# New Neutron-Deficient Isotopes of Rhenium*

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Three new activities have been observed in rhenium obtained by bombardment of rhenium and of tungsten with protons of energies from 40 to 240 Mev and of enriched $W^{180}$ with 10-Mev protons. Positron-emitting $Re^{177}$ of 17-minute half-life was identified through its daughter, the known 2.2-hr $W^{177}$. Evidence is presented for the assignment of $Re^{178}$ to a 15-min, 3.1-Mev positron activity and of $Re^{180}$ to a (20±1)-hour, 1.9-Mev positron activity. A previously reported unknown Re activity of approximately 1-hr half-life, which may possibly be an isomer of $Re^{186}$, was also observed.

## INTRODUCTION

A SEARCH has been made for new neutron-deficient isotopes of rhenium by bombarding both rhenium and tungsten with protons in the University of Rochester 130-in. synchrocyclotron. In addition to previously reported rhenium activities, three new activities were observed.

## EXPERIMENTAL

Tungsten as metal and oxide and rhenium as powdered metal were bombarded with protons of energies from 40 to 240 Mev. One bombardment with 10-Mev protons was made[1] on a sample of tungstic oxide enriched in $W^{180}$. This sample[2] had a reported isotopic analysis of 180–6.95%, 182–42.16%, 183–14.15%, 184–22.22%, and 186–14.52%.

Tungsten targets were dissolved, in the presence of potassium perrhenate as carrier, by heating with sodium hydroxide solution and hydrogen peroxide under constant stirring. Rhenium targets were dissolved in the minimum quantity of concentrated nitric acid, after which the solution was treated under constant stirring with an excess of sodium hydroxide solution and hydrogen peroxide. Tungsten carrier (20 mg) as sodium tungstate was then added. The two types of solutions thus prepared were scavenged with zirconium and lanthanum hydroxides and then made 4$N$ in NaOH. The resulting solution was equilibrated[3] once with an equal volume of pyridine previously shaken with 4$N$ NaOH. The pyridine layer, which contained the rhenium, was washed with an equal volume of 4$N$ NaOH solution, followed by scavenging with $Fe(OH)_3$. The solution was acidified with concentrated hydrochloric acid, heated to boiling, and saturated with hydrogen sulfide. The precipitated rhenium sulfide ($Re_2S_7$) was separated, washed with water, and dissolved in sodium hydroxide plus hydrogen peroxide. The resulting solution was heated, diluted, and scavenged with zirconium and lanthanum hydroxides. After neutralizing the solution with hydrochloric acid and cooling in ice water, tetraphenylarsonium chloride was added to precipitate tetraphenylarsonium perrhenate. The precipitate was separated, washed twice with ice-cold water, and mounted for counting.

In a few experiments rhenium was subjected to further purification by precipitating $Re_2S_7$ from concentrated hydrochloric acid solution several times. The solution obtained by dissolving the precipitate was evaporated with concentrated nitric acid and the residue was evaporated twice with concentrated hydrochloric acid. This $HNO_3$—HCl evaporation cycle was repeated. Finally rhenium was precipitated as tetraphenylarsonium perrhenate. In some cases rhenium was counted as nitron perrhenate. Counting of the rhenium samples which were subjected to the additional purification steps was begun about three hours after the end of the bombardment and thus no activity with a half-life of 15 min or less could be seen with these samples.

In the milking experiments, 20 mg of tungsten as sodium tungstate were added to the hydrochloric acid solution of purified rhenium and the precipitated tungstic acid was digested for 15 min. Tungstic acid separated only slowly from the solution and required at least 10 min for completion. Thus the tungsten exchange may not be all heterogeneous and the slow separation of the solid should be favorable for exchange. Furthermore, even if exchange were incomplete, identical conditions should yield the same proportion of exchange in each milking. At 17 min from the time of the previous separation of tungstic acid, the precipitate was separated by centrifuging and removed. Tungstic acid was separated from rhenium in this way at six 17-min intervals. The precipitate of tungstic acid was purified as follows. It was washed with 6$N$ nitric acid and dissolved in 4$N$ NaOH solution. Inactive rhenium carrier (10 mg) was added to the solution which was then extracted with an equal volume of pyridine previously shaken with 4$N$ NaOH solution. Rhenium carrier was again added to the aqueous layer and the extraction repeated. The aqueous solution

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[1] We wish to thank the Physics group at Princeton University for this bombardment.
[2] Kindly loaned to us by the Isotopes Division, Oak Ridge National Laboratory.
[3] W. Goishi and W. F. Libby, J. Am. Chem. Soc. **74**, 6109 (1952).

was scavenged with niobium hydroxide and then acidified with concentrated nitric acid. The tungstic acid precipitate was digested for a few minutes, separated, washed with $6N$ nitric acid, and dissolved in $6N$ ammonium hydroxide. Any residue left was removed by centrifugation. Rhenium hold-back carrier was added to the solution and tungstic acid was reprecipitated by addition of concentrated hydrochloric acid and heating. The precipitate was washed twice with water and mounted for counting.

The rhenium samples thus prepared from tungsten and rhenium targets by bombardment with protons of energies of 80 to 240 Mev and counted with beta-proportional and scintillation counters showed new activities of half-lives about 18 min, one hour, and 20 hours, besides the previously reported[4] activities of rhenium of mass number 186 or less. The 18-min activity actually turned out to result from a mixture of 17-min and 15-min positron emitters, which could not of course be separated from a gross decay curve.

### RHENIUM-177

Rhenium samples separated from tungsten targets bombarded with protons at energies of 120, 160, 200, and 240 Mev and from rhenium targets at 120 and 160 Mev showed activity decaying with a half-life of 15–20 min when measured with beta-proportional and scintillation counters. The positron spectrum, as determined with a survey $\beta$-ray spectrometer, was complex. On setting the magnetic field of the spectrometer at an energy corresponding to 0.4-Mev positrons and following the positron decay, the half-life was 17 min, accompanied by a long half-life tail for which correction was made. Correction at 0.4 Mev for the 15-min, 3.1-Mev positron activity (next section) could not be made but its contribution at 0.4 Mev should be small.

The identity of this 17-min half-life was determined from parent-daughter isolation experiments. On milking tungsten daughters from rhenium at 17-min intervals it was found that the activity associated with tungsten decayed with half-lives of 2.2 hr, 2.2 days, and 21 days. The yields of the 2.2-hr half-life tungsten obtained from six milkings decreased with a 17-min half-life. Milking experiments were also performed at 15- and 20-min intervals but the yields of the 2.2-hr activity fitted best with the 17-min interval. Since the 2.2-hr tungsten activity is assigned to mass number 177, the 17-min positron activity observed in rhenium at a spectrometer setting of 0.4 Mev must be associated with $Re^{177}$. The 2.2-day activity observed with the tungsten samples obtained from the milkings arose from $Ta^{177}$ formed by the decay of 2.2-hr $W^{177}$.

The maximum positron energies to be expected from the decay of various neutron deficient isotopes of rhenium have been calculated by the $\beta$-decay systematics of Coryell[5] and are given in Table I. According to the table[4] of nuclides, $Re^{182}$, $Re^{183}$, and $Re^{184}$ undergo electron capture. Recently, an isomer, $Re^{180m}$ of 2.42-min half-life and emitting 1.1-Mev positrons not in sequence with 0.88- and 0.11-Mev $\gamma$ rays has been reported.[6] While the maximum energy of the 17-min positron activity could not be determined because of the presence of at least two other positron decays, the calculated maximum positron energy of 2 Mev for mass 177 is in agreement with the mass assignment.

TABLE I. Maximum energy of positrons from rhenium isotopes calculated by Coryell $\beta$-decay systematics.

| Mass No. | Energy (Mev) | Mass No. | Energy (Mev) |
|---|---|---|---|
| 177 | 2.03 | 181 | E.C. |
| 178 | 3.14 | 182 | 1.14 |
| 179 | 1.22 | 183 | E.C. |
| 180 | 1.93 | 184 | 0.37 |

### RHENIUM-178

As already stated, the positron spectrum from rhenium samples was complex. The maximum energy observed with the $\beta$-ray spectrometer was 3.1 Mev. When positron activities were followed at magnet currents corresponding to energies of 2.1 and 1.7 Mev, rather than 0.4 Mev as in the preceding section, they were found to decay with a half-life of 15 min. At a setting of 1.7 Mev, but not at 2.1 Mev, the 15-min activity was accompanied by a weak tail of about one day ($Re^{180}$, next section). From Table I, any contribution of 17-min $Re^{177}$ to the 15-min positron activity at 2.1 Mev should be negligible. Thus the 15-min activity appears to be associated with positrons of 3.1-Mev maximum energy and is assigned to mass 178, the only isotope of rhenium of mass $>177$ that may be expected to emit such energetic positrons.

$Re^{178}$ should yield daughter $W^{178}$ of 21 day half-life. As mentioned in the preceding section, a 21-day daughter was observed in the tungsten milkings from rhenium. After two 17-min spaced milkings this activity was so low that the critical experiment of determining the decrease in yields of the 21-day daughter through several half-lives could not be done. However, if the 21-day tungsten activity observed is the daughter of the 15-min, 3.1-Mev positron emitting rhenium isotope, then tungsten milkings from rhenium performed one to ten days after the initial six 17-min milkings should show no activity, whereas if the 21-day tungsten activity is the daughter of the 20-hr rhenium positron emitter, the only other unknown rhenium activity present, such later milkings should show activity. The later milkings showed no activity, in

[4] Hollander, Perlman, and Seaborg, Revs. Modern Phys. **25**, 469 (1953). K. Way *et al.*, *Nuclear Data Cards* (National Research Council, Washington, D. C., 1955).

[5] C. D. Coryell, *Annual Review of Nuclear Science* (Annual Reviews, Inc., Stanford, 1953), Vol. 2, p. 305.

[6] V. K. Fischer, Phys. Rev. **99**, 764 (1955).

agreement with the assignment of mass 178 to the 15-min rhenium decay.

Rhenium activities with half-lives of 18±2 min, about 1 hr, 12.5 hr, 21±2 hr, 2.1 days, and 3.9 days were produced by bombarding tungsten enriched[2] in mass number 182 (180–0.017%, 182–92.33, 183–3.62, 184–2.71, 186–1.31) with 120-Mev protons. It was not always possible to separate 50-, 64-, and 91-hour activities but no trouble was experienced with the remainder. With 200-Mev protons only 18-min, 12-hr, 22.5-hr, and 2.83-day activities were observed. Aluminum absorption measurements on the latter set of activities were made with a beta-proportional counter 1.5 hr from the end of the bombardment. The absorption curve indicated the presence of short-lived betas of maximum energy 3.05 Mev, in agreement with beta-ray spectrometer measurements on this sample and on samples from bombardment of natural tungsten.

### RHENIUM-180

Natural tungsten bombarded with protons of energies from 160 to 240 Mev in six experiments gave in the rhenium fraction an activity of half-life 18–20 hr in a beta proportional counter and 20–24 hr in a scintillation counter. Three experiments in which rhenium was bombarded with protons of 60–160 Mev gave half-lives of 19 to 22 hr with a beta-proportional counter and 22 hr with a scintillation counter. Similar bombardments of rhenium at 40 and 50 Mev showed no approximately 20-hr activity. Beta-ray spectrometer measurements made on rhenium fractions 3.5 hr after the end of bombardment of rhenium at 60 and 160 Mev, by which time the short-lived positron emitting $Re^{177}$ and $Re^{178}$ had completely decayed, showed the presence of positrons of maximum energy 1.8 to 2.0 Mev. In the beta-ray spectrometer these positrons decayed with a half-life of the order of hours and were associated with the 20-hr activity.

The rhenium fraction obtained from bombardment of enriched $W^{182}$ by 200-Mev protons also showed the presence of the 20-hr half-life and, by beta-ray spectrometer measurements, positrons of 1.9-Mev maximum energy. Reference to Table I shows that aside from 17-min $Re^{177}$ and 15-min $Re^{178}$ the only rhenium isotope which, by Coryell's $\beta$-decay systematics, would be expected to emit positrons of 1.9-Mev energy is $Re^{180}$. The 20-hr half-life is thus assigned to this isotope.

Additional evidence for this assignment was obtained from the bombardment of $WO_3$ enriched in $W^{180}$ (6.95%, natural 0.135%) with 10-Mev protons.[1] Two samples of rhenium separated from the same target showed activities of half-lives 19.5 to 20.5 hr and 100 to 104 hr ($Re^{186}$) with a beta-proportional counter and 12 hr ($Re^{182}$), 19.5 hr and 6.6 days with a scintillation counter. Aluminum absorption measurements made 27 hr after the end of the bombardment yielded only three points of low intensity. If all three points are taken, a $\beta$ energy of 1.3 Mev results, while the two points of higher intensity yield 1.8–1.9 Mev, in agreement with the spectrometer measurements. The absorption measurements also showed the presence of approximately 0.8-Mev betas due to $Re^{186}$.

The intensities, calculated to saturation yields, of the 20-hr and 100-hr ($Re^{186}$) activities in the two samples compared favorably with the ratio of the relative abundances of $W^{180}$ (6.95%) and $W^{186}$ (14.52%) in the target, thus confirming the assignment by a $(p,n)$ reaction of mass 180 to the 20-hr half-life. Also in agreement with this assignment is the failure to obtain the 20-hr activity by bombarding rhenium with protons of energy less than 60 Mev.

### RHENIUM 1-HR ACTIVITY

When rhenium was bombarded with 40- and 50-Mev protons and $WO_3$ with 170-Mev protons, the rhenium fraction showed a growth of activity for a few hours after bombardment, followed by a decay of approximately 1-hr half-life. The appearance or nonappearance of the growth depended on the relative proportions of the various activities at different proton bombarding energies. Tungsten metal bombarded with 200- and 240-Mev protons as well as rhenium with 120- and 160-Mev protons also showed an 0.8–1.2-hr activity in the rhenium fraction. This 1-hr activity was observed in beta proportional, scintillation, and x-ray counters. Chu[7] has also reported a 1-hr activity in rhenium prepared from osmium by bombardment with 19-Mev deuterons and has suggested that an $Os(d,\alpha)$ product may be responsible. In view of these methods of preparation from rhenium, tungsten, and osmium, the 1-hr rhenium activity would appear to be associated with mass number 184 to 186. Since there appear to be isomers for each of Re-180,-182, and -184, possibly the 1-hr activity is an isomer of $Re^{186}$, analogous to the isomeric states in odd-mass-numbered tellurium isotopes from 119 to 133.

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[1] T. C. Chu, Phys. Rev. **79**, 582 (1950).