FUNDAMENTAL CHEMICAL CONSTANTS.¹

BY

PROF. EDWARD WILLIAMS MORLEY.

A MAN indulges in scientific research because it is fascinating. It gives more pleasure than golf; and, to have added to it so delightful a recognition as that given to me to-night, both in the medal and certificate, and also in the words introducing me, adds much even to the delight of successful research.

It was suggested that my topic should discuss the fundamental constants of chemistry. The importance of physical constants is, largely, that one of them holds condensed in small volume the essence of many observations, perhaps of all the observations which have ever been made in a given line. We have followed the motions of the planets with accurate observation for two hundred and fifty years. The number of observations is very great; the labor of consulting them would be enormous. But all their value has been extracted and condensed in a system of constants, seven for each planet. All planetary positions are wrapped up in these constants; from them, positions for the future can be unfolded as desired, with an accuracy corresponding to the accuracy with which the constants are known at a given time. A constant is compressed knowledge; it is like a seed, ready to grow and bud and blossom and fruit. The constants of chemistry are not so intricate as those of astronomy, and the labor of establishing them, although considerable in some cases, has not been so great as in the case of astronomy.

Chemical constants vary in nature and importance, and vary in their interest for the man who is not a chemist. Some are like words in a dictionary or figures in a mathematical table. It is needful that such constants be determined and tabulated, in order that a call for any one of them may be answered without delay and waste of time. For instance, a scientific man at present is endeavoring to find whether the properties of a compound are

¹Presented at the Stated Meeting of the Institute, Wednesday evening, May 15, 1912, when Prof. Morley received the Institute's Elliott Cresson Medal.

functions of the changes of energy taking place in its formation from its elements. To examine this matter, he will need to know the melting point and the boiling point and the critical temperature of some well-known elements and of their best-known compounds. Then he will doubtless need to know the density of each, in the solid form, and the liquid and the gaseous; and then greatly to enlarge this list of measurable and well-determined properties. If most of these constants are already determined, he may be able to enrich our conceptions of the nature of the material universe within some short time; if they are not ready for him, he cannot find what he desires, and the world will be the poorer.

Some chemical constants are tools with which to increase human comfort, or human wealth, or the effective power of human effort. The knowledge of some thermal constants of certain steels enables us to add immensely to the strength and durability of steel constructions under strain,—to double or quadruple the strength of a crank shaft.

Other chemical constants are poems, or prophecies, or histories. It is of such constants that I wish to speak. They show us something about the nature of matter, which is the most interesting thing in the world, except human nature with its varied expressions. Excepting the study of human nature, the study of the nature of matter is the most fascinating subject open to us.

The fundamental constants of chemistry are the atomic weights. These were first investigated in order to fill up the pages of our dictionary. They were further studied in order to increase the effective power of human effort, as tools in analytical processes. But, while these constants were obtained for these prosaic ends, we find, to our great delight, that they perform the added service of assisting somewhat our insight, limited as it is, into the nature of matter.

About a century ago, Prout announced the theory that all atomic weights are integral multiples of the atomic weight of hydrogen. For example, the atomic weight of lithium is nearly equal to seven. Prout asserted that, when it is determined with final accuracy, the number will be *exactly* seven, and not nearly seven. So the atomic weight of carbon is about twelve, and that of oxygen about sixteen. Prout asserted that these numbers, when exactly determined, will be the exact whole numbers, twelve and sixteen.

The suggestion was a valuable one. It stimulated some of the best work which has been bestowed on atomic weights, and was well worth the great labor which it has stimulated. It was a long time before results were obtained sufficient to settle decisively the matter. One early result caused a modification of the theory. The atomic weight of chlorine was found to be not a whole number, but a number nearly equal to 35.5. The result of many most rigorous and exhaustive experiments gives the value 35.45, when oxygen is taken 16.00; accordingly, Prout's hypothesis was modified to assert that, when finally determined, it will be found to be exactly 35.50, an integral multiple of *half* the atomic weight of hydrogen. Subsequent modifications of the original theory assume the fourth or even the eighth part of the atomic weight of hydrogen as the basis.

If the theory were known to be true, it would allow an immense saving of labor. For instance, in determining the atomic weight of oxygen, if we were authoritatively informed that it must be either 15.50 or 16.00 or 16.50, we need only to make experiments rigorous enough and numerous enough to show that it is more than 15.5 and less than 16.5. Instead of the difficult process of *measuring*, we merely have to use the simple process of *counting*. Measuring must always be attended with errors, which cannot be eliminated except in part, and the avoiding of errors and the reducing of errors till they are negligible is a long and difficult process. But counting is affected, not with errors, but with blunders, and blunders can be avoided. In case of objects like atoms, which we cannot see, counting has to be effected by weighing; but a hundred sovereigns can be counted by weight without seeing the individual sovereigns, and can be counted with absolute precision by weighing with an accuracy of one-fourth of one per cent. But to pay out the same value of uncoined gold, we must weigh to the hundredth part of one per cent. So, if Prout's hypothesis were known to be true, an accuracy of one or two per cent. would show that the truth was 15.50 or 16.00; while, if the hypothesis cannot be assumed for our guidance, an accuracy of one-hundredth of one per cent. is barely sufficient. So, if the theory were proved to be true, it would permit an immense saving of labor from the time it was adopted as a guide, but there is a more interesting result from the truth of the hypothesis. It suggests a theory of the structure of matter. It

suggests that the atoms of many elements, perhaps of all, consist of the same identical matter put up in packages of different weight. Hydrogen consists, according to one form of this theory, of two ultimate particles so adhering to each other that they are never separated in any chemical process known to us. Carbon consists, according to the theory, of twenty-four such ultimate particles, so held that chemical forces cannot separate them. So with oxygen, consisting of thirty-two; so with chlorine, consisting of seventy-one.

There has been much difficulty in determining atomic weights with a degree of accuracy sufficient to pronounce upon Prout's hypothesis. Even when they are determined as accurately as is now possible, some difficulty remains, at least in some minds, for many of the well-determined atomic weights were found to be curiously near to whole numbers. Perhaps the most serious difficulty, for a long time, was that we did not know the atomic weight of oxygen with sufficient accuracy. It so happens that most atomic weights are determined, as a matter of fact, by experimental comparison with oxygen, sometimes directly and sometimes indirectly. The atomic weight of carbon is determined by direct comparison with oxygen. Experiment shows that twice sixteen parts by weight of oxygen combine with twelve parts by weight of carbon. If, for the present, we assume sixteen as the atomic weight of oxygen, twelve is obviously the atomic weight of carbon, determined by direct comparison with oxygen. The atomic weight of potassium is determined by an indirect comparison. Five times sixteen parts by weight of oxygen combine with twice 35.45 parts by weight of chlorine, and 35.45 parts by weight of chlorine combine with 39.15 parts by weight of potassium, so that 39.15, by this indirect comparison, is the atomic weight of potassium.

Since oxygen is thus used as an intermediate term of comparison in most cases, we see that, in order to determine whether a given atomic weight is a multiple of the atomic weight of hydrogen, or of half of the same unit, we need to know with accuracy the atomic weight of oxygen referred to the same unit. To determine it has been difficult. Dumas, in a piece of work which will long be regarded as a classic of science, about the year 1842, made a series of determinations by the best method known at the time. As he was finishing the work, there was detected in his

laboratory a source of error attending all his experiments. He expressed the hope that his results were within the two-hundredth part of the truth, and his judgment was wonderfully accurate, for his final result was just the two-hundredth part too large. This result could by no means determine whether the atomic weight of oxygen is the whole number sixteen or is a tenth of a unit more or a tenth of a unit less. This same range of uncertainty becomes more troublesome in the case of larger atomic weights; it amounts to a quarter of a unit in the case of potassium.

To determine whether Prout's hypothesis or some of its modifications is true, it became necessary to determine the atomic weight of oxygen with far greater precision than attained by Dumas. It was found impossible to utilize the method of Dumas; although several of its sources of error can be removed, the annoying retention of water by the copper reduced from its oxide in the experiment could not be avoided in a workable apparatus. Using methods devised for the purpose, hydrogen was prepared containing less than $1/200,000$ part of impurity. That is a simple matter to mention, but it took many months to accomplish! The proving that the impurity was as stated took six months, and required more invention than a little. Next, oxygen was prepared, of corresponding purity. That was really easy. These two were then separately weighed, were combined to produce water, and the water was weighed. The weight of oxygen used divided by that of the hydrogen used gave the atomic weight of oxygen. The weight of water produced divided by that of the hydrogen gave a second value of the atomic weight of oxygen. The fact that these two determinations agreed showed that there was no source of important error in the experiment.

To confirm the result obtained, the density of hydrogen was compared with the density of oxygen, and the ratio of the volumes in which they combine was determined. Multiplying these two ratios together, we secure a new determination of the desired atomic weight. For determining the density of hydrogen, no method heretofore used was found to be sufficiently accurate. A process was invented, in which hydrogen was absorbed in palladium and sealed up in a glass vessel. Globes holding forty litres were exhausted and sealed up by fusion. Then the hydrogen, sealed up by fusion in one vessel, was introduced into the sealed globes, without opening them to the air, after which vessel and

globes were left sealed by fusion. Weighing the vessel before and after, we learned the weight of the hydrogen used in the experiment; measuring the temperature and pressure of the hydrogen in the globes, we had accomplished the determination of the density of hydrogen without the use of stop-cocks, which leak, and without introducing any impurity into the hydrogen derived from apparatus through which it is passed. The density of oxygen was easily determined by usual processes, carried out with many precautions to ensure precision. Now, if it were true that two volumes of hydrogen combine with one volume of oxygen, the ratio of the densities would be the ratio of the atomic weights. But it is not precisely true that two volumes combine with one; we had, therefore, to determine what the accurate ratio is, and then correct the ratio of the densities. Since the value thus determined agrees with the two previously found, and since all three agree much nearer than to one part in ten thousand, we are entitled to feel much confidence in the mean result. This value is 15.879.

I am moved to mention a little matter which shows how a scientific man tries to keep himself free from unconscious bias. The determination first mentioned consisted of twelve experiments, in three or four series. In order not to be biased, the results were not computed from the weights observed, until the experiments were all completed. When you test the accuracy of the sights of a rifle, it is well to fire the string of shots without inspecting the target; then it is made sure that one does not unconsciously draw a bead differently on learning of the ill success of the previous shot. So, also, the agreement between the result of the synthetical experiments and those on densities was not known to me till the manuscript had been accepted for publication by the Smithsonian Institution; after that time, I went to Washington and completed the computations and first knew how well the two results agreed. The scientific conscience is rather rigorous.

This fundamental chemical constant is, I think, somewhat more than a figure in a mathematical table, or than a tool to facilitate analyses. It tells us something about a long-discussed question, and asserts a proposition concerning the nature of matter. The atomic weight of oxygen is not exactly sixteen, not 15.50, nor 15.75. Prout's hypothesis finds no support in

the most carefully determined atomic weight of oxygen, the only weight which up to that time had been determined by direct comparison with hydrogen, and a determination in which no source of important error has been suggested.

Further, now that we know the atomic weight of oxygen, we are ready to compare other atomic weights with that of hydrogen. If the atomic weight of oxygen is 15.88, then the atomic weight of carbon becomes 11.93, and that is not a whole number, nor a number ending in the fraction one-half, nor one-quarter, nor three-quarters. The atomic weight of chlorine, now that we know the atomic weight of oxygen, becomes 35.18, and that of potassium becomes 38.82; neither of these numbers is in accord with Prout's hypothesis. There are two other well-determined small atomic weights which equally fail to support the hypothesis in question. The onus of proof lies with small atomic weights. If we imagine, for the sake of argument, that the atomic weights best determined are liable to an error of one part in a thousand it is obvious that a small atomic weight, like that of carbon, is liable to an error of not more than a hundredth of a unit, which still leaves its evidential value uninjured. But an atomic weight like that of lead, which is over two hundred, is liable to an error of two-tenths of a unit, from which no conclusion could be drawn as to Prout's hypothesis. The small atomic weights which are well determined utterly fail to support Prout's hypothesis. So far as chemical methods now known can throw light on the matter, Prout's hypothesis cannot be true.

I presume that it will still have its adherents. One cannot but wish that the theory had been true, even when he admits that no modification of it which is consistent with sound physical principles has any support in the facts. Ingenuity can still modify the theory, and can make a modified theory which could not be disproved by experiment. We might assert that all atomic weights are integral multiples of one-hundredth or one-thousandth the atomic weight of hydrogen. That is like striking a ship to escape capture; the ship is no longer of service. A child, learning that ten dimes make a dollar, and knowing that a bank sometimes pays out five dollars in the form of a rouleau containing fifty dimes, might form the whimsical theory that all our silver coins consist of the proper numbers of dimes compressed till they adhere. He may imagine that a half dollar consists of

five dimes, hammered together, and a dollar of ten, which retain their identity and could conceivably be separated, though perhaps somewhat flattened and defaced. If, now, the child learns that a dollar weighs more than ten dimes and a half, he may, if the theory has become attractive to him, form a modified theory, according to which the dime is made up of two half dimes, compressed and adherent, and the dollar of twenty-one half dimes. If he next learns, by more accurate weighing, that the dollar weighs as much as 10.82 dimes, he may say that the number really is $10\frac{3}{4}$, and that the dollar is made up of forty-three quarter dimes. He might equally well say that it is composed of fifty-four fifths of dimes, or of sixty-five sixths of dimes; there is no end of possible suggestions, if he must maintain his early belief without evidence or in the face of evidence.

But civilization and science tend to put away childish things. The humble efforts which you have this evening rewarded with the Elliott Cresson Medal have been efforts to obtain evidence on a most attractive but illusory theory. It is delightful to know that the work of J. J. Thomson and others in a new field affords a more promising basis for speculations on the nature of matter, and so takes away our regret that the theory of Prout has given only negative assistance in that inquiry.

Density of Aluminum. ANON. (*Amer. Mach.*, xxxvi, 10, 388.)—Owing to the high purity of commercial aluminum of the present day, as compared with that on the market several years ago, at which time the density and coefficient of linear expansion of the metal were determined, these data were re-determined by Dr. F. J. Brislee, who reported his results at the sixty-first general meeting of the Faraday Society. The metal used contained aluminum 99.5 per cent. and about 0.25 per cent. each of silicon and iron. The density of cast metal was 2.708, that of hard-drawn rod was 2.705. Remelted aluminum had a density of 2.68, perhaps due to absorbed nitrogen. The coefficient of linear expansion of hard-drawn aluminum is:

$$Lt = L (1 - 0.00002432 t),$$

and for annealed aluminum it is—

$$Lt = L (1 - 0.00002454 t).$$

The figures given above for density are much higher than that usually ascribed, 2.583, as is also Dr. Seligman's 2.727 for the density of rolled aluminum sheets.