2.5: Testing the Atomic Theory

Two criteria are usually applied to any theory. First, does it agree with facts which are already known? Second, does it predict new relationships and stimulate additional observation and experimentation? Dalton's atomic theory was able to do both of these things. It was especially useful in dealing with data regarding the masses of different elements which were involved in chemical compounds or chemical reactions.

To test a theory, we first use it to make a prediction about the macroscopic world. If the prediction agrees with existing data, the theory passes the test. If it does not, the theory must be discarded or modified. If data are not available, then more research must be done. Eventually the results of new experiments can be compared with the predictions of the theory.

Several examples of this process of testing a theory against the facts are afforded by Dalton's work. For example, postulate 3 in Dalton's Atomic Theory(opens in new window) states that atoms are not created, destroyed, or changed in a chemical reaction. Postulate 2 says that atoms of a given element have a characteristic mass: By logical deduction, then, equal numbers of each type of atom must appear on left and right sides of chemical equations such as

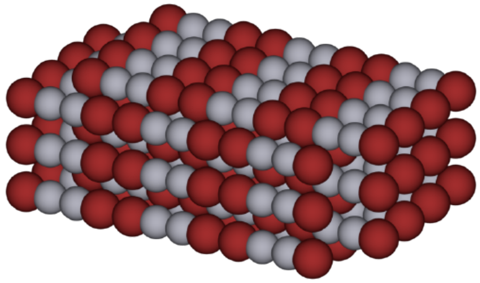
$$\mathrm{Hg}(l)+\mathrm{Br}_2(l) \rightarrow \mathrm{HgBr}_2(s) \tag{2.5.1}$$

and the total mass of reactants must equal the total mass of products. Dalton's atomic theory predicts Lavoisier's experimental law of conservation of mass.

A second prediction of the atomic theory is a bit more complex. A compound is a definite number of two or more types of atom. No matter how, when, or where a compound is made, it must always have the same ratios of different atoms. Thus mercuric bromide molecules always have the formula HgBr_2 no matter how much we have or where the compound came from, there will always be twice as many bromine atoms as mercury atoms. Since each type of atom has a characteristic mass, the mass of one element which combines with a fixed mass of the other should always be the same. In mercuric bromide, for example, if each mercury atom is 2.510 times as heavy as a bromine atom, the ratio of masses would be

$$\frac{\text{Mass of 1 mercury atom}}{\text{Mass of 2 bromine atoms}}=\frac{2.510 \times \text{ mass of } \cancel{\text{1 bromine atom}}}{2 \times \text{ mass of } \cancel{\text{1 bromine atom}}}=1.255$$

No matter how many mercury (II) bromide molecules we have, each has the same proportion of mercury, and so *any* sample of mercury (II) bromide must have that same proportion of mercury. We have just derived the **law of constant composition**, sometimes called the **law of definite proportions**. When elements combine to form a compound, they always do so in exactly the same ratio of masses. This law had been postulated in 1799 by the French chemist Proust (1754 to 1826) 4 years before Dalton proposed the atomic theory, and its logical derivation from the theory contributed to the latter's acceptance. The law of constant composition makes the important point that the composition and other properties of a *pure* compound are independent of who prepared it or where it came from. The carbon dioxide found on Mars, for instance, can be expected to have the same composition as that on Earth, while the natural vitamin C extracted and purified from rose hips has exactly the same composition as the synthetic vitamin C prepared by a drug company. Absolute purity is, however, an ideal limit which we can only approach, and the properties of many substances may be affected by the presence of very small quantities of impurities.



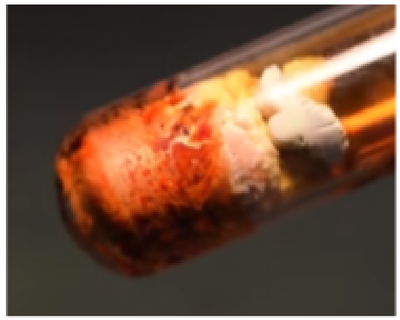
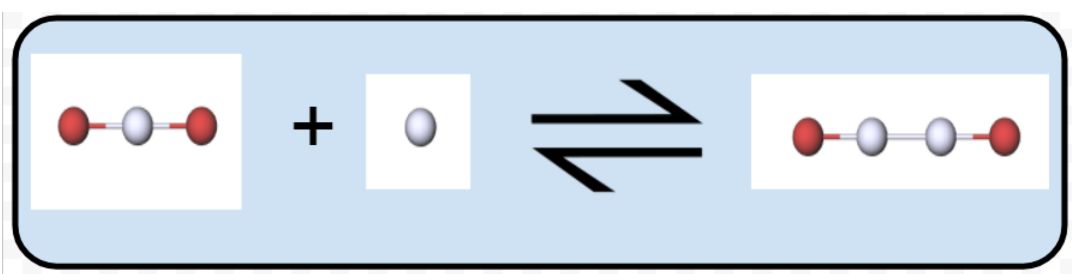


Figure 2.5.1:The arrangement of atoms and molecules in a crystal of mercury (I) bromide, Hg_2Br_2. from Wikipedia (Credit: CCoil). The image to the right is solid Hg_2Br_2, shown in macroscopic form.

A third law of chemical composition may be deduced from the atomic theory. It involves the situation where two elements can combine in more than one way, forming more than one compound. For example, if mercury (II) bromide is ground and thoroughly mixed with liquid mercury, a new compound, mercury (I) bromide (mercurous bromide), is formed. Mercury (I) bromide is a white solid which is distinguishable from mercury (II) bromide because of its insolubility in hot or cold water. Mercury (I) bromide also changes directly from a solid to a gas at 345°C. From the microscopic view of solid mercury (I) bromide in the above figure , you can readily determine that its chemical formula is Hg_2Br_2. (Since there are two atoms of each kind in the molecule, it would be incorrect to write the formula as HgBr.) The chemical equation for synthesis of mercurous bromide is

$$\mathrm{Hg}(l) + \mathrm{HgBr_2}(s) \rightarrow \mathrm{Hg_2Br_2}(s) \tag{2.5.2}$$



A chemical equation is expressed in terms of ball and stick structures. A white sphere bonded to two red sphere reacts with a single white sphere. The double sided arrow points to a structure with two bonded white spheres in the center bonded to two red spheres, one on the left and the right.

From the formulas $HgBr_2$ and Hg_2Br_2 (and the image above) we can see that mercury (II) bromide has only 1 mercury atom for every 2 bromines, while mercury (I) bromide has 2 mercury atoms for every 2 bromines. Thus, for a given number of bromine atoms, mercury (I) bromide will always have twice as many mercury atoms as mercury (II) bromide. Again using postulate 2 from Dalton's Atomic Theory, the atoms have characteristic masses, and so a given number of bromine atoms corresponds to a fixed mass of bromine. Twice as many mercury atoms correspond to twice the mass of mercury.

Therefore we can say that for a given mass of bromine, mercury (I) bromide will contain half the mass of mercury that mercury (II) bromide will (the doubled mass of mercury was provided by adding liquid mercury to mercuric bromide in Equation 2.5.2).

Example 2.5.1

Given that the mass of a mercury atom is 2.510 times the mass of a bromine atom, calculate the mass ratio of mercury to bromine in mercury (I) bromide.

Solution

The formula Hg_2Br_2 tells us that there are 2 mercury atoms and 2 bromine atoms in each molecule. Thus the mass ratio is

$$\frac{\text{Mass of 2 mercury atoms}}{\text{Mass of 2 bromide atoms}}=\frac{2\times(2.510\times\text{Mass of 1 bromide atom})}{2\times\text{Mass of 1 bromide atom}}=2.510$$

Note that the mass of mercury per unit mass of bromine is double that calculated earlier for mercury (II) bromide.

The reasoning and calculations above illustrate the law of multiple proportions. When two elements form several compounds, the mass ratio in one compound will be a small whole-number multiple of the mass ratio in another. In the case of mercury (II) bromide and mercury (I) bromide the mass ratios of mercury to bromine are 1.255 and 2.510, respectively. The second value is a small whole-number multiple of (2 times) the first.

Until the atomic theory was proposed, no one had expected *any* relationship to exist between mass ratios in two or more compounds containing the same elements. Because the theory predicted such relationships, Dalton and other chemists began to look for them. Before long, a great deal of experimental evidence was accumulated to show that the law of multiple proportions was valid. Thus the atomic theory was able to account for previously known facts and laws, and it also *predicted a new law*. In the process of verifying that prediction, Dalton and his contemporaries did many additional quantitative experiments. These led onward to more facts, more laws, and, eventually, new or modified theories. This characteristic of stimulating more research and thought put Dalton's postulates in the distinguished company of other good scientific theories.