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Report on Atomic Weights for 1954-55

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Introduction

The first section of this article reproduces verbatim those parts of the report of the Commission on Atomic Weights to the International Union of Pure and Applied Chemistry at Zurich, in July, 1955, that deal with the revision of the atomic weights of twelve elements and include the new International Table. The Commission also called attention to the problem arising from the coexistence of two scales of atomic weights, the chemical scale, which is based on natural oxygen, and the physical scale, which is based on the principal oxygen isotope, O¹⁶. The Commission invited consideration of this problem, and of its possible solution, by everyone interested. The second section of the present report, entitled "The Problem of Two Scales," provides a statement of the problem designed to stimulate such consideration among readers of this journal. Attention is earnestly invited to that section.

Report of the International Commission

During the period since the last report of the Commission on Atomic Weights, to the 17th Conference of the Union at Stockholm in 1953, one of the members of the Commission, A. O. Nier, has made a thorough and painstaking review¹ of all published physical measurements of the masses of nuclear species occurring in nature and of the relative abundances of isotopes. This review covered calculations of masses derived from the energy changes accompanying nuclear reactions as well as measurements made with mass spectrographs and mass spectrometers.

As a result of the study by Nier the Commission recommends the revision of the atomic weights of twelve elements, as follows: dysprosium, erbium, gadolinium, hafnium, indium, nickel, palladium, platinum, rhenium, samarium, tungsten, and xenon. It will be noted that most of these ele-

ments are among those that have presented unusual difficulties for the determination of atomic weights by chemical methods. Four are rare-earth elements, whose isolation from closely related elements has been not only difficult and laborious but often not subject to wholly satisfactory proof. For most of the others the difficulty of preparing compounds of exactly known composition has added to the problems of chemical isolation. No chemical determinations of the atomic weights of any of the twelve elements have been made in recent years, and none are known to be in progress or contemplated. In contrast, both mass determinations and isotopic abundance measurements have been made for each of the twelve elements, except rhenium, in recent years with advanced instruments and with procedures that have been subjected to much critical examination. Mass values for the rhenium isotopes were obtained by interpolation on the packing-fraction curve. Nier's review includes estimates of the accuracy of the results used to derive the recommended atomic weights. In converting values from the physical scale to the chemical scale the customary factor, 1.000275, has been used.

The following paragraphs give brief statements concerning the origins of the values previously used and the citations of the mass and abundance measurements used by Nier in choosing the values now recommended.

Recommended Revisions

Dysprosium.—The value 162.46 has been in use since 1930 and is based on the work of Hönigschmid and von Welsbach,² who compared the anhydrous chloride with silver. It displaced an earlier determination by Kremers, Hopkins and Engle,³ who used the same ratio and found 162.52.

(2) O. Hönigschmid and H. Frh. Auer von Welsbach, *Z. anorg. allgem. Chem.*, **165**, 289 (1927).

(3) H. C. Kremers, B. S. Hopkins and E. W. Engle, *THIS JOURNAL*, **40**, 598 (1918).

(1) A. O. Nier, *Z. Elektrochem.*, **58** (7), 559 (1954).

Recommended value, 162.51: mass determinations by Hogg and Duckworth⁴; isotopic abundance measurements by Inghram, Hayden and Hess.⁵

Erbium.—The value 167.2, adopted in 1938, was a compromise between Aston's⁶ mass spectrographic value, 167.15, and 167.24, obtained by Hönigschmid and Wittner⁷ by comparison of the chloride with silver and with silver chloride. It will be noted that the new value differs less from the chemical value cited than it does from the result of earlier mass spectrographic work.

Recommended value, 167.27: mass determinations by Hogg and Duckworth⁴; isotopic abundance measurements by Hayden, Hess and Inghram.⁸

Gadolinium.—The former value, 156.9, dates from 1936, when it was adopted as a result of agreement between a result reported by Aston⁶ and a chemical determination of the ratio between the chloride and silver made by Naeser and Hopkins,⁹ who found 156.85.

Recommended value, 157.26: mass determinations by Hogg and Duckworth⁴; isotopic abundance measurements by Hess¹⁰ and by Leland.¹¹

Hafnium.—The value 178.6 dates from 1925 and is based on two pairs of determinations of the ratio HfBr₄:4AgBr by Hönigschmid and Zintl,¹² which yielded 178.57 and 178.64 after correction for the "known zirconium content" of the hafnium preparations.

Recommended value, 178.50: mass determinations by Hogg and Duckworth⁴; isotopic abundance measurements by Hibbs.¹³

Indium.—The value 114.76 was adopted in 1934 on the basis of determinations by Baxter and Alter¹⁴ of the ratios of the chloride and the bromide to silver.

Recommended value, 114.82: mass determinations by Halsted¹⁵; isotopic abundance measurements by White and Cameron.¹⁶

Nickel.—The recommended change for nickel is the smallest in the list of twelve. The former value, 58.69, has been in use since 1925 and is based on highly concordant observations of the ratios NiO:Ni by Baxter and Parsons,¹⁷ and NiCl₂:2AgCl by Baxter and Hilton,¹⁸ which were later confirmed by determinations of the ratios NiBr₂:2Ag and NiBr₂:2AgBr, for both terrestrial and

meteoric nickel, by Baxter and Ishimaru.¹⁹ The change to 58.71 appears nevertheless to be justified because of the high accuracy of the measurements of isotopic masses and abundances, the over-all uncertainty of which Nier estimates to be ± 0.002 .

Recommended value, 58.71: mass determinations by Collins, Nier and Johnson²⁰; isotopic abundance measurements by White and Cameron.¹⁶

Palladium.—The old value [106.7] dates from 1909 and is based on a determination of the ratio Pd(NH₃Br)₂:Pd by Gutbier, Haas and Gebhardt.²¹ In 1912 Shinn²² obtained the identical value from the ratio Pd(NH₃Cl)₂:Pd.

Recommended value, 106.4: mass determinations by Halsted¹⁵; isotopic abundance measurements by Sites, Consolazio and Baldock.²³

Platinum.—The former value for this element, 195.23, was first adopted internationally in 1925 but is based on the work of Archibald,²⁴ who published in 1909 the results of an elaborate series of analyses of potassium and ammonium chloro- and bromo-platinates.

Recommended value, 195.09: mass determinations by Duckworth, Woodcock and Preston,²⁵ by Duckworth, Johnson, Preston and Woodcock,²⁶ and by Hogg and Duckworth⁴; isotopic abundance measurements by Inghram, Hess and Hayden,²⁷ and by Leland.²⁸

Rhenium.—The former value 186.31 was adopted in 1931 on the basis of the work of Hönigschmid and Sachtleben,²⁹ who determined the ratio between silver perchlorate and silver bromide.

Recommended value, 186.22: masses estimated by Nier¹ from the packing-fraction curve; isotopic abundance measurements by White and Cameron.¹⁶

Samarium.—The old value, 150.43, is based on identical results reported by Stewart and James³⁰ in 1917 for the ratio SmCl₃:3Ag, and by Owens, Balke and Kremers³¹ in 1920, who used the same ratio. In 1941 Hönigschmid and Hirschbold-Wittner³² reported a lower value, 150.38, based on the ratios of the chloride to silver and to silver chloride, but this value was not adopted for the International Table.

Recommended value, 150.35: mass determinations by Hogg and Duckworth⁴; isotopic abun-

(19) G. P. Baxter and S. Ishimaru, *ibid.*, **51**, 1729 (1929).

(20) T. L. Collins, A. O. Nier and W. H. Johnson, Jr., *Phys. Rev.*, **86**, 408 (1952).

(21) A. Gutbier, P. Haas and H. Gebhardt, *J. prakt. Chem.*, [2] **79**, 457 (1909).

(22) O. L. Shinn, *THIS JOURNAL*, **34**, 1448 (1912).

(23) J. R. Sites, G. Consolazio and R. Baldock, *Phys. Rev.*, **92**, 1096 (1953).

(24) E. H. Archibald, *Proc. Roy. Soc., Edinburgh*, **29**, 721 (1909).

(25) H. E. Duckworth, K. S. Woodcock and R. S. Preston, *Phys. Rev.*, **78**, 479 (1950).

(26) H. E. Duckworth, H. A. Johnson, R. S. Preston and R. F. Woodcock, *ibid.*, **78**, 386 (1950).

(27) M. G. Inghram, D. C. Hess, Jr., and R. J. Hayden, Plutonium Project Report ANL-4012, July, 1947, p. 7.

(28) W. T. Leland, *Phys. Rev.*, **76**, 992 (1949).

(29) O. Hönigschmid and R. Sachtleben, *Z. anorg. allgem. Chem.*, **191**, 309 (1930).

(30) O. J. Stewart and C. James, *THIS JOURNAL*, **39**, 2605 (1917).

(31) A. W. Owens, C. W. Balke and H. C. Kremers, *ibid.*, **42**, 515 (1920).

(32) O. Hönigschmid and Fr. Hirschbold-Wittner, *Z. physik. Chem.*, **189A**, 38 (1941).

(4) B. J. Hogg and H. E. Duckworth, *Can. J. Physics*, **32**, 65 (1954).

(5) M. G. Inghram, R. J. Hayden and D. C. Hess, Jr., *Phys. Rev.*, **75**, 693 (1949).

(6) F. W. Aston, *Proc. Roy. Soc. (London)*, **A146**, 46 (1934).

(7) O. Hönigschmid and F. Wittner, *Z. anorg. allgem. Chem.*, **232**, 113 (1937).

(8) R. J. Hayden, D. C. Hess, Jr., and M. G. Inghram, *Phys. Rev.*, **77**, 299 (1950).

(9) C. R. Naeser and B. S. Hopkins, *THIS JOURNAL*, **57**, 2183 (1935).

(10) D. C. Hess, Jr., *Phys. Rev.*, **74**, 773 (1948).

(11) W. T. Leland, *ibid.*, **77**, 634 (1950).

(12) O. Hönigschmid and E. Zintl, *Ber.*, **58B**, 453 (1925).

(13) R. F. Hibbs, "Mass-spectrometric Measurements of Natural Isotopic Spectra," U. S. Atomic Energy Commission Report 556, August, 1949.

(14) G. P. Baxter and C. M. Alter, *THIS JOURNAL*, **55**, 1943 (1933).

(15) R. E. Halsted, *Phys. Rev.*, **88**, 666 (1952).

(16) J. R. White and A. E. Cameron, *ibid.*, **74**, 991 (1948).

(17) G. P. Baxter and L. W. Parsons, *THIS JOURNAL*, **43**, 507 (1921).

(18) G. P. Baxter and F. A. Hilton, Jr., *ibid.*, **45**, 694 (1923).

dance measurements by Inghram, Hayden and Hess.³³

Tungsten.—In 1938 the value 183.92 was adopted as the result of a long series of comparisons of tungsten hexachloride with silver by Hönigschmid and Menn,³⁴ which agreed with the value derived by Aston³⁵ from mass spectrographic measurements.

Recommended value, 183.86: mass determinations by Duckworth, Johnson, Preston and Woodcock,²⁶ by Duckworth, Kegley, Olson and Stanford,³⁶ and by Geiger, Hogg, Duckworth and Dewdney³⁷; isotopic abundance measurements by Williams and Yuster.³⁸

Xenon.—In 1931 Whytlaw-Gray, Patterson and Cawood³⁹ reported 131.26 as the value of the atomic weight derived from measurements of the ratio of the pressures at which the densities of xenon and oxygen were equal. The rounded value, 131.3, was adopted for the 1932 table, noting the agreement of the above value with that obtained by Aston⁴⁰ with the mass spectrograph (131.27).

Recommended value, 131.30: mass determinations by Halsted¹⁵; isotopic abundance measurements by Nier.⁴¹

Hydrogen and Deuterium.—It is now occasionally found necessary to make stoichiometric calculations involving mixtures of hydrogen and deuterium of known isotopic composition differing significantly from natural hydrogen. In such calculations the recommended value, on the chemical scale, for the isotopic weight of H¹ is 1.0079 and of H², 2.0142.

The Problem of Two Scales

When the isotopes of oxygen, O¹⁷ and O¹⁸, were discovered by Giauque and Johnston in 1929,⁴² work was already under way on the precise inter-comparison of the masses⁴³ of nuclear species. These masses were quite naturally referred to 16 as the mass of "oxygen," because this was the base of reference for the scale of atomic weights. When the isotopic nature of oxygen became known it was immediately apparent that the scale being used by mass spectroscopists was not quite identical with the scale of atomic weights, because the compari-

(33) M. G. Inghram, R. J. Hayden and D. C. Hess, Jr., see Seaborg and Perlman, *Reviews Modern Physics*, **20**, 585 (1948).

(34) O. Hönigschmid and W. Menn, *Z. anorg. allgem. Chem.*, **229**, 49 (1936).

(35) F. W. Aston, "Mass Spectra and Isotopes," Arnold & Co., London, 1933, p. 150.

(36) H. E. Duckworth, C. L. Kegley, J. M. Olson and G. S. Stanford, *Phys. Rev.*, **83**, 1114 (1951).

(37) J. S. Geiger, B. J. Hogg, H. E. Duckworth and J. W. Dewdney, *ibid.*, **89**, 621 (1953).

(38) D. Williams and P. Yuster, *ibid.*, **69**, 556 (1946).

(39) R. Whytlaw-Gray, H. S. Patterson and W. Cawood, *Nature*, **127**, 970 (1931).

(40) F. W. Aston, *Proc. Roy. Soc. (London)*, **A126**, 511 (1930).

(41) A. O. Nier, *Phys. Rev.*, **79**, 450 (1950).

(42) W. F. Giauque and H. L. Johnston, *THIS JOURNAL*, **51**, 1436, 3528 (1929).

(43) Physicists commonly use the term atomic mass or isotopic mass, rather than atomic weight. This is especially appropriate to determinations not based on weighing. However, it is also correct in chemical usage because the property of interest is usually mass rather than the force exerted on mass in a gravitational field. In this report the terms will be used interchangeably. For isotopic elements it would also be more rigorous to say mean atomic mass (weight), but there is no evidence that any confusion results from the shorter designation commonly used by chemists.

sons were being made with the mass of the principal isotope of oxygen, not with the average mass of the three isotopic species. However, there seems to have been no clear recognition that this situation might lead to ambiguities, or even confusion, because of the coexistence of two scales so nearly identical. The following quotation from the Report of the International Commission on Atomic Weights for 1931⁴⁴ tells how the question was settled at that time.

"The discovery of the oxygen isotopes has created the undesirable situation that chemistry and physics are using two different scales for the determination of atomic weights. Because of this the question of an absolute standard has already been more or less widely discussed and various proposals made, for instance, H₁ = 1.00000; He₄ = 4.00000; O₁₆ = 16.0000 as well as the present chemical standard O = 16.0000.

"F. W. Aston, who discussed the question comprehensively before the British Association in 1931, concludes that it is advisable for chemists to retain the present chemical standard, since it amply satisfies all requirements of International Atomic Weights so far as accuracy is concerned. For the more exacting requirements of physics the oxygen isotope O₁₆ seems to him a better standard. The disadvantage that the two scales differ by one or two parts in ten thousand and that this difference will be subject to continual revision does not seem particularly important to him. Confusion may be easily avoided by speaking in one case of the 'atomic weight for chlorine' and in the other of the 'weight of the chlorine atom 35.'

"The Committee agrees unanimously with Aston's opinion and sees no reason for proposing a change in the present standard of atomic weights, O = 16.0000."

On the basis of today's knowledge of the isotopic composition of natural oxygen, the physical and chemical scales differ by nearly three parts in 10,000, instead of "one or two parts," as supposed in 1931. Since 1940 the International Commission has used the divisor 1.000275 in converting data from the physical scale to the chemical scale.

It is now also known that the isotopic composition of oxygen from different sources in nature is slightly variable. For this reason, if the chemical scale is regarded as based on natural oxygen, without qualification, it differs from the physical scale by a factor which ranges from 1.000268 to 1.000278.¹ By the International Commission's usage, however, oxygen for the purposes of the chemical scale of atomic weights has become that mixture of the isotopes of the element whose average mass is 1.000275 times the mass of O¹⁶. To confirm this usage by formal definition would suffice to remedy the logical defect of the chemical scale inherent in its variable base of reference. In recent years the International Commission has considered adopting this formal amendment of the chemical scale but has concluded that before such a step is taken the possibility of unifying the two scales should again be considered.

At this point it is pertinent to point out that the

(44) G. P. Baxter, M. Curie, O. Hönigschmid, P. LeBeau and R. J. Meyer, *THIS JOURNAL*, **54**, 1269 (1932).

INTERNATIONAL ATOMIC WEIGHTS 1955			Plutonium			
Symbol	Atomic Number	Atomic Weight ^a	Pu	94	[242]	
Actinium	Ac	89	Po	84	210	
Aluminum	Al	13	Potassium	K	19	39.100
Americium	Am	95	Praseodymium	Pr	59	140.92
Antimony	Sb	51	Promethium	Pm	61	[145]
Argon	A	18	Protactinium	Pa	91	231
Arsenic	As	33	Radium	Ra	88	226.05
Astatine	At	85	Radon	Rn	86	222
Barium	Ba	56	Rhenium	Re	75	186.22
Berkelium	Bk	97	Rhodium	Rh	45	102.91
Beryllium	Be	4	Rubidium	Rb	37	85.48
Bismuth	Bi	83	Ruthenium	Ru	44	101.1
Boron	B	5	Samarium	Sm	62	150.35
Bromine	Br	35	Scandium	Sc	21	44.96
Cadmium	Cd	48	Selenium	Se	34	78.96
Calcium	Ca	20	Silicon	Si	14	28.09
Californium	Cf	98	Silver	Ag	47	107.880
Carbon	C	6	Sodium	Na	11	22.991
Cerium	Ce	58	Strontium	Sr	38	87.63
Cesium	Cs	55	Sulfur	S	16	32.066 ^b
Chlorine	Cl	17	Tantalum	Ta	73	180.95
Chromium	Cr	24	Techetium	Tc	43	[99]
Cobalt	Co	27	Tellurium	Te	52	127.61
Columbium (see Niobium)			Terbium	Tb	65	158.93
Copper	Cu	29	Thallium	Tl	81	204.39
Curium	Cm	96	Thorium	Th	90	232.05
Dysprosium	Dy	66	Thulium	Tm	69	168.94
Erbium	Er	68	Tin	Sn	50	118.70
Europium	Eu	63	Titanium	Ti	22	47.90
Fluorine	F	9	Tungsten	W	74	183.86
Francium	Fr	87	Uranium	U	92	238.07
Gadolinium	Gd	64	Vanadium	V	23	50.95
Gallium	Ga	31	Xenon	Xe	54	131.30
Germanium	Ge	32	Ytterbium	Yb	70	173.04
Gold	Au	79	Yttrium	Y	39	88.92
Hafnium	Hf	72	Zinc	Zn	30	65.38
Helium	He	2	Zirconium	Zr	40	91.22
Holmium	Ho	67				
Hydrogen	H	1				
Indium	In	49				
Iodine	I	53				
Iridium	Ir	77				
Iron	Fe	26				
Krypton	Kr	36				
Lanthanum	La	57				
Lead	Pb	82				
Lithium	Li	3				
Lutetium	Lu	71				
Magnesium	Mg	12				
Manganese	Mn	25				
Mendelevium	Mv	101				
Mercury	Hg	80				
Molybdenum	Mo	42				
Neodymium	Nd	60				
Neon	Ne	10				
Neptunium	Np	93				
Nickel	Ni	28				
Niobium (Columbium)	Nb	41				
Nitrogen	N	7				
Osmium	Os	76				
Oxygen	O	8				
Palladium	Pd	46				
Phosphorus	P	15				
Platinum	Pt	78				

^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 abundance of the isotopes of sulfur the atomic weight of this element has a range of ± 0.003 .

variability of the isotopic composition of oxygen has had no practical effect on the values for atomic weights that appear in the International Table. There are three principal reasons for this. For those atomic weights that are derived either from stoichiometric ratios or from comparisons of gas densities, the experimental uncertainties are in most instances larger by about an order of magnitude than the known variation in the composition of natural oxygen. Furthermore, few of the chemically determined values now in use are derived from direct comparisons with oxygen. Most of them are based on comparisons with silver, chlorine, and bromine—three elements that have been intercompared in numerous series of exhaustive measurements. The relation of the three to oxygen rests mainly on the ratio $\text{AgNO}_3:\text{Ag}$. This comparison was made in an exceptionally thorough manner by Richards and Forbes⁴⁵ about fifty years ago, with results that were confirmed in several later investigations. Although the work on silver was of very high precision, and the concordance of values found by the several investigators suggests

(45) T. W. Richards and G. S. Forbes, *Publ. Carnegie Inst. Wash.* No. 69, 47 (1907); *THIS JOURNAL*, **29**, 808 (1907).

that it is probably of very high accuracy as well, it is unlikely that the unknown isotopic composition of the oxygen (and of the silver) involved in this determination contributed significantly to its total uncertainty. Since most of the currently accepted values for atomic weights rest on comparisons with silver and chlorine, or silver and bromine, they reflect the experimental errors of the secondary comparisons in addition to the uncertainties of the secondary reference numbers. Apart from those chemically determined atomic weights that are not based directly on natural oxygen, there are now 36⁴⁶ that are derived mainly or entirely from mass spectroscopic measurements or nuclear calculations. These 36 are therefore based on O¹⁶, rather than on natural oxygen. From this brief review of the origin of the currently accepted values for atomic weights, it can be concluded that in the use of natural oxygen as its base of reference the chemical scale suffers less from a practical than from a logical defect. This situation may change, however, as atomic weights become known with greater accuracy.

It seems desirable not to end this part of the discussion without brief comments about the nearly 50 values in the International Table that still rest on chemical determinations or gas-density measurements. The differences between these values and the "best" physically derived values, as compiled by A. O. Nier,¹ are not large. With nine exceptions they do not exceed 2 parts in 10,000. For the most part these differences will require for their resolution more accurate chemical determinations or more accurate measurements of isotopic abundances. It is an interesting corollary that for a few of the elements, such as silver, chlorine, and bromine, that occur in nature in the form of two isotopes of roughly equal abundance, the chemically determined atomic weights, together with the physically determined isotopic masses, may yield more accurate information on the isotopic abundances than is available thus far from mass spectroscopic measurements.

Let us now consider what might be done about unifying the two scales. In principle the solution is quite simple. To achieve a unified scale it is only necessary to agree on a single reference substance and to assign to its relative mass a fixed numerical value. The choice of the substance is not very important, provided its mass is invariant and can be reliably intercompared with the masses of other species. If the reference substance were O¹⁶ and its assigned mass the exact number 16, the chemical scale would be abandoned in favor of the physical scale. The atomic weight of natural oxygen would then be 16.0044, with some variation in the next decimal place, and all other atomic weights in the current International Table would be increased in the same proportion. Conversely, if the physical scale were merged with the existing

(46) Of the 36, 18 are elements that have no known natural isotopes. Such elements are sometime designated nonisotopic or monoisotopic. These adjectives are etymologically defective. H. E. Duckworth, in a private communication, has suggested anisotopic as being etymologically sound and justifiable by analogy with other scientific terms that have the prefix "an." The adjective "simple" has also been used but it lacks the specificity of anisotopic.

chemical scale, the mass of O¹⁶ would become some exact number close to 15.9956 instead of 16, and all atomic masses now reported on the physical scale would be decreased in the same proportion.

The practical difficulties involved in making this kind of transition from the present dual system to a single scale are considerable. If such a transition is made, there will be an inevitable period of confusion while those whose accustomed numbers have been discarded get used to the new ones. Above and beyond this will be the hard necessity of revising all important references and data related to the scale that is to be abandoned. On both scores it would seem that abandoning the chemical scale would involve much the greater difficulty. One need only consider the very large number of chemical textbooks, reference works, and handbooks, in all of which atomic and molecular weights form an important part of the content. In addition, there exists in the periodical literature a very large number of relatively permanent physicochemical data reported in terms of gram equivalents and moles, and of concentrations referred to these quantities. Many of these data are of sufficient accuracy so that a systematic change of nearly three parts in 10,000 could not be disregarded. By contrast, data based on the physical scale are still undergoing frequent revisions, and the number of scientists who use them must certainly be much smaller than of those who use the chemical scale.

The alternative of abandoning both existing scales and establishing a new one should not be dismissed without consideration, especially if a reference mass could be chosen that has no logical or practical disadvantages and that would minimize the revision of published material. In the 1931 report of the International Commission two possible new scales were mentioned. One used the exact number 1 as the relative mass of hydrogen-1.⁴⁷ Adoption of the hydrogen scale would change all data relating to the masses of atoms by about 8 parts in 1000—perhaps a sufficiently drastic change to minimize the resulting confusion. This scheme would also put an end to those curious quantities—negative mass defects—which are now attributed to the great majority of all nuclear species. However, on this scale the mass defects of the heavier elements become so large that the familiar and useful "mass numbers" would be displaced from the atomic masses of the respective nuclides by as much as two units.

A scale based on 4 as the relative mass of helium-4 does not appear in the light of present knowledge to offer any advantages over either of the existing scales and would change all numbers on both scales by about one part in 1000.

A scale based on fluorine-19, with an assigned exact mass of 19, would appear to offer more attractive possibilities.⁴⁸ In the current Inter-

(47) A scale based on hydrogen was advocated by Dole in 1937 (*J. Chem. Phys.*, **4**, 268 (1936)), in connection with his discovery of the difference between the isotopic composition of oxygen in air and in Lake Michigan water. It was not favorably considered by the International Commission (G. P. Baxter, O. Hönigschmid and P. LeBeau, *THIS JOURNAL*, **59**, 219 (1937)).

(48) This idea has been suggested by several persons, in particular J. I. Hoffman, Herbert J. Fleischmann, and F. L. Mohler, in private communications.

national Table the atomic weight of fluorine (which has no known natural isotopes) is given as 19.00, but its more exact value is 18.9992 ± 0.0002 .¹ The adoption of the exact number 19 for fluorine therefore would shift all numbers related to the current chemical scale upward by only about one part in 25,000. A change of this magnitude could be neglected for most of the data of chemistry, and the formal revision of books, etc., could proceed leisurely, with little confusion. On the current physical scale the mass of F^{19} is 19.0044. A change to 19 would shift all masses on the physical scale downward by about two parts in 10,000, an amount that would, of course, necessitate revision of all tabulations. Provided it offers no insurmountable obstacles for intercomparison with the masses of other nuclear species, a scale based on $F^{19} = 19$ might be more acceptable to physicists than one based on a non-integral value such as 15.9956 for O^{16} .

If a decision can be reached to unify the chemical and physical scales by one means or another, it would probably be desirable to set some fixed future time at which the change-over will be made, so

as to give authors, editors, and publishers adequate notice. If such a decision is not reached, all possible measures should be taken to minimize confusion and misunderstanding. In considerable areas of scientific work the context will indicate clearly the scale that is being used. For example, all data on the masses of individual nuclear species and quantities related to them would be recognized as based on the physical scale. Likewise, all the conventional atomic and molecular data of chemistry would be recognized as belonging to the chemical scale. In borderline areas, such as matters concerning the Faraday, or Avogadro's number, it should be possible to establish a uniform practice to use always one scale or the other. Some well-planned and conscientious efforts of this kind might make the situation tolerable.

It remains only to repeat the invitation to all concerned to give the problem thorough and objective consideration. Expressions of opinion will be welcomed.

U. S. BUREAU OF STANDARDS
WASHINGTON 25, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, DUKE UNIVERSITY]

Effects of X-Irradiation upon Some Organic Substances in the Solid State: Simple Alcohols, Amines, Amides and Mercaptans¹

BY CLARENCE F. LUCK AND WALTER GORDY

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Microwave magnetic resonance has been employed to study the effects of ionizing X-rays on some simple alcohols, amines, amides and mercaptans in the solid state. The proton hyperfine structure of the electron spin resonance allows fairly definite identification of the radicals produced in certain of these. For example, methyl alcohol, acetamide, sodium methoxide appear to form the radical $(CH_2)^+$, which, however, could be attached to some other molecule or group provided that the group has no nuclei which could interact with the electron spin. Ethyl alcohol and propionamide appear to form the radical $(C_2H_4)^+$. No such radicals are formed by the sulfur compounds, and it is believed that the odd electron (electron vacancy) in these remains on the S atom or atoms.

Microwave paramagnetic resonance has been used in this Laboratory to study the effects of ionizing radiations on many substances including amino acids,² proteins, carboxylic acids and metal organic compounds. A number of organic free radicals have been produced and identified in the solid state. A set of microwave "fingerprints" of organic radicals is thus being obtained which allows recognition of these same radicals when they are produced in other substances. In addition, experience is being gained which helps in the prediction of the primary effects of ionizing radiation in complex organic substances. The present work represents an extension of the method of microwave magnetic resonance to other classes of organic compounds.

The experimental methods are the same as those employed in the previous work.² The samples were irradiated several hours with 40 kv. X-rays. Most of the samples of the present study were studied at 77°K. and at 9 kMc./sec.

A general tendency already noted² previously is

(1) This research was supported by The United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

(2) W. Gordy, W. B. Ard and H. Shields, *Proc. Nat. Acad. Sci.*, **41**, 983 (1955); **41**, 996 (1955).

that whenever a given molecule of a solid is dissociated by ionizing radiations, the various parts, unable to escape rapidly, tend to react and re-react until the most stable assembly of simpler molecules and radicals is formed from the pieces. This useful generalization is borne out by several examples in the present study. The resonance of ethyl alcohol (see Fig. 1) consists of the characteristic quintet of the ionized ethylene radical $(C_2H_4)^+$. It is evident that in addition to $(C_2H_4)^+$ the stable H_2O molecule could be formed from ionized C_2H_5OH . Although the heat of formation of the $(C_2H_4)^+$ radical is unknown, its paramagnetic resonance pattern shows that the odd electron is in a symmetric molecular orbital which is spread all over the molecule. This delocalization of the odd electron wave function should enhance the stability of this radical over one of lower symmetry in which the odd electron would be essentially localized on a carbon.

A quintet like that for irradiated ethyl alcohol is found for irradiated propionamide and presumably it arises from the same radical, $(C_2H_4)^+$ (see Fig. 2). The spacing is slightly different, total spread 98 instead of 93 gauss. If this small difference is not due to error, it may arise from differences in internal