

Can the scales of atomic weights and nuclidic masses be unified?

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THE current discussion about a unified scale of nuclidic masses and atomic weights* grew out of a desire to correct the indefiniteness of the chemical scale of atomic weights which results from variations in the isotopic composition of natural oxygen. Oxygen, with a defined atomic weight of 16, has been the universally accepted reference element for atomic weights since early in the present century. Earlier many chemists favored a scale based on hydrogen, with a definite atomic weight of unity. The hydrogen scale originated with Dalton and doubtless enjoyed support on the basis of Prout's hypothesis that the hydrogen atom is the structural unit in the atoms of all other elements. However, the operational advantages of oxygen in stoichiometric determinations of atomic weights offset the logical arguments for hydrogen and in time brought about the general acceptance of the oxygen scale. It was natural to assign a whole number, sixteen, to oxygen, rather than the nonintegral number representing its atomic weight on the hydrogen scale. Thus the unit of atomic weight became one-sixteenth the weight of an atom of oxygen.

By the time of Aston's pioneer work in mass spectroscopy, the choice of oxygen as the reference element was firmly established. The atomic weights of silver, chlorine, and bromine, important secondary standards, had been related to that of oxygen by classical experimental work whose reliability has not yet been superseded by either chemical or physical measurements. Following these primary determinations, the atomic weights of many of the elements were determined by reference to these standards. This work, which enjoyed the attention of the most capable chemists of the time, had been largely accomplished before the isotopic nature of oxygen became known, and completed before the relative abundances of the three isotopes were at all well established.

In the beginnings of mass spectroscopy, the data on isotopic abundances were not reliable enough to supply useful information for the calculation of atomic weights. However, this situation changed rapidly, and the International Commission on Atomic Weights soon began to take mass-spectroscopic determinations of isotopic masses and abundances into account in its periodic revisions of the International Table of Atomic Weights. Up to the present time the atomic weights of 36 elements have been revised on the basis of physical measurements, mainly mass-spectroscopic. This list includes about 20 anisotopic elements, and therefore only about

16 isotopic ones. It follows that there are some 50 elements whose "official" atomic weights are derived from the classical stoichiometric and gas-density measurements. With a possible few exceptions the differences between the values derived from the chemical measurements and those calculated by Nier (1) from physical data exclusively are within the uncertainties of the respective methods and must await additional chemical and physical measurements, or both, for their resolution.

From 1940 on, when the proportions of O^{17} ** and O^{18} in natural oxygen were fairly well established, the International Commission has used a fixed factor in converting to the chemical scale, atomic masses reported on the physical scale. Thus those atomic weights in the International Table that are based on physical measurements are in fact related to O^{16} rather than to natural oxygen. The factor used for the conversion is 1.000275, which lies within the range of numbers resulting from the observed variations in the isotopic composition of natural oxygen. By this action of the International Commission values for atomic weights adopted since 1940 are not referred to a variable natural oxygen, but to oxygen of defined isotopic composition. Thus the present International Table of Atomic Weights is actually based in part on 16 as the atomic weight of undefined natural oxygen and in part on $16/1.000275$ as the atomic weight of oxygen isotope-16. However, this logical inconsistency has no practical significance because the uncertainties due to experimental errors of atomic weights derived from chemical determinations are, with a very few exceptions, greater by about an order of magnitude than the uncertainty arising from the variable isotopic composition of oxygen.

In its report for 1953 (2) the International Commission recognized that it would be desirable to correct the inexactness of the scale by formal definition rather than implicitly by the consistent use of a conversion factor such as 1.000275. Out of the discussion of this proposal there emerged the idea that the possibility of achieving a unified scale should once again be studied. This idea had been put forward from time to time by a number of persons, but without getting much favorable attention. A recent paper by Mattauch (3) reviews this history. It need only be noted here that the present existence of the two scales, unfortunate though it is, could not well have been avoided. When Aston realized that the oxygen whose atomic mass he was comparing with the masses of other atoms was not the same as the oxygen used in chemical determina-

* The term "atomic weight" is universally used by chemists instead of the more strictly correct term "atomic mass". It obviously derives from the fact that weighing was the only method of measurement originally available for the determination of atomic masses. Since such determinations are necessarily comparative and are made in a common gravitational field, the values obtained are numerically identical with the masses.

** In this article mass numbers are given as superscripts following the symbol for the element, in accordance with the usual American style, rather than preceding the symbol, as recommended by the International Union of Pure and Applied Chemistry.

tions of atomic weights, he could hardly have been expected to assign a provisional, nonintegral number to the mass of his oxygen pending the accurate determination of the difference between this atomic mass and that of natural oxygen. For even more obvious reasons the International Commission could not have abandoned its base of reference when there was as yet no evidence that isotopic abundance measurements would contribute significantly to the calculation of atomic weights. Thus it was quite natural that two scales should have emerged, with a relation to each other that was at first known only approximately. Now, however, this relation is so well known that the situation can be intelligently reviewed.

To adopt a defined ratio between the scales would provide an easy solution for the indefiniteness of the chemical scale. This could be done by defining the isotopic composition of the "natural" oxygen whose atomic weight is taken as 16. An even simpler definition would be to agree to take O^{16} as the reference species of the chemical scale, as it is of the physical scale, but with the defined mass of $16/1.000275$, which could be taken as 15.9956.

Such a decision would involve no revision of published data. For this reason it might be preferred by the two groups of scientists who now consistently use either one scale or the other and are never concerned with possible confusion of data based on the two. However, there is a considerable group of physical chemists who are not so fortunate. They are concerned with the calculation of thermodynamic functions from statistical, spectroscopic, and other molecular data, and the utilization of such functions. In such calculations and in the utilization of the derived functions, it is obviously necessary to use consistent atomic constants. However, the source literature frequently fails to specify the scale used and in some instances mixes data based on the two scales. The basic data are, in many instances, of sufficient accuracy to be significantly impaired by the uncertainties of nearly 3 parts in 10^4 introduced by the ambiguity of the scales. With the further improvement that is to be expected in the accuracy of physicochemical data of this kind the results of the confusion between the scales will become proportionately worse. Perhaps authors and editors could be persuaded to be unambiguous in these matters, but at present a substantial part of the pertinent literature is at fault.

Early in the recent discussion it became apparent that unification of the scales probably could not be accomplished by abandoning either of the existing scales in favor of the other. To retain a defined equivalent of the chemical scale would mean, for physicists, not only the revision of published values for nuclidic masses, but also the use of a nonintegral value (such as 15.9956) as the defined mass of O^{16} . Although this change might not have strictly logical objections (it can be argued that a single integral number can have no special sanctity in a series of a thousand or so nonintegral numbers), it would introduce an awkward

complication in defining the mass unit. Aesthetic objections to such a change also must be conceded, and there is the likelihood that in the years to come it would introduce one more pedagogical difficulty.

The alternative proposal of abandoning the chemical scale and retaining the physical scale met with widespread objection among chemists, primarily because of the enormous task of revising published data on atomic and molecular weights and on molar quantities. There are millions of such data. Although the accuracy of many of them is such as not to be seriously damaged by failure to make the necessary change of 275 parts per million, there remains a substantial body of physicochemical data for which the opposite is true. K. S. Pitzer (4) has estimated that there are as many as a million physicochemical data whose accuracy are of the order of 1 part in 10 000 and whose usefulness therefore would be impaired unless there were a prompt and systematic revision. Such a revision obviously could be accomplished only over an interval of some years in handbooks and reference works, and it is virtually impossible to revise data scattered through the periodical literature. For this sound reason, as well as the less logical but understandable reluctance of other chemists to abandon familiar numbers, it became apparent that unification on the basis of the present physical scale would not be acceptable to the chemical world.

Thus there remained only the alternative of finding a new scale acceptable to both physicists and chemists. For chemists the search would necessarily be limited to scales that would require much smaller changes in atomic weights, and the quantities related to them, than would the adoption of the present physical scale. The first of these to be considered was the one for which fluorine-19 would be the reference species, with a defined mass of 19. The adoption of this scale would involve revising numbers now based on the chemical scale (upwards) by 41 parts per million, a change far less objectionable than the 275 parts per million required by the use of O^{16} , with a defined mass of 16. Further, fluorine-19 constitutes the element fluorine, so far as is now known. This was considered advantageous from the chemist's point of view because, as an element, fluorine could be used directly as the reference species in certain stoichiometric determinations of atomic weights. Fluorine-19 does not appear to be acceptable as a reference nuclide to physicists, however, for reasons that are given by Kohman, Mat-tauch, and Wapstra, in another paper in this issue.

There is no anisotopic element other than fluorine whose atomic weight on the present chemical scale, if rounded to the nearest whole number, would not cause an excessively large revision of currently accepted atomic weights. There are, however, several nuclides whose masses, on the chemical scale, differ from their mass numbers by amounts no greater than 50 parts per million. They are C^{12} , N^{15} , O^{17} , and O^{18} . Of these, C^{12} is the only one that is the dominant isotope of the respective element.

J. Mattauch has given the problem of the scales much study during recent months. Simultaneously with A. Ölander he brought C^{12} to the attention of the International Commission on Atomic Weights. He has now concluded (see accompanying paper) that a scale based on 12 as the defined mass of C^{12} would not only be an acceptable substitute for the present physical scale, but that it actually has operational advantages for physical comparisons of nuclidic masses. Its use would cause a revision (downward) of presently accepted atomic weights by 43 parts per million. On this ground it is just as acceptable as the proposed fluorine-19 scale. Although its adoption would initiate a process of revision of innumerable tabulations of data, which would continue until all chemical handbooks and reference books now in use have been reissued or superseded, the results of a failure to use the revised values, or of mixing old and new values, would have little physical significance. If the C^{12} scale indeed proves acceptable to physicists, chemists should and probably will make up their minds to accept it also.

Carbon as an element would not have been considered a suitable reference element when stoichio-

metric determinations were the most important source of atomic weights, but this does not affect the present usefulness of C^{12} as the reference species. Chemical determinations of atomic weights are now very infrequently made. Even if this exacting art were to be revived, in order to get more accurate values for certain atomic weights than are presently obtainable by mass spectroscopy, no element or nuclide would have unique advantages as the reference species. All that is needed for this purpose is an accurate interrelation of the atomic weights of several elements. Such an interrelation is available through the highly accurate inter-comparisons, by physical methods, of the atomic weights of the anisotopic elements and certain others in which a single isotope is predominant.

If agreement can be reached on the carbon-12 scale, a very desirable simplification of scientific notation will have been accomplished.

References

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3. J. Mattauch, *Z. Naturforsch.*, **13A**, (7), 572 (1958).
4. Private communication.

C^{12} as a basis for a unified scale of nuclidic masses and atomic weights

By T. P. Kohman, J. H. E. Mattauch, and A. H. Wapstra

THERE exist at present three scales of atomic masses or weights: (1) the absolute scale based on the gram, (2) that defined by taking the mass of one atom of the nuclide O^{16} equal to 16 units (the "physical scale" of "atomic masses" or "nuclidic masses"), and (3) that taking the average atomic mass of the isotope mixture of "natural" oxygen as 16 units (the "chemical scale" of "atomic weights"). Of these, only the last two are in common and extensive use. The chemical scale is indefinite to the extent of the variation in the average atomic mass of oxygen from various natural sources (some 15 parts per million) resulting from variations in the relative proportions of O^{16} , O^{17} , and O^{18} .

Recently, proposals for improving this situation have been made and discussed. These discussions concern (1) how the definition of the chemical scale can best be made more precise, (2) whether the physical and chemical scales ought to be unified or not, and (3) whether the definition of the physical scale could perhaps be improved as well.

The most extensive recent discussion of the problem of the mass scales is that of Wichers,¹ who invites consideration and expressions of opinion by interested persons. Accordingly, we wish to bring into the light of public discussion a proposal which has received considerable consideration in private and which seems

to have merit with respect to all three of the above-mentioned points.

The existence of two sets of mass values differing slightly but significantly, even were the present uncertainty of the chemical scale to be eliminated by a more precise definition, in itself causes some confusion, which is often reflected in pedagogic difficulties. But more serious is the necessity of having two values, one for each scale, of the universal molar "constants", in particular the Avogadro number, the Faraday constant, and the gas-law constant. The necessity of matching the proper value of the Avogadro number with the mass values employed arises especially often in the domain of nuclear chemistry.

Proposals to unify the scales by adopting the physical scale for chemical atomic weights have been regarded with disfavor by many chemists because of the relatively large change (about 275 parts per million) which would have to be made in all of the quantities whose values depend on the size of the mole. There are many physicochemical data whose precision are greater than that and whose values would therefore have to be changed. On the other hand, the serious consideration which has been given by chemists² to the proposal of a new unified scale based on $F^{19} = 19$, which would result in a change of 41 parts per million, indicates that many chemists would be willing to accept a unified scale if the atomic weights would not be changed by more than about this amount. There are relatively few chemical data bearing such high precision.

Fortunately, there is a possible scale definition

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