Supplement

The Rational Choice of a Unified Scale for Atomic Weights and Nuclidic Masses

BY J. MATTAUCH

The Scale Proposal ^{19}F = 19.—There are in the main two reasons which would prevent physicists to adopt this scale.

(1) In the mass-spectroscopic determination of nuclidic masses the most important substandard is the mass of ^{12}C. In any instrument (mass-spectrograph, mass-spectrometer, time of flight) it is possible to measure the mass of ^{12}C in relation to that of ^{16}O by doublets containing no other nuclides; such doublets can be produced because the ratio of the mass numbers of ^{12}C and of ^{16}O is a simple one, namely, 3:4. It is therefore possible to tie the mass of ^{12}C directly to that of ^{16}O with an accuracy which is clearly superior to that of a measurement implying other nuclides besides ^{12}C and ^{16}O. The same is not true for the measurement of the mass of ^{12}C in relation to that of ^{19}F. Since the two mass numbers, 12 and 19, are incommensurable, one cannot produce a doublet containing no other nuclides. The accuracy with which, by mass-spectroscopic methods, the mass of ^{12}C can be linked to that of ^{19}F is therefore necessarily inferior to that of the measurement of ^{12}C in relation to ^{16}O. To lower the precision of the mass of the substandard ^{12}C has of course the consequence of degrading the accuracy with which the masses of many other nuclides can be determined.

(2) Very soon after Aston had carried out the first precise mass measurements with his mass-spectrograph, another method of computing masses of nuclides was developed. This method is based on the measurement of so-called Q-values, *i.e*, of the energies liberated in nuclear reactions leading to the ground state of the product nucleus of the reaction. Since its conception by Rutherford and others this method of Q-values has competed in accuracy with the mass-spectroscopic method. Again and again the comparison of the results of both methods and the tracking down of discrepancies between the two has furnished valuable clues for the elimination of errors (systematic and otherwise) of one or the other of the two methods. It would clearly be unwise to renounce voluntarily this advantage—as would be the case if ^{16}O were to be replaced by ^{19}F as the standard nuclide. The reason for this lies in a peculiarity of the evaluation of nuclidic masses for Q-values[1] which is not generally realized. It seems quite obvious that the Q-value method will be most useful if it is freed from assumptions as far as possible. In order to exclude assumptions about the correct form of an exact β-decay theory (which does not exist today), one is led to demand that for the calculation of masses so-called total β-decay energies should not be pooled with Q-values proper as defined above. However, from Q-values alone one can compute the masses of only those nuclides which have exactly the same ratio of mass number to atomic number (A/Z) as the standard nuclide. In other words, Q-values proper permit mass calculations of only those nuclides which in a plot of A versus Z lie on the straight line defined by the origin of the coördinate system and the standard nuclide. In such plots far more of the known nuclides lie on the straight line $A = 2Z$ than on any other; for these nuclides $A/Z = 2$. Starting with $^{2}_{1}$D there are, up to $^{60}_{30}$Zn, altogether 30 nuclides of this kind known (one for each element from hydrogen to zinc) of which 13 are stable. If one of the latter, *e.g.*, $^{16}_{8}$O or $^{12}_{6}$C is taken as standard, there remains for comparison a list of 12 stable nuclides, the masses of which can be determined from mass spectroscopic doublets *as well as* from Q-values as defined above. If $^{18}_{8}$O, having the ratio A/Z = 9/4, is chosen as the standard nuclide, then altogether 14 nuclides with this ratio are known (one for every fourth element from beryllium to barium) of which 8 are stable; excluding the standard, the list for comparison of the two methods is, therefore, reduced to 7 nuclides. To choose $^{19}_{9}$F with A/Z = 19/9 as the standard nuclide means that only every ninth element from fluorine to xenon has a known nuclide of this kind, so that there are 6 of them altogether. Since only two of these are stable, only one nuclide, $^{38}_{18}$A, remains for comparison with the standard.

Other Scale Proposals.—It appears that the idea of ^{19}F arose among chemists for two reasons: first, because fluorine-19 has no known natural isotopes; second, because assigning to it the exact relative mass 19 would require a shift (upward) of only 0.0041% in all numbers based on the present chemical scale. If the first argument can be neglected on the ground that in the future atomic weights will be derived almost entirely from physical measurements of nuclidic masses and isotopic abundances, and only the second argument is to be met, it is immediately clear that certain other nuclides can be considered. The several possibilities and the changes that their adoption would cause in the International Table of Atomic Weights are as follows: ^{12}C = 12 (−0.0042%), ^{15}N = 15 (−0.0030%), ^{17}O = 17 (+0.0008%), ^{18}O = 18 (+0.0004%). When the effects of these possible choices on the revision of published chemical data are compared with that of ^{16}O = 16 (+0.0275%), it is clear that ^{18}O = 18 would be the most advantageous. However, physicists would be reluctant to adopt it because both arguments mentioned earlier against ^{19}F = 19 apply also against ^{18}O = 18, even if to a somewhat lesser degree.

Of the four possibilities (besides ^{16}O = 16) only ^{12}C = 12 meets the desired $A = 2Z$ criterion mentioned earlier in paragraph 2. As might be inferred from what has been said in paragraph 1 above the advantages of the scale ^{12}C = 12 to the mass-spectroscopist would be tremendous. Not only do the doubly, triply and quadruply charged atomic ions of ^{12}C fall to integer mass numbers so

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[1] J. Mattauch, L. Waldmann, R. Bieri and F. Everling, "Annual Review of Nuclear Science," Vol. VI, 1956, p. 179.

that they can be paired in doublets with nuclides having mass numbers 6, 4 and 3, respectively; but —much more important—no other nuclide (with the exception of ^{13}C) can be found which forms polyatomic molecular ions with as many atoms (up to 10 and more) in the molecule. Therefore, the scale $^{12}C = 12$ would allow many more direct doublet-comparisons (as a matter of fact at every multiple of 12 up to $A = 120$ and more) of masses, especially of heavy nuclides, with the reference standard than any other scale. ^{12}C has the additional advantage that it forms many more hydrides than any other nuclide (again excepting ^{13}C) so that an easy reference line for doublets can be produced at almost every mass number up to $A > 120$ Thus for physicists the scale $^{12}C = 12$ would be much better even than $^{16}O = 16$ and by far better than any other scale proposal. It seems, therefore, that from all points of view a unified scale based on $^{12}C = 12$ deserves consideration.

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Max Planck Institut für Chemie
Mainz, Germany

[Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute]

Preparation and Thermal Stability of Lithium Titanium Fluoride[1]

By George J. Janz, Max R. Lorenz and Charles T. Brown

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The preparation and properties of Li_2TiF_6 have been reinvestigated. After two recrystallizations and high vacuum drying at 200°, 2.57% HF and 0.75% H_2O are still retained, most likely as solvates. When heated *in vacuo* at 365°, HF and H_2O are removed with little if any decomposition of Li_2TiF_6. At higher temperatures, Li_2TiF_6 undergoes a primary decomposition to form LiF and TiF_4. Thus a sample held under high vacuum at 485° for 21 hr. was found to be 42.5% decomposed. When exposed to atmospheric moisture and heated, Li_2TiF_6 decomposes by hydrolysis, with the formation of LiF, TiO_2 and HF.

Recent investigations on the cryoscopic behavior and electrical conductance of Li_2TiF_6 in chloride melts[2] in this Laboratory stimulated an interest in the thermal properties of lithium titanium fluoride. The present communication reports an investigation of the thermal stability of Li_2TiF_6 at temperatures up to 485°. Very little information on the preparation and physical properties of this compound are found in the literature. The work of Ginsberg and Holder[3,4] on the alkali titanium fluorides is most informative qualitatively. Preliminary experiments in this Laboratory indicated that the melting point of Li_2TiF_6 was in the region of 580° rather than 480° as reported by Ginsberg[3] and that when heated in air, hydrogen fluoride rather than elemental fluorine[4a] was evolved. The need for quantitative details in the preparation and the purity of Li_2TiF_6, and an investigation of its thermal stability when heated *in vacuo* or an inert atmosphere to establish the nature of the primary dissociation process was apparent.

Experimental

Preparation of Li_2TiF_6.—The method selected was that[4a] in which the salt is formed by the addition of Li_2CO_3 to a solution of TiO_2 in HF, *i.e.*

$$TiO_2 + 6HF \xrightarrow[HF]{excess} H_2TiF_6 + 2H_2O \qquad (1)$$

and

$$H_2TiF_6 + Li_2CO_3 \longrightarrow Li_2TF_6 + H_2O + CO_2\uparrow \qquad (2)$$

The procedure and results quantitatively were as follows. TiO_2 (40 g., reagent grade), dried at 100° for 3 hr., was dissolved in concentrated HF solution (48%) using a quantity 20% in excess (150.3 g.) of that required to form H_2TiF_6. Upon complete solution, Li_2CO_3 (reagent grade) was added until evolution of CO_2 subsided. To ensure complete solution of the Li_2TiF_6, the volume was made up to approximately 300 cc. with distilled water, and the mixture filtered to remove LiF. The solution was then made slightly acidic (1–2%) by the addition of some 48% HF solution (10 cc.). Evaporation to dryness was effected in polyethylene-lined vacuum kettles under reduced pressures at 25–30°. The crude Li_2TiF_6 was twice recrystallized in the same manner, using a minimum of distilled water slightly acidified with HF in each case. The water insolubles were removed by filtration after the Li_2TiF_6 had been redissolved in each case. The product thus gained was dried to constant weight at 200° under vacuum pumping. The composition of the product was: Li_2TiF_6, 93.8 ± 0.1%; Li_2TiOF_4, 1.2 ± 0.2%; LiF, 1.6 ± 0.2%; HF, 2.57%; and H_2O, 0.75%. The yield of product calculated on the above purity of Li_2TiF_6, 71.5 g., corresponds to 76.4% of that theoretically possible. The HF and H_2O undoubtedly are held as molecules of hydration, and the above amounts correspond to 4% of $Li_2TiF_6{\cdot}2H_2O$ and 24% of $Li_2TiF_6{\cdot}HF$ still present after vacuum drying to constant weight at 200°. The oxyfluoride is accounted for as a hydrolysis product of Li_2TiF_6. The presence of LiF is attributed to the finite solubility of this compound (0.3 g./100 g. H_2O). The identity of the water insoluble oxyfluoride as Li_2TiOF_4 was confirmed by X-ray powder diffraction patterns, and titanium analysis[5] (Li_2TiOF_4: calcd. Ti, 31.1%; found Ti, 30.7%).

Melting Point.—A platinum crucible containing approximately 10 g. of Li_2TiF_6 (93.8% purity) was heated under an inert (argon) atmosphere in a Hoskins furnace. Temperatures were measured with an automatically recording platinum–platinum, 10% rhodium thermocouple. The heating rate was quite rapid, 7°/minute in range 460–550°, and 20°/minute in the range 550–600°, to minimize decomposition of the sample before reaching the melting point. The sample sintered at 530 ± 5° and was completely molten at 580 ± 25°. Vigorous gas evolution occurred once the sample was fused. No attempt was made to gain a more precise estimate of the melting point in this work.

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[1] This work, supported by the U. S. Air Force, Air Office of Scientific Research, ARDC, Contract No. AF 49(638)-50, was initiated under the sponsorship extended by the Office of Naval Research, Contract No. Nonr 591(06).

[2] G. J. Janz *et al.*, *J. Phys. Chem.*, **62**, 823, in press (1958).

[3] H. Ginsberg, *Z. anorg. allgem. Chem.*, **204**, 225 (1932).

[4] (a) H. Ginsberg and G. Holder, *ibid.*, **201**, 193 (1931); (b) **196**, 188 (1931); (c) **190**, 407 (1930).

[5] J. A. Rahm, *Anal. Chem.*, **24**, 1832 (1952).