One of the greatest challenges that early chemists faced was trying to find a way to connect the mass of a substance to the number of particles in the sample. The findings that “elementary particles” combined in fixed ratios by weight led Dalton to his “atomic model” of matter. However, knowing that the mass ratio of oxygen to hydrogen in water is 8:1 doesn’t tell you *how many* atoms of each element are involved unless one knows the relative mass of each kind of atom.

The trick in assigning relative masses to elements is to be able to feel confident that the samples you are comparing have the same number of particles. It would not do, for example, to try to compare the mass of a baseball to a golf ball by weighing backpacks filled with each kind of ball. As we have seen earlier in the experiment comparing mass and volume of different metals, we could not say with certainty whether the iron was denser because it had more particles per given volume than a sample of aluminum, or that its individual particles were more massive than those of aluminum, or some combination of both.

In estimating atomic weights, Dalton was confronted with certain grave difficulties. Since it is impossible to weigh single atoms, any system of atomic weights must be formulated on a comparative basis. The atom of some element must be arbitrarily selected as the reference weight. Dalton chose the hydrogen atom and assigned *one* as its weight. The atomic weight of oxygen could then be found by either (1) comparing the weights of equal numbers of oxygen and hydrogen atoms or (2) finding by analysis the combining weights of oxygen and hydrogen in water. Dalton considered the first approach but rejected it. Since to him, atoms in a gas were analogous to a pile of shot, and since he believed that atoms of different gases varied in diameter, therefore equal volumes of gases could not contain equal numbers of atoms. The second approach he considered valid. However, reflection will show that it is valid only when the ratio of atomic combination is known.[[1]](#footnote-1)

The breakthrough came when Avogadro devised a hypothesis to account for the observations of Gay-Lussac regarding the reacting volumes of gases. Gay-Lussac had noted that gases appeared to react in simple integer ratios. It was observed that two volumes of carbon monoxide combined with one volume of oxygen to form two volumes of carbon dioxide, and ammonia contained nitrogen and hydrogen in a 1:3 ratio, and so on. Gay-Lussac’s law of combining volumes suggested that equal volumes of gases, at the same temperature and pressure, contained equal numbers of particles. However, there were problems. Two volumes of hydrogen gas combined with one volume of oxygen gas to produce *two* volumes of steam. If H combines with O in a 2:1 ratio and each volume contained *the same number of* particles of gas, one would expect only *one* volume of steam to be formed.

Avogadro’s paper of 1811, based on Gay-Lussac’s law and Dalton’s atomic theory, reconciled the … problems. Starting with the assumption that equal volumes of all gases contain equal numbers of molecules under similar conditions, Avogadro proceeded to analyze the facts of gaseous combination. Using the examples discussed by Gay-Lussac, he showed that the ambiguities disappeared if he assumed that the molecules involved in typical reactions might split into “half-molecules”; that is, he supposed the existence of molecules of elemental gases which contained more than a single atom. He did not use the term “atom”, but always used the term “half-molecule” as its equivalent. (Ihde)

Once we accept Avogadro’s Hypothesis, we can compare the mass of various gases and deduce the relative mass of the molecules. From there we can pick a weighable amount of the lightest element (say 1.0 g), then use mass ratios to assign the masses of the other elements. How many atoms are present in the sample? As unlikely as it might seem, it’s really not important to know. For if two volumes of hydrogen combine with one volume of oxygen gas, it’s reasonable to assume that two *molecules* of hydrogen are reacting with each *molecule* of oxygen. In fact, the word chosen to represent the standard weighable amount of stuff, the mole, comes from the Latin: *lump of stuff*.

For the purposes of Dalton’s theory their absolute sizes and weight were irrelevant. It was not necessary to know (e.g.) how many atoms there are in a gram of hydrogen, so long as one could assume that this number was very large indeed. For all one could infer by the application of Dalton’s ‘General Rules’ were the relative weights of atoms and molecules of different substances. One could establish that each oxygen atom weighed 4/3 times as much as each carbon atom – but there was no way of knowing whether they weighed 4 and 3 millionths, or 4 and 3 billionths, or 4 and 3 trillionths of a gram. The ‘atomic weights’ and ‘molecular weights’ of chemistry have always been expressed as multiples of an arbitrary unit – the weight of one hydrogen or carbon or oxygen atom being fixed by definition as ‘1’ or’12’ or ‘16’.[[2]](#footnote-2)

The unit builds on the use of Avogadro’s Hypothesis introduced in unit 4. However, instead of using the hypothesis to deduce formulas of compounds, we now use it to deduce the relative masses of elements. Unlike in solids, the particles of a gas are far enough apart that their size has little effect on the volume. The **Relative Mass activity** provided a tangible example of comparing masses of the same number of particles in the gaseous state

1. A. Ihde, The Development of Modern Chemistry, Harper & Row, 1964. [↑](#footnote-ref-1)
2. S Toulmin & J Goodfield, The Architecture of Matter, Harper & Row, 1962 [↑](#footnote-ref-2)