SCIENCE

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ARE FURTHER EXPERIMENTS NEEDED FOR DETERMINING THE ATOMIC WEIGHT OF OXYGEN?[*]

THE precision of experiments on the atomic weight of oxygen has been gradually so much increased that, in some cases, the mean error of a single determination is less than 1 part in 10,000. The agreement of different series of experiments is not so good, but if the work of different experimenters agreed well, the question, how accurately do we really know the atomic weight of oxygen, is not one which we can readily answer. Neither the concordance of the experiments of a given series, nor the agreement of the results of series of experiments by different observers, can excuse us from search for sources of error. All sciences which have to do with measurement afford sufficient instances of the fact that our conclusions are to be received with a certain suspense of judgment. And chemistry well illustrates that he is wise whose assertions regard the possibility of finding at some time evidence to the contrary.

The history of experiment on the atomic weight of oxygen affords an interesting example of the fact that neither the concordance of individual observations nor the agreement of different experimenters proves that a measurement is right. To-

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[*] President's address, delivered before the New Haven Meeting of the American Chemical Society.

ward the middle of the century, Dumas made his classic experiments on the composition of water. The probable error of a single experiment was, in round numbers, 1 part in 400, so that the probable error of the average of the 19 famous experiments was 1 part in 2250. Now, this means that his final value was not likely to differ more than a certain small quantity from the result of the repetition of even a very large number of experiments made in the same way, with the same skill and care. But as to the difference between this result of the 19 experiments and the unknown true value, we are told absolutely nothing by the proposition that the probable error of Dumas' result was 1 part in 2250. It is a commonplace to say, that the calculation of the probable error of a series of experiments does not show how nearly the result approaches the truth, but how near it is to the result of a greater number of similar experiments. It decides, not how nearly we approach the desired goal, but whether it is useful to persevere by the present method of approach. Dumas made 19 observations, and got the value, 15.96, with a probable error of 0.007; that is, if he had made 100 or 1000 experiments, it is unlikely that the final result would not have been between 15.95 and 15.97, and very unlikely indeed that it would not have been between 15.94 and 15.98. But he would never have obtained a value near that which now commands confidence.

It is interesting to recall that there is hardly any instance on record where the judgment of an experimenter as to the degree of approximation to the truth attained in his work has been better justified than in the case of Dumas' classic experiments. As we all remember, towards the end of his work, there was discovered in his own laboratory a source of error, not easy to eliminate, which had affected all his determinations. The amount of the error was not a fixed quantity, and no numerical correction could be applied to the results of observation. Dumas accordingly gave to the public the uncorrected and unmodified results of experiment. But he also stated his opinion as to the degree in which his results approximated, not to the mean of a larger number of experiments of the same kind, but to the unknown and unattainable true value. He expressed the hope that his value would be found not more than one part in 200 from the result of those subsequent experiments which should be thought satisfactory; and it is by just 1 part in 200 that his value differs from that which is now accepted.

So the concordance of Dumas' experiments did not prove that his result was right; neither did the agreement of experiments by different observers. Erdmann and Marchand made eight experiments by a method like that of Dumas, with some modifications. Their result was 15.973, with a probable error of 0.011. This value differs from that of Dumas by less than the sum of the probable errors, so that that agreement is perfectly satisfactory. So, also, Regnault determined the ratio of the densities of oxygen and hydrogen, from which was computed the atomic weight of oxygen as 15.963, with a probable error of 0.004. The results of Dumas, of Erdmann and Marchand, and of Regnault, show a very good agreement. But all of them, and the mean of all of them, we now know to be in error by 1 part in 200.

I adduce this example, somewhat in detail, to enforce the proposition that we must not excuse ourselves from looking for error because observations agree. We have experiments which give the atomic weight of oxygen with a probable error of 1 part in 50,000, but do we know it within 1 part in 1000? Each individual experimenter whose work would now be regarded as free from known and tangible error, agrees fairly well with the mean of all. For instance, Noyes' results show that degree of concordance which would justify us in expecting that, if he were to make 100 or 1000 experiments, his final mean would be as likely as not to be larger or smaller by 1 part in 9500, and his result differs from that which we accept by 1 part in 900. So Cooke and Richards assign a value which is just as likely as not to be within 1 part in 8000 of the result which they would have obtained by multiplying observations; and it differs from that which we accept by 1 part in 1500. But do we know that their means, and the means of all published results taken together, are not in error by 1 part in 900? The concordance of the results of a single experimenter, and the agreement of different experiments, does not justify us in asserting that we do.

In determining the atomic weight of oxygen, it has been somewhat difficult to determine directly all three of the quantities involved, and so to make what Stas called a *complete* synthesis. Berzelius, Dumas, and Erdmann and Marchand, weighed oxygen and weighed water, thus determining hydrogen by difference. More recently, Dittmar and Henderson and Leduc used the same method. Cooke and Richards, and Keiser weighed hydrogen and weighed water, while Rayleigh and Noyes weighed hydrogen and weighed oxygen. Any proceeding which weighs hydrogen directly has a great advantage in precision; different determinations in a given series agree better among themselves, and the series of different experimenters also agree better. But there is also a second, more important advantage. We have reason to believe that the constant errors involved in weighing hydrogen are small, for it is possible to obtain hydrogen with less than $\frac{1}{10000}$ or even $\frac{1}{20000}$ of its weight of impurity. There is no difficulty in weighing oxygen or water with accuracy, so if we weigh hydrogen and also weigh either oxygen or water, we may hope for a near approximation to the true value of the ratio sought.

We may hope, but we cannot *know*. We may believe that our hydrogen is pure, and that there was no error through leakage. But an unsafe stop-cock might make the apparent weight of the hydrogen in a series of experiments seem always smaller than the fact, and might yet leave the individual experiments so concordant with each other as to seem trustworthy.

If, however, we can weigh hydrogen and can weigh oxygen, and then combine them and weigh the water produced, we can at least give a better reason for our hope, if we find that the product is nearly equal to the sum of the components. The manipulation in this case is costly, and is so difficult, and involves so many minute details, that not many have patience and time sufficient for it, so that no great number of such complete syntheses has been made, and these few were made in conditions but little varied. When such complete syntheses shall have been made by different observers, with those variations of apparatus and method which may seem wise to them, we shall be able to judge of the magnitude of the errors to be feared. If such results are not concordant, we shall have much to learn as to sources of error; but we now see some reason to expect that they will not be discordant. However, even if they are not discordant, we are not to excuse ourselves from further study of sources of error.

Before repeating determinations so troublesome, and before studying unknown sources of errors not yet detected, the experimenter should receive all possible assistance from chemical theory and from criticism. For some, that criticism may be most profitable which is friendly and sympathetic; but, for the experimenter, the value of the criticism depends on the knowledge and the acuteness of the critic. Dr. Hinrichs published, some five years ago, a criticism of all determinations and computations of atomic weights since Dumas. As is well known, he is a most strenuous and insistent supporter of Prout's hypothesis. Looking hastily through the volume, there was found, towards the end, evidence that its author was one of those who, some thirty years ago, discerned that which, in the hands of Mendeléeff became the periodic law. It seemed possible that one who had early seen some indications of this law might, perhaps, also have discerned, even if obscurely, some principle relating to atomic weights. I therefore once spent some time and pains in carefully reading the book, and considered at length those passages, which, if any, contained valid criticism of the views which are generally accepted.

Hinrichs believes that the mean of a series of determinations of an atomic weight cannot give the true value sought. This proposition he deduces from a mathematical discussion. He believes that as larger and larger quantities are taken in our analytical operations, the results differ regularly from ideal accuracy; sometimes the difference continually increases as the quantity taken increases; sometimes the difference increases to a maximum and then decreases again. The proper computation of an atomic weight then, according to Hinrichs, consists not in taking the mean of different observations, made with different weight of materials, but in determining the limit towards which the series converges as the weight taken decreases. A good illustration is given: we cannot determine the weight of a new coin by weighing any number of old coins; every coin is worn and therefore light, and the mean weight of any number whatever is therefore necessarily below the mean weight of new coins. But if we weigh old coins and note the date of each, we may take the mean weights for each year separately. If we examine coins enough, these means when plotted as the ordinates with the years as the abscissas, will give us a "fairly regular curve, lowest for the oldest coins, gradually rising towards a *limit* which they would not quite reach. This higher limit would evidently be the mean weight of the new coin."

This is an intelligible proposition. It seemed to me worth while to examine it, for to this proposition one of the most enthusiastic and most active supporters of Prout's hypothesis, a man not lacking in shrewdness or ability or learning, has entrusted the defense of his favorite belief.

He asserts that an atomic weight as determined by experiment is variable, that it depends on the amount of substance taken for the analysis or other operation, and that it varies in a continuous and regular manner. His proposition is, that an atomic weight as determined by experiment is a function of the weight of substance taken. Is there any evidence in favor of it?

I answer, first: Theory does not afford any evidence for it. Hinrichs deduces this proposition from theory by a discussion which is mathematical in form. Whether the proof is sound need not be considered, for his theory does not attempt to show the order of magnitude of the regular and continuous variations which are affirmed to depend on the weight of substance taken, and to show whether they can be separated from the irregular and discontinuous errors due to accident. We are sure that accidental errors exist; we may concede for argument, that regular and continuous variations also exist; but this is far from implying that the actual errors in a given set of experiments will be largely or even perceptibly of the latter kind. Theory shows that there is a diurnal tide in the atmosphere; but theory does not show that the differences noted in a series of ten observations of the barometer at different hours of the day will follow the law of the diurnal tide.

But, secondly: Facts do not agree with the proposition. The accidental errors of the most precise experiments yet made are so much greater than any *systematic* variations, that nothing but accidental variations can be detected. To prove this, let us consider Stas' synthesis of silver nitrate from pure silver. This is one of the most important determinations ever made; Hinrichs has discussed it twice in his volume; he asserts that the ratio of silver nitrate to silver found in each analysis depends on the weight of silver taken, and twice draws curves to show this. I assert, on the contrary, that the errors, which average only 1 part in 40,000, are purely accidental, and that they follow no law. This can be proved by proving that the ratios obtained depend on any other quantities selected by accident just as much as they depend on the weights of silver taken. Hinrichs plots the results of the ten determinations, using for abscissas the weights of silver taken, and so obtains tolerable curves. I plotted the same ten observations, using for abscissas not the weights of silver taken but ten numbers selected by *sortes Virgilianæ*, and get curves quite as tolerable as before; and this I did with ten different sets of abscissas, all selected by pure accident. Now, quantities which depend on any one of eleven sets of abscissas, ten of which are selected by accident, are themselves accidental in their variations, and the variations follow no law. So far as the facts are examined, they give no evidence in favor of Hinrichs' proposition; we have seen that theory is equally chary of her support, and we may safely dismiss the suspicion that any source of systematic error can be detected in deducing atomic weights from the means of good experiments.

Within the limits of convenience, it is well to vary the amount of substance taken in analytical determinations. This has been a frequent practice in the finest investigations. But that this practice derives any support from the so-called 'limit method' cannot be conceded.

This criticism, this attempt at a theory, then, removes no obstacles and reveals no threatening pitfalls. If we desire a firmer foundation for our system of atomic weights we must simply enlarge the experimental basis of our knowledge.

If it is only by further experiment that we can make surer of the atomic weight of oxygen, we are to consider what kind of experiments is most desirable. It is chiefly for the sake of eliciting discussion on this point that the subject of this address has been chosen.

Our present value for the ratio between oxygen and hydrogen rests on one single chemical combination, and upon two processes for determination. The first is, the synthesis of water from its components. The second is, the determination of the densities of the gases and of their volumetric ratio. Let us consider these in order.

What synthetic experiments should be repeated? We are met by the fact that a complete synthesis, in which hydrogen and oxygen and water are all three weighed, can be made with errors only about one-fourth as large as the errors in any of the syntheses where only two substances are weighed out of the three concerned. Other things being equal, then, this process is by far the most promising. But, so far it has been carried out adequately by only one experimenter. Conditions were varied somewhat, it is true, but by no means so much as they would be varied if the same person repeated the experiments after an interval of years; by no means so much as if others were to undertake such complete syntheses. Lately, Keiser has devised a process which varies in many particulars from that already executed; it is very desirable that he should make a series of experiments, after adequate study of sources of error and of means of avoiding them. It is also desirable that, if possible, the original process of complete synthesis should be repeated with the little modifications which time is sure to introduce. These two would be enough, as far as synthesis is concerned; unless, indeed, through the invention of another process by a third experimenter, we could have still more. Other syntheses of water than by a *complete* synthesis seem less likely to be of much service, except as a school of experimentation.

What further work is desirable on the ratio of densities and of combining volumes of hydrogen and oxygen? Three constants are involved: the density of oxygen, the density of hydrogen, and the volumetric ratio.

The density of oxygen is known with a probable error of about 1 part in 50,000. It is very probable that no number whatever of further determinations would change this value by 1 part in 10,000. No further work upon this density seems at present desirable, except that whoever determines the density of hydrogen cannot well fail to determine that of oxygen also.

The density of hydrogen demands further experiment. It is possible to make, by some one of three or four slightly different processes, a series of experiments whose average variation shall be less than 1 part in 3000 or 5000, or even 10,000; but different series do not agree sufficiently with each other. We are far from knowing the density of hydrogen so well that more observations might not change our value by 1 part in 2000 or 3000. It is very desirable that further observations should be undertaken by at least two different methods. In one method, hydrogen should be weighed while absorbed in palladium, should be then transferred to a measuring apparatus without the use of stop-cocks, and should be there measured. This process should be repeated with measuring apparatus of varied volumes. In another method, hydrogen should be weighed after Regnault's method, in a counterpoised globe, but with such precautions that leakage through a stop-cock, and contamination with vapor of mercury, should be excluded. The globe should be exhausted till the remaining air is a small fraction of a millionth, should be sealed off from the pump, and should be connected with a condenser at the temperature of liquid air, so as to remove mercurial vapor. After this hydrogen is to be admitted without the use of stop-cocks. The manipulation is not difficult, and the method would confirm the results of the previous method.

The ratio of the combining volumes of hydrogen and oxygen is not known with the degree of confidence which is desirable. The history of the matter is not an uninteresting one. Further continuance of the two series of experiments on which the present value depends would be most unlikely to change it by 1 part in 10,000, for its probable error is 1 part in 40,000. But one of the experimenters has obtained results differing from that finally adopted by as much as 1 part in 220. The other experimenter has entirely discarded the result of one series and replaced it, not by a better series of the same kind but by one of a quite different nature, not carried to its proper completion, and accordingly reduced by the use of the constants of van der Waals' equation. It is desirable that experiments be made to furnish means for a new reduction by measuring the change of volume when 2 volumes of hydrogen and 1 volume of oxygen are mixed, being at the same pressure before and after mixing. This experiment has lately been made by Berthelot, whether with sufficient precision for the purpose is not known at this moment. It is also desirable that the ratio of the combining volumes of oxygen and hydrogen should be measured with the gases contained in vessels of the dimensions of those used for obtaining their densities.

If these syntheses and these studies of ratios of densities and combining volumes should agree as well as it is safe to expect, we should know the atomic weight of oxygen as confidently as we can know it while the value rests on a single chemical process, the combination of the two gases to form water.

But this is not so much as is desirable. We know the atomic ratio between silver and oxygen with considerable confidence, because this rests not on a single chemical process but on eight different chemical processes, which give eight independent results, and because these eight results agree. Is there, then, any chemical process by which the atomic ratio of oxygen and hydrogen can be determined, other than the analysis or synthesis of water? Is there any element whose atomic ratio to oxygen is well known, whose ratio to hydrogen is capable of accurate direct determination?

It is probable that, given an adequate equipment, the direct ratio of hydrogen to chlorine, of hydrogen to sodium, of hydrogen to magnesium, or of hydrogen to aluminum, could be determined with sufficient precision for the purpose, provided that the ratio of chlorine to oxygen, of sodium to oxygen, of magnesium to oxygen, and of aluminum to oxygen are well enough known. This may not now be the case with aluminum or magnesium, but is the case with chlorine and with sodium, whose atomic ratios to oxygen may be fairly assumed to be known within 1 part in 2500. If, now, we can determine the ratio of chlorine to hydrogen, or of sodium to hydrogen, to 1 part in 5000, we could compute, by a new method, the ratio between hydrogen and oxygen. If this should agree with the present value, within some such quantity as 1 part in 2000, we should be as confident of the truth of our value of the atomic weight of oxygen as we can well hope to be.

The difficulties in making a complete synthesis of hydrochloric acid are not small, nor are they all well understood. Some unexpected circumstance may be prohibitive. But there is good reason to hope that 3 or 4 or 5 grams of hydrogen could be weighed, that a nearly equivalent quantity of chlorine could also be weighed, that the two could be combined, and that the product could be weighed. One serious difficulty would be found in attempting to prepare pure chlorine, but the difficulty does not seem insuperable. The manipulation of the corrosive element requires invention, but seems not difficult. For the collection of the hydrochloric acid in a weighable form, there seem to be alternative methods, not very troublesome of execution, unless unforeseen difficulties are encountered. If the ratio between hydrogen and chlorine could be determined to 1 part in 5000 or to 1 part in 10,000, it would be a very interesting addition to our list of known constants, most helpful in establishing confidence in the ratio between oxygen and hydrogen.

So, also, if sodium can be prepared of sufficient purity, or of sufficiently constant impurity, it seems possible to weigh 100 or 200 grams, to act on with water in such a way as to produce a slow evolution of hydrogen, and to determine the weight of this hydrogen by loss. Whether sodium can be obtained sufficiently free from absorbed hydrogen and whether it can be prepared for weighing without attacking the vessels which contain it, are questions which need further experiment. It is probable that a vessel of platinum-iridium alloy could be made which would make success almost certain, but at considerable cost. In this case also, if the ratio between sodium and hydrogen can be determined to 1 part in 5000, or 1 part in 10,000, the result would inspire confidence, or, if it must be, distrust, in our present value for the ratio between oxygen and hydrogen.

These suggestions, necessarily tentative in their nature, are submitted to the American Chemical Society, in the hope of obtaining from those who do me the honor to listen to them or to read them, expressions as to the desirability of making experiment in the lines described, and discussions of the new methods indicated as possible.

Edward W. Morley.

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CRUISE OF THE ALBATROSS.

III.

Mr. Agassiz's third letter written from the *Albatross* to Hon. George M. Bowers, U. S. Commissioner of Fish and Fisheries, is dated Suva Harbor, Fiji Islands, December 11, 1899, and is as follows:

We left Papeete, November 15th, after coaling and refitting on our return from the Paumotus. During our trip to Suva we made a few soundings from Tahiti to Tonga, striking the northern extension of the deep basin lying to the eastward of Niue; the depths ranged from 2472 to 2882, the bottom being red clay. This would indicate a greater extension westward of the zone over which the manganese-nodule bottom extends.

After leaving Niue we steamed for the deep hole of the Tonga-Kermadec Deep, about 75 miles to the eastward of Tonga-Tabu, and in 4173 fathoms made a haul with the Blake beam-trawl, by far the deepest trawl haul yet made. The gear was carefully inspected and strengthened as far as practicable by Captain Moser, and it was with considerable anxiety that we laid out 5000 fathoms of wire rope for our haul. Fortunately, everything went off successfully and we landed the trawl safely back on deck. To my great surprise we found in the bag a number of large fragments of a silicious sponge belonging probably to the genus *Crateromorpha* which had been obtained by the *Challenger* in the Western Pacific, but in depths less than 500 fathoms. We also brought up quite a large sample of the bottom; it consisted of light brown volcanic mud mixed with radiolarians.

We decided to trawl at 4173 fathoms rather than wait for a possibly deeper sounding, as the conditions for work were admirable and we did not care to run any risk from a change of weather. After our haul we made a still deeper sounding in the proximity of the 4762-fathom sounding marked on the chart, and found 4540 fathoms with the bottom of the same character as at the place where we trawled. We also took a couple of soundings in the line from Vavau to the southern extremity of the Lau Group in Fiji, but found, as we expected from the soundings given further south, comparatively shoal water, viz., 1381 fathoms. In the channel north of Yangasá, where we crossed the Lau Plateau between Yangasá and Mothe, we found 453 fathoms, with bottom composed of coral sand, pteropod ooze and a few globigerinæ. Between Namuka and Yangasá we obtained 324 fathoms, between Namuka and Marambo 600 fathoms, and between it and Kambara 450 fathoms, and finally about 15 miles west of Kambara we sounded in 990 fathoms. These soundings would indicate a continuous plateau of moderate depths from Wailangolala south upon which the islands of the Lau Group rise.

On our way back to Papeete from the Paumotus we examined the eastern coast of Tahiti, and from Papeete examined the western coast as far as Port Phaeton at Tararao Isthmus. We examined in a general way the Leeward Society Islands: Murea, Huaheine, Raiatea, Tahaa, Bora-Bora, Motu Iti and Maupiti. There are