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ATOMIC WEIGHTS.[1]

BY THEODORE W. RICHARDS.

Mr. Chairman, Ladies and Gentlemen;

I cannot find words to tell you how highly I appreciate the great honor which you have conferred upon me by the presentation of this valuable medal. I shall prize it among my choicest treasures, and its possession will always be to me an incentive and an inspiration to further effort. No earthly reward is greater than the good will of one's friends and nearest colleagues; and this medal brings with it a message of just such good will. Your kind act has deeply touched me, and the memory of this evening, of your most hospitable reception, and of all the kind words and acts which you have showered so bounteously upon me, will remain to cheer me throughout all the years which are to come. Once more, let me express my heartfelt appreciation of this very high honor, and my very sincere and grateful thanks.

We have come together to-night in memory of the genius of Josiah Willard Gibbs. As long as our civilization persists, the name of this eminent man will stand high on the roll of the great thinkers of all nations. Born in New Haven seventy-three years ago, of excellent stock, Willard Gibbs lived the quiet and uneventful life of a professor of mathematical physics in Yale University; and when he died in 1903, the nation as a whole little realized that we had lost one of our greatest minds. So it was with that great Italian nobleman of the last century—the physicist Amadeo Avogadro di Quaregna—who like Willard Gibbs left a chemical legacy of priceless value, and whose fame was destined to reach its full magnitude long after his mortal career was finished. Doubtless the

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[1] An address presented before the Chicago Section of the Society on the occasion of the award of Willard Gibbs Medal, May 17, 1912.

future has still much to discover in the recondite works of our present hero; and that which is now understood by the few, will later be magnified by the many.

The competent testimony of my honored predecessor, Svante Arrhenius (who is, as Willard Gibbs was, a towering figure among the leaders of physical chemistry), emphasizes the unique position of the Connecticut thinker. Arrhenius declared him to have been ahead of the great Helmholtz, both in chronological order and in the fulness of his mathematical analysis; and no one who has really studied his abstract discussions will be apt to dispute this estimate. The generous founder of the present occasion, William A. Converse, is to be congratulated for commemorating the extraordinary services of this remarkable man.

As you are aware, the Willard Gibbs Address to-night has to do with atomic weights. We all know that the atomic weights are those multiples of the chemical combining proportions which are generally taken to represent the relative weights of the imaginary atoms of the tangible chemical elements. But what do we mean by "atoms" and "elements?"

Within the last fifteen years the definition of these two words has been rendered somewhat uncertain, and bids fair to suffer even further change. Both of them are ancient words, and both even a century since had acquired meanings different from those of long ago. Thales thought of but one element, and Aristotle's elements—earth, air, fire, water and the quintessence, derived perhaps from yet more ancient philosophy—were not plentiful enough to account for all the manifold phenomena of nature. Democritus's old idea of the atom was associated rather with the philosophical conception of indivisibility than with the idea of chemical combination in definite proportions. To-day many chemists and physicists think that the chemical atoms of the last century are no longer to be considered as indivisible. In that case, the old Greek name "atom" is no longer fitting, because it denotes indivisibility. Moreover, if our so-called atoms are really divisible, we cannot but be somewhat doubtful as to our definition of the ultimate elements of the Universe.

But, after all, interesting and significant as are these considerations, the fact remains that the ordinary reactions upon which life depends, and the ordinary phenomena which take place immediately around us on the earth, are explicable by reference to the chemical atoms of Dalton and Avogadro. For all practical purposes the elementary substances may still be regarded as undecomposed (even if not perhaps absolutely incapable of decomposition) in all our chemical considerations concerning earthly phenomena, except concerning the very small fraction of those phenomena which involve the abnormal changes associated with radioactivity. Therefore, we may safely retain the term *chemical elements*, as applied to the eighty or more substances which are not decomposed in any of the ordinary changes of life, and which mankind has hitherto been powerless to alter. Whether we should call radium and its extraordinary cousins elements or not is less clear; but no new discoveries in radioactivity seem likely to suggest any essential change in our present explanation of definit and multiple combining proportions—laws which our idea of the chemical atom so satisfactorily elucidates.

To-night we have to do with the determination of the relative weights of these chemical atoms—a field of chemical research in which great precision has been sought. The reason for attempting to attain unusual accuracy in the evaluation of atomic weights is not always understood. Some evidently think that in this case great precision is striven after merely for its own sake. This is a commendable aim, but as in the case of all commendable aims, its prosecution should be kept within due bounds. An experimenter, dominated by the love of accuracy alone, is likely to fritter away his time on trivialities. Although at all times sufficient precision for the case in hand should be faithfully sought, very high accuracy is not always needful. Where an approximate result will amply suffice, it would be a waste of time to seek the highest order of exactness.

In the case of atomic weights, on the other hand, no degree of accuracy can be too great; the greatest attainable should be the object of the quest. The reason for this search after a maximum degree of precision lies in the peculiar nature of these numerical magnitudes. They are properties of matter in the most general sense, and not the properties of any particular bodies. For example, the atomic weight of copper in a milligram of copper sulfate is the same as that in a ton. They are, moreover, quantities which no man by taking thought can change, and so far as we know they are quantities not to be annihilated by any cosmic cataclysm. In more than one case I have been able to show that material from very different parts of the earth gives always the same results. We have reason to believe that under the conditions familiar to us the values are the same in the most distant worlds as in our own. Not only stellar spectra, but also the identity of meteoric with terrestrial iron, as proved by Baxter, demonstrate this fact.

The objection has been raised that perhaps, even if constant in a given place at a given time, the atomic weights may be subject to cosmic variations over great periods of time. To this argument, recent research on radioactivity has added emphasis. If they are thus variable, is it worth while to expend much labor in determining the values which they happen to possess at any one time under any one set of conditions?

To this question, an emphatic negative must at once be answered. If atomic weights are capable of change "the circumstances accompanying each possible variation must be determined with the utmost precision in order to detect the ultimate reason for its existence. As Democritus said long ago, 'the word chance is only an expression of human ignorance.' No student of natural science who perceives the dominance of law in the physical universe would be willing to believe that such variation in a fundamental number could be purely accidental. Every variation must have a cause, and that cause must be one of profound effect throughout the physical universe. Thus the idea that the supposed constants may possibly be variable instead of invariable adds to the interest which one may reasonably take in their accurate determination, and enlarges the possible field of investigation instead of contracting it."[1] As yet, however, no evidence is at hand indicating any appreciable changes in the atomic weights under circumstances known to us.

Although, apparently, these numbers were determined at the birth of the universe, they are, philosophically speaking, in a different class from the purely mathematical constants such as the relation of circumference to the diameter of a circle. 3.141592 is a geometrical magnitude entirely independent of any kind of material, and it therefore belongs in the more general class of numbers, together with simple numerical relations, logarithmic and trigonometric quantities, and other mathematical functions. On the other hand, the atomic weights, although less general than these, are much more general and fundamental than the constants of astronomy, such as the so-called constant of gravity, the length of the day and year, the proper motion of the sun, and all the other incommensurable magnitudes which have been more or less accidentally ordained in the cosmic system. The physicochemical constants, such as the atomic weights, lie in a group between the mathematical constants and the astronomical "constants," and their values have a significance only less important than the former.

In dealing with this question we need not venture far into the domains of philosophy. For our present purpose it matters not if the whole universe is the figment of a dream. Supposing this to be the case, then our problem is to compare the practical numerical relations of certain definit images in this dream. Thus one may study the atomic weights in a way entirely independent of any ultimate philosophy of the universe; but on the other hand no creditable philosophy of nature can afford to ignore our results or our conclusions.

As I have more than once said, the atomic weights seem to be concerned with the ultimate nature of things, and must have been fixed at the very beginning of the universe, if indeed the universe ever had any beginning. They are silent, apparently unchanging witnesses of the transition from the imagined chaos of old philosophy to the existing cosmos. The prime object of the most searching work upon the atomic weights is to attain

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[1] Inaugural lecture at the University of Berlin, May 4, 1907. *Science*, Sept. 6, 1907.

knowledge which may disclose their real meaning, and therefore make clear the underlying causes of those undoubted family relationships between the elements which are partly exhibited and partly hidden by that great cosmic puzzle, the periodic system. No trouble is too great to be devoted to this discovery, for it would "afford us an immeasurably precious insight into the ultimate nature of things."[1]

But how can such remote scientific knowledge, even if it satisfies our ever-insistent intellectual curiosity, be of any practical use? Who can tell? "Faraday had no conception of the electric locomotive or the power-plants of Niagara when he performed those crucial experiments with magnets and wires that laid the basis for the dynamo. When mankind discovers the fundamental laws underlying any set of phenomena, these phenomena come in much larger measure than before under his control and are applicable for his service. Until we understand the laws, all depends upon chance. Hence, merely from the practical point of view of the progress of humanity, the exact understanding of the laws of nature is one of the most important of all the problems presented to man; and the unknown laws underlying the nature of the elements are obviously among the most fundamental of these laws of nature."[2]

In any study of this sort one must always base his labors upon the foundation already reared by others, and it is a pleasure to acknowledge here the debt which the modern work owes to those who have gone before. To Dalton, whose idea inspired Berzelius, to that great Swede himself, to Marignac, who improved some of Berzelius's work, and to Stas, who combined the knowledge of Dumas, his teacher, with that of Marignac, we owe a great debt of gratitude for their painstaking and unprejudiced search after the true values of the atomic weights. I am glad, too, to express my obligation to my own old teacher, Josiah Parsons Cooke, who was during forty-four years Erving Professor of Chemistry at Harvard, as well as to the succession of earnest and able collaborators, assistants, and students, whose devoted help has greatly augmented both the quality and the quantity of the Harvard work.

Besides the chemical knowledge inherited and acquired by the old masters, the modern investigator of atomic weights must possess an acquaintance with many physicochemical relations undreamt of in those early days. As Böttger declared in his recent comparison of Winkler's work on the atomic weight of nickel with that at Harvard, the more recent experimenter, if he experiments with his eyes open and his brain alert, is bound to penetrate more deeply into a chemical subject than the chemist of fifty years ago. Accordingly, as Böttger points out, the Harvard work was successful, whereas Winkler's was not.

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[1] Faraday lecture, *Trans. Chem. Soc.*, 99, 1202 (1911).

[2] "Methods Used in Precise Investigation," *Carnegie Inst. Pub.*, 125, 98 (1910).

This physicochemical knowledge is nowhere of greater service than in the first step which every one must take, at the beginning of a research upon the atomic weights, namely, the choice of the material upon which he is to experiment. It is not too much to say that much of the success of modern work is due largely to the wise choice of material. From some compounds, owing to their tendency to hydrolyze, or to absorb water which may not be driven off without decomposition, or perhaps on account of the variable valence of one of the elements concerned, or for some other reason, no results of any value can be obtained. Usually the choice narrows down to one or two compounds, which are so much the best—either on account of the ability to prepare them in a pure state or because, after they have been prepared, they may be analyzed with exactness—that no others deserve consideration. F. W. Clarke has more than once expressed an earnest desire that as many different compounds of each element as possible should be analyzed so as to have as many checks and cross-references as may be, and I heartily sympathize with this wish. On the other hand, a bad result is worse than nothing in such matters; and many compounds can only be got to give a bad result, no matter how carefully the analysis is conducted. A few good results of a really reliable nature, even if they are somewhat similar and involve but few elements, are far more significant than any number of figures derived from uncertain substances or doubtful analyses. For this reason the work at Harvard has largely confined itself to the halides of the metals, because these may be analyzed with unusual precision. One great advantage from this similarity of method in the different cases may perhaps be mentioned, namely, the fact that since the metals are compared under similar circumstances, we may suppose that relatively to one another the results may be very trustworthy. Even if one should discover some now wholly unsuspected fault in the relation of the metals to the halogens, this fault would probably appear in all cases, and all the results would be similarly affected. Therefore the relative values of the various metals are likely to be correct, even if the absolute ones should be proved to be in error. At present, fortunately, one is not driven to take advantage of this comforting conclusion, because all the evidence from many points of view seems to indicate that analyses of the halides yield not only relatively accurate results but also figures of great absolute trustworthiness.

There is not time to-night to review in detail all the modern work on atomic weights, or even to discuss minutely that concerning the revision of the atomic weights of the thirty elements which have been investigated at Harvard; nor is there time to treat adequately all the sources of error to which special determinations are liable, nor all those devices which must be used in order to render these innocuous. Those of you who desire a more comprehensive idea are referred to a book published by the Carnegie Institution of Washington, called "Determinations of Atomic Weights."[1] This Institution has generously subsidized the work in recent years, and without its help the results would have been much poorer both in quality and quantity.

Although details must be omitted, a sketch of my work may nevertheless be of interest. The first problem which I undertook, more than a quarter of a century ago, was the determination of the ratio between oxygen and hydrogen, under the guidance of Cooke. We weighed the hydrogen directly in large glass globes and, after having burnt it with copper oxide, determined the weight of water formed. The outcome, when all corrections had been applied, gave a result for hydrogen only 0.0004 different from the value 1.0078 now generally accepted, since the publication of the later magnificent work of Morley and W. A. Noyes. This error is less than one-twelfth as large as the error of the result previously considered as the best.

During the work on oxygen and hydrogen it was necessary to study very carefully the preparation of the oxide of copper, which was found to exhibit so many peculiarities as to cause doubt concerning the accepted atomic weight of copper, partly derived from the analysis of the oxide. Thus began a research which lasted four years and involved the study of many methods and many compounds of copper.

It was proved conclusively that the copper oxide which had been previously used for determining the exact ratio of copper to oxygen must have contained included gases. Thus it contained less copper than the pure compound, and the atomic weight of the element appeared to be lower than the true value.

Besides applying this correction to the older result, entirely new methods were used. The relation of copper to silver, of copper to bromine, and of copper to sulfuric acid were all determined with care, and all yielded essentially the same new value, thus leaving no doubt that the old value for copper was nearly half a per cent too low.

The next element to be investigated was barium, to which attention had been called because of certain anomalies in an attempt to find the ratio between barium and copper sulfates in the previous research. Both barium chloride and barium bromide were analyzed, taking great care to drive off all water without decomposing the salts. Much time was spent upon the preparation of pure silver, and every step of the analysis was tested, taking great heed especially of the solubility of silver chloride. The result showed that barium was previously almost as inexact as copper, the new value being about 0.3 of a unit higher than the old one. In this case as in the other not only were new results obtained, but also the reasons for the deviations in the old ones were made clear.

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[1] This work is *Publication* 125 of the Carnegie Institution of Washington.

Next among the atomic weights strontium was undertaken because of a suspicion that the same errors vitiating previous work on barium were also at work here. Moreover, I wished especially to obtain accurate values for those elements which form well-marked series in the periodic system, because among such elements it seems reasonable to suppose that a possible numerical relation is most likely to be found. The salts used were the same as those employed for barium, namely the chloride and bromide, but distinct improvements in manipulation were introduced. In this work on strontium the earliest forms of the so-called "bottling apparatus" were used, and also the nephelometer—the first being a device for drying hygroscopic salts without contact with the moisture of the air, and the second being an instrument which made possible the detection of faint traces of precipitate suspended in liquids. A puzzling outcome of this research lay in the fact that the results from the chloride and the bromide did not seem to be exactly alike; they differed by an amount too great to be ascribed to the probable error in analysis. The reason for this was found nearly ten years afterwards in the discovery that the error lay not in the results for strontium but rather in the accepted value of the atomic weight of chlorine as determined by Stas.

Next the study of a new series in the periodic system was begun, namely, the magnesium-zinc series. The accepted values for these metals were suspected, because they depended largely upon the synthesis of the oxides through the nitrates, a method which had been shown in the research upon copper to cause the retention of gases in the oxides. This impurity would cause the observed values for both zinc and magnesium to be distinctly lower than the true one. Accordingly, zinc bromide and magnesium chloride were analyzed with great care, with the assistance respectively of E. F. Rogers and H. G. Parker, and the suspicion was found to be justified. The "bottling apparatus" was modified during the latter research in such a way as to permit a sublimation of ammonium chloride from ammonium magnesium chloride, and this form of the instrument has been used, with slight modifications, ever since.

"The simple device consists of a hard glass or quartz ignition tube fitted to a soft-glass tube which has a projection or pocket in one side. A weighing-bottle is placed at the end of the latter tube, and its stopper in the pocket. The boat containing the substance to be dried is heated in the ignition tube, surrounded by an atmosphere consisting of any desired mixture of gases. These gases are displaced, after partial cooling, first by nitrogen, and then by pure dry air, and the boat is pushed past the stopper into the weighing-bottle, the stopper being then forced into place, and the substance thus shut up in an entirely dry atmosphere. The weighing bottle may now be removed, placed in an ordinary desiccator and weighed at leisure. The substance is really dry, and its weight has definit significance."[1]

Nickel, cobalt and iron, attacked with the help of Allerton Cushman and Gregory P. Baxter, formed the next subjects of investigation, each metal bringing its own new problem. The bromides of the first two were prepared by sublimation and were analyzed both for bromine and for the metal contained in them, so that a complete analysis was available. The satisfactory summation to make 100.00% was reassuring, not only with regard to these elements themselves, but also with regard to the other elements which had been previously studied by somewhat similar processes. It was conclusively proved that nickel and cobalt really have different atomic weights, and that the value for iron is much lower than it had been supposed to be.

Simultaneously with this work another of quite a different nature was in progress. The question as to whether the chemical combining proportions agree exactly with the electrolytic equivalents was one which had never been satisfactorily settled. According to the atomic hypothesis there was every reason to believe that they should precisely agree, but the matter was one which could not be settled without actual experiment. The electrochemical equivalent offers an entirely new method of approach with regard to the combining proportions; and with this in mind (as well as with the hope of simplifying and making more certain the determination of the quantity-factor of electricity) I sought, with the efficient help of E. Collins and G. W. Heimrod, to compare the weight of silver and copper precipitated from their salts by an identical current.

In this way, by taking original precautions too numerous to recite, we found for the atomic weight of copper the value 63.58 if silver is taken as 107.88—a result which confirms with reasonable precision the value 63.57, found for the atomic weight of copper by the chemical methods of eight years before.[2]

Later the precipitation of silver was studied much more in detail under varying circumstances and the former results were confirmed and amplified.[3] With the help of W. N. Stull it was shown also that precisely the same quantity of silver is precipitated from a solution of silver nitrate in fused sodium and potassium nitrates at 250° as from an aqueous solution at 20°, when the proper correction has been made for traces of solvent included in the crystals.[4] This is perhaps the most striking confirmation of the exact and universal precision of Faraday's law which has ever been offered.

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[1] Faraday lecture, *Science, N. S.*, 34, Oct. 27 (1911).

[2] *Proc. Am. Acad.*, 35, 123 (1899).

[3] *Ibid.*, 37, 415 (1902).

[4] *Ibid.*, 38, 409 (1902).

Thus the atomic weights are shown to represent numerical relations which persist under widely differing conditions.

Two other elements were then studied, calcium, in order to complete the series of the alkalin earths, and uranium, because of the interest stimulated by its unique property of possessing the greatest of all the atomic weights. Neither of these investigations was completed at the time, although the former was finished ten years afterwards at Harvard with the help of Otto Hönigschmid, whose results with both the bromide and chloride essentially confirmed those found during the earlier part of the work.

Curiosity concerning uranium was heightened by Becquerel's and the Curies' brilliant discoveries, and by the recent disintegration theory which imagines that uranium and radium are merely aggregates that may be called "elemental compounds" of helium with lead. Ramsay has emphasized the fact that the atomic weights alone of these elements are capable of finally solving the puzzle.

Radium has recently been determined with great precision by Hönigschmid at Vienna, using the Harvard methods, learned during the study of its analog calcium, and found to be 225.95. If uranium should be found to be 237.83—different from radium by just three times the atomic weight of helium—the theory concerning the relation of the two so-called elements would receive substantial support. Hence, a systematic and searching repetition of the early careful Harvard work on uranium of B. S. Merigold is now in progress in Cambridge; and with the help of quartz tubes and other modern appliances, we hope to obtain more conclusive results either for or against the hypothesis. Incidentally it may be said that the old Harvard work pointed to the value 238.4, a quantity over half a unit higher than the value demanded by the disintegration theory.

The new method of purifying cesium salts through the dichloriodide, devised by H. L. Wells, led to the investigation of the atomic weight of cesium, and this generous chemist put at our disposal large quantities of pure material prepared by his method, which proved to be highly satisfactory. E. H. Archibald undertook the work with cesium and not only used methods already familiar but also devized several new ones.

This research marked the end of what may be called the first period of the investigations at Harvard—the time during which the work of Stas was considered as impeccable. Confidence in Stas had been engendered largely because the most important point in which we had tested his work (namely, as to the relation between silver and bromine) had been proved to have brought a result apparently without reproach. In 1904, however, our confidence received a rude shock. During a series of investigations upon the transition temperatures of hydrated salts, undertaken for the purpose of obtaining new exact points in thermometry, a sample of very pure sodium bromide was obtained. This substance, by undergoing transition at a perfectly definit point, gave evidence of great purity; but its analysis yielded an atomic weight of sodium almost 0.2% lower than that of Stas. Evidently new investigation was necessary. Thus, a physicochemical problem demanding great purity of material led to a quantitative research of unexpected magnitude; and in turn this quantitative investigation depended continually upon physicochemical methods and considerations, many of them having been acquired since the days of Stas. There is not time to go into the details to-night either of our new precautions or the errors into which Stas had unwittingly fallen, but the outcome was that common salt prepared in the state of great purity was found to yield the same low atomic weight of sodium as the pure bromide; and simultaneously Stas's atomic weight of chlorine as referred to silver was found to be appreciably too low. Turning back now to strontium where I had previously found a discrepancy between the chloride and the bromide, it appeared as I have already said that this had been due to the erroneous value for chlorine; with the new value the result from the chloride agreed with that from the bromide. Other elements also into which chlorine entered needed correction, but fortunately these were very few in number, because we had intentionally almost always employed the bromide on account of its greater analytical certainty. Moreover, metals with high equivalents are affected less by the error in chlorine than those like sodium with low equivalents.

The discovery of error in two of Stas's most accurately determined results led to a natural suspicion that the others also needed revision. Accordingly, redeterminations of potassium with the help of A. Staehler and E. Mueller, of sulfur with that of Grinnell Jones, and of nitrogen, first with the help of G. S. Forbes, and finally in collaboration with Köthner and Tiede during my term of service at the University of Berlin, were undertaken. Potassium chloride and bromide were both analyzed with all the care used in the case of sodium; sulfur was approached by a new method involving the conversion of silver sulfate into the chloride; and nitrogen was attacked both by the synthesis of silver nitrate and by the analysis of ammonium chloride. In each case Stas's results were found to be somewhat in error. The work on silver nitrate was in some ways the most convincing of all, because in this case it was possible to prove that the salt was essentially free from water, by decomposing it and passing the products of decomposition, suitably treated, through a phosphorus pentoxide tube. No more concordant results have ever been secured in the Harvard Laboratory than the six successive experiments by which the silver was converted into silver nitrate—the extreme variation between the results being less than one-thousandth of a percent. If any error existed in them, it was an error of amazing constancy.

The most recent finished problem with which I have been concerned was the atomic weights of lithium and silver, a research conducted with the help of H. H. Willard, now at Ann Arbor. This has been so recently published that it seems hardly necessary to review it now, but perhaps I may remind you that we determined not only the ratio of lithium chloride to silver, but also that of the same salt to lithium perchlorate, which was easily made from it in a remarkably pure state. The relation of silver to oxygen was thus directly obtained according to the equation

$$\frac{Ag}{LiCl} \times \frac{LiCl}{LiClO_4 - LiCl} = \frac{Ag}{O_4}.$$

Incidentally, the atomic weight of lithium was found to be almost a whole per cent less than that obtained by Stas. This seems to have been his most grievous error, and came to pass only because all the defects in his processes accumulated on the head of this lightest of all metals.

During the last ten years Gregory P. Baxter, as independent investigator, has studied successfully at Harvard a number of other atomic weights, but these do not form part of this evening's program. Neither do those other excellent researches of a similar nature which are carried on from time to time in other laboratories throughout the world.

In all, about thirty atomic weights have been investigated in the Chemical Laboratory of Harvard College. The earlier of the investigations were of course less accurate than the later, for many reasons. Lack of time, of proper facilities, and of chemical knowledge all contributed in greater degree to cause imperfection in the older work than in that of recent years. Nevertheless it is pleasant to think that as yet no serious error has been discovered in any of the slowly accumulated data. Further researches are now in progress at Harvard University, and it is hoped that the procuring of better conditions in the Wolcott Gibbs Memorial Laboratory, now being built in Cambridge, will make possible the application of yet more effective refinements.

If I were to sum up in a few words the lessons of these protracted investigations, I should be inclined to say that the secret of success in the study of atomic weights lies in carefully choosing the particular substances and processes employed, and in checking every operation by parallel experiments so that every unknown chemical and physical error will gradually be ferreted out of its hiding place. The most important causes of inaccuracy are: the solubility of precipitates and of the material of containing vessels; the occlusion of foreign substances by solids, and especially the presence of retained moisture in almost everything. Each of these disturbing circumstances varies with each individual case. Far more depends upon the intelligent choice of the conditions of experiment than upon the mere mechanical execution of the operations, although that too is important. I have often quoted the innocent remark which has occasionally been made to me: "What wonderfully fine scales you must have to weigh atoms!" To-night I have endeavored to point out that the purely chemical work, which precedes the introduction of the substance into the balance-case, is far more important than the mere operation of weighing. Moreover, speculation and the higher mathematics are as yet of little service to us in this quest; I cannot help thinking that any ultimate general conclusion must rest upon careful laboratory work. Chemistry is still largely an inductive science; when we have discovered the realities, we shall be in a position to attempt to explain them. In the meantime more accurate values, discovered little by little through patient investigation, will be of use to the thousands of men throughout the world who daily employ these fundamental data of chemistry.

This method of working is very different from that of the great man whose memory we are celebrating to-night. Willard Gibbs went always from the abstract to the concrete; his whole point of view was deductive rather than inductive. Perhaps herein we may find one reason why his extraordinary generalizations have so often remained hidden until other investigators have come upon them inductively. Nevertheless, the radical difference of method brings with it no real contradiction of aim and outcome. The mathematical logic of Gibbs supplements but does not supplant the work in the laboratory; both have the same object, and each helps the other toward the ultimate goal. This goal—a more fundamental understanding of the mechanism of the universe in which our lot is cast—is worthy of the highest endeavor of mankind.

COMPRESSIBILITIES OF CERTAIN HYDROCARBONS, ALCOHOLS, ESTERS, AMINES, AND ORGANIC HALIDES.

BY THEODORE W. RICHARDS, W. N. STULL, J. H. MATHEWS AND C. L. SPEYERS.

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Introduction.

In previous papers from this laboratory the compressibilities of certain inorganic compounds as well as of a number of the elementary substances have been discussed.[1] It has been demonstrated that compressibility is a property having chemical relations of importance; and accordingly it becomes a matter of interest to compare the compressibilities of a wide variety of organic substances. Unfortunately, however, the existing data concerning this subject are incapable of throwing light upon it be-

[1] Richards and Stull, *Pub. Carnegie Inst.*, **7** (1903); *Z. physik. Chem.*, **49**, 1 (1904); Richards, THIS JOURNAL, **26**, 399 (1904); Richards, Stull, Brink, and Bonnet, *Pub. Carnegie Inst.*, **76** (1907); *Z. physik. Chem.*, **61**, 77 (1907); *Ibid.*, **61**, 183 (1907); THIS JOURNAL, **31**, 154 (1909); Richards and Mathews, *Ibid.*, **30**, 8 (1908); *Z. physik. Chem.*, **61**, 449 (19 8); Richards and Jones, THIS JOURNAL, **31**, 158 (1909); *Z. physik. Chem.*, **71**, 52 1910 .