A COMPARISON OF THE CHEMICAL AND PHYSICAL ATOMIC WEIGHT VALUES OF THE MONOISOTOPIC ELEMENTS

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This review is an attempt to compare systematically the chemical and physical atomic weight values of the twenty-two elements which are known to be composed of only one stable isotope. It is found that of this group there are only five elements whose atomic weight values on both the chemical and the physical scales deserve the highest confidence. It is concluded that these data are too limited to permit a significant comparison of the two atomic weight scales to be carried through. Attention is directed to the question of the atomic weight of silver, because this constant is the practical basis of many chemical atomic weight values; here also no unqualified conclusion can be drawn.

The question of the validity or accuracy of the chemical atomic weights has naturally been a vital one ever since the acceptance of the atomic theory. Until fairly recently these chemical constants could be found only by the chemical analysis of a pure substance or from a determination of the density of a pure gaseous compound, and the test of the validity of the atomic weight values so obtained became in effect a test of their self-consistency. In the last two decades the development of new physical methods (e.g., mass-spectrographic and nuclear reactions) for measuring isotopic masses has, for the first time, opened up the possibility of checking the values of chemical atomic weights against an entirely independent set of values. Indeed, reports on the results of an atomic weight investigation nowadays usually present comparisons of the chemical and physical values.

The isotopic constitution of the elements is now fairly well established. Twenty-two elements are believed to be composed of a single atomic species, and are referred to as monoisotopic or simple elements; the remaining seventy-odd elements are mixtures of two or more isotopes, the largest number being ten in the case of tin. A direct general comparison of all chemical and physical atomic weight values is out of the question at this time, owing to the fact that the estimation of the physical values for the multi-isotopic elements involves the measurement of abundance of isotopes as well as measurement of isotopic masses. Fortunately, however, the group of twenty-two elements known to be monoisotopic is quite representative, and a comparison of their atomic weight values might be regarded as a sample comparison for all the elements. The study reported in this article is a first, exploratory step toward carrying out the comparison of chemical and physical atomic weight values of this limited group of elements.

Data regarding the chemical and physical atomic weight values of the twenty-

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TABLE 1

Atomic weights of the monoisotopic elements

(1) ELEMENT	(2) SYMBOL	(3) CHEMICAL VALUE	(4) PHYSICAL VALUE	(5) ESTIMATED ERROR $\times 10^{+3}$		(6) DIFFERENCE CHEMICAL — PHYSICAL
Aluminum	Al	26.97	26.9826	0.80	(b)†	−0.01
			26.98335	0.43	(c)	−0.01
Arsenic	As	74.91	74.913	–	(d)	(0.00)
Beryllium	Be	9.013	9.01258	0.20	(a)	0.000
			9.01255	0.06	(b)	0.000
			9.012481	0.062	(c)	+0.001
Bismuth	Bi	209.00	208.999	8.6	(c)	0.00
Cesium	Cs	132.91	132.897	–	(d)	(+0.01)
Cobalt	Co	58.94	(58.94)*	–		(0.00)
Fluorine	F	19.00	18.99927	0.26	(b)	0.00
			18.99932	0.12	(c)	0.00
Gold	Au	197.2	(196.99)	–		(+0.2)
Holmium	Ho	164.94	(164.94)	–		(0.00)
Iodine	I	126.92	126.897	–	(d)	(+0.02)
Manganese	Mn	54.93	54.942	–	(b)	−0.01
			54.9502	–	(d)	(−0.02)
Niobium	Nb (Cb)	92.91	(92.92)	–		(−0.01)
Phosphorus	P	30.98	30.9758	0.50	(b)	0.00
			30.97589	0.27	(c)	0.00
Praeseodymium	Pr	140.92	(140.91)	–		(+0.01)
Rhodium	Rh	102.91	102.921	5.2	(b)	−0.01
Scandium	Sc	45.10	44.9545	–	(b)	+0.15
			44.95740	0.63	(c)	+0.14
Sodium	Na	22.997	22.98974	0.31	(b)	+0.007
			22.99012	0.18	(c)	+0.007
Tantalum	Ta	180.88	180.878	–	(d)	(0.00)
Terbium	Tb	159.2	(158.93)	–		(+0.3)
Thorium	Th	232.12	(232.06)	–		(+0.06)
Thulium	Tm	169.4	(168.95)	–		(+0.4)
Yttrium	Y	88.92	(88.92)			(0.00)

* Values in parentheses were taken from the report of Hahn, Fluegge, and Mattauch (6).

† These letters identify the sources of the figures used by Covey (5):

(a) Bainbridge (1).

(b) Mattauch and Fluegge (9).

(c) Massachusetts Institute of Technology Staff (8).

(d) Seaborg Wall Chart, (1939), Gilman Hall, Department of Chemistry, University of California, Berkeley, California. Regarding this chart, Covey (5) writes: "For most of the values taken from this wall chart, the supporting references unfortunately cannot be located. Thus it is impossible to recheck and verify values given for several of the isotopes for which no other source reports confirmatory data."

two monoisotopic elements have been assembled in table 1. In the following discussion it will be shown that a high degree of confidence can be placed in only nine of the physical atomic weight values and in twelve of the chemical

values. Only five elements appear in both the physical and the chemical "high confidence" groups.

The chemical atomic weight values (column 3) have been taken from the 1950 Report of the International Committee (7). Following the presentation below of the data relating to the physical values, the chemical values will be considered and their background will be reviewed.

The physical atomic weight values (column 4), all of which are expressed in terms of the chemical scale (i.e., assigning the weight 16.0000 to the naturally occurring mixture of oxygen isotopes), have been obtained from two sources. The values in parentheses have been taken from the 1940 report of Hahn, Fluegge, and Mattauch (6) and were presumably derived from their packing-fraction curve. The other values in column 4 were taken from Covey's compilation (5); the estimated uncertainty for each of these values, as given by Covey, is shown in column 5.

From a consideration of the sources of the physical atomic weight values given in column 4, it must be concluded that, from the standpoint of reliability, they fall into two distinct groups. The figures in which the greatest confidence can be placed are those of Covey derived from sources (a), (b), and (c), which presumably stem back to direct measurements; the values in parentheses and Covey's figure from source (d) are probably first-rate estimates but cannot be accorded the same confidence as the values in the first group, as defined above. In column 6 of table 1 are given the differences between the chemical and physical atomic weight values. Those differences which are derived from the more reliable group of physical values, as described above, are not placed within parentheses, while those differences which involve the less certain physical values are given in parentheses.

As an examination of the data in the last column of table 1 will show, there are only nine different values which are not in parentheses and which, therefore, might be regarded as significant in a critical comparison of chemical and physical atomic weight values. In other words, as a consequence of the uncertainties in the physical atomic weight values, the group of twenty-two monoisotopic elements which ideally might serve as a basis for a comparison of chemical and physical atomic weight values is cut down to nine. We shall return to an examination of the differences of this reduced group of elements after a review of the background of the chemical atomic weights.

Although the chemical atomic weight values (column 3) recommended by the International Committee can be regarded as the most acceptable values to be derived from existing experimental data, their experimental foundations vary over a very wide range. Since this matter of experimental foundation is of considerable importance in any comparison of chemical and physical atomic weight values, we shall undertake in what follows to review and examine the experimental data on which the chemical atomic weight values of the monoisotopic elements are based.

Before presenting the results of the many chemical determinations of the atomic weights of these elements, there is one point to consider regarding these

determinations, either by analysis or by the gas-density method. Determinations based upon the chemical analysis of a pure compound can be viewed as consisting of two parts:

(a) The experimental determination of the stoichiometrical ratio R between the substance which contains the element A whose atomic weight is sought and some other substance X which may or may not contain A.

(b) The calculation of the atomic weight of A from the experimental ratio R and assumed values for the atomic weights of *all* elements besides A which are present in the compounds.

As this breakdown shows, the atomic weight value derived from any given determination will depend on the atomic weight values accepted as correct for the other elements involved in the analysis. Similarly, the atomic weight derived from a given determination by the gas-density method depends upon the atomic weight values accepted for the other elements present in the substance whose molecular weight is found by experiment. The point to be made here is that all chemical atomic weight values are closely interrelated and that the values derived from experimental measurements will depend on the set of atomic weight values accepted in making the computations. For the purpose of the present study the results of all experimental determinations of the atomic weights of the monoisotopic elements have been recalculated, using the set of atomic weight values accepted by the International Committee in 1947. In this way, all the chemical atomic weight values used in this article have been made consistent with the modern set of chemical atomic weights. The detailed results of these extensive and rather laborious recalculations are summarized in the thesis of one of the authors (2).

In an attempt to simplify the consideration of the results of the rather large number of atomic weight determinations, the data are presented graphically in figure 1. For the purposes of this figure, the atomic or isotopic weight values have been converted to mass deviations ΔM, defined as $(M - A)$ where M is the mass of the isotope and A is its mass number. In figure 1 the ΔM values, expressed in atomic weight units, are plotted as ordinates against the corresponding mass numbers (A) of the elements as abscissae. To avoid any misunderstanding, it should be noted here that all "weight" values are on the chemical scale.

By way of introduction to figure 1, attention is directed first to the plotted solid and dashed lines which depict, respectively, the physical and chemical atomic weight values given in table 1. The bases for the physical atomic weight points which determine the solid line have been considered above.

In plotting the chemical atomic weight values many instances were naturally encountered where the results of two or more determinations were so close that the values could not be plotted clearly. To help matters in these cases the following device was adopted: On the main scale of figure 1 a solid black rectangle has been plotted to cover the range of the cluster of atomic weight values. For each black rectangle there is then inserted in the figure a secondary magnified scale, connected with the black rectangle by a dotted tie-line, and on this scale,

magnified by a factor of ten, are plotted the individual points of the cluster of values comprised in the solid black rectangle.

A second point to be noted in connection with figure 1 is that in plotting the chemical atomic weight values a code has been followed so as to indicate the general nature of the method used in each determination. For the purpose of this code the various methods have been classified according to the following scheme:

TYPE OF PLOTTED POINT	DESCRIPTION OF METHOD USED IN ATOMIC WEIGHT DETERMINATION
◒	Nephelometric-silver comparisons: these represent the results of analyses of chlorides or bromides by the Harvard or Richards method
●	All other analyses involving silver: most of these are gravimetric determinations involving silver chloride or silver bromide; some of these determinations are incidental to nephelometric analyses (see above) and involve the identical sample of material
○	General chemical methods not involving silver: these comprise *all* chemical methods not included in the first two classes of methods described above
△	Physicochemical methods: these results are derived from gas-density measurements

Finally, it may be noted that each plotted point is identified by a two-digit number which refers to the year in which the atomic weight determination was published. Since no publication antedated 1850 or occurred after 1950, there should be no confusion regarding the century of the publication. In a few instances the results of several atomic weight determinations carried out in the same year coincide. In these cases, the number of coincident values is indicated by a superscript to the two-digit date numbers.

A scrutiny of the chemical atomic weight values plotted suggests certain general conclusions regarding the experimental foundations for the accepted atomic weight values.

(*a*) The greatest deviations between the chemical and physical atomic weight values are those for four elements: scandium, terbium, thulium, and gold. With these elements the fault would appear to lie on the chemical side. In the case of the first three of these elements the difficulty is due, no doubt, to the fact that these elements are rare earths, and the compounds analyzed were probably contaminated with other rare earths. In the case of gold, since there has been no determination since 1889, the difficulty may be attributed to the lack of a modern determination of its atomic weight. The accepted atomic weight value of gold seems to represent some sort of average of all the values that are available and coincides also with the weighted general mean of Clarke's last recalculations (4). It may be observed here that the element scandium, which falls

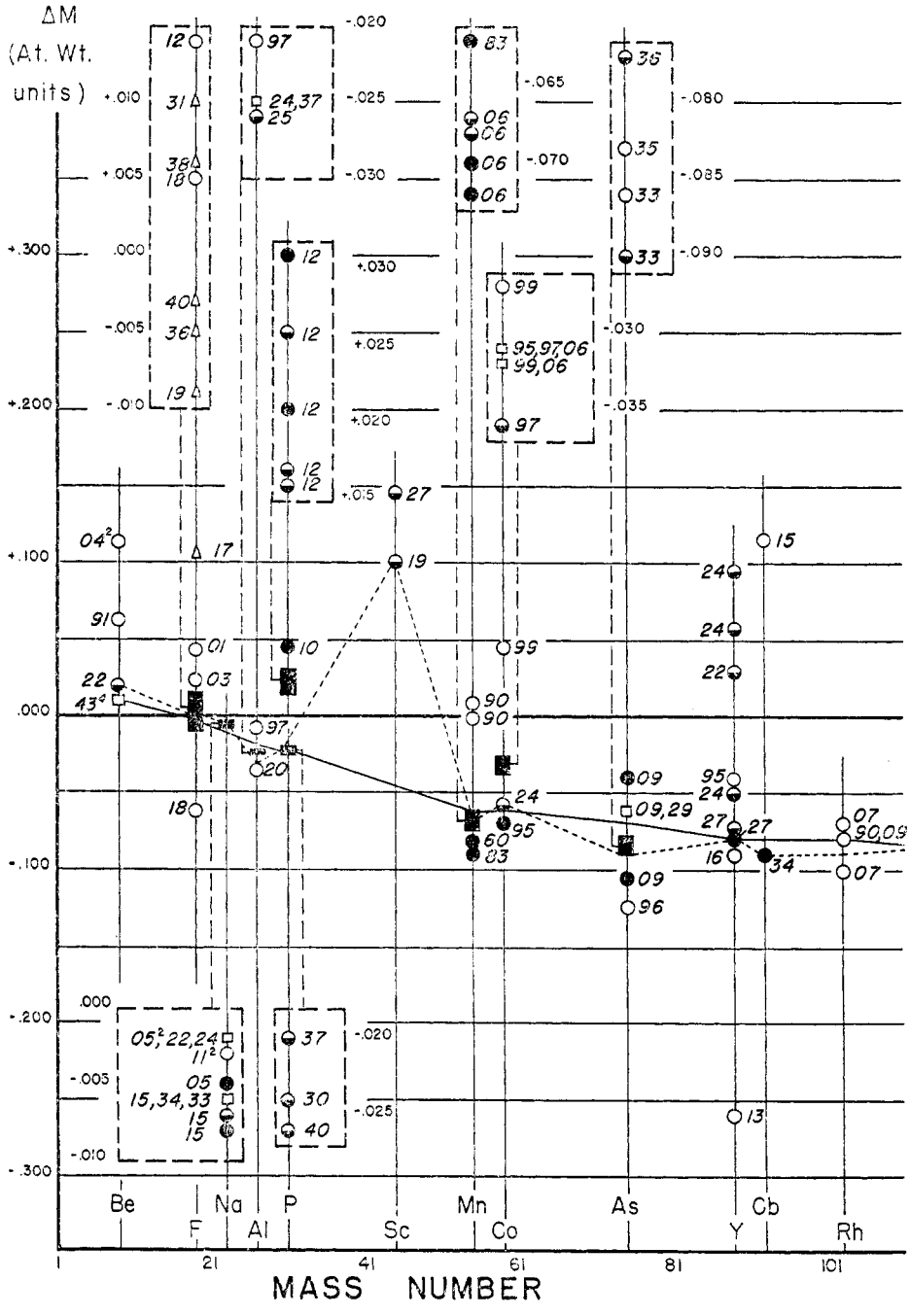
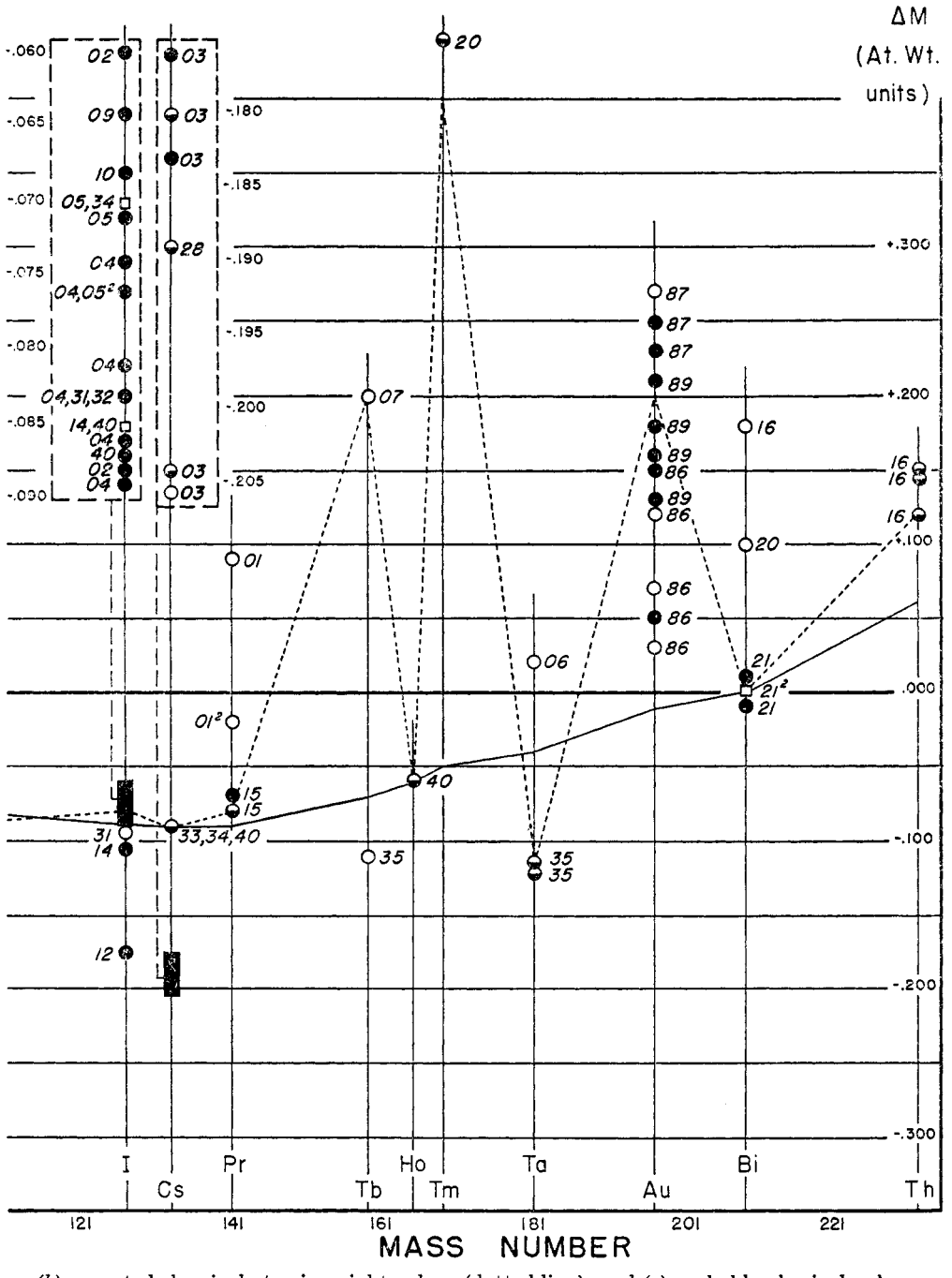


FIG. 1. Atomic weight values of monoisotopic elements expressed as ΔM, the difference between the atomic weight on the chemical scale and the mass number of the element. The plot shows: (*a*) results of all chemical atomic weight determinations for each element;



(*b*) accepted chemical atomic weight values (dotted line); and (*c*) probable physical values (solid line).

in this doubtful group, is one of the elements whose weight has been established by physical methods to a comparatively high degree of certainty.

(*b*) The chemical atomic weight values of two elements, tantalum and thorium, also differ appreciably from the given physical values, but the deviations are less than in the group named above. The experimental basis for the chemical value for tantalum does not seem too firm. The values plotted for thorium are all from Hönigschmid's careful series of measurements made in 1916. Although it would be desirable to have Hönigschmid's results confirmed, there is no reason to expect a lower value which would be necessary to reduce the deviation from the physical value. Indeed, eight earlier determinations, whose results are not plotted, yielded atomic weight values considerably higher than Hönigschmid's.

(*c*) The seventeen elements not considered in paragraphs (*a*) and (*b*) have accepted chemical atomic weight values which do not differ appreciably from the corresponding physical values. However, of these seventeen elements, there are five whose chemical atomic weights either rest upon a single set of measurements or represent the mean of several, not very consistent, sets of measurements. These five elements are listed below with a brief comment in each case:

F	No single chemical determination fully satisfactory
Nb	The accepted value rests upon the single 1934 determination by Hönigschmid and Wintersberger
Rh	The value is an average of the results of old (latest one, 1909) analyses of pentaammine rhodium halides
Ho	The value is based solely on 1940 measurements of Hönigschmid and Hirschbold-Wittner
Bi	The value is based on 1921 analyses of Hönigschmid and Birchenbach; there are certain grounds for questioning this result and a new determination is currently under way in the laboratory of one of the authors (A. F. S.)

(*d*) The foregoing process of elimination leaves twelve elements whose chemical atomic weights rest upon a substantial experimental foundation. The only comment to be made regarding the values for these elements is that in the case of two of them the accepted atomic weight value might be revised slightly if the International Committee reviewed the results of all determinations on record. These cases are given below:

Na	It seems clear that the evidence (which will be presented later in this article) points to a value of 22.994 rather than the accepted value of 22.997.
As	The present accepted value, 74.91, is based upon two sets of measurements by Baxter and his students, published in 1933. Subsequent work by Baxter and by Krepelka yielded a value of 74.92. All measurements previous to 1933 gave values greater than 74.92. It would appear, therefore, that possibly too much weight has been accorded Baxter's value of 74.91 and that a fairer value would be 74.92.

To summarize the foregoing discussion of the experimental background of the chemical atomic weights, the elements are classified in table 2 into three groups

on the basis of the degree of confidence in the experimental basis of their accepted chemical atomic weight values.

In the discussion up to this point the physical and chemical atomic weight values of the twenty-two monoisotopic elements have been reviewed, and those physical and chemical values in which the greatest confidence can be placed have been identified. Clearly, a meaningful comparison of the chemical and physical values can be carried out only with those elements whose atomic weight values on *both* scales deserve the fullest confidence. Of the twenty-two monoisotopic elements there are only five which, according to the analysis of the

TABLE 2

Classification of the elements on the basis of degree of confidence in atomic weight values

HIGHEST CONFIDENCE IN VALUE	HIGH CONFIDENCE IN VALUE; ONLY QUESTION IS LACK OF SUPPORTING DETERMINATIONS	VALUES WHICH ARE OPEN TO QUESTION FOR VARIOUS REASONS
Be	Nb	F
Na	Ho	Sc
Al	Th	Rh
P		Tb
Mn		Tm
Co		Ta
As		Au
Y		Bi
I		
Cs		
Pr		

authors, meet this condition. These elements and their differences are given below:

ELEMENT	CHEMICAL ATOMIC WEIGHT	DIFFERENCE IN VALUES: CHEMICAL MINUS PHYSICAL
Be	9.013	0.000
Na	22.997	+0.007
	(22.994)	(+0.004)
Al	26.97	−0.01
P	30.98	0.00
Mn	54.93	−0.01 to −0.02

Of the five elements included in the above table there are two (beryllium and phosphorus) in which the chemical and physical atomic weight values are identical; two (aluminum and manganese) whose chemical values are smaller than the physical; and just one element (sodium) whose chemical value is greater than its physical value. Although these data suggest that the chemical values tend to be smaller than the physical values by 0.0–0.3 part per 1000, this apparent trend cannot be credited with any significance whatever because of the small number of elements involved in the comparison and also because none of the elements is a heavy one. Briefly, there do not exist at the present time suffi-

cient chemical or physical data to enable a significant comparison of the chemical and physical atomic weight values to be carried through.

When the present comparison of the chemical and physical atomic weights was initiated it was hoped that it would throw some light on the question of the correct value for the atomic weight of silver. A clear presentation of this interesting and complex problem has been given by Birge (3) in his 1941 report on "The General Physical Constants," which is quoted below:

> "But the value of F (the faraday) depends upon the adopted atomic weights of iodine and silver, and the most accurate determinations of I depend in turn on the value of Ag. Since 1925 the internationally-accepted value of Ag has been 107.880, and there appears to be nothing in any recent report of the International Committee on Atomic Weights to indicate that any change is contemplated or needed in the adopted value. Hence in working up the present list of constants, I merely accepted the value 107.880 ± 0.001, which I had adopted in G. C. 1929. Then, after my calculations were completed, I happened to read something in my notes that aroused my suspicions about the value of Ag. As the result of a subsequent but hasty and still incomplete investigation, it appears to me that the best value is far more likely to be 107.878 than 107.880. To get out of this difficulty with a minimum of recalculation, I have increased the probable error and now adopt Ag = 107.880 ± 0.002, thus covering the possibility of 107.878. Since the atomic weight of silver is the basis for nearly all atomic weights, it is not to be changed without due consideration."

Unfortunately, our present analysis of atomic weight results does not furnish a firm basis for a critical judgment of the atomic weight of silver—again, mainly owing to lack of sufficient data in the right places. It may be noted first that the chemical atomic weight values of the five monoisotopic elements in the tabulation all involve the atomic weight of silver to some extent, and it will be of interest to consider them with the question of the atomic weight of silver in mind. The chemical atomic weight values for beryllium, phosphorus, and manganese are all derived from analyses of halides by the Harvard method and therefore rest on the atomic weight of silver. Unfortunately, the chemical bases of these atomic weight values are not sound enough to justify their use in evaluating the atomic weight of silver; in other words, the fact that the atomic weight of none of these three elements exceeds the corresponding physical value cannot be viewed as significant.

The chemical atomic weight values of aluminum and sodium are both better established than those of the three elements just considered, but they lead to ambiguous conclusions so far as the atomic weight of silver is concerned. In the case of aluminum the following modern determinations are on record:

YEAR	ANALYSIS OF HALIDE BY HARVARD METHOD	VALUE	YEAR	DETERMINATIONS BY OTHER METHODS	VALUE
1920	Richards and Krepelka $AlBr_3$:3Ag	26.963	1937	Hoffman and Lundell $2Al:Al_2O_3$	26.975
1924	Krepelka $AlCl_3$:3Ag	26.975			
1925	Krepelka and Nikolic $AlCl_3$:3Ag	26.974			

Here, since the values based on silver are in complete agreement with the value based only on oxygen, it is not reasonable to attribute the fact that the chemical value is lower than the physical value (26.982) to the assumption of too low a value for silver. Turning now to sodium we find the following record of modern determinations:

YEAR	ANALYSIS OF HALIDE BY HARVARD METHOD	VALUE	YEAR	ANALYSIS OF SODIUM COMPOUNDS OTHER THAN HALIDES	VALUE
1905	Richards and Wells		1915	Richards and Hoover	
	NaCl:Ag	22.998		Na_2CO_3:2AgBr	22.992
	NaCl:AgCl	22.995		Na_2CO_3:2Ag	22.993
				Na_2SO_4:Na_2CO_3	22.994
1933	Johnson				
	NaCl:Ag	22.994	1924	Zintl and Meuwsen	
				$NaNO_3$:NaCl	22.998
			1934	Baxter and Hale	
				Na_2CO_3:I_2O_5	22.994

As a careful examination of this tabulation will show, there is exceedingly strong experimental evidence to support a chemical atomic weight value of 22.994 for sodium, which is 0.004 unit larger than the physical value (22.990). Although a high value for the chemical atomic weight of sodium would be the consequence of too high a value for silver, the difference of 0.004 unit cannot be attributed to that cause alone; for to suppose that silver is solely at fault would imply that the correct value for the atomic weight of silver is about 107.85, a figure which is much too low to be reasonable. In the case of sodium at least, since the chemical evidence is so strong, it is logical and reasonable to suspect that the physical value is not so well established as the estimated uncertainty indicates it to be.

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REFERENCES

(1) BAINBRIDGE, K. T.: "Isotopic Weights of the Fundamental Isotopes," Nuclear Science Series, Preliminary Report No. 1. National Research Council, Division of Mathematical and Physical Sciences, November, 1947.
(2) BETTMAN, MAX: "A Critical Review of the Atomic Weights," Thesis, Reed College, 1948.
(3) BIRGE, R. T.: Reports on Progress in Physics **VIII**, 90 (1941).
(4) CLARKE, F. W.: "A Recalculation of Atomic Weights," Smithsonian Inst. Pubs., Misc. Collections **27**, No. 441 (1920).
(5) COVEY, E. H.: "A Compilation of the Non-Radioactive Nuclear Properties of the Naturally Occurring Isotopes," AECU-190 (UCRL-290).
(6) HAHN, O., FLUEGGE, S., AND MATTAUCH, J.: Ber. **73A**, 1 (1940).

(7) INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS (CHEMICAL ELEMENTS): Statements attributed to this Committee are taken from their reports published in the year specified in the Journal of the American Chemical Society.
(8) MASSACHUSETTS INSTITUTE OF TECHNOLOGY STAFF: Notes for Seminar in Nuclear Science and Engineering, Appendix A (8.44), 1946.
(9) MATTAUCH, J., AND FLUEGGE, S.: *Nuclear Physics Tables and an Introduction to Nuclear Physics*. Interscience Publishers, Inc., New York (1946).