Natural Radioactivity of Rhenium*†

CLARENCE J. WOLF‡ AND W. H. JOHNSTON§
Department of Chemistry, Purdue University, Lafayette, Indiana
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The natural radioactivity of rhenium (rhenium-187) was investigated by the method of internal gas-tube low-level Geiger counting. A half-life of $(1.2\pm0.4)\times10^{11}$ yr was found for the direct beta decay of this isotope. Gas-tube proportional measurements suggest a value of about 3 kev for the maximum beta energy. This value of the endpoint energy, the lowest known, suggests that it may be a rhenium atom and not the nucleus alone which is decaying.

NUMEROUS investigators[1–12] have studied the interesting nuclide rhenium-187 in an attempt to ascertain its half-life and mode of decay. Although the half-life and energy of the direct beta disintegration are not well known, it has been fairly well established that rhenium-187 does undergo beta minus decay emitting an extremely weak beta particle, of less energy than the tritium beta.[5,7,8,10,11]

The present paper describes work on the determination of the rhenium-187 half-life and maximum beta energy. A maximum beta energy of about 3 kev and a half-life toward beta emission of $(1.2\pm0.4)\times10^{11}$ yr is reported. Low-level internal gas-tube Geiger and proportional counting techniques were used. The results obtained are in fair agreement with most of the previous work and in particular can be correlated with the work of Herr and Merz[10] who found a half-life of about 6×10^{10} yr by studying the osmium-187 enrichment in old rhenium-containing ores.

In 1948 Naldrett and Libby[1] reported a half-life of $(4\pm1)\times10^{12}$ yr and a maximum beta energy of 43 kev. Since technetium is so similar to rhenium chemically, Sugarman and Richter[2] showed that the Naldrett and Libby[1] sample did not contain traces of technetium. They obtained the same disintegration rate after careful purification. Later Suttle and Libby[5] attempting to refine the measurements of Naldrett and Libby found that the beta energy previously reported (43 kev) was due to trace impurities in the aluminum absorbers. They were unable to determine the energy of the rhenium beta, but assigned it an upper limit of 8 kev ($E_{\beta\ \max}<8$ kev). According to their observed counting rates, a beta energy of a few kev would yield a half-life of about 10^{11} yr. In 1952 Curran[3] quoted preliminary results obtained by Dixon and McNair who had found a maximum beta energy of 400 kev. In 1953 Gauthe and Blum[4] used the perrhenate of methylene blue to study the tracks produced in photographic emulsions by the rhenium-187 beta. They found evidence for a maximum beta energy of 34 kev.

In 1954 Herr, Hintenberger, and Voshage[6] measured the enrichment of osmium-187 in an old rhenium-containing ore. Since the age of the ore was not accurately known, they were only able to place limits on the half-life of the rhenium: $5\times10^{9}\leq t_{\frac{1}{2}}\leq2.5\times10^{11}$. Later Herr and Merz,[10] by determining the ages of several rhenium-containing ores and then using the enrichment technique, obtained a half-life greater than 5.5×10^{10} but less than 6.8×10^{10} yr.

Also in 1954 Dixon and McNair[7] and later Dixon, McNair, and Curran[8] reported that they were unable to detect any radioactivity with energy greater than 1 kev and assigned a minimum half-life for the beta decay of rhenium-187 to be 1.3×10^{16} yr. At about the same time, Curran[9] explained the high value he had previously reported for the maximum beta energy of rhenium-187 (400 kev)[3]; this value was attributed to radioactive impurities in the aluminum foil which held the rhenium sample.

Recently, Walton[11] found a half-life of $(2.1\pm0.5)\times10^{11}$ yr and a maximum beta energy of 2.4 ± 0.5 kev and in 1958 Naldrett[12] reported a rhenium-187 half-life of $(3.2\pm0.7)\times10^{11}$ yr with a maximum beta energy of about 20 kev.

For convenience, a summary of all the experimental investigations on rhenium-187 is given in Table I.

EXPERIMENTAL

The technique of internal gas-tube low-level counting requires that the radioactive substance in question be inside the counter as a gas. Only four compounds of rhenium have been reported which are volatile at room

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† Taken in part from a thesis submitted by Clarence J. Wolf to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
‡ Present Address: Research Division, McDonnell Aircraft Corporation, St. Louis, Missouri.
§ Present Address: W. H. Johnston Laboratories, Inc., Baltimore, Maryland.

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TABLE I. Summary of half-life and beta energy studies on rhenium-187.

Half-life (yr)	Maximum beta energy (kev)	Detection method	Investigators	Reference
$(4\pm1)\times10^{12}$	43	Solid sample, Geiger counting	Naldrett and Libby	1
$\simeq5\times10^{12}$	...	Solid sample, Geiger counting	Sugarman and Richter	2
...	400	Solid sample, proportional counting	Curran	3
...	34	Tracks in photographic emulsions	Gauthe and Blum	4
$\simeq10^{11}$	<8	Solid sample, Geiger counting	Suttle and Libby	5
$5\times10^{9}\leq t_{\frac{1}{2}}\leq2.5\times10^{11}$	...	Os^{187} isotope enrichment	Herr *et al.*	6
$>1.3\times10^{16}$	<1	Solid sample, proportional counting	Dixon *et al.*	7,8
$5.5\times10^{10}\leq t_{\frac{1}{2}}\leq6.8\times10^{10}$	...	Os^{187} isotope enrichment	Herr and Merz	10
$(2.1\pm0.5)\times10^{11}$	2.4±0.5	Internal gas-tube	Walton	11
$(3.2\pm0.7)\times10^{11}$	≃20	Solid sample, Geiger counting	Naldrett	12
$(1.2\pm0.4)\times10^{11}$	~3	Internal gas tube	Present work	

temperature, rhenium trimethyl and triethyl,[13] rhenium hexafluoride,[14] and rhenium oxychloride.[15] The rhenium trimethyl and triethyl have proved difficult, if at all possible, to prepare[16] and the hexafluoride has proven recalcitrant as a counting gas.[11,12] Although rhenium (VII) oxychloride (ReO_3Cl) has been previously prepared, it was always contaminated with the rhenium VI oxychloride ($ReOCl_4$). It was necessary to prepare the rhenium VII oxychloride by a procedure in which the rhenium VI oxychloride was held to a minimum. This was accomplished by the direct chlorination of rhenium VI oxide at 170°C.[17] The rhenium VI oxide was prepared by the reduction of rhenium VII oxide with dioxane. Since rhenium-187 is 62.93% abundant in nature,[18] it is not necessary to use enriched rhenium samples. The oxychloride, which has a vapor pressure of 4.5 mm of mercury at room temperature,[17] was purified by several vacuum distillations.

Numerous gas mixtures were studied in order to find an acceptable counting gas. The counting gas selected had to fill four requirements: (1) stability over a 24-hr period, (2) sensitivity to external radiation, (3) uniform height of Geiger pulses (determined with an oscilloscope), and (4) a plateau length of at least 25 v. Gas mixtures containing up to 4.5 mm of mercury of rhenium oxychloride, 650 mm neon, 0.1 mm chlorine, and 0.5 mm of argon were found to be acceptable for Geiger counting, although these counters were inefficient with respect to the number of ionizing events necessary to produce a single pulse. The determination of the counting efficiency was indeed a major part of this work.

The efficiency of most gas counters is 100%, that is, every ionizing event which occurs in the active volume of the counter gives rise to a pulse. However, it is well known that in halogen quenched counters the efficiency decreases below 100% as the halogen content increases.[19] This phenomenon is also present in counters containing rhenium oxychloride, here the gas efficiency varied from about 6 to 85%.

The internal gas efficiency was measured with standardized cobalt-60 and iron-55 external sources together with the "mesonic" background counting rate. The latter efficiency is equal to the ratio of the canceled anticoincident pulses in the rhenium counter to that in the reference counter. In Table II a few typical efficiencies are compared to efficiencies obtained with a gas filling of isobutane-helium, a commercial mixture known as "Q gas" which is well known to be one hundred per cent efficient. The gas efficiency seems to be independent of the energy of the ionizing event since mesons, iron-55 and cobalt-60 yield essentially the same value. The decrease in efficiency seems to be equivalent to a reduction in the effective volume of the counter.

Although the oxychloride is very reactive chemically, nickel and stainless steel counters were found to be inert when pretreated with an atmosphere of chlorine and then with the oxychloride at its saturation pressure. Both counters were rather large, the active volumes of the nickel and stainless steel counters were 1.74 and

TABLE II. Comparison of gas efficiencies for various partial pressures of ReO_3Cl for mesons, iron-55, and cobalt-60.

$P(ReO_3Cl)$[a] (mm Hg)	Percent efficiency[b] Mesons	Iron-55	Cobalt-60	Average
4.5[c]	4.6	...	5.6	5.1
0.52[c]	14.7	17.4	18.0	16.7
0.22[c]	19.8	20.3	20.6	20.3
3.5[d]	5.0	6.8	6.9	6.2
1.6[d]	6.1	7.5	7.9	7.2
0.015[d]	85.1	86.1	85.8	85.7

[a] Partial pressure of the ReO_3Cl in mm of mercury.
[b] Percent efficiency as compared to isobutane-helium (a commercial premixed gas: Q gas).
[c] Using the nickel counter.
[d] Using the stainless steel counter.

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3.04 liters, respectively. These volumes were determined by the addition of an accurately known specific activity of argon-37, which was calibrated in a Libby-type counter[20] in which end corrections were applied. Each counter was equipped with a holder for the standard sources.

The low-level counting equipment used in this work consisted of 17 anticoincidence counters placed around the sample counters. The anticoincidence counters were housed in an iron shield which had a "roof" consisting of 8 in. of iron and 2 in. of lead, sides of 4 in. of iron and 2 in. of lead, and a "floor" of 1-in. iron. The shield alone reduced the background to about 300 counts per minute in the stainless steel counter (active volume, 3 liters) and the anticoincidence shielding reduced this another factor of ten (to 33 counts/min).

Although inefficient counters are believed to be useless as proportional counters, several hundred attempts were made at internal gas proportional beta-ray spectrometry. The spectrometer consisted of the nickel or steel counter, a preamplifier, a stable 5000-v power supply, a high-gain nonoverloading linear amplifier, and a memory core 100-channel pulse-height analyzer. In one of the numerous attempts to determine the beta-ray spectrum of rhenium-187, proportionality was obtained. Although the spectrum could not be obtained again, the results are worth noting. Argon-37 was admitted to the counter after the rhenium spectrum was obtained and the 2.8-kev x ray of chlorine resulting from K capture in argon, was used for the energy calibration. Since the uncertainties in this procedure are large, we have not included the experimental observations, but shall merely quote the results.

RESULTS AND DISCUSSION

The results of the half-life determinations are shown in Table III. The first column shows the partial pressure of the oxychloride in the counter; the second the observed low-level counting rate; the third column gives the average efficiency determined from the cobalt-60, iron-55, and mesons (see preceding section); the fourth column shows the calculated half-life from each of the measurements. The average of these half-lives is 1.22×10^{11} yr with a standard deviation of 0.36×10^{11} yr. This can best be reported as $(1.2 \pm 0.4) \times 10^{11}$ yr for the half-life of rhenium-187 toward direct beta emission. The rather large error is not inherent in the gas-tube method but rather arises from the low internal efficiency of the counter.

Figure 1 shows the specific activity in disintegrations per minute per liter of counting volume plotted against the partial pressure of the rhenium oxychloride. The linearity of the resulting plot shows that the mechanism by which the internal efficiency is lowered is independent of the energy of the ionizing event, at least in the range studied here.

When a nucleus undergoes beta decay, the nuclear charge increases by one unit. This increase in charge results in an increase in the binding energy of the

TABLE III. Calculated half-lives of rhenium-187 for various internal gas efficiencies and partial pressures of ReO_3Cl.

$P(ReO_3Cl)$[a] (mm Hg)	Observed[b] counting rate (counts/min)	Average[c] efficiency	Calculated[d] half-life (10^{11} yr)
	Nickel counter		
4.5	90.86	5.1	1.17
4.5	96.31	5.4	1.16
1.6	80.13	12.1	1.16
2.1	89.61	11.4	1.27
4.5	85.95	5.4	1.31
2.53	60.45	6.6	1.30
1.37	45.30	8.2	1.20
0.52	46.94	21.7	1.32
0.52	30.49	16.7	1.63
0.24	35.61	20.5	0.80
0.52	36.82	17.0	1.32
0.22	25.61	20.2	1.13
0.086	24.21	26.7	0.63
	Steel counter		
4.5	140.61	4.4	1.08
2.33	122.93	7.3	1.06
1.18	95.31	9.5	0.97
0.32	49.61	15.3	0.89
3.5	121.39	6.2	1.48
1.6	72.31	7.2	1.31
0.76	40.61	10.4	1.70
0.32	42.67	17.4	1.22
0.039	21.51	33.6	0.51
0.015	37.61	85.7	2.43
0.31	40.11	16.6	1.20
0.16	27.34	18.6	1.17

[a] Pressure of ReO_3Cl in mm of mercury.
[b] Observed low-level counting rate in counts per minute.
[c] Percent efficiency as compared to isobutane helium (Q gas); average of the gas efficiency for mesons, iron-55, and cobalt-60.
[d] Half-life for rhenium-187 corrected for efficiency and background, in units of 10^{11} yr.

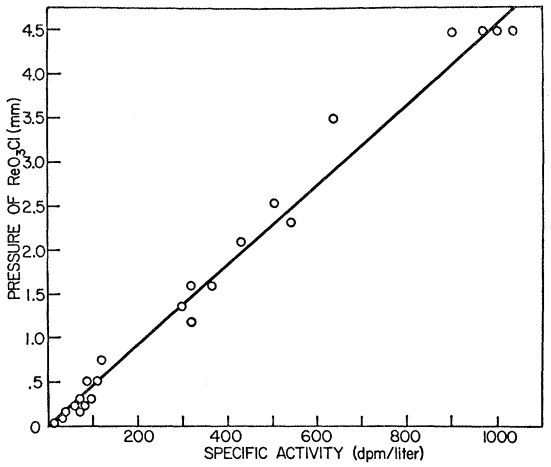

FIG. 1. Specifity activity [in (disintegrations/minute) per liter] as a function of the rhenium oxychloride pressure.

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atomic electrons. According to Foldy[21] this atomic rearrangement energy is proportional to $Z^{12/5}$. In the case of the rhenium to osmium transition the rearrangement energy is 14 kev, considerably more than the maximum beta energy.

Since energy must be conserved, we must account for the electronic rearrangement energy. This energy could manifest itself in one of five places: (1) all the energy could be carried away by the emitted electron, (2) the neutrino could take it all, (3) electromagnetic radiation (which we shall call rearrangement radiation) could be emitted, (4) it could be shared by the neutrino and the electron, or (5) the energy could be used directly in the creation of the beta transition. Postulates (4) and (5) are essentially equivalent when the maximum beta energy exceeds the rearrangement energy. However, they are different when the rearrangement is greater than the maximum beta energy. In this latter case the rearrangement supplies part of the energy necessary for particle creation.

In essence the first four postulates are discussed by Schwartz[22] and our line of reasoning is quite similar to that presented by him. The first postulate can be eliminated by noting that it would cause a displacement of the beta spectrum by an amount equal to the difference in electronic energy of the final and initial atoms. This has not been observed in lead-210[23,24] nor plutonium-241[25] nor in the present work. In lead-210 and plutonium-241 the rearrangement energy and the maximum beta energy are of the same order of magnitude and one would expect a discrete beta spectrum if the electron received all the rearrangement energy. The beta spectrum of lead-210 was measured by Jaffe and Cohen[23] and Huster.[24] The observed spectrum was not discrete but was in agreement with theory. Shliagin,[25] who studied plutonium-241, did not observe a discrete beta spectrum, but found that this result agreed with theory. The second postulate, that the neutrino might take all the energy, can be eliminated because of the extremely weak coupling between the neutrino and electron cloud. The third postulate, emission of rearrangement radiation, cannot be ruled out on the basis of our work, but can be disregarded by the findings of previous workers. In the rhenium decay the electromagnetic radiation resulting from the change in binding energy of a K electron alone would be 2 kev. Radiation of this magnitude would have been easily detected in the counters of Libby and Suttle[5] and Dixon *et al.*[7,8] If the fourth postulate is correct (electron and neutrino sharing the energy), we can easily see that the rearrangement energy is the lower limit for the maximum beta energy. There appears to be little doubt that this is not the case in the rhenium-187 decay. Thus, we are led to the fifth postulate that the rearrangement energy is involved in the creation of the electron-neutrino pair. This implies that it is the atom and not just the nucleus which is undergoing beta decay.

Serber and Snyder[26] have considered the effect of rearrangement energy of the beta particle as it passes through the electron cloud. They conclude that only a small fraction of the energy (approximately 120 ev in case of rhenium) could be transferred to the beta particle. Energies of this magnitude would not perturb the shape of the beta spectrum. However, our interpretation suggests that the beta is created in the electron field of the final atom and therefore does not move through a changing electron cloud.

In the case of rhenium, the bare nucleus would be stable and the decay is only possible because of the electron cloud. The calculation of the overlap between the nuclear and atomic wave functions is a problem beyond the scope of this paper. However, Gilbert[27] has theoretically considered the rhenium-187 beta transition and has calculated for beta energies in the neighborhood of 1 kev that two processes of equal probability occur. The first is direct beta emission and the second is so-called indirect electron creation, here the electron is created in a state bound to the daughter atom. Electron creation would not produce an ionizing electron and, therefore, would not be counted in a Geiger or proportional counter. The measurements of Herr and Merz[10] did not involve the detection of ionizing radiation but determined the total amount of osmium-187 produced by the decay of rhenium-187. Thus, if we accept the Herr and Merz total rhenium-187 half-life of 6×10^{10} yr and consider our value of 1.2×10^{11} yr (neglecting the error) as the partial half-life for direct beta decay, we see that the partial half-life for electron creation is 1.2×10^{11} yr. A ratio of unity for electron creation to direct beta decay is well within the computational limits of Gilbert and the experimental errors of our work. The errors involved are of such a magnitude that we have been unable to prove the existence of electron creation; however, our findings are consistent with that postulate.

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