

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

Journal de Physique, **73**, 58-76 (1811)

From: <http://lem.ch.unito.it/chemistry/essai.html>

I.

M. Gay-Lussac has shown in an interesting Memoir (*Mémoires de la Société d'Arcueil*, Tome II.) 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 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 *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.

II.

There is a consideration which appears at first sight to be opposed to the admission of our hypothesis with respect to compound substances. It seems that a molecule composed of two or more elementary molecules should have its mass equal to the sum of the masses of these molecules; and that in particular, if in a compound one molecule of one substance unites with two or more molecules of another substance, the number of compound molecules should remain the same as the number of molecules of the first substance. Accordingly, on our hypothesis, when a gas combines with two or more times its volume of another gas, the resulting compound, if gaseous, must have a volume equal to that of the first of these gases. Now, in general, this is not actually the case. For instance, the volume of water in the gaseous state is, as M. Gay-Lussac has shown, twice as great as the volume of oxygen which enters into it, or, what comes to the same thing, equal to that of the hydrogen instead of being equal to that of the oxygen. But a means of explaining facts of this type in conformity with our hypothesis presents itself naturally enough; we suppose, namely, that the constituent molecules of any simple gas whatever (i.e., the molecules which are at such a distance from each other that they cannot exercise their mutual action) are not formed of a solitary elementary molecule, but are made up of a certain number of these molecules united by attraction to form a single one; and further, that when molecules of another substance unite with the former to form a compound molecule, the integral molecule which should result splits itself into two or more parts (or integral molecules) composed of half, quarter, etc., the number of elementary molecules going to form the constituent molecule of the first substance, combined with half, quarter, etc., the number of constituent molecules of the second substance that ought to enter into combination with one constituent molecule of the first substance (or, what comes to the same thing, combined with a number equal to this last of half-molecules, quarter-molecules, etc., of the second substance); so that the number of integral molecules of the compound becomes double, quadruple, etc., what it would have been if there had been no splitting up, and exactly what is necessary to satisfy the volume of the resulting gas.¹

On reviewing the various compound gases most generally known, I only find examples of duplication of the volume relatively to the volume of that one of the constituents which combines with one or more volumes in the other. We have already seen this for water. In the same way, we know that the volume of ammonia gas is twice that of the nitrogen which enters into it. M. Gay-Lussac has also shown that the volume of nitrous oxide is equal to that of the nitrogen which forms part of it, and consequently is twice that of the oxygen. Finally, nitrous gas, which contains equal volumes of nitrogen and oxygen, has a volume equal to the sum of the two constituent gases, that is to say, double that of each of them. Thus in all these cases there must be a division of the

¹ Thus, for example, the integral molecule of water will be composed of a half-molecule of oxygen with one molecule, or what is the same thing, two half-molecules of hydrogen.

molecule into two; but it is possible that in other cases the division might be into four, eight, etc. The possibility of this division of compound molecules might have been conjectured *à priori*; for otherwise the integral molecules of bodies composed of several substances with a relatively large number of molecules, would come to have a mass excessive in comparison with the molecules of simple substances. We might therefore imagine that nature had some means of bringing them back to the order of the latter, and the facts have pointed out to us the existence of such means. Besides, there is another consideration which would seem to make us admit in some cases the division in question; for how could one otherwise conceive a real combination between two gaseous substances uniting in equal volumes without condensation, such as takes place in the formation of nitrous gas? Supposing the molecules to remain at such a distance that the mutual attraction of those of each gas could not be exercised, we cannot imagine that a new attraction could take place between the molecules of one gas and those of the other. But on the hypothesis of division of the molecule, it is easy to see that the combination really reduces two different molecules to one, and that there would be contraction by the whole volume of one of the gases if each compound molecule did not split up into two molecules of the same nature. M. Gay-Lussac clearly saw that, according to the facts, the diminution of volume on the combination of gases cannot represent the approximation of their elementary molecules. The division of molecules on combination explains to us how these two things may be made independent of each other.

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 $7\frac{1}{2}$ to 1 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, $8\frac{1}{2}$, 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

² In what follows I shall make use of the exposition of Dalton's ideas given in Thomson's System of Chemistry.

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 $6 + 2 \times 5 = 16$, whilst according to our method it should be $(15.074+2 \times 13.238)/2 = 20.775$, 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 (Société d'Arcueil, same volume) it appears that this acid is formed from 1 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 1 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.

IV.

We may now look at a few more compounds, which on our hypothesis can give us at least conjectural information concerning the relative masses of the molecules and their number in these compounds, and compare our results with the suppositions of Dalton.

M. Gay-Lussac has shown that if we assume that dry sulphuric acid is composed of 100 parts of sulphur and 138 of oxygen by weight, as the most recent work of chemists has established, and that the density of sulphurous acid gas is 2.265 referred to air as unity (Kirwan's determination), and if we admit, as the result of Gay-Lussac's experiments, that sulphuric acid is composed of two parts by volume of sulphurous acid is nearly equal to that of the oxygen which entered into it; and this equality would be exact if the bases on which the calculation rests were the same. If we suppose Kirwan's determination to be exact, throwing the whole error on the analysis of sulphuric acid, we find that in sulphurous acid 100 parts of sulphur take 95.02 of oxygen, and consequently in sulphuric acid $95.02 + (95.02/2) = 142.53$, instead of 138. If, on the contrary, we suppose the analysis of sulphuric acid to be exact, it follows that sulphurous acid contains 92 of oxygen for 100

of sulphur, and that its specific gravity should be 2.30314, instead of 2.265.

One consideration would appear to weigh in favour of the first assumption until the density of sulphurous acid gas has been confirmed or rectified by fresh experiments,—namely, that there must have been in the determination of the composition of sulphuric acid, a source of error tending to increase the quantity of the radical, or, what is the same thing, diminish the quantity of oxygen. The determination was made from the quantity of dry sulphuric acid produced. Now it seems almost certain that ordinary sulphur contains hydrogen; the weight of this hydrogen, which must have been converted into water in the operation, has therefore been added to the true weight of the radical. I shall therefore assume sulphurous acid to be composed of 95.02³ of oxygen to 100 of sulphur, or rather of sulphuric radical, instead of 92.⁴

In order now to determine the mass of the molecule of the sulphuric radical, it would be necessary to know what proportion by volume this radical in the gaseous state would bear to the oxygen in the formation of sulphurous acid. The analogy with other combinations already discussed, where there is in general a doubling of the volume or halving of the molecule, leads us to suppose that it is the same in this case also, *i.e.* that the volume of the sulphur as gas is half that of the sulphurous acid, and consequently also half that of the oxygen with which it combines. On this supposition the density of sulphur gas will be to that of oxygen as 100 to 95.02/2, or 47.51; which gives 2.323 for the density of gaseous sulphur, taking that of air as unity. The masses of the molecules being according to our hypothesis in the same ratio as the densities of the gases to which they belong, the mass of the molecule of the sulphuric radical will be to that of hydrogen as 2.323 to 0.07321, or as 31.73 to 1. One of these molecules combined, as we have said, with two of oxygen, will form sulphurous acid (division of the molecule being left out of account), and combined with yet another molecule of oxygen, will form sulphuric acid. Accordingly, sulphurous acid should be analogous to nitric acid, with regard to the relative number of molecules of its constituents, sulphuric acid having no analogue amongst the nitrogen compounds. The molecule of sulphurous acid, having regard to division, will be equal to $(31.73 + 2 \times 15.074)/2$, or 30.94, as would also be obtained directly by dividing the density 2.265 of sulphurous acid gas by that of hydrogen gas. As for the molecule of sulphuric acid, it cannot be determined, for we do not know whether there is further division of the molecule on its formation, or not.⁵

³ Erroneously 92.02 in the original.

⁴ This was written before I had seen the Memoir of Davy on oxymuriatic acid, which also contains new experiments on sulphur and phosphorus. In it he determines the density of sulphurous acid gas, and finds it to be only 2.0967, which gives new force to the above considerations. If we adopt this density, we find that in sulphurous acid 100 parts by weight of sulphur take 111 of oxygen, and in sulphuric acid 167 instead of 138; but perhaps this density of sulphurous acid, according to Davy, is somewhat too low.

⁵ Davy in the Memoir alluded to, has made the same suppositions as to the relative number of molecules of oxygen and radical in sulphurous and sulphuric acids. From his determination of the density of sulphurous acid gas, the density of the sulphuric radical would be 1.9862, and its molecule 27.13, that of hydrogen being taken as unity. Davy, by a similar calculation, fixes it at about half, *viz.*, 13.7, because he supposes the molecule of oxygen to be equal to about half our molecule, using Dalton's hypothesis with respect to water.

He finds nearly the same mass, *viz.*, 13.4, by taking as his starting-point the density of sulphuretted hydrogen; which his experiments make equal to 1.0645, a result only slightly different from Kirwan's, and by assuming that this gas (which contains, as we know, its own volume of hydrogen combined with sulphur) is composed of one molecule of sulphur and one of hydrogen. As we suppose the molecule of sulphur to be nearly twice as great, we must assume that this gas is the product of the union of one molecule of the radical with two at least of hydrogen, and that its volume is twice that of the gaseous radical, as in so many other cases. I say *at least* with two molecules of hydrogen, for if there were hydrogen already in ordinary sulphur, as known experiments on this substance indicate, its quantity

Dalton had supposed that sulphuric acid was composed of two molecules of oxygen to one of radical, and sulphurous acid of one molecule of oxygen to one of sulphur. These two assumptions are incompatible, for according to Gay-Lussac's results the quantities of oxygen in these two acids for a given quantity of radical, are represented by 1 and 1 1/2. Besides, in his determination of the molecule he set out from a wrong value for the composition of sulphuric acid, and it is only by chance that the mass 15 which he assigns to it, bears to his value for the mass of the oxygen molecule a ratio which approaches that presented by these two substances on our hypothesis.

Phosphorus has as much analogy with sulphur that we might apparently assume that phosphoric acid also is composed of three molecules of oxygen to one of radical, and phosphorous acid of only two of oxygen to one of radical. On this assumption we may calculate approximately the mass of the molecule of the phosphoric radical. Rose found by a method analogous to that which had been employed for sulphuric acid, that phosphoric acid contains about 115 parts by weight of oxygen to 100 of phosphorous. There ought to be a little more oxygen in it if we suppose that phosphorus, like sulphur, contains hydrogen. As an approximation we can make this increase in the same proportion as we have seen holds good for sulphuric acid in accordance with the specific gravity of sulphurous acid, and thus bring the quantity of oxygen up to 120. We then find from our hypotheses that the mass of the molecule of the phosphoric radical is about 38, that of hydrogen being taken as unity. Dalton also has adopted for phosphorous and phosphoric acids, hypotheses analogous to those he had made for sulphurous and sulphuric acids; but since he used different values for the elements of these acids by weight, he arrived at a determination of the molecule of phosphorus, which does not bear the same ratio to his determination of the molecule of sulphur as ought to exist, according to us, between these molecules: he has fixed that of phosphorus as 8, hydrogen being unity.⁶

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

also must be added. If, for instance, ordinary sulphur were composed of one molecule of sulphuric radical and one of hydrogen. Sulphuretted hydrogen would be composed of three molecules of hydrogen and one of radical. This could be decided by the comparison of the specific gravities of sulphuretted hydrogen and sulphurous acid gas, if both were known exactly. For example, supposing Davy's determination for sulphuretted hydrogen to be exact, the molecule of the sulphuric radical, on the supposition of only two molecules of hydrogen, would be 27.08, that of hydrogen being taken as unity; but on the supposition of three molecules of hydrogen, 27.08 would still be the sum of one molecule of radical and one of hydrogen, so that the former would be reduced to 26.08. If the exact density of sulphurous acid gas confirmed one or the other of these results, it would confirm by that means one or other of these hypotheses: but we are not sufficiently agreed about these densities to be able to draw any conclusion in this respect from the determinations hitherto existing.

⁶ Davy has adopted the same suppositions as ourselves for the number of molecules of oxygen and radical in phosphorous and phosphoric acids; and by still taking the molecule of oxygen nearly half ours, he finds 16.5 for the molecule of phosphorus, which would give about 33 on our evaluation of the molecule of oxygen, instead of 38. The difference arises from Davy having taken from his own experiments 34 parts to 25, *i.e.* 136 to 100 of phosphorus, as the quantity of oxygen in phosphoric acid instead of 120 as we have assumed. Further experiments will clear up this point.

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 notwithstanding 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.

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 same 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:

$$(11.36 + 15.074)/2 = 13.22 = 0.96782/0.07321$$

V.

Amongst the simple non-metallic substances there is still one of which we have to speak. This substance, being naturally gaseous, can leave no doubt, on our principles, as to the mass of its molecule; but the latest experiments of Davy upon it, and even the earlier experiments of MM. Gay-Lussac and Thenard, force us to depart from ideas hitherto received, although the last named chemists have attempted to explain them in accordance with these ideas. This is the substance hitherto known by the name of *oxygenated muriatic acid*, or *oxymuriatic acid*. In the present state of our knowledge we must now regard this substance as still undecomposed, and muriatic acid as a compound of it with hydrogen. It is in accordance with this theory, therefore, that we shall apply our principles regarding combinations to these two substances.

The density of oxymuriatic acid according to MM. Gay-Lussac and Thenard is 2.470 referred to atmospheric air as unity; this gives for its molecule referred to that of hydrogen as unity, 33.74, adopting the density of hydrogen determined by MM. Biot and Arago. According to Davy 100 English cubic inches of oxymuriatic gas weigh 74.5 grains, and an equal volume of hydrogen gas 2.27. This would give for the molecule of the former $74.5/2.27 = 32.82$. These two estimates differ very little from the mass that Davy himself, from other considerations, assigns to this substance, viz., 32.9. It follows from the experiments both of Gay-Lussac and Thenard, and of Davy, that muriatic acid gas is formed by the combination of equal volumes of oxymuriatic gas and hydrogen, and that its volume is equal to their sum. This means, according to our hypothesis, that muriatic acid is formed of these two substances united molecule to molecule, with halving of the molecule, of which we have already had so many examples. Accordingly the density of muriatic acid gas, calculating from that given above for oxymuriatic gas, should be 1.272; it is 1.278 according to the experiments of MM. Biot and Gay-Lussac. If we suppose this last determination to be exact, the density of oxymuriatic gas should be 2.483, and the mass of its molecule 33.91. Should we prefer to adopt this value, the mass of the molecule of muriatic acid will be $34.91/2 = 17.45 = 1.278/0.07321$. The determination of the specific gravity of the muriatic acid gas by Davy, according to which 100 cubic inches of that gas weigh 39 grains, would give numbers only slightly different, viz., 33.36 for the mass of the molecule of oxymuriatic acid, and 17.18 for that of muriatic acid.

VI.

Let us now apply our hypothesis to some metallic substances. M. Gay-Lussac assumes that mercurous oxide, in the formation of which 100 parts by weight of mercury absorb 4.16 of oxygen, according to Fourcroy and Thenard, is analogous to nitrous oxide, *i.e.*, that the mercury, supposed gaseous, is combined in it with half its volume of oxygen gas, which on our hypothesis is to say that one molecule of oxygen combines with two molecules of mercury. Supposing this to be the case, the density of mercury gas ought to be to that of oxygen as 100 to 8.32, which would give 13.25 as its density taking that of air as unity, and for the mass of the molecule of mercury 181 taking as unity that of hydrogen. On this supposition mercuric oxide, which contains twice as much oxygen, should be formed of mercury and oxygen united molecule to molecule; but some reasons lead me to think that it is mercurous oxide which represents this last case, and that in mercuric oxide one molecule of mercury combines with two of oxygen. Then the density of mercury gas, and the mass of its molecule, would be double what they are on the preceding hypothesis, viz., 26 1/2 for the first, and 362 for the second. In this assumption I am supported by analogies drawn from other metals, and particularly from iron. It follows from the experiments of different chemists, carefully discussed by Hassenfratz, that the two best known oxides of iron, the black oxide and the red oxide, are composed respectively of 31.8 and 45 parts by weight of oxygen to 100 of iron. We see that the second of these two quantities of oxygen is nearly half as great again as the first, so that we are naturally led to suppose that in the first oxide one molecule of iron combines with two molecules of oxygen, and in the second with three. If that is so, and if we admit the proportion for the black oxide to be the more exact, the proportion for the red oxide would be 47.7 for 100 of iron, which comes very near the proportion found directly by Proust, viz., 48. The mass of a molecule of iron will therefore be to the mass of a molecule of oxygen as 100 to 15.9, which gives about 94 with regard to hydrogen as unity. It would appear from this that there should be another oxide of iron which would contain 15.9 of oxygen to 100 of iron, and this is perhaps the white oxide, although the experiments hitherto performed point to this substance containing a greater proportion of oxygen. Now the two oxides of mercury of which we have spoken, one of which contains twice as much oxygen as the other, should apparently be analogous to this last oxide of iron and to the black

oxide, the red oxide having no analogue in the case of mercury.

In the same way the other metals present for the most part two oxides in which the quantities of oxygen are as 1 to 2, so that from the proportions of their elements by weight, we may determine in the same manner the mass of their molecules. I find for example, 206 for the molecule of lead, 198 for that of silver, 123 for copper etc. ⁷

VII.

We shall now make a few applications of our principles to saline compounds, which will furnish us with the opportunity of examining an important point in the theory of these compounds. M. Gay-Lussac has shown that the neutral carbonate, fluoborate, and muriate of ammonia are composed of equal volumes of ammonia gas and of the respective acids. Let us pause to consider the carbonate. On our hypothesis, this salt is composed of one molecule of carbonic acid with one molecule of ammonia—*i.e.* (according to the values previously given and independently of any division), of one molecule of carbon, two of oxygen, one of nitrogen, and three of hydrogen, which would give 57.75 for the mass of its molecule; but admitting the division into two which had already taken place in the components, this molecule is reduced to 28.87. It would be brought down again to half this number, if there were another division on the union of the acid with the alkali.

M. Gay-Lussac has suspected that the equality of volume between a gaseous alkali and acid, which by their union form a neutral salt, may be general. That is as much as to say on our hypothesis, that neutral salts are composed of acid and alkali united molecules to molecule; but certain considerations appear to be opposed to the admission of this principle in all its generality. The idea of acidity, alkalinity, and neutrality, which still seems to me the most conformable to the phenomena, is that which I have given in my Memoir on this subject (Journal de Physique, tome lxi.). According to it, all substances form amongst themselves a series, in which they play in part of acid or alkali with respect to one another; and this series is the same as that on which depends the positive or negative electricity they develop on mutual contact. I express by the term of *oxygenicity* the property in virtue of which substances are ranked in the scale, placing first those which play the part of an acid with respect to the others. In this scale there is a point about which are placed the substances we term *neutral*, above it are those which are absolutely acid, below it are those which are alkaline, when their state of aggregation permits them to exhibit these qualities.

⁷ I shall here add a few words regarding the molecule of potassium. Davy, assuming that potash is formed from potassium and oxygen united molecule, has fixed the mass of the molecule of potassium at 40.5, in accordance with the quantity of oxygen by weight in the substance, and has taken the molecule of oxygen to be 7.5. Assuming, as we have done, this last molecule to be nearly twice as great, the molecule of potassium will also be doubled, viz., about 81, if we adopt the other assumptions of Davy. But it may be that in potash one molecule of potassium takes two of oxygen, in which case we should again have to double the last value and make it 162. It might also be (for the analogy drawn from other metals is not in this case a very safe guide) that two molecules of potassium combine with one oxygen, which would bring back the molecule of potassium to 40.5.

It is on the assumption of this last value for the molecule of potassium that Davy finds 32.9 for that of oxymuriatic acid, calculating from the composition of muriate of potash, and assuming that this salt is formed of one molecule of potassium with one of acid. If we suppose the molecule of potassium to have a different mass, we must admit another relative number of molecules in the muriate, since both from our hypothesis and from the density of the gas, 32.9 is very nearly the molecule of oxymuriatic acid. On the supposition that the molecule of potassium is 81, and that in sulphide of potassium the combination is molecule to molecule, the molecule of sulphur will be about 27 instead of 13 1/2 as found by Davy on the later assumption, which will bring about between this result and that derived from sulphurous acid according to our calculations the agreement which exist between Davy's values.

Lastly, composite substances occupy in this scale a place intermediate between those of which they are composed, having regard to the degree of oxygenicity and to the proportion by weight of these constituents substances; so that a neutral substance results from the combination of two substances, one acid, the other alkaline, in a certain proportion (see the Memoir referred to).⁸

The recognition of the simple ratios observed on combination, and in particular in cases where neutral substances are the result, leads us now to a more exact manner of conceiving the state of neutrality. The oxygenicity in two bodies which combine, cannot be supposed to have such a relation to the masses of their molecules, that from the union of certain definite numbers of these molecules there should result a certain definite degree of oxygenicity which would be that of neutrality, and would only depend, as we have already assumed for oxygenicity in general, on the proportion by weight and the degree of oxygenicity of the components. It appears, then, that we must admit that the degree of oxygenicity which corresponds to neutrality is not quite fixed, although approximating more or less to a fixed limit, and that this state depends on the excess of mass of one of the components (from which the acid or alkaline quality might result) being prevented from exercising these qualities by the simple combination with the contrary principle which retains it by its attraction, although the compound otherwise might have a state of aggregation permitting it to act as an acid or an alkali, if it were endowed with these qualities. The excess of mass thus held back is that which is necessary to complete a certain simple relation between the number of combining molecules. Thus amongst the different simple ratios in which molecules can combine, there is one which gives neutrality; that, namely, which gives the compound approximating most closely to the definite point of oxygenicity mentioned above, so that if in the compound formed according to this ratio, one of the component principles let one molecule of the other escape, or took up one in addition, the compound would diverge further from this precise point, about which there oscillate, as it were, the oxygenicities of the various neutral compounds; and it is this point which would give the neutral state in the combination of two substances which could combine in all proportions, or in ratios expressible by any number of molecules whatever. It is evident that this way of regarding the neutrality of compound substances reconciles the theory given in the Memoir quoted with the ideas put forward by M. Haüy in his *Traité de Physique*.

According to this theory it is evident that if the oxygenicity of two acids and two alkalis which combine respectively in pairs, is not extremely different, and if at the same time the mass of the molecule of one of the acids is not in a different ratio to its alkali from that of the other acid with regard to its own alkali, the ratio between the numbers of molecules which gives neutrality may be the same in both compounds; but in the contrary case, the ratio may vary in such a way that instead of the equality of volumes, or of combination molecule to molecule which we see between carbonic and a few other acids on the one hand and ammonia on the other, there may be other simple ratios such as 1 to 2, etc., which give the neutral state. Nevertheless, the simplicity which will always exist amongst these ratios, in conjunction with the information we may obtain from other sources as to the mass of the molecules and the degree of oxygenicity of the components, will sometimes put us in a position to determine, or at least conjecture, what are the simple ratios which may occur in a given case; but it is the task of experiment to confirm or correct these theoretical estimates.

VIII.

⁸ The properties of oxymuriatic acid, as Davy conceives them being analogous to those of oxygen, are not at all extraordinary from this point of view; they simply show that this substance is very oxygenic. I had already remarked in my Memoir that the properties of the alkalis, supposed to be oxides, are easily explained according to these ideas.

It will have been in general remarked on reading this Memoir that there are many points of agreement between our special results and those of Dalton, although we set out from a general principle, and Dalton has only been guided by considerations of detail. This agreement is an argument in favour of our hypothesis, which is at bottom merely Dalton's system furnished with a new means of precision from the connection we have found between it and the general fact established by M. Gay-Lussac. Dalton's system supposes that compounds are made in general in fixed proportions, and this is what experiment shows with regard to the more stable compounds and those most interesting to the chemist. It would appear that it is only combinations of this sort that can take place amongst gases, on account of the enormous size of the molecules which would result from ratios expressed by larger numbers, in spite of the division of the molecules, which is in all probability confined within narrow limits. We perceive that the close packing of the molecules in solids and liquids, which only leaves between the integral molecules distances of the same order as those between the elementary molecules, can give rise to more complicated ratios, and even to combinations in all proportions; but these compounds will be so to speak of a different type from those with which we have been concerned, and this distinction may serve to reconcile M. Berthollet's ideas as to compounds with the theory of fixed proportions.