[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE COLLEGE OF WASHINGTON]

The Identification of W^{188} formed in Neutron-Activated Tungsten by a Chemical Separation of Re^{188}

BY MANFRED LINDNER AND JAMES S. COLEMAN[1]

A new radioisotope of tungsten, mass 188, which was formed by successive neutron capture by the heaviest stable tungsten isotope, W^{186}, has been indirectly established in the presence of very large levels of other radio-tungsten isotopes. This was accomplished by observing the activity of the known Re^{188} which arises as a result of the decay of the W^{188}. The chemical method consisted of precipitation of the tungsten as oxide and isolation of the rhenium as tetraphenylarsonium perrhenate. The equilibrium level of separable rhenium activity was found to diminish with a half-life of 65 days, which is thus the half-life of the W^{188}. The isolation of the Re^{188} in pure form led to a new value of the half-life of this isotope of 16.9 hours as contrasted to previous values of 18 and 18.9 hours.

Introduction

The quantitative determination of perrhenate ion by the use of tetraphenylarsonium chloride has been described in detail by Willard and Smith.[2] They report no detectable interference by anions such as tungstate and chloride, and cations such as sodium and potassium. This specificity suggests that if, in a long, thermal-neutron irradiation of tungsten metal, W^{188} should be formed in detectable amounts from the stable isotope W^{186} as a result of the capture of two successive neutrons, a procedure for determining the half-life of the mass 188 tungsten isotope could be worked out by separation of the known Re^{188} "daughter" radioactive isotope.[3]

Study of the decay characteristics of W^{188} by direct observation of the radioactivity present in the neutron-irradiated tungsten sample itself was impossible because of the presence of comparatively high levels of activity of the radioisotopes W^{181} and W^{185}, both formed from stable isotopes of tungsten as the result of the capture of a single neutron. The neutron excess of W^{188} must lead to β-particle emission and formation of Re^{188}, which, in turn, decays with a known half-life to stable Os^{188}. Detectable concentrations of other rhenium daughter activities would not be expected to result from thermal neutron bombardment of natural tungsten.

If the assumption, subsequently proved justifiable, is made that the half-life of W^{188} be much longer than that of Re^{188}, the following relationship among the intensity of radioactivity of the Re^{188}, A_{Re}, the activity of the W^{188}, A_W, from which the Re^{188} would originate, and the time following chemical purification of the tungsten, is applicable for the growth of the rhenium daughter.

$$A_{Re} = A_w(1 - e^{-0.69t/T_{Re}}) \qquad (1)$$

T_{Re} is the half-life of the Re^{188}. After a time t, long compared with T_{Re}, equation (1) becomes

$$A_{Re} = A_W \qquad (2)$$

i.e., the parent and daughter activities approach equality. It is this relationship upon which the present method is based. Since A_W is a function only of the half-life of W^{188} and the time, t, *i.e.*, since

$$A_W = C'e^{-0.69t/T_W} \qquad (3)$$

where C' is a proportionality constant, it follows that

$$\log A_{Re} = C - 0.30t/T_w \qquad (4)$$

Thus, a plot of log A_{Re} as defined by (2) *versus* t should give a straight line from whose slope might be calculated the value for T_W.

Experimental

A chemically pure sample of irradiated tungsten was allowed to stand for about 1 week, after which time any Re^{188}, whose half-life is 16.9 hours, would essentially obey equation (2). The tungsten and rhenium were then separated chemically, and the radioactivity of the rhenium, A_{Re}, was measured on a suitable counter apparatus. Such a procedure, when repeated at intervals of time on the same sample of irradiated tungsten, gave a series of points which obeyed equation (4). The data thus justified the original assumption concerning the relative half-lives of the W^{188} and Re^{188}.

About 0.85 g. of potassium perrhenate[4] was dissolved in 100 ml. of water, and to a 1.00-ml. aliquot in 0.5 N NaCl was added an excess of tetraphenylarsonium chloride.[5] The resulting precipitate was filtered on a small weighed filter paper, dried in an air oven at 110° and weighed as $(C_6H_5)_4AsReO_4$. The standardization was done in triplicate and the perrhenate solution was thus found to contain 5.38 mg. of Re present per ml. of perrhenate solution.

Two weighed samples of slow-neutron-irradiated tungsten metal were separately dissolved in a 2:1 mixture of 27 N HF and 16 N HNO_3. The resulting solutions were evaporated to dryness, taken up in dilute NaOH solution and the tungsten precipitated as yellow tungstic oxide from a boiling solution of 3 N HCl. The resultant yellow precipitate was centrifuged, dissolved in dilute NaOH solution, and "scavenged" by addition of ferric chloride solution and subsequent centrifugation and disposal of the resultant precipitate of ferric hydroxide.

These purified tungstate solutions were then denoted as samples A and B, and independent determinations of the half-life of W^{188} were made on both of these.

In a typical run, 2.00 ml. of the standard perrhenate solution was added to one of the active tungstate solutions, which had been allowed to stand for at least 1 week, the resultant mixture made 3 N in HCl and heated in a hot water-bath for about 20 minutes. This procedure generally brought about the precipitation of the bulk of the tungsten as the yellow oxide, and consequently the time was noted as the time of tungsten-rhenium separation. However, the solution, in addition to containing all of the perrhenate, also contained an appreciable quantity of tungsten, and it was necessary to boil the solution quite vigorously to ensure further precipitation and minimum solubility of the tungstate. (Any such precipitate was of course centrifuged, combined with the original precipitate and set aside for a future run.) In spite of such treatment, the final tungstate solubility was often considerable, although it varied from run to run. In any case, tungstate which thus remained in solution with the perrhenate had to be considered as lost as a source for all future separations, and furthermore had to be removed from the perrhenate, since even a very small quantity of tungsten which might have remained in the perrhenate solution was sufficiently active to completely mask the radioactivity due to the isotope Re^{188}.

This loss of tungsten was determined by measuring the radioactivity left in an aliquot of this solution after the Re^{188}

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[1] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

[2] Willard and Smith, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 305 (1939).

[3] Seaborg and Perlman, *Rev. Mod. Phys.*, **20**, 628 (1948).

[4] Obtained from A. D. Melaven, University of Tennessee.

[5] Obtained from the Hach Chemical Corporation, Ames, Iowa.

had decayed. Then, after the conclusion of all Re–W separations, the radioactivity remaining in the tungsten sample itself was determined. In this way, the per cent. of the final total tungsten activity lost in each run was determined. In practice, all radiochemical assaying was done on the same date to avoid corrections which would be necessary because of the gross radioactive decay of the tungsten itself.

The second problem—that of removing all traces of active tungsten—was met by boiling off the excess hydrochloric acid from the perrhenate-containing solution, making the solution barely alkaline with sodium hydroxide, and adding about 50 mg. of sodium tungstate reagent to the solution. This was then made 3 *N* in hydrochloric acid and the solution boiled vigorously to ensure as nearly complete a precipitation of tungstic oxide as possible. This precipitate was discarded, and the cycle repeated on the supernatant solution.

The final acidic perrhenate solution was made barely alkaline with sodium hydroxide, 100 mg. of sodium tungstate added, and perrhenate then precipitated with tetraphenylarsonium chloride. This precipitate was filtered, dried and weighed as in the standardization procedure. The weight of the precipitate determined the chemical yield of rhenium throughout the procedure. Since the chemical yield was never completely quantitative, the actual weight of precipitate indicated the amount of rhenium which was lost in the separation procedure, and hence a correction for this could be applied.

The filter paper was suitably mounted on a small card which could be placed below a mica end-window type Geiger counter, and the radioactive decay of the rhenium sample thus followed. Similarity of mounting and counting procedures in all runs eliminated the effects of counter geometry, back-scattering and self-absorption. The same counter was used throughout the investigation.

Results

Table I contains all data pertinent to the rhenium–tungsten separations as described above. In the first column, the origin of the time coördinate was arbitrarily taken to be that of the first separation for each of the samples. The second column gives the activity, in counts registered per minute on the Geiger counter, of the rhenium samples. The activities of the Re samples were found to decrease with the half-life expected for the isotope, Re^{188}. Furthermore, the values in column 2 were the values of this activity when extrapolated back to the time of the chemical separation.

The third column gives the chemical yield of the rhenium in the separation and the fourth column lists the per cent. of tungsten which was lost in the run due to tungstic oxide solubility. It should be noted that any experimental value in the second column must be corrected by the *sum* of all the preceding loss values given in column four.

TABLE I

Day	Activity Re^{188} c./m.	Chem. yield, %	Tungsten loss, %	Corrected activity, A_{Re}	log A_{Re}
		Sample A			
0	3,170	8.7	20.2	36,400	4.561
16	23,000	79.8	13.3	34,600	4.539
29	8,200	40.2	1.8	27,200	4.436
49	15,300	86.7	1.1	23,900	4.378
77	10,800	81.2	0.5	18,100	4.258
92	9,100	87.5	9.2	14,200	4.154
112	6,940	90.2	..	11,200	4.052
		Sample B			
0	11,900	39.0	20.2	30,500	4.484
14	17,100	92.7	2.5	22,300	4.348
28	14,200	83.7	2.3	20,900	4.320
48	12,000	86.5	19.2	17,400	4.241
76	6,750	75.2	0.7	13,000	4.114
90	6,250	87.0	0.7	10,400	4.017
97	6,000	86.5	1.3	10,100	4.004
104	5,600	87.9	..	9,350	3.972

Discussion

Figure 1 is a plot of the log A_{Re} *versus* time, *t*, for both samples. It is obvious that straight lines result and that for both samples, these have the same slopes. From these lines it is found that the W^{188} has a half-life T_W, calculated from equation (5) as 66 and 64 days, respectively.

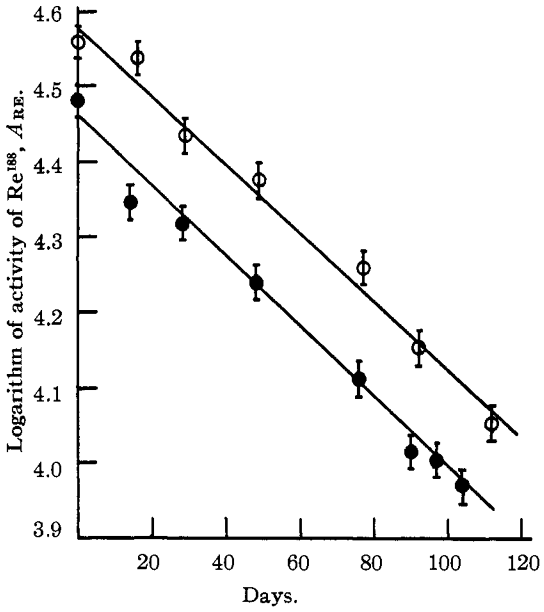

Fig. 1.—Change, with time, of yield of Re^{188} separable from slow-neutron-irradiated tungsten: hollow circles, sample A; full circles, sample B; vertical lines through points represent estimated experimental error.

The vertical line through each point represents an estimate of the experimental errors involved, including those from the gravimetric determination, the radiochemical assays of the tungsten, and the extrapolations of the decay curves of the rhenium activity to the time of the separation. These combined errors amounted to about 5%. We therefore report a half-life for the nuclide W^{188} as 65 ± 5 days.

The present investigation also showed that the mean half-life value for Re^{188}, as determined from fifteen rhenium samples extracted from tungsten, was 16.9 hours as contrasted with the values of 18 and 18.9 hours[3] previously reported. The values obtained ranged from 16.7 to 17.1 hours.

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