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Decay of Rhenium-187

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The end-point energy for ^{187}Re has been determined to be 2.62±0.09 keV by use of $(C_5H_5)_2$ReH vapor in a proportional-counter spectrometer. The ^{187}Re half-life determined from the proportional-counting experiments is $(6.6\pm1.3)\times10^{10}$ year. This is identified as the β^- half-life for decay to continuum states only. When this is combined with the total half-life of $(4.3\pm0.5)\times10^{10}$ year obtained from ^{187}Re/^{187}Os ratios in geologically dated minerals, the ratio of bound-state to continuum-state decays is found to be 0.5±0.3.

SYMBOLS

A DISCUSSION of the $^{187}\text{Re}\rightarrow{}^{187}\text{Os}$ β^- transition is complicated by the fact that the energy of the emitted β^- particle is less than the change in the atomic binding energy. The more important of the symbols which will be used in this discussion are listed below.

$\langle E_{\text{ex}}\rangle$ = the average atomic excitation energy of the final atom immediately following β^- decay. This energy is the result of imperfect overlap between initial and final atomic states.[1] It ranges in value from zero for an adiabatic transition to $23Z^{2/5}$ (130 eV for Re) for a nonadiabatic transition.[2]

$Q\equiv W_0-1+\Delta E$, where W_0 is the difference between the initial and final nuclear masses, and ΔE is the difference between the initial and final atomic binding energies.[3] Since the neutrino rest mass is assumed zero, Q is the sum of $\langle E_{\text{ex}}\rangle$ and the kinetic energies of the emitted neutrino and β^- particle.

T = the apparent β^- kinetic energy. Because the Os atom is expected to de-excite during the resolving time of the proportional counter (10^{-6} sec), in our experiments $T\cong p^2/2+\langle E_{\text{ex}}\rangle$, where p is the true momentum of the β^- particle.

$q_0\equiv Q-p^2/2$, which will be taken to be the neutrino energy (or momentum) until the overlap correction is considered.

E_0 = the end-point energy, i.e., the value of T at which the extrapolated Kurie plot of the spectrum crosses the energy axis. The difference between E_0 and the maximum β^- energy $Q-\langle E_{\text{ex}}\rangle$ is less than the errors in previously reported maximum energies, so all will be designated as E_0 values.

INTRODUCTION

Rhenium-187 has been studied many times by Geiger and proportional counting. Half-lives[4,5] from 3×10^{10} to more than 1.3×10^{16} yr and E_0 values from less than 1 to 400 keV[4] have been reported. Solid samples have been used extensively because all Re compounds which are volatile at room temperature and can be synthesized reproducibly have proven to be counter "poisons," i.e., they attach electrons. However, all of the half-life, and most of the E_0 measurements with solid sources depend on the determination of the half-thickness of the very soft beta spectrum. This has never been done accurately because of experimental difficulties caused by the small value of E_0. As an example, Suttle and Libby[6] determined the activity per cm^2 of a (thick) Re metal sample with a Geiger counter and reported 10 times the activity observed by Watt and Glover[5] with a proportional counter, yet the first authors used their data to calculate a half-life 3 times as large. This is owing to the fact that the half-thickness Suttle and Libby observed corresponds to an E_0 value 7 times as large as Watt and Glover's.

Watt and Glover obtained their seemingly accurate value of E_0 (actually, maximum β^- energy) by examining the spectrum from a Re metal foil placed inside a proportional-counter spectrometer. However, two reasons can be given for suspecting that their value 1.2±0.1 keV may be in error: (1) The E_0 could not be determined by the usual linear extrapolation (Kurie plot) because self-absorption caused the spectrum to be distorted. This distortion accentuated the normal asymptotic approach of the spectrum to the energy axis. (2) The statistical uncertainties were rather large since the sample activity was only $\frac{1}{4}$ of background.

The uncertainties due to self-absorption can be eliminated by the use of an internal, gaseous sample. Probably the best of the earlier half-lives is Wolf and Johnston's value of $(12\pm4)\times10^{10}$ year obtained with the volatile counter "poison," ReO_3Cl.[4] Brief mention has been made of the two determinations of E_0 where volatile samples were used [$Re(CH_3)_3$? and ReO_3Cl],[4] but neither spectrum could be confirmed by a second experiment.

EXPERIMENTAL

Several attempts were made to find a reasonably volatile compound of Re which could be used at room

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[1] J. N. Bahcall, Phys. Rev. **129**, 2683 (1963).

[2] R. Serber and H. S. Snyder, Phys. Rev. **87**, 152 (1952).

[3] Energy is given in mc^2 unless otherwise stated, length is in $\hbar/mc$, and momentum is in mc. The fine structure constant $\alpha\equiv e^2/\hbar c$.

[4] C. J. Wolf and W. H. Johnston, Phys. Rev. **125**, 307 (1962). These authors summarize the previous results, so only the experiments believed to be the more significant will be discussed here.

[5] D. E. Watt and R. N. Glover, Phil. Mag. **7**, 105 (1962).

[6] A. D. Suttle, Jr. and W. F. Libby, Phys. Rev. **95**, 866 (1954).

temperature. By a method previously described,[7] ReO_3Cl[8] and $CH_3Re(CO)_5$[9] were shown to be very efficient electron scavengers, so that if either of these compounds were to be used to obtain relatively undistorted spectra, their pressures would need to be so low that the ^{187}Re activity would be much lower than background.

Thus far, all metal alkyls and cyclopentadienyl compounds have proven to be good counting gases, so many attempts were made to prepare the volatile $Re(CH_3)_3$ reported by Druce.[10] Reactions were tried using a halide ($ReCl_3$, $ReCl_5$, or ReI_3-ReI_4) and a methylating agent (CH_3MgI or $LiCH_3$) in diethyl ether under anaerobic conditions. All volatile compounds were removed by one vacuum distillation, and most of the ether was stripped off by a second. However, it was found by gas-liquid chromatography, a flame test, or (once) mass-spectrometric analysis, that the volatile Re in the remaining liquid corresponded to less than several tenths of a percent yield. These negative results confirm those of earlier workers.[6,11]

Finally, biscyclopentadienylrhenium hydride, $(C_5H_5)_2ReH$, was synthesized as described by Wilkinson and Birmingham.[12] Because of the low volatility of this compound, it had to be used at elevated temperatures. There was evidence of decomposition of the $(C_5H_5)_2ReH$ at the higher temperatures used, so an excess of the $(C_5H_5)_2ReH$ was distilled into the counter, and its pressure was controlled by the counter temperature.

In order to be able to calculate the ^{187}Re half-life, this procedure necessitated that the vapor pressure of the $(C_5H_5)_2ReH$ be determined. A sample of the $(C_5H_5)_2ReH$ was sealed under high vacuum in a small system, which included a Hg manometer. The system was placed in an oil bath, and the vapor pressure was determined from 90 to 140°C with a cathetometer. The error due to decomposition during the measurements was negligible as shown by the fact that the manometer returned to zero on cooling. The data were fitted to the equation

$$\log_{10}P_i(\text{Torr}) = -3279/T_i + 8.36 \qquad (1)$$

obtained by the method of least squares with the error in $\log_{10}P_i$ weighted by P_i. Equation (1) fits the data with a standard deviation of ± 0.050 Torr.

The counter was constructed from a stainless steel tube with an inside diameter of 4.0 cm. It was fitted with a metal valve, Stupakoff electrodes, and a 0.002-in.-diam tungsten anode. The distance between the ends of the guard electrodes was 41.3 cm, which was taken to be the sensitive length of the counter in volume calculations. For greater temperature uniformity the counter was clad with $\frac{1}{2}$ in. of brass and placed completely in an oven. The temperature error, including nonuniformity along the counter, was less than ±1°C, which corresponds to ±5% in P_i.

For proportional counting a trace of ^{37}Ar was used for energy calibration (K-peak energy = 2.82 keV); and 25 Torr of ethane, as the counting gas. A multichannel analyzer was used for pulse analysis. The resolution (full width at half-maximum) of the K peak was 24% in the background runs and 36% in the presence of $(C_5H_5)_2ReH$, so computed K peaks of 36% resolution were used in background subtraction. In other measurements in which Geiger counting was tried, the counting gas was 5-Torr butane and 45-Torr He; and here an electronic quench circuit (dead time, 2.9 msec) had to be used to stop multiple pulsing.

RESULTS AND DISCUSSION

Theoretical Spectrum Shape

Since the spins and parities of the ground states of ^{187}Re and ^{187}Os are $\frac{5}{2}+$ and $\frac{1}{2}-$, respectively, the beta transition is first forbidden (unique). Therefore, the spectrum shape is given by[13,14]

$$N(W) \propto F(Z,W)pW[L_0q_0^2/3 + 3L_1]q_0^2, \qquad (2)$$

where $F(Z,W)$ is the relativistic Coulomb correction factor and W is the total β^- energy, including rest mass. The L_n represent combinations of electron radial wave functions.

It will be shown that $E_0 = 2.62$ keV for ^{187}Re. By extrapolating the tabulated values[15] of L_n below 2.5 keV, it was found that $3L_1 \gg L_0q_0^2/3$ and[16] that L_1 is independent of energy to within ±2% for $T < 2.6$ keV. (The same results were obtained when the less exact[17] analytical representations[13,14] for L_n were used.[18]) Thus, Eq. (2) reduces to

$$N(W) \propto F(Z,W)pWq_0^2. \qquad (3)$$

From tabulated values of the Fermi function,[19] it can be shown that $pWF(Z,W)$ is constant below 2.6 keV, so

$$N(W) \propto q_0^2. \qquad (4)$$

The effect of the electron cloud on the shape of the

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[7] C. F. Smith, Jr., and D. C. Conway, Rev. Sci. Instr. **33**, 726 (1962).

[8] H. Kocol, M. S. thesis, Purdue University, 1961 (unpublished).

[9] L. Finkel, M. S. thesis, Purdue University, 1964 (unpublished).

[10] J. G. F. Druce, J. Chem. Soc., 1129 (1934).

[11] H. Gilman, R. G. Jones, F. W. Moore, and M. J. Kolbezen, J. Am. Chem. Soc. **63**, 2525 (1941).

[12] G. Wilkinson and J. M. Birmingham, J. Am. Chem. Soc. **77**, 3421 (1955).

[13] E. J. Konopinski and G. E. Uhlenbeck, Phys. Rev. **60**, 308 (1941).

[14] E. Greuling, Phys. Rev. **61**, 568 (1942).

[15] M. E. Rose, C. L. Perry, and N. M. Dismuke, Oak Ridge National Laboratory Report No. ORNL-1459, 1953 (unpublished).

[16] This inequality shows that the electron carries off the unit of orbital angular momentum. The centrifugal potential $l(l+1)/2r^2$ is equal to the Coulomb potential at $r = 1/\alpha Z$, so the β^- particles leak through the centrifugal barrier in the region of the 1s shell.

[17] M. E. Rose and C. L. Perry, Phys. Rev. **90**, 479 (1953).

[18] The numerical evaluation of the expression for L_1 has been discussed by Macklin *et al.* [P. Macklin, L. Lidofsky, and C. S. Wu, Phys. Rev. **87**, 391 (1952)].

[19] U. Fano, Natl. Bur. Std. (U.S.) Appl. Math. Ser. **13**, (1952).

spectrum must now be considered. Good[20] has obtained screening corrections for forbidden transitions by use of the WKB approximation. The screened potential was taken to be[3]

$$V_{\mathrm{SC}}=-\alpha Z/r+V_0\,, \tag{5}$$

where V_0 is the potential produced by the electron cloud in the region of the nucleus. The (screening) corrected spectrum is obtained by using the corrected functions $\bar{F}$, $\bar{p}$, $\bar{W}$, and $\bar{L}_n$ in Eq. (2), where $\bar{K}(Z,W)\equiv K(Z,W-V_0)$. However, $V_0\cong 13$ keV,[19] and this method (method A) is not applicable when $V_0>T$.[20]

A less accurate method (method B) of correcting for the screening effect would be to use the approximate potential

$$V_{\mathrm{SCA}}=-\alpha Z'/r \tag{6}$$

for V_{SC}. Here the corrected functions are $\bar{F}$ and $\bar{L}_n$, where $\bar{K}(Z,W)\equiv K(Z',W)$. Below 85 keV the corrected (reduced) $N(W)$ values obtained by method A are 0 to 8% larger than those obtained by method B with $Z'=0.8Z$. If the ^{187}Re spectrum is corrected by the latter method, the spectrum shape is not changed appreciably, although the magnitude of $N(W)$ is reduced about 30%. An exact calculation of the screening correction would be of interest, as the value of E_0 and the upper limit to the half-life are dependent upon the spectrum shape.

It is possible for beta decay to occur by the indirect (exchange) process where an electron is created in a previously occupied bound state with the simultaneous transfer of the bound-state electron to a continuum state. Gilbert[21] has calculated that exchange emission is much less probable than direct decay to continuum states for ^{187}Re, so the spectrum shape is not affected by exchange emission.

By essentially the same derivation as used for allowed transitions,[1] it is found that the effect of imperfect atomic overlap on the ^{187}Re spectrum can be accounted for by multiplying Eq. (4) by $(1\text{-}2\langle E_{\mathrm{ex}}\rangle/q_0)$. This correction factor consists of the first two terms in a Taylor series expansion. Therefore, let us limit our discussion to the region of the spectrum below 2 keV, since reliable experimental data were not obtained above this point. In this region, $1-2\langle E_{\mathrm{ex}}\rangle/q_0\cong(1-\langle E_{\mathrm{ex}}\rangle/q_0)^2$. Therefore, the corrected spectrum is

$$N(W)\propto(Q-T)^2\,, \tag{4'}$$

which identifies the extrapolated E_0 as Q.

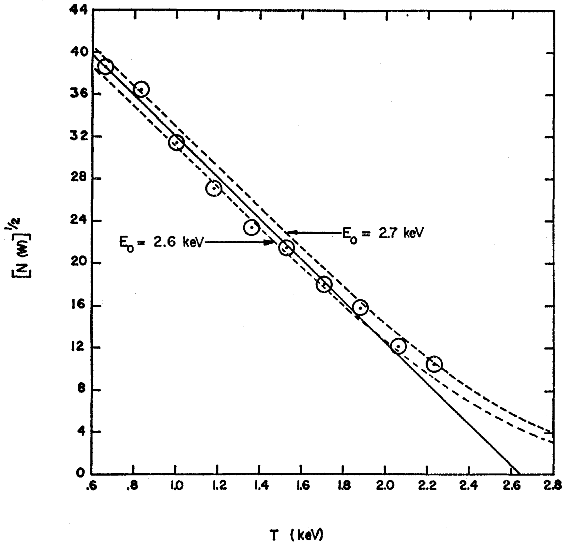

FIG. 1. Kurie plot of the ^{187}Re spectrum where $E_0=2.67$ keV. The curve is concave upward at lower energies. Computed (resolution-distorted) spectra for $E_0=2.6$ and 2.7 keV are also shown.

End-Point Energy

Proportional-counter spectra. Kurie plots were made of the spectra. Figure 1 shows such a plot for $T>0.6$ keV. At energies below 0.6 keV the data points fell above the extrapolated linear region and were not as reproducible. This was due in part to electrical breakdown pulses which fed into these lower energy channels. This effect appeared to be worse in the presence of $(C_5H_5)_2$ReH. The points at energies above 2 keV were not considered in evaluating E_0 because of the low ratio of sample activity to background. This ratio varied from 2 to $\frac{1}{2}$ from 0.6 to 2 keV and dropped off rapidly above this because of the wing of the ^{37}Ar peak. The E_0 values obtained by a least-squares fit of the data from 0.6 to 2 keV are given in Table I.

Systematic errors. The effect of the finite resolution $R(T)$ of the spectrometer on the shape of the spectrum was evaluated on a computer. $R(T)$ was evaluated from the observed value of 36% for the K peak of ^{37}Ar by assuming it to be proportional to $T^{-1/2}$. The Kurie plot of the computed (resolution distorted) spectrum was practically linear from 0.6 to 2 keV (Fig. 1), although the extrapolated E_0 obtained by a least-squares fit to a linear curve was 1.4% too high. Considering also the small variation in L_1, the corrected value of E_0 is found to be 2.62 ± 0.09 keV.

Other systematic errors, such as those caused by the nonlinearity of the amplifier or the ADC unit of the multichannel analyzer, do not cause a significant increase in the standard deviation. If correcting for the wing of the ^{37}Ar peak had introduced a significant error in E_0, the 130° data would not agree with the 140° data, as the ratio of the ^{187}Re activity to the ^{37}Ar activity was 40% smaller at the lower temperature. The average values at the two temperatures differ by 0.09 keV, which is not considered significant.

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[20] R. H. Good, Jr., Phys. Rev. **94**, 931 (1954).

[21] N. Gilbert, Compt. Rend. **247**, 868 (1958).

Half-Life

Proportional-counter half-life. One estimate of the true total counting rate of the source was obtained by integrating under the curve of Fig. 1, extrapolated linearly back to $T=0$. The half-lives computed with this estimate are designated t_E in Table I.

Another estimate of the total counting rate was obtained by integrating under the observed spectrum. The half-lives computed with this estimate are designated t_0 in Table I. Extensive electrical breakdown caused one of the t_0 values to be much too low, so it has not been tabulated.

Systematic errors. During the counting experiments, a steady state existed in which the rate of mass transport of $(C_5H_5)_2ReH$ vapor into each unit volume of the counter was equal to its rate of loss by decomposition and mass transport. If the decomposition was too rapid, the average $(C_5H_5)_2ReH$ pressure would have been significantly less than that given by Eq. (1). This effect is expected to be worse at 140°C and would cause the half-lives to be too large. It is seen (Table I) that the half-lives obtained at 140° are larger than the average of the values obtained at 130°, $t_E=(7.2\pm0.5)\times10^{10}$ year and $t_0=(6.0\pm0.6)\times10^{10}$ year. To determine if the deviations are significant, Chauvenet's criterion was used.[22] Although two of the deviations are just small enough to pass this statistical test, it appears that sample decomposition may have affected the half-lives at 140°, so the 130° data will be used.

It has been shown that the theoretical spectrum is expected to have the shape given by Eq. (4′) from 0 to 2 keV. Nevertheless, the t_E half-lives are 10 to 20% too large. This is due to the fact that the gas gain is too low at each end of the proportional counter (end-effect) over a region with a length somewhere between the radius and the diameter of the cylinder.[23] Pulses from these regions appear in the low-energy region of the spectrum, so the extrapolated values of $N(W)$ are actually too low.

The pulses from the regions of low gas gain at the ends of the counter were counted in computing t_0. However, the t_0 values are only lower limits to the true half-life because the electrical breakdown pulses were also counted. Therefore, the half-life determined from the proportional counter spectra t_p is taken to be $(6.6\pm1.2)\times10^{10}$ year, which is the average of the values of t_E and t_0 obtained at 130°. When the standard deviation in P_i and the uncertainty in the counter temperature are included in the error, $t_p=(6.6\pm1.3)\times10^{10}$ year.

Geiger counter half-life. In the absence of Re the Geiger pulses were 3 to 5 V high in the plateau region. With $(C_5H_5)_2ReH$ in the counter, the activity was determined at 10° intervals from 110 to 140°C at 4 V pulse height. The values obtained for the half-life in two series of experiments are $(3.2\pm0.1)\times10^{10}$ and $(6.9\pm0.2)\times10^{10}$ year. Since no plateau was taken in the first series of experiments, and the "plateau" was found to be an inflection point on a steeply rising curve in the second, the results are not reliable estimates of the half-life. However, the fact that the results appear to be independent of temperature is evidence that the counter gas was saturated with $(C_5H_5)_2ReH$ vapor at temperatures as low as 130°.

TABLE I. Proportional-counter data for the end-point energy and half-life of ^{187}Re.

Temperature (°C)	E_0 (keV)	$t_E\times10^{-10}$ (year)	$t_0\times10^{-10}$ (year)
130	2.74	7.21	6.59
130	2.77	6.70	5.38
130	2.61	7.76	6.13
140	2.67	7.95	...
140	2.57	8.40	6.89
Average	2.67 ± 0.09[a]	7.6 ± 0.7[a]	6.2 ± 0.7[a]

[a] The errors are standard deviations. Systematic errors are considered in the text.

Ratio of Bound-State to Continuum-State Decays

Let Γ_B/Γ_C be defined as the ratio of the rate of bound-state decay to previously unoccupied atomic states to the rate of decay to continuum states. Gilbert[21] has calculated Γ_B/Γ_C ratios for ^{187}Re using Slater orbitals. He finds that the most probable mode of bound-state decay is by the indirect (exchange) process where an electron is created in a previously occupied bound state with the simultaneous transfer of the bound-state electron to an unoccupied bound state. For this process, the theoretical value of Γ_B/Γ_C at $E_0=2.6$ keV is 1/9.

It is presumed that bound-state beta decay was not detected in the proportional-counter experiments, so t_p will be taken to be the half-life t_C for decay to continuum states only.[24] From $^{187}Re/^{187}Os$ ratios in 10 geologically dated molybdenites, the geological half-life t_{Geo} for ^{187}Re has been determined to be $(4.3\pm0.5)\times10^{10}$ year.[25] Of course, t_{Geo} is the total half-life for both types of decay. Therefore, $1/t_{Geo}=1/t_C+1/t_B$, from which $\Gamma_B/\Gamma_C=0.5\pm0.3$. The agreement between this value and the theoretical value is close enough, considering the experimental accuracy and the approximate nature of Gilbert's computation.

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[22] Crumpler and Yoe, *Chemical Computations and Errors* (John Wiley & Sons, Inc., New York, 1940).

[23] S. C. Curran, *Beta- and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (Interscience Publishers, Inc., New York, 1955), p. 166.

[24] If shake-off electrons were produced in bound-state decay, they would be produced in no more than about 20% of the transitions, as found for β^- decay [T. A. Carlson, Phys. Rev. **131**, 676 (1963), and the earlier references quoted therein]. However, it is likely that only the undetectable neutrino escapes the Os atom, as the transition between initial and final atomic states is probably adiabatic. One can picture (classically) the electron moving to an outer orbital with a velocity of the same order of magnitude as the orbital velocities of the electrons in each shell it passes, so the electron cloud probably has time to readjust.

[25] B. Hirt, G. R. Tilton, W. Herr, and W. Hoffmeister, Helv. Phys. Acta **35**, 320 (1962).