PHYSICAL REVIEW VOLUME 73, NUMBER 5 MARCH 1, 1948

Natural Radioactivity of Rhenium

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(Received November 14, 1947)

An attempt to confirm the reported K capture activity of Os^{187}, using OsO_4 mixed with argon as the counter gas, failed to reveal any activity corresponding to a half-life of less than 5×10^{11} years. This method assumed that any K capture in Os would be followed by the emission of Auger electrons which would be recorded. The sensitivity of the system to soft Auger electrons was demonstrated by using 34.0-day A^{37} which decays by K capture. Rhenium then was examined for beta-activity, Re^{187} being isobaric with Os^{187}. An activity was found in two samples of different origin which resisted chemical purifications, including distillation of the perrhenic acid from concentrated sulfuric acid solution. The half-life appears to be $4\pm 1\times 10^{12}$ years calculated for Re^{187} isotope, and the range is 3.5 mg of Al/cm² corresponding to an upper energy limit of about 43 kev.

INTRODUCTION

ACCORDING to the rules of nuclear stability, it is not expected that two neighboring elements will have stable isotopes of the same nominal mass. In the cases of ${}_{18}A^{40}{}_{19}K^{40}{}_{20}Ca^{40}$, ${}_{37}Rb^{87}{}_{38}Sr^{87}$, and ${}_{70}Yb^{176}{}_{71}Lu^{176}{}_{72}Hf^{176}$ it has been shown that radioactive transformations occur. In three of the four other cases where neighboring isobars have been found to exist, there has not yet been any report of instability of either member of the pairs. These four pairs and their natural isotopic abundances[1,2] are as follows:

${}_{48}Cd^{113}$ (12.3 percent)	${}_{49}In^{113}$ (4.5 percent)
${}_{49}In^{115}$ (95.5 percent)	${}_{50}Sn^{115}$ (0.4 percent)
${}_{51}Sb^{123}$ (44 percent)	${}_{52}Te^{123}$ (0.85 percent)
${}_{75}Re^{187}$ (61.8 percent)	${}_{76}Os^{187}$ (1.64 percent)

A series of experiments was carried out by Zingg[3] in which particular attention was given to the detection and identification of the characteristic x-radiation of Cd, In, Sb, or Re, respectively, which would be expected to follow the capture of an orbital electron by In, Sn, Te, or Os, respectively. The observations were made by placing the subject element or one of its compounds around the outside of a cylindrical Geiger-Müller tube of 0.05-mm copper containing 10 cm Hg pressure of dry air. Copper was chosen to give the highest yield of photoelectrons from the x-rays which were sought. Within the error of his measurements Zingg found no activity in In or Te. With three samples of Sn a slight activity was found (corresponding to a half-life greater than 0.9×10^{12} years) and, moreover, absorption measurements with Cu foils gave data which fit fairly well the absorption of the In K line in Cu. However, a fourth sample of Sn gave no activity even when used as the actual counter wall, and Zingg concluded that the activity could not positively be ascribed to Sn. With Os an activity of about $\frac{1}{3}$ that found with the Sn samples was observed, but the absorption characteristics were not as predicted.

An attempt to detect the x-ray emission attending K capture was made also by Rusinov and Igelnitsky.[4] These authors used an aluminum G-M counter which was filled with 95 percent krypton and 5 percent xenon at a pressure of two atmospheres to give a high counting efficiency for soft gamma-rays. The subject material was placed around the outside of the counter. A counting yield of 100 percent is claimed for 20 kv photons (0.6A), dropping to 12 percent for 50 kv (0.24A). The K radiation of Cd, In, and Sb is 0.4 to 0.5A, within the region of high counting efficiency, but for Re, for which the K radiation is 0.2A, the efficiency would be poor. The background count was reduced over 10 times to about 9 counts per minute by shielding plus anticoincidence circuit methods. The Os-Re pair

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[1] K. T. Bainbridge and E. B. Jordan, Phys. Rev. **50**, 282 (1936).

[2] A. O. Nier, Phys. Rev. **52**, 885 (1937).

[3] E. Zingg, Helv. Phys. Acta **13**, 219 (1940).

[4] L. I. Rusinov and J. M. Igelnitsky, Comptes Rendus U.R.S.S. (Akademia Nauk C.R.) **47**, 333 (1945) and **49**, 343 (1945).

was not examined by these authors, but for the other three pairs, the x-rays sought were not observed, and they estimate that the half-lives must at least be greater than as follows: for In^{113}, 1×10^{14} years; for Sn^{115}, 1×10^{13} years, and for Te^{123}, 2×10^{14} years.

Neither of these investigations would have succeeded in detecting low energy beta-particles nor Auger electrons since these would have been stopped by the wall of the counter (except in Zingg's experiment in which he used Sn as the counter wall). Lougher and Rowlands[5] placed Os directly inside a cloud chamber and observed a group of electrons with a range in air of 5.0 ± 0.5 cm and with an energy of 61 ± 6 kv, both in excellent agreement with values for Re K x-radiation. They concluded Os^{187} was radioactive by K capture, and estimated the half-life as 3×10^{8} years.

The present investigation was undertaken to establish the existence of natural K capture more conclusively by placing the element inside the counter volume as a gaseous compound so that the Auger electrons emitted after the nuclear transformation might trip the counter with an efficiency high for the nuclear events. From known data it seems extremely likely that in an element such as osmium nearly every instance of K capture would be followed by the emission of at least one Auger electron, the thought being that even if the K vacancy should happen to fill by x-ray emission, the L vacancy so produced would have an even better chance of filling by the Auger process and that if even the L shell filled by x-ray emission, the M shell would not be as likely to, etc. Therefore, if the x-ray probabilities ("fluorescence yields") are W_K, W_L, etc., the chance of obtaining at least one Auger electron per nuclear event would be $(1-W_KW_LW_M\cdots)$ which from known data approaches unity for Os and most elements. This point is discussed more quantitatively later. The present report deals with an investigation of the Os-Re isobaric pair.

I. EXAMINATION OF OSMIUM

Description of Apparatus

Geiger-Müller gas counters of conventional type were used. Preliminary observations were made in a counter about 14 cm long and 2 cm in diameter; a larger counter about 30 cm long and 5 cm in diameter was then made to obtain greater sensitivity. In both cases the center wire was 0.010-in. tungsten wires, the cathode was silver, chemically deposited on the inside wall of the tube over an area which gave an effective counting volume for the small counter 70 mm long and 18 mm diameter and for the large counter 150 mm long and 50 mm in diameter. The Pyrex wall of the counter tube was pulled out in a flame to a thickness of about 30 mg/cm^2 for the small counter, and of 100 mg/cm^2 for the large counter, in order to permit the passage of some of the beta-particles from a uranium sample which could be mounted on the outside of the tube as a standard. Osmium tetroxide, purified by successive sublimations, was evaporated into the counter volume to a pressure of about 3 cm; argon was then added to bring the total pressure to 10 to 15 cm. The counter tube was kept in an oven at 60°C to prevent condensation of the osmium tetroxide. It was not found practicable to use any further shielding.

The counting equipment consisted of a scale of 64 with a stabilized high voltage supply of 2500 volts which it was necessary to supplement with a 600 volt supply from a series pack of "B" batteries, in order to provide the operating voltage required of about 3000 volts. An electronic quenching device of the Neher-Harper type was used, and an oscilloscope was connected to the center wire of the counter so that the pulses could be observed, and correct operating conditions maintained.

Procedure and Results

Observations were made with the same counter tube filled alternately with the OsO_4-argon gas mixture and with a conventional counting gas mixture of 10 mm of ethanol and 90 mm of argon. In order to check the counting efficiency of the OsO_4-argon mixture, a standard sample of uranium could be affixed to the outside of the counter tube in a reproducible manner. However, it was considered possible that the OsO_4-argon counting gas might have a sufficiently different absorption coefficient for uranium gamma-radiation so that a uranium standard would give a different count rate than with

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[5] E. T. Lougher and S. Rowlands, Nature **153**, 374 (1944).

TABLE I. Comparison of count rate observed with EtOH-A and with OsO_4-A.

	Alcohol-Argon			OsO_4-Argon			
(1) Date of observation	(2) Count with *U* standard	(3) Background	(4) Date of observation	(5) Count with *U* standard	(6) Background	(7) Normalized background	(8) Apparent increment, counts/min. due to OsO_4 (7)-(3)
Small counter tube							
10 Jan. 47	663.5±1.7	49.2±0.4	8 Jan. 47	533.0±1.5	41.6±0.4	51.6±0.5	2.4±0.6
20 Jan. 47	670.8±1.3	59.0±0.3	24 Jan. 47	647.1±2.0	55.0±0.3	57.0±0.3	− 2.0±0.4
Large counter tube							
			19 Mar. 47	1931.3±6	295.6±2		
			22 Mar. 47	1934.9±7	299.6±2		
			23 Mar. 47	1899.4±5	301.1±3		
20 Mar. 47	1699.7±7	279.3±1.3	24 Mar. 47	1921.4±3.3	298.6±1.1		
21 Mar. 47	1692.3±4	271.4±1.4					
Average of above	1696.4±3.5	274.9±1.0	*Average of above*	1926.0±2.4	297.6±0.9	262.1±0.9	−12.8±1.4
15 Mar. 47	1653.2±5	260.6±2	14 Mar. 47	1672.1±1.9	257.3±0.5	254.4±0.5	− 6.2±2.1

alcohol-argon counting gas. Therefore, only the uranium beta-radiation was used for standardization. Absorption experiments showed that not over ten percent of the effect attributable to the uranium standard was due to gamma-radiation with either gas, and for this small percentage it was shown that the efficiences were similar.

Even with the use of an electronic quenching device the counting characteristics of the OsO_4-argon mixture are very sensitive to the voltage applied, or, in other words, the "plateau" of the Geiger-Müller counting region is very steep, and the count rate obtained with the uranium standard varied considerably depending upon the part of the plateau at which the counting was done. Table I shows the counting results obtained with both the small counter tube and a large one, and for each case two sets of figures are presented. The first set of results was obtained by setting the operating voltage at what appeared to be the middle of the Geiger-Müller plateau, at which voltage a higher counting rate was obtained for both the standard uranium sample and the background than with the alcohol-argon counting gas mixture. The second set of observations was made with the voltage set at the lower part of the G-M plateau, at a voltage which gave as nearly as possible the same counting rate for the uranium standard as was obtained with the alcohol-argon counting gas. In order to compare the background count obtained with OsO_4-argon and with the alcohol-argon, the count with OsO_4-argon (column 6) was multiplied by the ratio of the standard count with alcohol-argon (column 2) to the standard count with OsO_4-argon (column 5), giving the normalized OsO_4-argon background (column 7). Any activity caused by Os should be manifested in an increase of this quantity over the background with alcohol-argon (column 3).

Actually, as shown in column 8 of Table I, no increase in the counting rate was observed with OsO_4-argon as compared with that observed with alcohol-argon, which can only be interpreted as indicating that Os is not radioactive by either orbital capture or particle emission processes within the limits of error of the observations. Because of the high reactivity of OsO_4 with organic matter, it was necessary to pump out the counter tube for a long interval when fillings were changed, and, therefore, the observations with OsO_4-argon and alcohol-argon were made on different days as shown in Table I. Some fluctuation in the background counting rate of an unshielded counter under these conditions is unavoidable, and the apparent deficit in counting rate with OsO_4-argon is probably a result of such fluctuations. Better shielding of the counter, and averaging a protracted series of observations would permit the elimination of this uncertainty. However, a half-life of Os^{187} of 3×10^8 years as previously estimated (5) would have resulted in an extra activity in the large counter described above of 8,000 counts per minute. The data here presented would indicate

TABLE II. Relative response of argon-alcohol and argon-OsO_4 counting mixtures to radioactive argon.

Counter filling	Pressure of active argon mixture	Count rate	Count due A^{37}	Count per mm Hg pressure of A^{37} mixture
Argon-alcohol	none	275.0±1.7		
	115.1 mm	2782.5±4.3	2507.5	21.79
Argon-OsO_4	none	238.8±1.7		
	115.0 mm	2786.6	2547.8	22.15

a half-life about 1000 times as long. Moreover, in the second part of this report it is shown that Re, the other member of this isobaric pair, is active by beta-particle emission, and that actually the Os is therefore stable. Further evidence that the Os is inactive is presented in the following section. Refinements of technique therefore did not seem warranted.

Proof That Auger Electrons are Counted in an OsO_4-Argon Filled Geiger Counter

In order to establish that the OsO_4-argon counting mixture would respond to soft Auger electrons, some observations were made using an argon isotope, A^{37}, which was found to be radioactive by *K* electron capture by Weimer, Kurbatov, and Pool.[6] These authors consider that *K* electron capture accounts for over 99.9 percent of the total number of disintegrations; the probability of Auger emission is said to be 0.96±0.3. The sample of A^{37} for our observations was prepared by bombarding potassium chloride with deuterons in the University of Chicago 37-inch cyclotron, causing the reactions ${}_{19}K^{39}(d,\alpha){}_{18}A^{37}$ and ${}_{17}Cl^{37}(d,2n){}_{18}A^{37}$. The irradiated potassium chloride was placed in a tube with ice at liquid nitrogen temperature. After air had been removed from the system the ice was allowed to melt and the potassium chloride dissolved to free the A^{37} trapped in the crystals. Some inert argon was added and the gas was transferred by a Toepler pump, through a trap at −78°C to remove moisture, to a storage volume. The decay rate of a sample of the gas was followed for a period of three months and gave a half life of 34.0 days in good agreement with the value of 34.1 days reported originally.[6]

The counting rates found when similar amounts of this radioactive gas mixture were used in a standard alcohol-argon counting mixture, and in OsO_4-argon mixture are presented in Table II. The count rate obtained from the *K* capture process in A^{37} is the same with both counting gas mixtures.

It is, therefore, quite certain that Auger electrons from orbital capture in Os would also have been detected if they had occurred. No counting increment due to Os was observed, however. Therefore, it can be said either that no *K* capture process occurs in Os, or that if *K* capture occurs, the refilling of the orbital vacancy results only in the emission of x-rays, and never of Auger electrons, a very unlikely situation. Of course the absorption in the OsO_4-argon gas mixture of the *K* x-rays of Re would be slight. From observations reported for other elements it would appear that the probability of at least one Auger electron being emitted is high, although the fluorescence yields for rhenium have not been reported. For transitions to the *K* orbit no elements of atomic number close to rhenium have been reported, but for those examined no fluorescence yield close to unity has been reported. For example for ${}_{27}Co$, ${}_{42}Mo$, and ${}_{52}Te$, it is 0.29, 0.65, and 0.56, respectively, for transitions to the *K* orbit.[7] Moreover, for transitions to the *L* level, which will inevitably follow the *L* to *K* transitions, fluorescence yields are lower and have been reported to be 0.298 and 0.348 for ${}_{74}W$ and ${}_{76}Os$, respectively.[8] For succeeding orbits the fluorescence yield is still lower, being only 0.06 for the *M* orbit in ${}_{92}U$.[8] Therefore, we can say that for ${}_{75}Re$ at least two thirds and more likely more than 90 percent of the *K* capture will result in the emission of Auger electrons.

Conclusion

Assuming the limit of detectability in the above experiments to be ±10 counts per minute, a conservative limit, we are led to a lower estimate for the half-life of Os^{187} for orbital capture or positron emission of 5×10^{11} years The observations reported in the following section, however, indicate that Os^{187} is completely stable.

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[6] P. K. Weimer, J. D. Kurbatov, and M. L. Pool, Phys. Rev. **60**, 209 (1944).

[7] R. J. Stephenson, Phys. Rev. **46**, 73 (1934).

[8] H. Lay, Zeits. f. Physik **91**, 533 (1934).

II. EXAMINATION OF RHENIUM

Description of Apparatus

The rhenium counts were made using solid compounds of rhenium, either metallic rhenium or rhenium heptasulfide in a "screen-wall counter," a device which has been fully described elsewhere.[9, 10] In effect this type of counter avoids the loss of particles by absorption in the counter wall, since only a wire screen is interposed between the sample and the active counting volume. The sample cylinder is twice the length of the wire screen cathode and slides concentrically within the confining tube and over the wire screen, so that in one position of the sliding cylinder, the sample, which is fastened to the inside wall of the cylinder over one-half of its length, is in counting position, whereas by sliding the cylinder the sample is moved out of the counting region and the background count is obtained. The counter was operated with the sample cylinder at about 50 volts negative potential with respect to the screen, so that the sample cylinder itself became the counter wall and the geometrical efficiency was increased to nearly 50 percent.

Observations were made on rhenium received from the University of Tennessee in the form of potassium perrhenate and sintered rhenium metal. These samples were purified as described below. A sample of rhenium metal of European origin received from Johnson-Matthey Company, London, England, was also examined. The absorption characteristics of the activity found were determined by placing aluminum foils inside the slide cylinder covering both the sample and the background areas.

Method of Chemical Purification

Rhenium heptasulfide was precipitated by passing hydrogen sulfide gas into a solution of the rhenium compound which had been made 4*N* in hydrochloric acid. The rhenium heptasulfide precipitate after thorough washing was dissolved in sodium hydroxide plus hydrogen peroxide and the solution filtered to separate sulfides not soluble in this mixture. Concentrated sulfuric acid was added to the solution and perrhenic acid distilled off in a stream of carbon dioxide and steam.[11] Two such cycles resulted in a product which appeared to have no radioactivity resulting from potassium as judged by the absorption characteristics of the activity found, for certainty four such cycles were completed on the American sample of potassium perrhenate.

This purification scheme is believed to be adequate for the removal of all other elements with the possible exception of element 43, which can be expected to follow rhenium at least in part in the above separations. However, it appears doubtful in any case that this element exists in nature since the isotopes of atomic weights 97, 99, and 101, which are those most likely to be stable, have been shown to be radioactive with half-lives of 93 days,[12] 4×10^6 years and 14.0 minutes,[13] respectively. The sample was mounted simply by painting a slurry of rhenium heptasulfide in alcohol on the slide cylinder.

The sample of European rhenium was not further purified. According to a spectrographic examination of the sample made by the Johnson-Matthey Company the sample is exceedingly

TABLE III. Absorption in aluminum of activity of American and European rhenium samples.

Area of sample and thickness (1) Counts per minute (2) Percentage of original count rate	American rhenium 300 cm², 2.5 mg/cm² of Re_2S_7 (1)	 (2)	European rhenium 180 cm²; 5.6 mg/cm² of Re (1)	 (2)
Through 0 mg/cm² aluminum	31.5±1.2	100 ±3.8%	38.5±2.6	100 ±6.7%
0.8 mg/cm² aluminum	9.7±1.6	30.8±5.0%		
1.5 mg/cm² aluminum	5.6±1.4	17.8±4.3%	8.2±1.7	21.3±4.4%
2.4 mg/cm² aluminum	3.2±1.1	10.3±3.5%	4.3±1.4	11.1±3.7%
3.4 mg/cm² aluminum	0.0±0.7	0 ±2.3%	0.76±1.3	2.0±3.4%

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[9] W. F. Libby, Phys. Rev. **46**, 496 (1934).

[10] D. D. Lee and W. F. Libby, *ibid.*, **55**, 245 (1939).

[11] L. C. Hurd and C. F. Hiskey, Ind. Eng. Chem. Anal. Ed. **10**, 623 (1938).

[12] E. E. Motta, G. E. Boyd, and A. R. Brosi, Phys. Rev. **71**, 210 (1947).

[13] J. M. Siegel, J. Am. Chem. Soc. **68**, 2411 (1946).

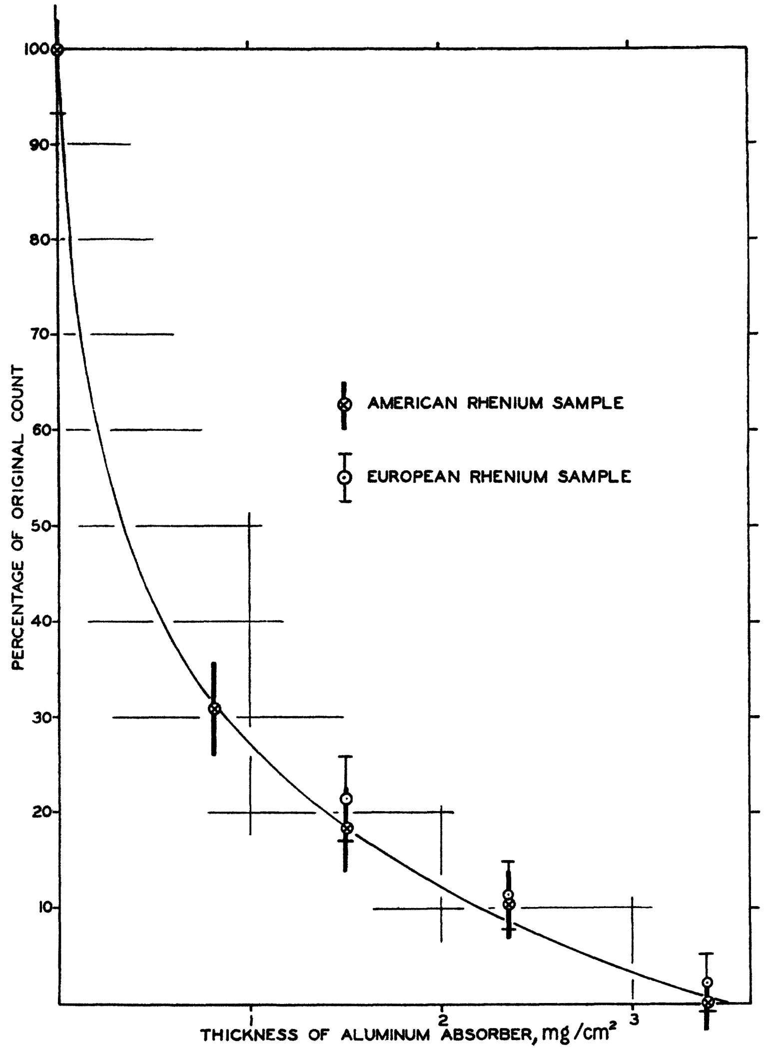

FIG. 1. Absorption in aluminum of rhenium activity.

pure, the only lines being attributed to traces of the elements calcium, silicon, magnesium, copper, and iron.

RESULTS

Table III presents the activity found in the two samples of diverse origin, *viz.*, American rhenium heptasulfide and European rhenium metal as described above. The effect of the same aluminum absorbers on the counting rates of each of these samples is also presented. The data from both samples are plotted together in Fig. 1. From this figure it can be seen that the same activity is possessed by the two widely different samples of rhenium. From these data the range of the beta-particles is estimated to be 3.5 ± 0.5 mg/cm² of aluminum. From an empirical range-energy relation,

$$\text{Range (mg/cm}^2) = \frac{[E(KV)]^{5/3}}{150},$$

which is known to hold for some other low energy beta-particle emitters,[14] the energy of the rhenium beta-particle is estimated to be 43±6 kev.

Possibility That Acticity Is Caused by Emission of Alpha-Particles

The low range of these particles invited the suspicion that the activity might be alpha-particles. For this reason an attempt was made

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[14] W. F. Libby, Ind. Eng. Chem. Anal. Ed. 19, 2 (1947).

to determine whether alpha-particles were involved, by determining whether the intensity of ionization produced by the particles emitted was sufficient to be observed in a counter operating in the proportional region.

The screen wall counter was used for these observations. In order to provide some known alpha-particles for comparison, a sample of samarium nitrate was mounted on the end of the sample cylinder opposite to the rhenium, in the normal background position. Under conditions which gave very well defined pulses on the oscilloscope screen when the Sm was in position, no pulses were observed when the counter was tipped to slide the Re into position, and it was concluded that the activity of Re is not emission of alpha-particles. The possibility that the activity might be due to positron emission or K capture must be eliminated, since ${}_{74}W^{185}$ and ${}_{74}W^{187}$ are both known to be radioactive by beta-emission. This leaves only the possibility of emission of beta-particles from either ${}_{75}Re^{185}$ or ${}_{75}Re^{187}$. The former process would lead to ${}_{76}Os^{185}$, which is known to be radioactive (I.T. 99 days; 30 hours). Since this activity is not observed, we conclude that the activity of natural rhenium is due to beta-emission from ${}_{75}Re^{187}$.

Half-Life of Rhenium^{187}

Estimated from European Rhenium Metal Sample

A count rate of 38.5±2.6 counts per minute was given by a sample 180 cm^2 in area and 5.6 mg/cm^2 thick (Table III), of which only a layer of thickness equivalent to the range, 3.5±0.5 mg/cm^2 will have contributed to the counting rate. Because of absorption and geometry factor the count observed is about 10 percent of the total disintegrations from a layer of a depth equal to the range.[84] We therefore have an indicated disintegration rate of 385±26 per minute from 630 mg of rhenium of which 61.8 percent is the isotope Re^{287}. The half-life calculated from these data is 4.3×10^{82} years.

Estimated from American Rhenium Heptasulfide

A count rate of 31.5±1.2 counts per minute was given by a sample 300 cm^2 in area and 2.5 mg/cm^2 thick (Table III). The total disintegration rate indicated[14] is then 320±12 per minute from a calculated 1050 mg of rhenium heptasulfide, of which $373/598\times61.8/100$ is the weight of the isotope Re^{187}. The half-life calculated from these data is 2.6×10^{12} years.

This sample of rhenium sulfide covered a greater area than the sample of rhenium metal, and the counting efficiency was somewhat less because of greater end effect. A second observation was therefore made, using an infinitely thick layer of rhenium sulfide covering the same area as the rhenium metal sample. A count rate of 3.1±1.4 counts per minute was observed, which gives a value for the half-life of Re^{187} of 3.3×10^{12} years.

In view of the different origins and chemical natures of the samples, the estimates of the half-life are in good agreement. Part of the discrepancy which appears is probably due to the difficulty of applying the sample in a completely uniform layer and without additives to assist adhesion. This was more difficult with the rhenium metal, which was a hard, sintered material, and the lumpiness of the sample layer probably contributed to the lower apparent activity and higher apparent half-life in this case. The average value for the half-life of Re^{187} indicated by the three observations is $3\pm1\times10^{12}$ years.