The Atomic Weights of Radioactive Substances

Forrest Western and Arthur E. Ruark

Citation: The Journal of Chemical Physics **1**, 717 (1933); doi: 10.1063/1.1749234
View online: http://dx.doi.org/10.1063/1.1749234
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/1/10?ver=pdfcov
Published by the AIP Publishing

The Atomic Weights of Radioactive Substances[1]

FORREST WESTERN AND ARTHUR E. RUARK, *University of Pittsburgh*

(Received June 16, 1933)

(1) The isotopic weights of Pb^{206}, Pb^{207}, and Pb^{208}, on the chemical scale O = 16.0000, are obtained by three distinct methods, using in each case the assumption that they differ by an amount very close to unity. The results for Pb^{206} are these: (1) from packing fraction of lead, 205.96_5; (2) from study of the packing fraction curve, 205.99_2; from relative abundance of isotopes in leads of known atomic weight, 206.00_3. Mean, $205.98_7 \pm 0.03$. By taking into account a recent atomic weight determination on lead from Bedford cyrtolite, reasonable rounded values for the three isotopes are 205.98, 206.98 and 207.98 ± 0.03. (2) From these values the isotopic weights of the radioactive substances are obtained by adding the mass (and the mass-equivalent of the energy) lost in disintegration. The calculated values for radium and thorium, 226.02 ± 0.03 and 232.03 ± 0.03, do not agree with the International values 225.97 ± 0.01 and 232.12 ± 0.01. The calculated weights for U^{238} and U^{234} are 238.04 ± 0.03 and 234.04 ± 0.03, respectively, while the heretofore accepted atomic weight of U is 238.14 ± 0.01. In view of Aston's conclusion that U does not contain more than 3 percent of U^{239} or any higher isotope, it appears probable that the accepted value for uranium is somewhat too high. (3) $W - N$ is plotted as a function of N, for the three radioactive series, W being the isotopic weight and N the nearest integer. The graphs obtained are almost linear, and their slopes are nearly identical. In an average way they conform to the equation $W - N = -0.02 + 0.00214\ (N - 206)$.

I. INTRODUCTORY

IF we know the atomic weight of any member of a radioactive series, we can obtain that of any other member by taking account of the masses of the particles emitted, and the mass equivalent of the energy liberated in the disintegrations leading from one of these substances to the other. The errors involved are very small, now that we have precise values for the masses of the electron and the helium atom. Unless otherwise stated, we shall use the chemical scale of atomic weights throughout this paper. Mass-spectrograph results are usually expressed on the scale $O^{16} = 16.0000$. To reduce them to the chemical scale we subtract a correction of 2.2 parts in 10^4, based on the relative abundances of the oxygen isotopes given by Mecke and Childs.[2] Further, we assume that the atomic weight of helium on the chemical scale $= 4.00128 \pm 0.0004$; this is obtained from Aston's value, 4.00216 on the O^{16} scale.[3]

Computations of the atomic weights of radioactive substances were made by Stefan Meyer,[4] but his results differ considerably from those reported here, because he did not have available all the data now at our disposal and because the distinction between the chemical atomic weight scale and the O^{16} scale was not known. Meyer treats uranium as a mixture of U^{238} and 3 percent of a hypothetical isotope U^{239}, thereby computing the weight of U^{238} as 238.011 or 238.010. From this he obtains 226.09 or 226.08 for the atomic weight of radium, a value almost 0.1 unit higher than the accepted one, 225.97. We agree with his conclusion that the chemically-determined atomic weight of radium is wrong, but his value for U^{238} may be questioned, being based on the idea that uranium contains a percentage of U^{239} equal to the actinium-uranium branching ratio, whereas the latter is a ratio of activities, not of masses. Further, Meyer computes the loss of mass between U^{238} and Pb^{206} as 32.07, in close agreement with our value. He then states that if one takes the atomic weight of Pb^{206} + 3 percent Pb^{207} to be 206.05, and adds 32.07, one arrives at 238.12 for the atomic weight of the uranium complex consisting of U^{238} and 3 percent of U^{239}. This lies within the range covered by Hönig-

[1] Preliminary communications may be found in Phys. Rev. **42**, 903 (1932); **43**, 205 (1933).

[2] Mecke and Childs, Zeits. f. Physik **68**, 362 (1931); Aston, Nature **130**, 22 (1932); Naudé, Phys. Rev. **36**, 333 (1930).

[3] See also Bainbridge, Phys. Rev. **43**, 103 (1933).

[4] Meyer, Wien Ber. (IIA) **137**, 647 (1928).

schmid's chemical determinations, and Meyer concludes that no discrepancy exists in regard to the atomic weights of uranium and uranium lead. However, the figure 206.05 is the atomic weight of a lead extracted from Katanga pitchblende (Table I). We know now that it contains 6.7 percent of Pb^{207} instead of 3 percent. Further, as we shall see, there is some evidence against the assumption that uranium contains 3 percent of U^{239}. The entire subject, therefore, must be reconsidered.

II. Weights of the Lead Isotopes

We shall derive the weights of radioactive substances by using the weights of lead isotopes as a base. The latter will be obtained in three ways, namely, from Aston's packing fraction for lead; from the packing-fraction curve; and from the chemically-determined atomic weights of radioactive leads, together with their isotopic compositions.

(1) Aston[5] stated that the packing-fractions of lead isotopes are indistinguishable from the value he gives for mercury, 0.8×10^{-4}. Later he said[6] that the lead packing fractions would be difficult to measure and that they probably lie between zero and $+1\times10^{-4}$. If we place them in the middle of this range we obtain 205.965, 206.965, and 207.965 ± 0.02 for the weights of the principal lead isotopes.

(2) Let W be the weight of an isotope and N the integer nearest to that weight. It is possible to determine the value of $W-N$ for the lead isotopes by studying the dependence of this quantity on atomic weight. The values of $W-N$ are not available for all the individual isotopes of heavy elements. The numbers we shall use are average values for all the isotopes of an element, or values for individual abundant isotopes. Accordingly, we shall simply speak of the $W-N$ value for an element. Aston[7] determined the packing fractions of tungsten, rhenium, osmium and thallium by comparing their lines, or those of their oxides, with the mercury lines; so that any change in the value of $W-N$ for mercury requires corresponding changes in the values for these other elements. Now, from the relative abundances of mercury isotopes and their packing fractions we find the atomic weight $200.60_2\pm0.05$, while the International atomic weight is 200.61 ± 0.004.[8] Thus it seems reasonable to increase Aston's isotopic weights for these heavy elements by half the difference between these numbers, or 0.004. Then for the isotope Hg^{200}, $W-N$ is -0.024. If we plot the resulting $W-N$ values against N, it is found that they do not lie even approximately on a straight line, and it would be difficult to determine $W-N$ for lead by extrapolating the general trend. Accordingly, we adopt another procedure, as follows. In Section III, we shall obtain the differences of the values of $W-N$ for radioactive elements from disintegration data. If we arbitrarily assign a $(W-N)$ value to the lead isotopes, higher than the correct one by an unknown amount, c, a knowledge of these differences makes it possible to plot $W-N+c$ as a function of N. The plotted points can be shifted up and down as a body, until a straight line representing their average trend passes through the plotted point for Hg^{200}. This line crosses the abscissa 206 at an ordinate of -0.008, so we take 205.992 ± 0.03 as a value of the isotopic weight of Pb^{206}. These relations are shown by the line marked XX' in Fig. 1. However, all the other data in this figure are plotted on the basis of the value 205.98 for the weight of Pb^{206}. This is a mean value obtained from all three methods outlined in this section. Accordingly, the $W-N$ values plotted for tungsten, rhenium, osmium, mercury and thallium are 0.004–0.012 or 0.008 lower than those obtained directly from packing fraction data, above.

(3) Our third method makes use of the relative abundances of the isotopes in ordinary and radioactive leads,[9] together with the atomic weights of these leads, determined chemically. Data are given in Table I. The assumption is made that the weights of these three isotopes differ by integers on the chemical scale, so that

[5] Aston, Nature **123**, 313 (1929).
[6] Aston, Nature **129**, 649 (1932).
[7] Aston, Proc. Roy. Soc. **A126**, 511 (1930); **132**, 487 (1931); **134**, 571 (1932).
[8] Hönigschmid, Birckenbach and Steinheil, Ber. **56B**, 1212 and 1219 (1923).
[9] Aston, Nature **120**, 224 (1927); **123**, 313 (1929); **129**, 649 (1932).

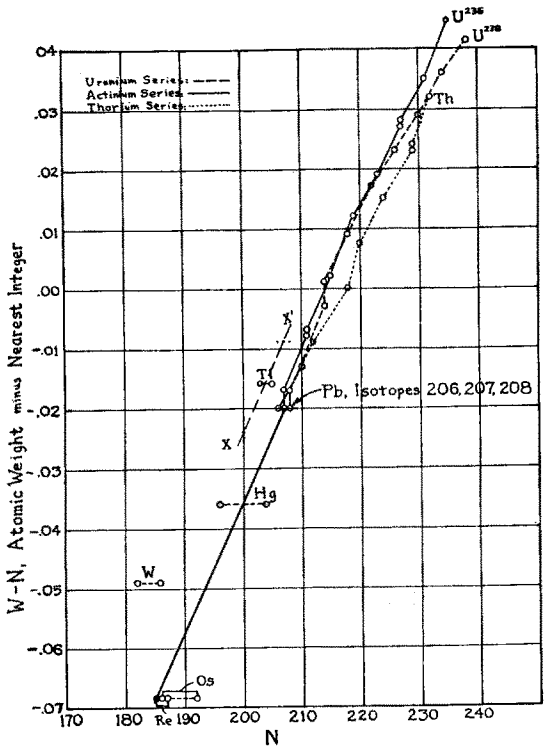

FIG. 1. Deviation of atomic weights of heavy elements from the nearest integer. Chemical scale, O = 16.0000.

they may be written $206+x$, $207+x$, and $208+x$, respectively.[10] We may use Wilberforce uraninite as an illustration. From Table I, $206.195 = 0.859(206+x)+0.83(207+x)+0.058(208+x)$. Then $x=-0.004$; that is, the calculated weight of Pb^{206} is 205.996.

On the basis of this assumption the four samples of lead in Table I yield the following values for the weight of Pb^{206}:

Material	*Isotopic weight of Pb^{206}*
Ordinary lead	206.030
Katanga pitchblende	205.981
Wilberforce uraninite	205.996
Norwegian thorite	206.005
Average	206.003 ± 0.035

Weighting all three methods equally, the final mean for Pb^{206} is 205.987 ± 0.03. Simultaneously with our announcement of the above results, a paper by von Grosse[11] appeared, in which he gives $205.96+0.02$ as the weight of Pb^{206}. This is obtained from the data of Table I; the method of computation is not explained. We believe our mean is better supported *by the data above*, than the lower value of von Grosse. However, recent atomic weight determinations by Baxter and Alter[12] yield a *lower* value for Pb^{206} than any so far obtained. They have determined the atomic weight of lead extracted from a thorium-free cyrtolite occurring at Bedford, N. Y., with the result 205.924 ± 0.02. An isotopic analysis of the Bedford material is much to be desired, for the discrepancy between this value and our mean may be due to the presence of the isotopes 203, 204, or 205, found by Aston.[13] Meanwhile, we shall give the cyrtolite value some weight by adopting the rounded value 205.98 for Pb^{206}. This mean depends on the results of three independent methods of attack, employing a number of atomic weight determinations, including Baxter and Bliss' work on Wilberforce lead, but it is quite possible that a lower value may be confirmed by later developments. If so, the effect will be to bring our calculated value for the atomic weight of radium (see Table II) into better agreement with the observed one; but the calculated and observed values for uranium will still disagree.

TABLE I. *Isotopic constitution of ordinary and radiogenic leads.*

Source of lead:	Ordinary lead	Katanga pitchblende	Wilberforce uraninite	Norwegian thorite
Chemical Atomic weight:	207.22[a]	206.048[b]	206.195[c]	207.90[d]
Percentage 206:	27.75	93.3	85.9	4.6
Percentage 207:	20.20	6.7	8.3	1.3
Percentage 208:	49.55	(0.02)	5.8	94.1
Other isotopes:	2.50	—	—	—

[a] International value.
[b] Hönigschmid and Birckenbach, Ber. **56**, 1837 (1923).
[c] Baxter and Bliss, J. Am. Chem. Soc. **52**, 4851 (1930).
[d] Fajans, Sitz. Heidelb. Akad. Wiss. **3** (1918); Hönigschmid, Phys. Zeits. **19**, 437 (1918); Zeits. f. Elektrochemie **25**, 91 (1919).

[10] Study of data on lighter elements indicates the degree to which this assumption may be trusted; the $(W-N)$ values determined by the mass-spectrograph for the isotopes of a single element never differ by more than 0.005 of a unit, and usually the departure is only 0.001 or 0.002. In the radioactive domain, however, the differences are larger, as we can see from Fig. 1. It appears likely that our assumption is correct within 0.01 of a unit of atomic weight. It should be considered merely as a convenient working hypothesis.

[11] von Grosse, Phys. Rev. **42**, 565 (1932).
[12] Baxter and Alter, Science **76**, 524 (1932).
[13] Aston, Nature **129**, 649 (1932).

III. Computation of the Isotopic Weights of Radioactive Substances

We shall now consider mass losses in disintegration. When an alpha-particle is emitted, two planetary electrons must leave the atom, so the atomic weight of a neutral helium atom plus the weight equivalent of the energy loss must be subtracted from the atomic weight of the parent atom to obtain that of the daughter. However, when a beta-particle is emitted, the planetary shells of the daughter atom pick up an electron. The only mass lost is that associated with the kinetic energy of the beta-particle and the energy of the gamma-rays.

In computing the energy loss in beta-ray transformations we use the average energy of the disintegration electrons rather than the maximum. It is well known that the average energy obtained with the beta-ray spectrograph is in agreement with the energy loss determined calorimetrically. The experimental facts require that we adopt one of several suppositions:

Either it is true that (1) energy is conserved only statistically in beta-ray transformations; or (2) an atom which sends out a slow disintegration electron must rid itself of surplus energy by the emission of penetrating rays or particles which are not detected in the calorimetric measurements or indeed in any others so far made; or (3) nuclei of a given species do not all have the same energy. Several other hypotheses, more or less complicated, might be mentioned. Our method of procedure corresponds to the first assumption, but if we were to use the maximum energy of the disintegration electrons, none of the atomic weights we calculate would be altered by more than a few thousandths. This is negligible in comparison with the uncertainty of 0.03 involved in the weights of the lead isotopes.

In the case of isotopes whose gamma-ray spectra are known, we have used the energy loss corresponding to the shortest gamma-ray recorded, in the hope that its energy is fairly close to the average surplus possessed by the excited nucleus just after disintegration. A detailed understanding of nuclear energy levels is not necessary for our purpose because the loss of energy by radiation corresponds in most cases to a negligible mass-loss. Where the spectrum is not known, we neglect the loss of energy by radiation. Inspection of known gamma-ray spectra shows that this procedure cannot possibly introduce an error greater than about 0.005 in any isotopic weight. Probably the average error thus introduced is closer to 0.001 unit.

The factors used in computation are these: Mass energy of atom having unit chemical atomic weight, $1.482\ 10^{-3}$ ergs, or $932\ 10^{6}$ electron-volts. One electron-volt corresponds to $1.074\ 10^{-9}$ chemical atomic weight units. Energies of alpha-particles, recoil atoms and beta-particles are taken from Gamow's[14] *Atomic Nuclei and Radioactivity*, with few exceptions. The data for U^{238}, U^{234}, and Th are those of Kurie, and of Kurie and Knopf,[15] while the values for U^{239} and U^{255} are assumed to be the same as those for U^{238} and U^{234}, respectively. For the hypothetical beta-rayers between U^{239} and U^{235}, we assume the disintegration electrons have the same energies as those of UX_1 and UX_2, respectively. A similar assumption is used in dealing with $MsTh_1$ and $MsTh_2$. No information is available concerning the gamma-rays of UY, Ac, An and AcA. We assume they are negligible.

Most of the gamma-ray energies were taken from *Radiations from Radioactive Substances*, by Rutherford, Chadwick and Ellis.[16] In a few cases it was necessary to estimate them from absorption coefficients given on page 456 of the same work, by use of the Klein-Nishina formula. The uncertainties thus introduced are negligible for our present purpose.

The results are shown in Table II.[17] The isotopic weights are given to a higher accuracy than the data warrant, to avoid error in rounding off. The outstanding facts which emerge from a study of these numbers are: (1) that in a gross

[14] Gamow, *Atomic Nuclei and Radioactivity*, pages 35 to 54, Oxford University Press.

[15] Kurie, Phys. Rev. **41**, 701 (1932); Kurie and Knopf, Phys. Rev. **43**, 311 (1933).

[16] Rutherford, Chadwick and Ellis, *Radiations from Radioactive Substances*, pp. 360–377, Cambridge University Press, 1930.

[17] Phys. Rev. **43**, 38–59 (1933) contains a group of papers by F. Allison and his associates, in which large numbers of new radioactive isotopes are proposed. These are fitted by Miss Bishop into four radioactive series. Independently Piggot proposes a somewhat similar arrangement. These schemes are highly hypothetical. We base our discussion on the disintegration sequences generally accepted.

TABLE II. *Mass losses and isotopic weights for the radioactive elements.* (*Chemical scale.*)

Isotope	Mass equivalent of energy loss: Alpha-particle and recoil atom	Beta-particle	Gamma-ray	Total mass loss	Isotopic weight
U^{238}	0.0044			0.0044+He	238.04
UX_1		0.0001		.0001	234.04
UX_2		.0004	0.00015	.00055	234.04
U^{234}	.0050			.0050+He	234.04
Io	.0050			.0050+He	230.03
Ra	.0052			.0052+He	226.02
Rn	.0059			.0059+He	222.02
Ra A	.0065			.0065+He	218.01
Ra B		.00025	.0005	.00075	214.00
Ra C		.0008	.0024	.0032	214.00
Ra C′	.0084			.0084+He	214.00
Ra D					209.99
Ra E		.0004		.0004	209.99
Ra F	.0058			.0058+He	209.99
Ra G					205.98
U^{239}?	.004(?)			.004+He	239.05
Beta-Rayer?		.0001(?)		.0001?	235.04
Beta-Rayer?		.0004(?)		.0004?	235.04
U^{235}	.005(?)			.005+He	235.04
UY					231.03
Pa	.0055		.0003	.0058+He	231.03
Ac					227.03
RdAc	.0065		.0007	.0072+He	227.03
AcX	.0062			.0062+He	223.02
An	.0075			.0075+He	219.01
Ac A	.0081			.0081+He	215.00
Ac B		.0002	.0005	.0007	210.99
Ac C	.0072		.0005	.0077+He	210.99
Ac C″		.0004	.0022	.0026	206.98
Ac D					206.98
Th	.0040			.0040+He	232.03
$MsTh_1$		.0001?		.0001	228.03
$MsTh_2$		.0004?	.0021	.0025	228.02
RdTh	.0058		.0001	.0059+He	228.02
ThX	.0062			.0062+He	224.02
Tn	.0068			.0068+He	220.00
Th A	.0073			.0073+He	216.00
Th B		.0001	.0003	.0004	211.99
Th C	.0066			.0066+He	211.99
Th C″		.0007	.0027	.0034	207.98
Th D					207.98

way, $W-N$ is a linear fraction of atomic weight for each radioactive series, and (2) that the mean rate of increase of $W-N$ with atomic weight is nearly the same for the three series. The equation $W-N=-0.02+0.00214(N-206)$ is a fair average representation of the atomic weights in the three series.

Isotopic weights of UI, Ra, Rn, and Ra F have also been computed by von Grosse,[18] whose results are 0.02 lower than ours.

The chemically-determined atomic weight of radium is 0.05 unit lower than our calculated value, and about 0.15 unit lower than the value obtained by calculation, on any reasonable basis, from the chemically-determined atomic weight of uranium. For thorium the discrepancy is 0.09 unit. In both cases the discrepancies are larger than the sum of the estimated uncertainties of the calculated and experimental values.

The value determined chemically for uranium is higher than one would expect on any assumption which appears probable in view of known facts. It can be understood if sufficient amounts of isotopes heavier than U^{238} are present, but Aston[19] found only the isotope U^{238}, and says, "uranium is probably simple to at

[18] von Grosse, Phys. Rev. **42**, 565 (1932).

[19] Aston, Nature **128**, 725 (1931).

least two or three percent." Wahlin[20] also found only a single isotope. It is possible, however, that several percent of U^{239} would have escaped detection in his experiment. If uranium were composed of the isotopes 238, 234 (in negligible amount), and 3 percent of 239, the atomic weight of the mixture calculated from our isotopic weights would be 238.07, which is 0.06 lower than the chemical value. Of course, small percentages of several higher isotopes would suffice to bring about agreement, but there is no positive evidence for their existence. As to U^{239}, we have summarized[21] the evidence on the origin of the actinium series, concluding that it is quite improbable that this isotope exists.

IV. Conclusions

Our conclusion is that the calculated values for the atomic weights of radium and thorium should be used in preference to those determined chemically, and that the accepted value for uranium appears too high on the basis of present information as to the isotopes of this element. In making this judgment, we wish to express admiration for the work of Hönigschmid and his collaborators on these atomic weights. In the case of uranium, for example, Hönigschmid and Schilz[22] made 37 determinations by several methods. For all three elements the inner consistency of the results leaves little to be desired, but it appears that systematic errors beyond the control of the chemist must have played a part. The only other possibilities are to assume that Einstein's energy-mass relation is not strictly valid or that energy is not even *statistically* conserved, in radioactive disintegration. Against both of these assumptions, a wealth of experimental evidence can be adduced.

[20] Wahlin, Phys. Rev. **39**, 183 (1932), and private communication.

[21] Western and Ruark, Phys. Rev. **43**, 205 (1933).

[22] Hönigschmid and Schilz, Z. anorg. chem. **170**, 145 (1928).