Avogadro was essentially a theoretical scientist, not an experimentalist. A few years earlier to the time around which Avogadro started his scientific career, Dalton's atomic theory had been announced, and Gay-Lussac had published his memoir on combining volumes. The sharp analytical intellect of Avogadro could quickly grasp the import of uniting the two ideas. He had noted Dalton's pitfalls in applying the atomic theory to the formation of molecules. He had, on the other hand, great faith in Gay-Lussac's experimental results which led to the law of combining volumes. (Gay-Lussac was one of the most respected scientists of his time. The quality and the amount of work he had produced on gases was unmatched. He undertook hot-air balloon flights for experimental purposes, and having achieved a height of 7000 m, a record at that time, he was a house-hold name.)

The following excerpts taken from the paper of Avogadro published in 1811 provide an insight into his extraordinary clarity of vision, clear understanding of the particulate nature of matter, and the interaction of particles (elementary as well as compound) during combination (reaction). He has shown how he used Gay-Lussac's results to calculate the atomic and molecular weights of many substances and the defects in Dalton's concepts. The narration is simple, highly inspiring and enjoyable.

G Nagendrappa

Essay on a Manner of Determining the Relative Masses of the Elementary Molecules of Bodies, and the Proportions in Which They Enter into These Compounds

Amedeo Avogadro (1776-1856)

I.

M Gay-Lussac has shown in an interesting *Memoir* (Mémoires de la Société d'Arcueil, Tome 11.) that gases always unite in a very simple proportion by volume, and that when the result of the union is a gas, its volume also is very simply related to those of its components. But the quantitative proportions of substances in compounds seem only to depend on the relative number of molecules which combine, and on the number of

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composite molecules which result. It must then be admitted that very simple relations also exist between the volumes of gaseous substances and the numbers of simple or compound molecules which form them. The first hypothesis to present itself in this connection, and apparently even the only admissible one, is the supposition that the number of integral molecules in any gases is always the same for equal volumes, or always proportional to the volumes. Indeed, if we were to suppose that the number of molecules contained in a given volume were different for different gases, it would scarcely be possible to conceive that the law regulating the distance of molecules could give in all cases relations as simple as those which the facts just detailed compel us to acknowledge between the volume and the number of molecules. On the other hand, it is very well conceivable that the molecules of gases being at such a distance that their mutual attraction cannot be exercised, their varying attraction for *caloric* may be limited to condensing the atmosphere formed by this fluid having any greater extent in the one case than in the other, and, consequently, without the distance between the molecules varying; or, in other words, without the number of molecules contained in a given volume being different. *Dalton*, it is true, has proposed a hypothesis directly opposed to this, namely that the quantity of caloric is always the same for the molecules of all bodies whatsoever in the gaseous state, and that the greater or less attraction for caloric only results in producing a greater or less condensation of this quantity around the molecules, and thus varying the distance between the molecules themselves. But in our present ignorance of the manner in which this attraction of the molecules for caloric is exerted, there is nothing to decide us a *à priori* in favour of the one of these hypotheses rather than the other; and we should rather be inclined to adopt a neutral hypothesis, which would make the distance between the molecules and the quantities of caloric vary according to unknown laws, were it not that the hypothesis we have just proposed is based on that simplicity of relation between the volumes of gases on combination, which would appear to be otherwise inexplicable.

Setting out from this hypothesis, it is apparent that we have the means of determining very easily the relative masses of the molecules of substances obtainable in the gaseous state, and the relative number of these molecules in compounds; for the ratios of the masses of the molecules are then the same as those of the densities of the different gases at equal temperature and pressure, and the relative number of molecules in a compound is given at once by the ratio of the volumes of the gases that form it. For example, since the numbers 1.10359 and 0.07321 express the densities of the two gases oxygen and hydrogen compared to that of atmospheric air as unity, and the ratio of the two numbers consequently represents the ratio between the masses of equal volumes of these two gases, it will also represent on our hypothesis the ratio of the masses of their molecules. Thus the mass of the molecule of oxygen will be about 15 times that of the molecule of hydrogen, or, more exactly as 15.074 to 1. In the same way the mass of the molecule of nitrogen will be to that of hydrogen as 0.96913 to 0.07321, that is, as 13, or more exactly 13.238, to 1. On the other hand, since we know that the ratio of the volumes of hydrogen and oxygen in the formation of water is 2 to 1, it follows that water results from the union of each molecule of oxygen with two molecules of hydrogen. Similarly, according to the proportions by volume established by M Gay-Lussac for the elements of ammonia, nitrous oxide, *nitrous gas*, and *nitric acid*, ammonia will result from the union of one molecule of nitrogen with three of hydrogen, nitrous oxide from one molecule of oxygen with two of nitrogen, nitrous gas from one molecule of nitrogen with one of oxygen, and nitric acid from one of nitrogen with two of oxygen.

Dalton has made the same supposition as we have done regarding the composition of *carbonic acid*, and has consequently been led to attribute to carbon a molecule equal to 4.4, which is almost in the name ratio to his value for that of oxygen as 11.36 is to 15, the mass of the molecule of oxygen according to us.

Assuming the values indicated for the mass of the molecule of carbon and the density of its gas, carbonic oxide will be formed, according to the experiments of M Gay-Lussac, of equal parts by volume of carbon gas and oxygen gas; and its volume will be equal to the sum of the volumes of its constituents: it will accordingly be formed of carbon and oxygen united molecule to molecule, with subsequent halving – all in perfect analogy to nitrous gas.

The mass of the molecule of carbonic acid will be –

$(11.36 + 2 \times 15.074)/2 = 20.75 = 1.5196/0.07321$,

and that of carbonic oxide will be –

$(I\ 1.36 + 15.074)/2 = 13.22 = 0.96782/0.07321$

III.

Dalton, on arbitrary suppositions as to the most likely relative number of molecules in compounds, has endeavoured to fix ratios between the masses of the molecules of simple substances. Our hypothesis, supposing it well-founded, puts us in a position to confirm or rectify his results from precise data, and, above all, to assign the magnitude of compound molecules according to the volumes of the gaseous compounds, which depend partly on the division of molecules entirely unexpected by this physicist.

Thus Dalton supposes [2] that water is formed by the union of hydrogen and oxygen, molecule to molecule. From this, and from the ratio by weight of the two components, it would follow that the mass of the molecule of oxygen would be to that of hydrogen as 7 1/2 to I nearly, or, according to Dalton's evaluation, as 6 to 1. This ratio on our hypothesis is, as we saw, twice as great, namely, as 15 to 1. As for the molecule of water, its mass ought to be roughly expressed by 15+2=17 (taking for unity that of hydrogen), if there were no division of the molecule into two; but on account – of this division it is reduced to half, 8 1/2, or more exactly 8.537, as may also be found by dividing the density of aqueous vapour 0.625 (Gay-Lussac) by the density of hydrogen 0.0732. This mass differs from 7, that assigned to it by Dalton, by the difference in the values for the composition of water; so that in this respect Dalton's result is approximately correct from the combination of two compensating errors,--the error in the mass of the molecule of oxygen, and his neglect of the division of the molecule.

Dalton supposes that in nitrous gas the combination of nitrogen and oxygen is molecule to molecule: we have seen on our hypothesis that this is actually the same. Thus Dalton would have found the same molecular mass for nitrogen as we have, always supposing that of hydrogen to be unity, if he had not set out from a different value for that of oxygen, and if he had taken precisely the same value for the quantities of the elements in nitrous gas by weight. But supposing the molecule of oxygen to be less than half what we find, he has been obliged to make that of nitrogen also equal to less than half the value we have assigned to it, viz., 5 instead of 13. As regards the molecule of nitrous gas itself, his neglect of the division of the molecule again makes his result approach ours; he has made it 6+5=11, whilst according to us it is about (15+13)/2 = 14, or more exactly (15.074+13.238)/2 = 14.156, as we also find by dividing 1.03636, the density of nitrous gas according to Gay-Lussac, by 0.07321. Dalton has likewise fixed in the same manner as the facts has given us, the relative number of molecules in nitrous oxide and in nitric acid, and in the first case the same circumstance has rectified his result for the magnitude of the molecule. He makes it 6 + 2 × 5 = 16, whilst according to our method it should be (15.074 + 2 × 13.238)/2 = 20.775, a number which is also obtained by dividing 1.52092, Gay-Lussac's value for the density of nitrous oxide, by the density of hydrogen.

In the case of ammonia, Dalton's supposition as to the relative number of molecules in its composition is on our hypothesis entirely at fault. He supposes nitrogen and hydrogen to be united in it molecule to molecule, whereas we have seen that one molecule of nitrogen unites with three molecules of hydrogen. According to him the molecule of ammonia would be 5+1= 6; according to us it should be (13+3)/2 = 8, or more exactly 8.119, as may also be deduced directly from the density of ammonia gas. The division of the molecule, which does not enter into Dalton's calculations, partly corrects in this case also the error which would result from his other suppositions.

All the compounds we have just discussed are produced by the union of one molecule of one of the components with one or more molecules of the other. In *nitrous acid* we have another compound of two of the substances already spoken of, in which the terms of the ratio between the number of molecules both differ from unity. From Gay-Lussac's experiments (Societe d'Arcueil, same volume) it appears that this acid is formed from I part by volume of oxygen and 3 of nitrous gas, or, what comes to the same thing, of 3 parts of nitrogen and 5 of oxygen; hence it would follow, on our hypothesis, that its molecule should be composed of 3 molecules of nitrogen and 5 of oxygen, leaving the possibility of division out of account. But this mode of combination can be referred to the preceding simpler forms by considering it as the result of the union of I molecule of oxygen with 3 of nitrous gas, i.e. with 3 molecules, each composed of a half-molecule of oxygen and a half-molecule of nitrogen, which thus already included the division of some of the molecules of oxygen which enter into that of nitrous acid. Supposing there to be no other division, the mass of this last molecule would be 57.542, that of hydrogen being taken as unity, and the density of nitrous acid gas would be 4.21267, the density of air being taken as unity. But it is probable that there is at least another division into two, and consequently a reduction of the density to half : we must wait until this density has been determined by experiment.

Let us now see what conjecture we may form as to the mass of the molecule of a substance which plays in nature a far greater part than sulphur or phosphorus, namely, that of carbon. As it is certain that the volume of *carbonic acid* is equal to that of the oxygen which enters into it, then, if we admit that the volume of carbon, supposed gaseous, which forms the other element, is doubled by the division of its molecules into two, as in several combinations of that sort, it will be necessary to suppose that this volume is the half of that of the oxygen with which it combines, and that consequently carbonic acid results from the union of one molecule of carbon and two of oxygen, and is therefore analogous to sulphurous and phosphorous acids, according to the preceding suppositions. In this case we find from the proportion by weight between the oxygen and the carbon, that the density of carbon as gas would be 0.832 with respect to that of air as unity, and the mass of its molecule 11.36 with respect to hydrogen. There is, however, one difficulty in this supposition, for we give to the molecule of carbon a mass less than that of nitrogen and oxygen, whereas one would be inclined to attribute the solidity of its aggregation at the highest temperatures to a higher molecular mass, as is observed in the case of the sulphuric and phosphoric radicals. We might avoid this difficulty by assuming a division of the molecule into four, or even into eight, on the formation of carbonic acid; for in that way we should have the molecule of carbon twice or four times as great as that we had just fixed. But such a composition would not be analogous to that of the other acids; and, besides, according to other known examples, the assumption or not of the gaseous state does not appear to depend solely on the magnitude of the molecule, but also on some other unknown property of substances. Thus we see sulphurous acid in the form of a gas at the ordinary temperature and pressure of the atmosphere not withstanding its large molecule, which is almost equal to that of the solid sulphuric radical. Oxygenated muriatic acid gas has a density, and consequently a molecular mass, still more considerable. Mercury, which as we shall see further on, should have an extremely large molecule, is nevertheless gaseous at a temperature infinitely lower than would be necessary to vaporise iron the molecule of which is smaller. Thus there is nothing to prevent us from regarding carbonic acid to be composed in the manner indicated above, – and therefore analogous to nitric, sulphuric, and phosphoric acids, – and the molecule of carbon to have a mass expressed by 11.36.

Information and Announcements

Sagar

The National Institute of Oceanography (NIO) dedicated to ocean research, attracts visitors, particularly students, who come to learn about oceanography. A pocketbook, *Sagar*, was recently prepared to enable the visitor to pursue the fascinating world of the oceans. It provides an overview of the oceans: their formation, characteristics, and the dynamics that determine their evolution. It also contains information on how the interested reader can pursue these topics further through books and websites.

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