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Report of the Committee on Atomic Weights of the American Chemical Society

BY EDWARD WICHERS

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The Commission on Atomic Weights of the International Union of Pure and Applied Chemistry, at its Meeting in New York in September, 1951, adopted changes in the atomic weights of seven elements. The new values and the reasons for the changes are stated in the following paragraphs. In this discussion conversions to the chemical scale, of mass data reported on the physical scale, have been made with the divisor 1.000275. Unless otherwise noted, the values of atomic weights used in the review or recalculation of chemical ratios are those given in the 1949 table.

Aluminum.—The former value, 26.97, has been in use since 1925. It resulted from the determination by Richards and Krepelka[1] of the ratio $AlBr_3:3Ag$, which yielded 26.963, and similar work by Krepelka[2] on the ratio $AlCl_3:3Ag$, which yielded 26.975. The next year Krepelka and Nikolic[3] published 26.974 as the result of a series of comparisons of silver with aluminum chloride prepared in a different manner. Hoffman and Lundell[4] from 13 observations of the ratio $2Al:Al_2O_3$, found 26.975. In 1943 Mattauch and Ewald[5] reported mass-spectrographic measurements of the single isotope of aluminum with the result, on the chemical scale, of 26.982. This work was recently reviewed and confirmed in a study of a series of elements by Motz.[6] In view of the inherently high accuracy of modern mass-spectrographic determinations of atomic masses, it appears reasonable to weight the value of Mattauch and Ewald somewhat more heavily than the chemically determined values. Consideration of the work of Hoffman and Lundell also suggests a greater likelihood of a negative than a positive error in the calculated value. The value 26.98 was accordingly chosen for the 1951 table.

Silicon.—The value 28.06 was first adopted in 1925, as a change from 28.1. It was based largely on the work of Baxter, Weatherill and Scripture,[7] who determined the ratio $SiCl_4:4Ag$. In 1924 Hönigschmid and Steinheil[8] published the results of four determinations of the same ratio, with an average value of 28.105. In 1932 Weatherill[9] obtained 28.103 as the average of 11 determinations of the ratio $SiCl_4:SiO_2$.

Three separate determinations of the molecular weight of silane in Professor Whytlaw-Gray's Laboratory, by the method of limiting densities, all yielded 28.11 as the atomic weight of silicon. By the same procedure Moles and Toral[10] obtained 28.089 from the molecular weight of silicon tetrafluoride, if the atomic weight of fluorine is taken as 18.999.

Bainbridge and Nier,[11] in a recent report on the relative isotopic abundances of the elements, reviewed the measurements of isotope abundances and chose as the best values: Si^{28}, 92.27 ± 0.09; Si^{29}, 4.68 ± 0.05; Si^{30}, 3.05 ± 0.03 (all in atom per cent.). No other isotopes have been detected in sufficient amount to influence the atomic weight. Duckworth and co-workers[12] have determined the masses of the three isotopes (on the physical scale) as Si^{28}, 27.9858; Si^{29}, 28.9858; Si^{30}, 29.9831, each with an uncertainty of about 1 in the 4th decimal place. The atomic weight (chemical scale) derived from these masses and abundances is 28.086. In the light of this evidence, and taking into account the discrepancies among the chemically determined values, the value 28.09 was chosen for the 1951 Table.

Phosphorus.—The accepted value has been 30.98 since 1939, when it was changed from 31.02 on the basis of the comparison by Hönigschmid and Menn[13] of phosphorus oxychloride with silver, and of close agreement of their average value, 30.981, with that obtained from a measurement by Aston of the packing fraction. The new value was also in better agreement with that obtained by Ritchie[14] from the limiting density of phosphine. Ritchie's work yielded 30.977, which at the time of its publication was considered too much at variance with the atomic weight obtained from chemical ratios.

Hönigschmid and Hirschbold-Wittner[15] obtained the value 30.974 from a comparison of phosphorus oxybromide with silver but considered this value less reliable than that obtained from their earlier work on the oxychloride. H. Motz[6] reports a value computed from nuclear reaction data supplemented by mass spectroscopic measurements that yields 30.975 on the chemical scale. The evidence seems conclusive that the previously accepted value is somewhat high and the new value was accordingly taken as 30.975.

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(1) T. W. Richards and H. Krepelka, THIS JOURNAL, **42**, 2221 (1920).

(2) H. Krepelka, *ibid.*, **46**, 1343 (1924).

(3) H. Krepelka and N. Nikolic, *Chem. Listy*, **19**, 158 (1925).

(4) J. I. Hoffman and G. E. F. Lundell, *Nat'l. Bur. Standards J. Research*, **18**, 1 (1937).

(5) J. Mattauch and H. Ewald, *Physik Z.*, **44**, 181 (1943).

(6) H. T. Motz, *Phys. Rev.*, **81**, 1061 (1951).

(7) G. P. Baxter, P. F. Weatherill and E. W. Scripture, Jr., *Proc. Am. Acad. Arts and Sciences*, **58**, 246 (1923).

(8) O. Hönigschmid and M. Steinheil, *Z. anorg. allgem. Chem.*, **141**, 101 (1924).

(9) P. F. Weatherill, THIS JOURNAL, **54**, 3932 (1932).

(10) E. Moles and T. Toral, *Z. anorg. allgem. Chem.*, **236**, 225 (1938).

(11) K. T. Bainbridge and A. O. Nier, "Relative Isotopic Abundances of the Elements," Preliminary Report No. 9 (1951), Nuclear Science Series, Division of Mathematical and Physical Sciences, National Research Council, U. S. A.

(12) H. E. Duckworth and co-workers, *Phys. Rev.*, **79**, 188, 402 (1950).

(13) O. Hönigschmid and W. Menn, *Z. anorg. allgem. Chem.*, **235**, 129 (1937).

(14) M. Ritchie, *Proc. Roy. Soc. (London)*, **A128**, 551 (1930).

(15) O. Hönigschmid and F. Hirschbold-Wittner, *Z. anorg. allgem. Chem.*, **243**, 355 (1940).

Potassium.—The value 39.096 has been accepted since 1934. It was also in use for many years prior to 1929, but during the interval 1929–1933 the value used was 39.10. This temporary change resulted from the work of Hönigschmid and Goubeau,[16] who obtained 39.104 from an extensive series of comparisons of potassium chloride with silver and the same value from the comparison of potassium bromide with silver. However, Baxter and MacNevin[17] found 39.094 from the ratio of potassium chloride to silver and a new investigation by Hönigschmid (and Sachtleben)[18] yielded 39.097 from comparisons of both the chloride and the bromide with silver. A few years later, Johnson[19] obtained 39.100 from an extremely concordant series of 15 comparisons of the chloride with silver. A new investigation by Baxter (with Harrington)[20] of the ratio KCl:Ag yielded 39.098. McAlpine and Bird[21] decomposed potassium bromate to the bromide and thus obtained a molecular weight of potassium bromide which yielded 39.095 for the atomic weight of potassium.

It will be seen that the numerous chemical determinations made over many years have ranged from 39.094 to 39.104. Bainbridge and Nier,[11] in their 1951 report, reviewed measurements of the abundance ratio of K^{39} to K^{41} and chose as the best value 13.48 ± 0.07. This ratio, together with the masses reported by Collins, Nier and Johnson[22] yields 39.104. If the ratio of K^{39} to K^{41} were 13.9, as found by Paul and Pahl,[23] the atomic weight would be lower by 4 in the third decimal place. The value adopted by the Commission was 39.10.

Scandium.—The previously accepted value for scandium, 45.10, which was based on a comparison by Hönigschmid[24] of scandium bromide with silver, and which was confirmed by Smith,[25] who found 45.14 as the average of a series of comparisons of scandium chloride with silver, cannot be reconciled with the apparently well established fact that scandium is a simple element with a negative packing fraction. The mass-spectrographic determination reported by Collins, Nier and Johnson,[22] recalculated to the chemical scale, is 44.958. The value adopted for the table was rounded off to 44.96.

Krypton.—The previously accepted value, 83.7, was adopted in 1932 on the basis of density measurements by Watson.[26] By the same method Allen and Moore[27] found 83.6 and Heuse and Otto[28] obtained 83.66. The value obtained from mass measurements by Nier (as yet unpublished) and Nier's abundance ratios as given in the Nier–Bainbridge report[11] is 83.805 ± 0.004. This value was accepted by the Commission, but rounded to 83.80.

Iodine.—The previous value, 126.92, was adopted in 1933, in replacement of 126.932. This change was strongly influenced by the work of Hönigschmid and Striebel,[29] who obtained 126.917 as the average of seventeen concordant measurements of the ratio AgI:AgCl. This work followed a series of seven earlier determinations of the same ratio by the same authors,[30] whose average was also 126.917. Aston's packing fraction measurement of that period[31] yielded 126.905 (on the chemical scale) but the method was not regarded as being of sufficiently established accuracy. The same value was obtained by Baxter and Butler[32] from the ratio $2I:I_2O_5$, but was "believed to be impossibly low" (Baxter, *et al.*[33]).

Chemical determinations made after 1933 tended in the direction of a lower value. Baxter and Hale[34] compared iodine pentoxide with sodium carbonate. The average of 9 determinations yielded 126.930 if sodium is taken as 22.997 and carbon as 12.010. However, if the values for sodium and carbon are used that are currently regarded by physicists as the most reliable (Na = 22.991 and C = 12.011), the work of Baxter and Hale leads to 126.912. Baxter and Titus[35] redetermined the ratio AgI:AgCl and found for iodine 126.915. Baxter and Lundstedt[36] measured the ratios Ag:AgI, and AgI:AgCl. From the former they found 126.9135 and from the latter 126.916.

Recent and as yet unpublished measurements by Nier of the packing fraction of iodine yield for the atomic weight, on the chemical scale, 126.911, with an estimated uncertainty of 1 in the third decimal place. Consideration of this evidence and of the chemical work reported above led the Commission to accept 126.91 as the present best value.

For several other elements there is evidence, principally from mass spectrographic measurements, that the values given in the table for 1949 deserve reconsideration. In view of the fact that some of this evidence was unpublished at the time the International Commission met, and because of uncertainties arising from disagreements between this evidence and the results of earlier work on chemical ratios or limiting densities, the Commission decided not to make changes in the values in question at its New York meeting but to include in its report the direction and probable magnitude of changes likely to be made the next time a formal report is presented. Meanwhile workers who are concerned with uncertainties of the magnitude indicated should use the best current evidence in choosing the values to be used.

THE ELEMENTS TO WHICH THIS DISCUSSION APPLIES

Element	Present Value	Comment
Carbon	12.010	Probably low by 0.001
Nitrogen	14.008	Probably high by 0.0005
Sodium	22.997	Slightly high, probable best value between 22.990 and 22.994
Manganese	54.93	Probably low by 0.01
Terbium	159.2	Best value near 158.9
Thulium	169.4	Best value near 169.0
Gold	197.2	Best value near 197.0
Iridium	193.1	Best value near 192.2

The Commission took note of recent work on natural variations in the abundance ratios of isotopes, an excellent report on this subject having been prepared by Marble.[37] Abundance ratios of the isotopes of many of the elements vary in some degree. However, it was considered necessary in only one instance to call attention to this variation as affecting the internationally accepted value of an atomic weight. This is in the case of sulfur, to whose atomic weight a range of ±0.003 was attached, in order to indicate the range of values that may apply to sulfur from different natural sources.

The new table has a minor departure in the way

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(16) O. Hönigschmid and J. Goubeau, *Z. anorg. allgem. Chem.*, **163**, 93 (1927), and **177**, 102 (1928).

(17) G. P. Baxter and W. M. MacNevin, THIS JOURNAL, **55**, 3185 (1933).

(18) O. Hönigschmid and R. Sachtleben, *Z. anorg. allgem Chem.*, **171**, 1 (1928).

(19) Clyde R. Johnson, *J. Phys. Chem.*, **39**, 781 (1935).

(20) G. P. Baxter and C. D. Harrington, THIS JOURNAL, **62**, 1836 (1940).

(21) R. K. McAlpine and E. J. Bird, *ibid.*, **63**, 2960 (1941).

(22) T. L. Collins, Alfred O. Nier and Walter H. Johnson, Jr., *Phys. Rev.*, **84**, 717 (1951).

(23) Walter Paul and M. Pahl, *Naturwiss.*, **32**, 228 (1944).

(24) O. Hönigschmid, *Z. Elektrochem.*, **25**, 93 (1919).

(25) N. H. Smith, THIS JOURNAL, **49**, 1642 (1927).

(26) H. E. Watson, *Nature*, **127**, 631 (1931).

(27) F. J. Allen and R. B. Moore, THIS JOURNAL, **53**, 2512 (1931).

(28) W. Heuse and J. Otto, *Physik. Z.*, **35**, 57 (1934).

(29) O. Hönigschmid and H. Striebel, *Z. angew. allgem. Chem.*, **208**, 53 (1932).

(30) O. Hönigschmid and H. Striebel, *Z. physik. Chem.*, Bodenstein Festband, 282 (1931).

(31) F. W. Aston, *Nature*, **127**, 233, 519, 813 (1931); **128**, 149 (1931).

(32) G. P. Baxter and A. Q. Butler, THIS JOURNAL, **53**, 968 (1931).

(33) G. P. Baxter, *et al.*, *ibid.*, **54**, 1275 (1932).

(34) G. P. Baxter and A. H. Hale, *ibid.*, **56**, 615 (1934).

(35) G. P. Baxter and A. C. Titus, *ibid.*, **62**, 1826 (1940).

(36) G. P. Baxter and O. W. Lundstedt, *ibid.*, **62**, 1829 (1940).

(37) J. P. Marble, National Research Council Committee on Measurement of Geologic Time, Rept. for 1950–1951, Exh. D, pp. 108–139.

the value for oxygen is expressed. Since this is a defined value, and therefore an exact number, it is given as 16, rather than (as formerly) 16.0000. To further distinguish it from the values determined in relation to it, the value is printed in bold-faced type and centered in the column.

From time to time proposals are made to change the basis of the chemical scale to 16 as the weight of the oxygen isotope of mass number 16 and thus to end the difference between the chemical and physical scales. The atomic weight of natural oxygen, with which the chemist is usually concerned, would then become 16.0044, and all the other values of the present table would be similarly multiplied by the factor 1.000275. This would affect nearly all relatively recently published values of atomic and molecular weights, as well as a great mass of data on the properties of systems recorded on a molar or "equivalent" basis. It is believed that the confusion that would result would be too high a price to pay for the advantage gained. Relatively few scientists are concerned with both the chemical and physical scales. Those who are must remember, for the present at least, when to use 1.000275 (or a similar number of slightly different magnitude) as a multiplier and when as a divisor.

INTERNATIONAL ATOMIC WEIGHTS

1951

	Symbol	Atomic number	Atomic weight[a]
Actinium	Ac	89	227
Aluminum	Al	13	26.98
Americium	Am	95	[243]
Antimony	Sb	51	121.76
Argon	A	18	39.944
Arsenic	As	33	74.91
Astatine	At	85	[210]
Barium	Ba	56	137.36
Berkelium	Bk	97	[245]
Beryllium	Be	4	9.013
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Californium	Cf	98	[246]
Carbon	C	6	12.010
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Columbium (see Niobium)			
Copper	Cu	29	63.54
Curium	Cm	96	[243]
Dysprosium	Dy	66	162.46
Erbium	Er	68	167.2
Europium	Eu	63	152.0
Fluorine	F	9	19.00
Francium	Fr	87	[223]
Gadolinium	Gd	64	156.9
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	197.2
Hafnium	Hf	72	178.6
Helium	He	2	4.003
Holmium	Ho	67	164.94
Hydrogen	H	1	1.0080
Indium	In	49	114.76
Iodine	I	53	126.91
Iridium	Ir	77	193.1
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.92
Lead	Pb	82	207.21
Lithium	Li	3	6.940
Lutetium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.93
Mercury	Hg	80	200.61
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neptunium	Np	93	[237]
Neon	Ne	10	20.183
Nickel	Ni	28	58.69
Niobium (Columbium)	Nb	41	92.91
Nitrogen	N	7	14.008
Osmium	Os	76	190.2
Oxygen	O	8	**16**
Palladium	Pd	46	106.7
Phosphorus	P	15	30.975
Platinum	Pt	78	195.23
Plutonium	Pu	94	[242]
Polonium	Po	84	210
Potassium	K	19	39.100
Praseodymium	Pr	59	140.92
Promethium	Pm	61	[145]
Protactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.31
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.7
Samarium	Sm	62	150.43
Scandium	Sc	21	44.96
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.880
Sodium	Na	11	22.997
Strontium	Sr	38	87.63
Sulfur	S	16	32.066[b]
Tantalum	Ta	73	180.88
Technetium	Tc	43	[99]
Tellurium	Te	52	127.61
Terbium	Tb	65	159.2
Thallium	Tl	81	204.39
Thorium	Th	90	232.12
Thulium	Tm	69	169.4
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	183.92
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

[a] A value given in brackets denotes the mass number of the isotope of longest known half-life. [b] Because of natural variations in the relative abundances of the isotopes of sulfur the atomic weight of this element has a range of ±0.003.

It may be pointed out that because of existing variations in the relative abundances of the isotopes of oxygen there is a slight inexactness in referring to the atomic weight of "natural" oxygen (defined as 16) as the basis of the chemical scale. As yet this does not affect the table of atomic weights because of the limited accuracy with which the values are given. This situation can be remedied, when it is deemed desirable to do so, in either of two ways. One is to agree on a particular kind of oxygen; for example atmospheric oxygen or ocean-water oxygen, as "natural" oxygen. Another and probably better way is to use as the basis a defined mixture of oxygen isotopes, possibly that representing the best knowledge, at the time the decision is made, concerning the average isotopic composition of terrestrial oxygen.

In 1949 the practice was introduced of including in the table, but as bracketed values to distinguish them from true atomic weights, selected mass numbers for "synthetic" elements. This is continued in the new table. Discoveries of isotopes of certain of these elements that have longer half-lives than the previously chosen isotopes, have resulted in four changes in these values. They are as follows: americium, 243[38]; curium, 243[39]; plutonium, 242[40]; and promethium, 145.[41] Two new elements appear for the first time, berkelium (symbol Bk, atomic number 97), and californium (symbol Cf, atomic number 98).

The name wolfram, as the preferred name for the element more commonly known as tungsten in the English-speaking countries, has been dropped from the table because it has failed to gain acceptance in the United States. Both names, tungsten and wolfram, are now recognized by the International Union.

(38) K. Street, Jr., *et al.*, *Phys. Rev.*, **79**, 531 (1950).

(39) S. G. Thompson, *et al.*, *ibid.*, **80**, 781 (1950).

(40) S. G. Thompson, *et al.*, *ibid.*, **80**, 1108 (1950).

(41) F. D. S. Butement, *Nature*, **167**, 400 (1951).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, POLYTECHNIC INSTITUTE OF BROOKLYN]

Cerium(III) Sulfide and Selenide and Some of their Solid Solutions[1]

BY E. BANKS, K. F. STRIPP, H. W. NEWKIRK AND R. WARD[2]

The relationship between the complex and cubic phases of cerium(III) sulfide has been investigated by the use of molten salts to extract the oxide from the complex form. It has been shown that the complex phase is not a mixture containing the cubic phase. Some solid solution of flux constituents in the Ce_2S_3 crystals occurs. Cerium(III) selenide, Ce_2Se_3 and oxyselenide, Ce_2O_2Se have been prepared and shown to be isomorphous with the corresponding sulfides. Cerium(II) selenide has been prepared by the sodium reduction of cerium(III) selenide, and is isomorphous with CeS. Solid solutions of strontium sulfide and selenide in the corresponding cerium(III) compounds have been shown to exist up to complete filling of the defect structure of the cerium compounds (50 mole per cent.) with an increase in lattice constant. In the case of the sulfides, calcium and magnesium sulfides show lower solubility limits, with a contraction of the Ce_2S_3 lattice.

The authors' attention was first focused on rare earth sulfides in an investigation of the state of cerium and samarium ions in alkaline earth sulfide phosphors.[3] In this investigation, preparations of rare earth sesquisulfides were made by standard methods (*e.g.*, heating the oxides or anhydrous salts in an atmosphere of hydrogen sulfide at temperatures in the range 900–1100°. Under these conditions the products are brown to red powders whose X-ray powder patterns are very complex—"linienreich"—in the words of Klemm,[4] who first reported the X-ray investigation of a series of rare earth sulfides prepared in the conventional manner.

Eastman, Brewer, *et al.*,[5] have reported the preparation of cerium(III) sulfide and similar compounds at higher temperatures (*ca.* 1300–1500°) in carbon vessels in a hydrogen sulfide atmosphere. Under these conditions any moisture or oxygen present in the system is converted to carbon monoxide and the resulting sulfide is free of oxide impurity. The cerium(III) sulfide prepared in this way was found by Zachariasen[6] to have a defect structure of the Th_3P_4 type (space group T_D^6; $I\bar{4}3d$) with $10\,^2/_3$ cerium atoms statistically distributed over 12 equivalent positions in the unit cell. The ideal composition is Ce_3S_4, with all twelve cerium positions filled. Ce_3S_4 is prepared by combining cerium(III) sulfide with cerium(II) sulfide. The latter compound was prepared by Eastman, *et al.*, by allowing cerium(III) sulfide to react with finely divided cerium metal formed by the decomposition of cerium hydride. It has a rock-salt structure with $a_0 = 5.76$ Å. Zachariasen also reports the existence of a continuous homogeneity range between the compositions Ce_2S_3 and Ce_3S_4, having the Th_3P_4 structure.

In the above work, Eastman, *et al.*, state that a very complex X-ray pattern is obtained from cerium(III) sulfide containing very small traces of oxygen, which might be added in the form of the oxysulfide, Ce_2O_2S.[5] Under ordinary conditions our laboratory gases contain enough moisture to convert 5 g. of cerium(III) sulfide to the oxysulfide in about 30 hours at 1000°. Thus, any preparations made without special precautions should yield the complex phase, as observed.

The object of the present work was to determine, if possible, the relation between the cubic cerium (III) sulfide and the complex oxide-containing

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(1) (a) Supported in part by the Signal Corps; (b) presented at the XII International Congress of Pure and Applied Chemistry, New York, N. Y., September 12, 1951.

(2) The University of Connecticut, Storrs, Connecticut.

(3) (a) E. Banks and R. Ward, *J. Electrochem. Soc.*, **96**, 247 (1949); (b) H. L. Yakel, E. Banks and R. Ward, *ibid.*, **96**, 304 (1949).

(4) W. Klemm, K. Meisel and H. von Vogel, *Z. anorg. allgem. Chem.*, **190**, 123 (1930).

(5) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles and N. Lofgren, THIS JOURNAL, **72**, 2248 (1950).

(6) W. H. Zachariasen, *Acta Cryst.*, **2**, 57 (1949).