

Characteristics of Some Radionuclides of Tungsten, Rhenium, and Osmium Formed by Second-Order Thermal Neutron Capture*

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The identification and characteristics of several beta-emitting nuclides are reported. The half-life of W^{188} is 65 days, Os^{194} about 700 days, while Re^{189} might be either of two isotopes having half-lives of about 150 days or of at least five years. The mass assignment of W^{181} has been confirmed in view of its presence in thermal-neutron irradiated tungsten. Re^{188} was found to have a half-life of 16.9 hours. No gamma-radiation could be found by absorption measurements to be associated with the 18-hour Ir^{194} daughter of Os^{194} . Thermal-neutron activation cross sections are reported for most of the nuclides.

I. INTRODUCTION

IF we consider the thermal-neutron capture reactions

$$Z^A(n, \gamma)Z^{A+1} \quad \text{and} \quad Z^{A+1}(n, \gamma)Z^{A+2}, \quad (1)$$

then if Z^{A+1} is unstable with a half-life short compared with the time of exposure to the neutron flux, a fixed amount of Z^{A+1} will be present after "equilibrium" has been reached. Under these conditions it can be shown that

$$(\lambda N)_{A+2} = I^2 \sigma_A \sigma_{A+1} n [1 - \exp(-\lambda_{A+2} t)] / \lambda_{A+1}, \quad (2)$$

where the λ 's are the respective decay constants, I is the intensity of the neutron flux, the σ 's are the activation cross sections, and n is the number of target nuclei of the isotope Z^A .

Therefore, the factors favorable to an increasingly large value of $(\lambda N)_{A+2}$ are (1) large activation cross sections for both reactions shown above, (2) an intense neutron flux, (3) a large natural isotopic abundance, (4) a small value for λ_{A+1} (even though Eq. (2) was simplified for the case in which $1/\lambda_{A+1} \ll t$), and (5) an exposure time, t , long enough such that the factor in parentheses in Eq. (2) is of the order of magnitude of unity.

Yaffe, *et al.*,¹ using the heavy water pile at Chalk River, were able to thus produce Ba^{140} from second-order capture of thermal neutrons by Ba^{138} . By chemically purifying the irradiated barium and then making periodic separations of lanthanum, they were able to establish the presence of Ba^{140} through its La^{140} daughter,

and to calculate the thermal-neutron activation cross section for Ba^{139} . However, since Ba^{139} has a half-life of only 85 minutes and an activation cross section calculated by them to be four barns, it is evident that only the most intense neutron flux could produce feasible amounts of activity of the second-order capture products.

Inspection of an isotope chart shows that, owing either to a small value for σ , a low natural abundance, or a large value for λ_{A+1} , or to a combination of these factors, $(\lambda N)_{A+2}$ would likely be vanishingly small with anything but the largest values of I , for most regions of the isotopic chart. However, the elements tungsten, rhenium, osmium, and iridium appear to have large thermal-neutron activation cross sections for their heaviest isotopes (which are, moreover, relatively abundant) and reasonably long half-lives for the first-order products of neutron capture. The data in Table I, taken from Seren, Friedlander, and Turkel² illustrate these conditions.

It seemed worth while to investigate second-order capture in these elements, studying the decay periods of any new nuclides thus formed, and also to calculate the thermal-neutron activation cross sections for the $A+1$ nuclides, as well as several cross sections that have not hitherto been calculated for first-order reactions.

II. EXPERIMENTAL PROCEDURE

Samples of W, Re, and Os metals were irradiated in a nuclear reactor and, after the period of irradiation, were allowed to stand for several months until the shorter-lived activities had effectively disappeared. The materials were then chemically purified and examined for products of second-order neutron capture. As reported in a previous note,³ definite proof for the formation of new beta-emitters was found.

Tungsten

The nuclide of interest in the irradiated tungsten would be W^{188} arising from second-order capture by

TABLE I. Relative abundances and cross sections for some heavy isotopes.

Nuclide	Percent abundance	$\sigma \times 10^{24}$ cm ²	$T_{1/2}(A+1)$, hours
W^{186}	28.7	34.2	24
Re^{187}	62.9	75.3	18
Os^{192}	41.0	5.3	30
Ir^{193}	61.5	79.0	18

* This work was performed under contract with the AEC.

¹ Yaffe, Sargent, Kirsch, Standil, and Grunlund, *Phys. Rev.* **76**, 617 (1949).

² Seren, Friedlander, and Turkel, *Phys. Rev.* **72**, 888 (1947).

³ M. Lindner and J. S. Coleman, *Phys. Rev.* **78**, 67 (1950).

W^{186} . The product would necessarily decay by beta-emission to the well-known 18-hour Re^{188} . Since the level of any W^{188} activity would be orders of magnitude smaller than that of the 75-day W^{185} formed by first-order capture, direct observation of the radiations of W^{188} was not possible; but the half-life was determined by measuring the equilibrium level of the separated Re^{188} daughter activity at various intervals of time. The chemical separation procedure and the results of the measurements have been described elsewhere,⁴ but the latter will be repeated below for convenience.

Osmium

Since the principal long-lived activity present in thermal-neutron activated osmium is the 97-day Os^{185} , the difficulty encountered in observing a second-order product such as Os^{194} is similar to that described for tungsten. Again, however, because Os^{194} would necessarily decay to the known 18-hour Ir^{194} , the elucidation of the parent through its radioactive daughter seemed the most feasible approach.

The chemical method used for the separation of any possible Ir^{194} consisted in initial purification of the osmium by dissolving it in, and distilling it from, boiling aqua regia, the volatile osmium tetroxide being absorbed in dilute sodium hydroxide. The distillation procedure was repeated several times from nitric acid to insure a pure osmium fraction, and the final solution of sodium perperosmate made to a definite volume. Equal aliquots of this solution and equal volumes of a standardized iridium chloride solution were added to each of seven test tubes. The tubes were then sealed. One of the tubes was analyzed several weeks after this procedure, the succeeding tubes at intervals of from three to five months.

Analysis consisted of transferring the contents of the opened tube to a distillation apparatus provided with a stream of air, adding perchloric acid, and distilling the osmium tetroxide. This simple method proved to be so effective in removing osmium that factors of 10^6 in purification were achieved with no difficulty. The residue, consisting only of unvolatilized iridium perchlorate, was taken up in water and the iridium reduced to metallic form with zinc metal, filtered, weighed, and counted. The counting rate extrapolated to the time of the osmium distillation was, together with the chemical yield correction, taken as the equilibrium level of Ir^{194} .

Rhenium

Rhenium was purified by distillation of the dissolved irradiated metal from boiling concentrated sulfuric and phosphoric acids, this being followed by precipitation of the rhenium as tetraphenylarsonium

perrhenate. Decay and absorption data were obtained from this material.

III. EXPERIMENTAL DATA

As reported elsewhere,⁴ periodic tungsten-rhenium separations led to the isolation of a Re^{188} daughter the yield of which decreased with a half-life of 65 days. Of at least 15 such separations, the average half-life for the Re^{188} was 16.9 hours rather than 18 or 18.9 hours.⁵ The lowest value was 16.7 hours, the highest, 17.2 hours.

The purified tungsten itself showed residual radiation when the beta-particles from W^{185} were stopped with Lucite absorbers. This residual radiation consisted of, principally, x-rays characteristic of the tungsten region, a lesser amount of undetermined hard gamma-radiation, and decayed with a half-life of about 120 days. This thus confirms the assignment made by Wilkinson⁶ of W^{181} made by deuteron bombardment of tantalum. The x-ray energy was determined by absorption in aluminum and in lead.

Periodic osmium-iridium separations also led to the isolation of the 18-hour beta-emitter Ir^{194} . A plot of the decrease of the specific activity of the iridium samples due to the decay of the Os^{194} is shown in Fig. 1. An accurate value for the half-life of the Os^{194} has not thus far been feasible by this method because its very long half-life still renders errors in mounting and counting from sample to sample appreciable as compared with the fraction decayed. However, the half-life appears to be around 700 days. Since direct decay measurements of the osmium itself indicate that the shorter-lived Os^{185} is gradually giving way to the Os^{194} , it will be possible within two years to observe the latter directly.

Of some interest is the absorption curve for the Ir^{194} daughter taken through Lucite absorbers, shown in Fig. 2. It is to be noted that no gamma-radiation is detectable which exceeds 0.1 percent of the intensity of the beta-activity. This is in contrast with observations

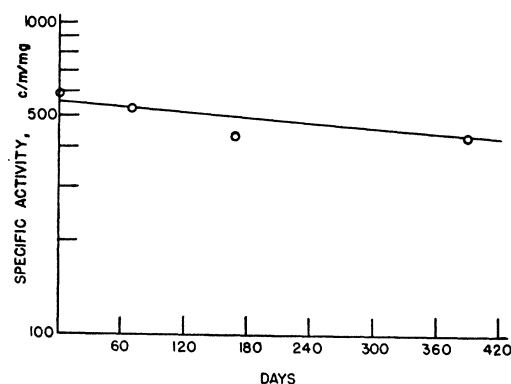


FIG. 1. Decrease with time of specific activity of iridium samples in equilibrium with Os^{194} .

⁴ M. Lindner and J. S. Coleman, *J. Am. Chem. Soc.* **73**, 1610 (1951).

⁵ G. T. Seaborg and I. Perlman, *Revs. Modern Phys.* **20**, 585 (1948).

⁶ G. Wilkinson, *Nature* **160**, 864 (1947).

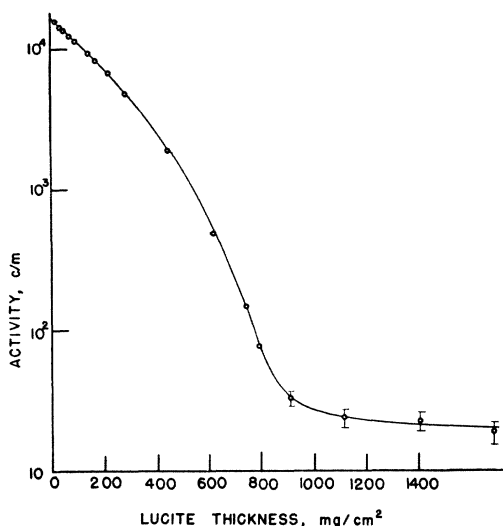


FIG. 2. Lucite absorption curve of Ir^{194} separable from thermal-neutron-irradiated osmium metal.

made on the isotope produced directly,⁵ the most recent being that of Cork⁷ wherein it is reported that a single gamma-ray of 327.5 keV follows the beta-transition of Ir^{194} . The evidence from Fig. 2 would seem to indicate no electromagnetic radiation other than bremsstrahlung can be found associated with this nuclide. The question of efficiency of detection of the gamma-radiation has been ruled out through the use of both a helium-filled and an argon-filled mica end-window counter. Identical absorption curves were obtained in both cases.

The second-order capture product of interest in irradiated rhenium is the nuclide Re^{189} . Because of the absence of a parent-daughter relationship, such a nuclide would have to be observed by direct decay of the activity remaining in the purified rhenium. Figure 3

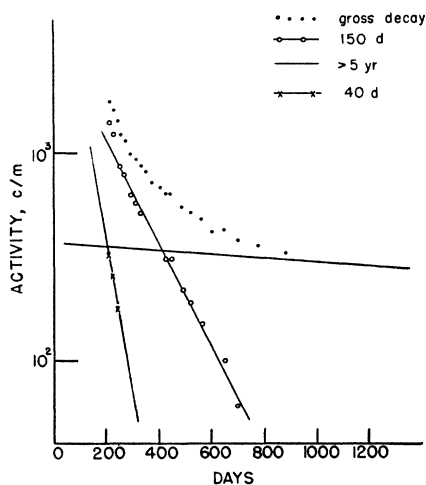


FIG. 3. Decay curve of long-lived rhenium isotopes produced in thermal-neutron irradiation of rhenium metal.

⁷ Cork, LeBlanc, Stoddard, Childs, Branyan, and Martin, *Phys. Rev.* **83**, 222 (1951).

shows the decay curve of rhenium followed for about two years. Although resolution is difficult, and the accuracy rather low, the most careful resolution indicates three components: (1) one of about 40 days, (2) a 150-day component, and (3) a component of at least five years in half-life.

The forty-day period is undoubtedly Re^{184} formed by the comparatively rare ($n, 2n$) reaction. However, the presence of two other long-lived activities in presumably purified rhenium poses a more difficult problem in mass assignment. One of these two is probably Re^{189} formed by second-order capture by Re^{187} , although no daughter activities exist which could prove the point. While the remaining period might be an independent isomer of either Re^{186} or Re^{188} , another possibility seemed to be an independent isomer of Re^{187} formed either from second-order capture by Re^{185} or by inelastic scattering of fast neutrons by Re^{187} . The latter isotope is known to decay to Os^{187} with a half-life of 10^{12} years.⁸

Although the total amount of the two long-lived activities was very low, it was possible to gain further limited information from careful absorption measurements after the 40-day component had become negligible. Figure 4 shows absorption curves taken on a nucleometer methane flow-type windowless proportional counter⁹ with aluminum absorbers up to a thickness of about 200 mg/cm^2 .

Curve *B* was taken one year after curve *A*, and therefore represents a greater contribution from the longer-lived component. It is significant that points on these two curves in the region from 40 to 60 mg/cm^2 of aluminum indicate very little decay over the time interval between measurements. In fact, two such corresponding points indicate a minimum half-life of at least four years, in good agreement with the value obtained as the minimum necessary to resolve the decay curve of Fig. 3. Curve *C* is the difference between curves *A* and *B*, and represents the absorption of the shorter-lived, or 150-day, component. It appears to consist of electrons or beta-particles of roughly a 50- mg/cm^2 range. Although these results are comparatively crude, they do indicate that the shorter-lived isotope emits particles of lesser energy than the longer-lived one.

Absorption data were also taken on a more conventional, mica end-window type, helium-filled Geiger counter. These are shown in Fig. 5 for curves taken one year apart on the same dates as the curves of Fig. 4. It is seen that, in addition to a trend similar to that of Fig. 4, the range of the longer-lived beta-particle is 300 mg/cm^2 , corresponding to an energy of about 0.75 MeV.

It is not possible to decide further from the information above concerning the mass assignments of these two nuclides, other than to postulate that one of them be Re^{189} . If Re^{187} be the other one, then there existed the possibility that, in the irradiation of tungsten with

⁸ S. N. Naldrett and W. F. Libby, *Phys. Rev.* **73**, 487 (1948).

⁹ Radiation Counter Laboratories, Chicago, Illinois.

TABLE II. Activation cross sections for nuclides of W, Re, and Os.

Nuclide	$T_{1/2}$	Type	Part. energy (Mev)	$\sigma \times 10^{24} \text{ cm}^2$
W^{181}	120 days	<i>K</i>	...	<i>2</i>
W^{188}	65 days	β^-	...	80
$\text{Re}^{187, 189}$	150 days	β^-	0.2	...
	$\geq 5 \text{ yr}$	β^-	0.75	...
Os^{185}	97 days	<i>K</i>	...	20
Os^{194}	700 days	β^-	...	190

thermal neutrons, at least some of the first-order capture product, W^{187} , might decay to such an isomeric Re^{187} . To test this point, a sample of the irradiated tungsten metal was dissolved and, without initial purification, rhenium carrier was added to, and separated chemically from, the tungsten as described for W-Re separations.⁴ Although, in addition to the Re^{188} , a relatively small amount of an activity which seemed to correspond roughly to the absorption and decay characteristics of the shorter-lived component of the irradiated rhenium, the rhenium carrier could be separated from the activity by volatilization, indicating that there is no evidence supporting the postulate of the existence of another long-lived isomeric state of Re^{187} .

Turner and Morgan¹⁰ report that rhenium activities

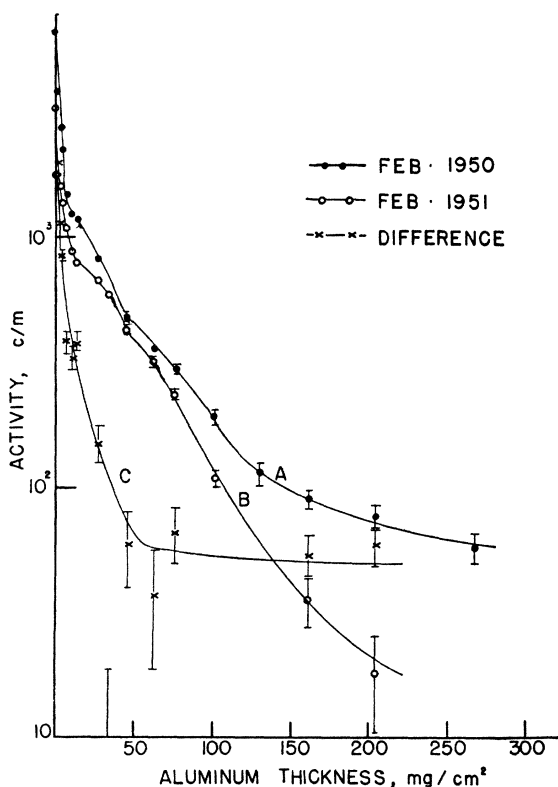


Fig. 4. Absorption curves of long-lived rhenium activities taken on a windowless flow-type proportional counter.

¹⁰ S. E. Turner and L. O. Morgan, Phys. Rev. 81, 881 (1951).

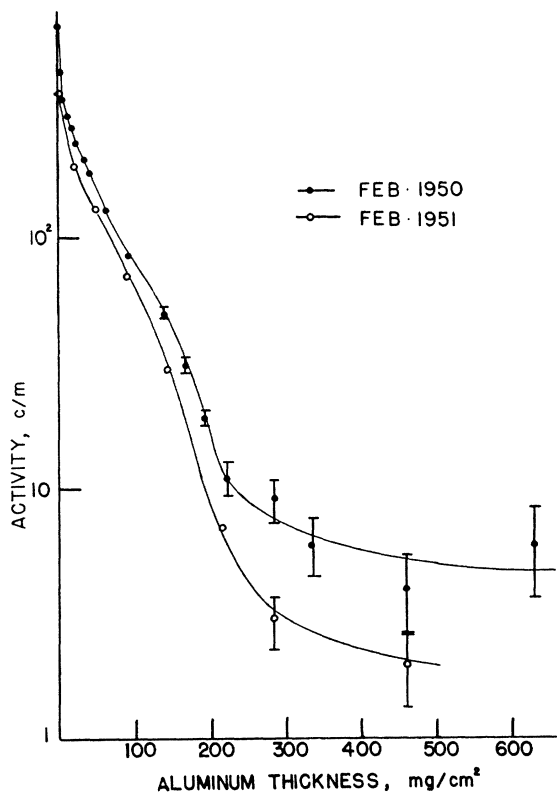


Fig. 5. Absorption curves of long-lived rhenium isotopes taken on a mica end-window counter.

produced in irradiation of tungsten with deuterons and helium ions yield a decay curve consistent with a 120-day Re^{183} and a 250-day component which they suggest may be Re^{189} . Their absorption data differ from those shown above, so that it must be assumed that two entirely different activities were being investigated by them.

Thermal-Neutron Activation Cross Sections

The cross sections, σ , for their formation, and the decay characteristics for the new activities formed from second-order capture, are reported in Table II, together with the cross sections for formation of the two nuclides W^{181} and Os^{185} , whose decay characteristics have been previously reported. The new data are shown in italics.

Column 3 serves to indicate the decay mode rather than to describe the radiations involved. The values in the last column were calculated from the activation data using Eq. (2).

The cross-section values for W^{181} and Os^{185} are subject to an additional uncertainty arising from the inability to determine the absolute number of disintegrations per minute in the samples containing these nuclides. W^{181} , for example, showed considerable x-ray activity when detected with a counter filled with argon and

alcohol, but only electron and hard gamma-rays when a counter filled with helium and alcohol was used. A one-percent counting efficiency was assumed for these x-rays determined with the argon-alcohol-filled counter. This figure could probably be in error by a factor of ten. An analogous situation existed for Os¹⁸⁵. In this case,

the 0.75-Mev gamma-ray was assumed to be detectable with a one percent counting efficiency.

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On Nuclear Quadrupole Moments

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The correction to nuclear quadrupole moments on account of the quadrupole moment induced in the electron shells has been obtained by solving the Schroedinger equation for the perturbed core wave functions for Li, Al, and Cl. The correction factor by which the average $\langle 1/r^3 \rangle$ over the valence electron function in the equation for the quadrupole coupling should be multiplied to take account of the induced effect is 1.11, 0.83, and 0.68, respectively. The previously described Thomas-Fermi calculation of this effect has been carried out for 13 additional elements.

I. INTRODUCTION

THE correction to nuclear quadrupole moments on account of the quadrupole moment induced in the electron shells has been previously estimated by means of the Thomas-Fermi model.¹ In the first part of this paper we present a calculation of this effect by solving the Schroedinger equation for the cases of Li, Al, and Cl. It was found that the inclusion of exchange, which is not contained in the Thomas-Fermi model, may change the quadrupole correction considerably. In general, the exchange terms have sign opposite to the direct terms. For Al and Cl they are larger than the direct terms, so that the sign of the effect is reversed, the complete quadrupole correction being such as to increase the interaction energy for a given value of the nuclear quadrupole moment. Moreover, it was found that the statistical model represents only a part of the perturbation of the electron core by the nuclear moment Q , namely, those excitation modes in which there is only angular displacement of the charge, the charge contained in any spherical shell remaining constant. This part always gives rise to a shielding of Q . The other part of the perturbation consists of radial displacements of the charge which may shield or reinforce the effect of the nucleus, depending on the shell structure and the valence electron wave function.

In the second part of the paper, we discuss the effect of including the induced moment in the perturbation which rearranges the electron cloud. We also list the results of calculations of the Thomas-Fermi value of the correction for 13 additional elements, which make it possible to interpolate the Thomas-Fermi correction for all elements.

II. WAVE FUNCTION CALCULATIONS

The perturbed wave function of the core electrons was obtained by solving numerically the Schroedinger equation for the atomic potential as perturbed by the nuclear Q . The procedure will be shown first by considering the perturbation of the $1s$ state for Al. Let H_0 and H_1 be the unperturbed and the perturbed part of the hamiltonian, respectively; u_0 and u_1 will denote the unperturbed and the perturbed part of the wave function times r . We have

$$H_0 = -(\hbar^2 \nabla^2 / 2m) + V_0, \quad (1)$$

where V_0 is the central potential of the atom which was taken as the Thomas-Fermi potential. The perturbation H_1 is given by

$$H_1 = -Q(3 \cos^2 \theta - 1) / 2r^3, \quad (2)$$

where r is the length of the radius vector from the nucleus and θ is the angle included by this vector and the axis of the nuclear quadrupole moment Q ; lengths are in units of the Bohr radius a_H , and H_1 is in ry units. If E_0 denotes the unperturbed $1s$ energy, the Schroedinger equation becomes

$$(H_0 + H_1)(u_0 + u_1) = E_0(u_0 + u_1), \quad (3)$$

since the first-order perturbation of the energy is zero for s states. Upon subtracting $H_0 u_0 = E_0 u_0$, and to the first order in Q , we obtain

$$(H_0 - E_0)u_1 = -H_1 u_0. \quad (4)$$

In the following the zero-order functions u_0 will be written

$$u_0 = u_0'(r) \Theta(\theta, \phi), \quad (5)$$

where u_0' is the radial and Θ is the angular part of the

* Research carried out under contract with the AEC.

¹ R. Sternheimer, Phys. Rev. **80**, 102 (1950).