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The Isotopic Constitution of Uranium and the Half-Lives of the Uranium Isotopes. I†

Alfred O. Nier*
Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts

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A mass spectrographic determination of the relative abundances of the uranium isotopes has been made. The following abundance ratios were found: $U^{238}/U^{235}=139\pm1$ percent; $U^{238}/U^{234}=17{,}000\pm10$ percent. A search was made for other isotopes but none was found. From the above values, together with the results of the alpha-particle counting experiments of Kovarik and Adams, and the assumption that the actinium series is 4.6 percent as active as the uranium, the following decay constants are computed: U_{I}, 1.520×10^{-10} yr.$^{-1}$; U_{II}, 2.6×10^{-6} yr.$^{-1}$; AcU, 9.72×10^{-10} yr.$^{-1}$. The corresponding half-lives are, respectively, 4.56×10^{9} yr., 2.7×10^{5} yr. and 7.13×10^{8} yr.

In evaluating the decay constants of the three naturally occurring uranium isotopes, $U^{238}(U_{\text{I}})$, $U^{234}(U_{\text{II}})$, and U^{235}(AcU), a knowledge of the relative abundances would be extremely useful. Although two mass-spectrographic studies of uranium have been made, there is no record of any direct determination of the abundances. Aston[1] showed that at least 97 percent of the uranium atoms had the mass 238, while Dempster,[2] who was able to detect U^{235}, estimated that it must have an abundance less than one percent that of U^{238}. U^{234} has not until the present been detected mass-spectrographically. The present paper concerns itself with a mass-spectrographic study from which it is possible to make determinations of the relative abundances of all three isotopes.

Apparatus

A description of the mass spectrometer used in this work has already been given.[3] It may be described briefly as an apparatus in which positive ions are formed by the collision of a controlled beam of low energy electrons with the vapor or the gas of the substance to be investigated. The ions formed by the impact of the electrons are drawn out of the ionizing region, are accelerated and sent around a 180° magnetic analyzer. The analyzed ion current is measured with an electrometer tube amplifier. For the study of relatively nonvolatile substances use is made of a small furnace located inside of the mass-spectrometer tube just above the ionizing region. A compound containing the element to be studied is placed in the furnace which when heated to a suitable temperature volatilizes its contents. Through an opening in the furnace a molecular beam passes into the electron stream where ionization then takes place.

UCl_4 and UBr_4 were found to be satisfactory as sources of ions. A typical mass spectrum is shown in Fig. 1. Three peaks are clearly visible in the figure. The most abundant isotope is, of course, U^{238}, the parent of the uranium-radium family (for obvious reasons, only the lower portion of this peak is shown). The second most abundant isotope is U^{235}. U^{234}, the isotope in radioactive equilibrium with U^{238}, is just visible in the spectrum.

Results

In view of the fact that it was at one time thought[4] that the U_{I}/AcU ratio might be a function of the age of the mineral in which the uranium is found this ratio was measured for three different samples of widely different geologic age. Table I gives the results obtained. Each of the numbers given is the average of ten determinations of the ratio. The relatively large random variations noted in the table are caused principally by the fact that it was difficult to maintain an absolutely constant stream of vapor from

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† Preliminary report, Phys. Rev. **53**, 922 (1938).

* This work was done while the writer was a National Research Fellow at Harvard University. Present address, Department of Physics, University of Minnesota, Minneapolis, Minnesota.

[1] F. W. Aston, Nature **128**, 725 (1931).

[2] A. J. Dempster, Nature **136**, 180 (1935).

[3] A. O. Nier, Phys. Rev. **53**, 282 (1938).

[4] National Research Council Bulletin No. 80, *Age of the Earth* (1931), p. 113.

the furnace. Not only did the pressure in the vapor beam fluctuate randomly, but it also decreased steadily as time progressed. In the case of the uranium from the Swedish Kolm, two compounds, UCl_4 and UBr_4 were tried as sources of ions and gave the same ratio within the experimental errors. As the UBr_4 was found to be more satisfactory as far as steadiness of evaporation was concerned, it alone was used for studying the Wilberforce and Dakeite uranium. Practically all of the readings given correspond to abundances determined for U^+ ions. However, a few determinations (as noted) were made in the UBr^+ and UCl^+ part of the spectrum. The values obtained here are seen to be in good agreement with those found for the U^+ ions when one considers that the UBr^+ and UCl^+ ions are not as plentiful as the U^+, and that, moreover, the resolution of the peaks for these higher mass numbers is not as good as for the lower masses. From this study it seems safe to conclude that within the experimental errors the ratio does not depend upon the compound used nor upon the particular type of ion investigated.

The close agreement between the average values found for the three samples indicates that the ratio does not depend upon the source of the uranium. Allowing for systematic errors such as errors in calibration, discrimination of apparatus against different mass numbers, etc., one can probably safely assume that the best value for the ratio is 138.9 or 139, with a limit of error of one percent.

TABLE I. U^{238}/U^{235} *ratio in different minerals.*

Source of Uranium Approximate Age	Kolm* (Sweden) 4×10⁸ yr.		Uraninite† (Wilberforce, Ont.) 1.0×10⁹ yr.		Dakeite‡ 1×10³ yr.	
	Ratio	Type of Ion Studied	Ratio	Type of Ion Studied	Ratio	Type of Ion Studied
	139.0	U^+ in UCl_4	140.8	U^+ in UBr_4	139.7	U^+ in UBr_4
	139.4	"	135.3	"	139.7	"
	139.1	"	135.3	"	136.6	"
	139.4	"	142.3	"	138.0	"
	137.5	UCl^+ in UCl_4	137.1	"	137.8	"
	138.0	U^+ in UBr_4	139.4	"	138.2	"
	138.8	"	139.1	"	141.3	UBr^+ in UBr_4
	140.7	UBr^+ in UBr_4	139.7	"		
			139.6	"		
			139.4	"		
			140.3	UBr^+ in UBr_4		
Averages	139.0		138.9		138.8	

* Baxter and Bliss, J. Am. Chem. Soc. **52**, 4848 (1930).
† Baxter and Bliss, J. Am. Chem. Soc. **52**, 4851 (1930).
‡ Larson, Mineralogist, Feb. 1937; American Mineralogist, May 1937; Dake, Mineralogist, March 1938.

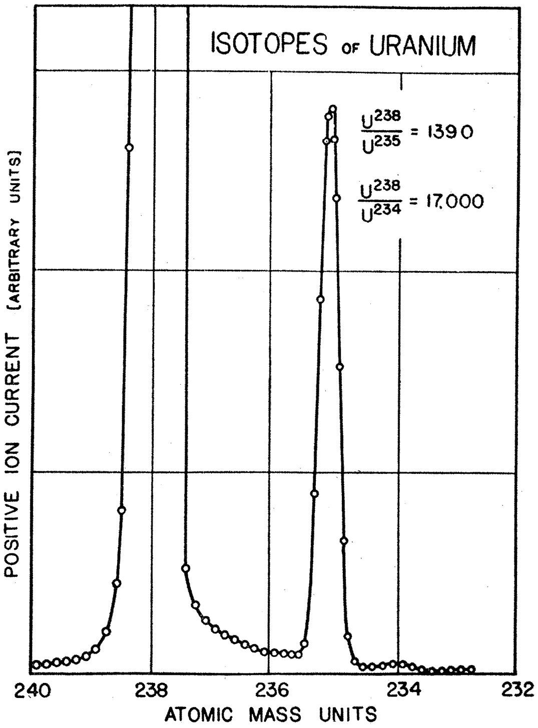

FIG. 1. Mass spectrum showing isotopes of uranium. The experimental points are obtained by plotting positive ion current passing through the exit slit of the analyzer as a function of the energy of the ions while the magnetic field is held constant. As there is a definite relation between the energy and the mass of the ions collected, namely, energy×mass = a constant, the voltage scale can be readily changed to a mass scale, as was done in the figure. The width of the peaks is, of course, caused by the finite width of the slits used and the imperfections in focusing.

The U^{238}/U^{234} ratio was determined only for the uranium found in the Swedish Kolm. Table II gives the results obtained. Each number is the result of one carefully made determination. Because of the extreme rarity of the U^{234} isotope great accuracy in the measurement of this ratio cannot be hoped for. It was not possible to determine the ratio for the U^+ ions formed from the UCl_4 as an unknown rare impurity contributed to the 234 peak. During the time that the UCl_4 was in the tube the apparent U^{238}/U^{234} ratio measured for the U^+ ions increased steadily and appeared to be approaching the values given in the table, indicating the impurity was gradually being eliminated. In view of the fact that the ratios as measured in three different ways

TABLE II. *Individual determinations and average value of the* U^{238}/U^{234} *ratio.*

18,400	14,500	17,000	18,300	16,000
17,600	16,300	20,800	15,700	13,000
				Average 16,800

agreed as well as they did leads the writer to believe that the average given is not far from correct. The final result may be taken as $U^{238}/U^{234} = 17{,}000$, with a limit of error of ten percent.

In addition to the measurement of the abundance ratios a search was made for other isotopes. None was found, and it was possible to set the following upper limits of abundance relative to U^{238}: U^{242}, U^{241}, and U^{240}, 1/65,000; U^{239} and U^{237}, 1/12,000; U^{236}, U^{233}, U^{232}, and U^{231}, 1/35,000.

The mean mass number computed from the relative abundances is 237.977. With a packing fraction of 5.6[5] for uranium, and a conversion factor 1.000275 in going from the physical to the chemical scale an atomic weight of 238.045 is derived for uranium. The chemically determined value is given as 238.07.

The half-life of U_I

Kovarik and Adams[6] found 24,770 alpha-particles given off by a gram of uranium per second, a determination from which they computed a decay constant $=1.532\times10^{-10}$ yr.$^{-1}$ or a half-life $T=4.52\times10^9$ yr. for U_I. In view of recent developments, their computations should be modified to include: (1) a change in the electronic charge from 4.77 to 4.80×10^{-10} e.s.u.;[7] (2) a change in the atomic weight of uranium from 238.17 to 238.045; (3) the results of the present investigation that only approximately 139 out of every 140 uranium atoms are those of U_I; (4) the fact that approximately 4.6 out of every 204.6 alpha-particles[8] counted were caused by the decay of U^{235}. If these corrections are made one finds the decay constant of U_I to be 1.520×10^{-10} yr.$^{-1}$, a value which corresponds to a half-life, $T=4.56\times10^9$ yr.

The half-life of U_{II}

Two methods have been employed in making determinations of the half-life of U_{II}. The first of these makes use of the Geiger-Nuttall law, an empirical relation between the decay constant of an alpha-raying substance and the range of the particles. From older range determinations[9] a half-life of 10^8 yr. was computed for U_{II}. More recent determinations[10] lead to values around 10^4 yr.

The second method employed in measuring $T(U_{II})$ is to separate chemically a known amount of U_{II} and to measure its specific activity. By this method Collie[11] found the half-life to be something over 10^6 yr. Walling[12] determined a value of 3.4×10^5 yr., while Gratias,[13] in repeating Collie's experiment, discovered an inaccuracy in the method employed and arrived at the value 1.7×10^5 yr.

From the present work $T(U_{II})$ may be determined from the formula (1)

$$\lambda(U_I)N(U_I)=\lambda(U_{II})N(U_{II}), \qquad (1)$$

which expresses the fact that U_I and U_{II} are in radioactive equilibrium. Substituting the known quantities given earlier in the paper in the formula one obtains a value $\lambda(U_{II})=2.60\times10^{-6}$ yr.$^{-1}$. The corresponding half-life is 2.7×10^5 yr. This new and highly direct measurement is thus seen to be in essential agreement with the results obtained from the chemical separation experiments and adds considerable weight to the conclusion of Sizoo and Wytzes[14] that the Geiger-Nuttall relation is not accurate enough for a determination of $T(U_{II})$. The writer's computation is, of course, based upon the tacit assumption that all U^{238} and U^{234} atoms are radioactive.

The half-life of AcU

Several attempts have been made to determine the half-life of actino-uranium. In each case the

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[5] A. J. Dempster, Phys. Rev. **53**, 869 (1938).

[6] A. F. Kovarik and N. I. Adams, Phys. Rev. **40**, 718 (1932).

[7] J. W. M. Du Mond and V. L. Bollman, Phys. Rev. **50**, 524 (1936); G. Kellström, Phil. Mag. **23**, 250 (1937); Bond, Proc. Roy. Soc. **A149**, 206 (1937); P. J. Rigden, Nature **141**, 82 (1938); W. V. Houston, Phys. Rev. **52**, 751 (1937); G. B. Banerjea and B. Pattenaik, Nature **141**, 1016 (1938); J. A. Bearden, Phys. Rev. **51**, 378 (1937).

[8] See following paper.

[9] B. Gudden, Zeits. f. Physik **26**, 110 (1924).

[10] G. C. Laurence, Phil. Mag. **5**, 1027 (1928); F. N. D. Kurie, Phys. Rev. **41**, 701 (1932); H. Zeigert, Zeits. f. Physik **46**, 669 (1928); S. Bateson, Can. J. Research **5**, 567 (1931).

[11] C. H. Collie, Proc. Roy. Soc. **A131**, 541 (1931).

[12] E. Walling, Zeits. f. physik. Chemie **10**, 467 (1930).

[13] O. A. Gratias, Phil. Mag. **17**, 491 (1934).

[14] G. J. Sizoo and S. A. Wytzes, Physica **4**, 791 (1937).

method employed made use of the knowledge that the uranium and actinium series end ultimately as isotopes of lead having the masses 206 and 207, respectively. From the isotopic analysis of the lead found in a uranium mineral of known age, the relative activities of the actinium and uranium series at the present time and the decay constant of U_I, it was possible to find the decay constant of AcU. As the result of calculations of this sort, Rutherford[15] arrived at the value $T(\text{AcU})=4.2\times 10^8$ yr.; Kovarik,[16] 2.7×10^8 yr.; v. Grosse,[17] 4×10^8 yr.; Western and Ruark,[18] 4.45×10^8 yr.; Meyer,[19] 7.0 and 6.3×10^8 yr.

From the relative abundances of the uranium isotopes it is possible to obtain this quantity by a quite independent method requiring only as additional information a knowledge of the decay constant of U_I and the present activity ratio of the actinium and uranium series. The careful investigation of large number of radiogenic lead samples indicates[8] that the actinium series is 4.6 percent as active as the uranium series. This fact is conveniently expressed by means of Eq. (2). Making the necessary substitution one finds $\lambda(\text{AcU})=9.72\times 10^{-10}$

$$0.046=\lambda(\text{AcU})N(\text{AcU})/\lambda(U_I)N(U_I), \qquad (2)$$

yr.$^{-1}$ or $T(\text{AcU})=7.13\times 10^8$ yr.

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[15] Lord Rutherford, Nature **123**, 313 (1929).

[16] A. F. Kovarik, Phys. Rev. **35**, 1432 (1930).

[17] A. v. Grosse, Phys. Rev. **42**, 565 (1932); J. Phys. Chem. **38**, 487 (1934).

[18] F. Western and A. E. Ruark, Phys. Rev. **44**, 675 (1933); **45**, 628 (1934).

[19] S. Meyer, Wien Ber. IIa, **146**, 175 (1937); **146**, 581 (1937).

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The Isotopic Constitution of Radiogenic Leads and the Measurement of Geological Time. II

Alfred O. Nier[*]
Research Laboratory of Physics, Harvard University, Cambridge, Massachusetts

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The isotopic constitution of 21 samples of radiogenic lead has been determined with a mass spectrometer and the results have been correlated with mineral analysis data available for the specimens from which the leads were extracted. The common lead contamination in the samples was found, on the whole, to agree closely with that estimated from earlier atomic weight determinations. The AcD/RaG ratios (Pb^{207}/Pb^{206} ratios corrected for common lead contamination) appear to be in better agreement with a value 4.6 percent for the present day ratio of the activity of the actinium series to that of the uranium series than with the directly determined and commonly accepted value 4.0 percent. The results indicate that AcU was not nearly as abundant in the early days of the earth as was at one time believed.

The measurement of geologic age from AcD/RaG ratios is discussed and it is shown that in the event of mineral alteration the ages obtained are more reliable than those found from the Pb/U ratios.

The relatively small amount of Pb^{204} present in samples containing a large amount of thorium indicates that it is extremely unlikely that Pb^{208} decays to Pb^{204}.

IT IS a well-known fact that the natural disintegration of uranium results in the ultimate formation of two stable isotopes of lead, Pb^{206}(RaG) and Pb^{207}(AcD), while the

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[*] This work was done while the writer was a National Research Fellow at Harvard University. Present address, Department of Physics, University of Minnesota, Minneapolis, Minnesota.