corresponding to the electronic reaction, $Te(s) + H_2O = TeO(OH)^+ + 3H^+ + 4E^-$, was found to be —0.5590 volt.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OBSERVATIONS ON THE RARE EARTHS. XVI. THE PURIFICATION AND ATOMIC WEIGHT OF HOLMIUM[1]

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Introduction

The object of the work described in this paper was (1) to continue the purification of holmium material and (2) to determine the atomic weight of holmium using the chloride-to-silver ratio.

Only one determination of the atomic weight of holmium has previously been made. This work was carried out by Holmberg[2] in 1911 who purified the holmium obtained from 29 kg. of euxenite and determined its atomic weight using the oxide-to-sulfate ratio. Two analyses gave the values 163.57 and 163.40.

Sources of Material

The material used in the study of this element was obtained from three different sources.

1. **Texas Gadolinite.**—The rare earths were extracted from this ore in 1917 by L. F. Yntema. The finely powdered mineral was extracted with hot hydrochloric acid and the rare earths were precipitated with oxalic acid. The cerium group earths were separated as the double alkali sulfates and any cerium remaining in the yttrium group was removed by the bromate method of James.[3] The yttrium group earths were then converted to the bromates by the usual method.

2. **Norway Fergusonite.**—Forty-five kg. of Norway fergusonite was treated in 1.5kg. lots with hydrochloric and nitric acid and the rare earths were precipitated with oxalic acid. Since the percentage of cerium in this ore was exceedingly small there was no necessity for the removal of this element. The oxalates were converted to the bromates by the usual method.

3. **Series M (Bromates).**—This was an yttrium group bromate series, the previous history of which is a little uncertain. It was derived from double alkali sulfate residues furnished by the Welsbach Company,

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[1] This communication is an abstract of a thesis submitted by Frank H. Driggs, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Holmberg, *Z. anorg. Chem.*, **71,** 226 (1911).

[3] James, THIS JOURNAL, **34,** 757 (1912).

of Gloucester, New Jersey. It had been fractionated several times in 1915 and contained mainly yttrium group elements with small amounts of neodymium and praseodymium.

Fractionation of the Bromates

The general plan of procedure in this Laboratory for the purification of any rare earth has been to make a preliminary separation, usually by fractional crystallization, until fractions are obtained which consist of the element desired, together with one or possibly two other elements. If the final purification is to depend upon differences in basicity, then the basicity of both impurities present must be either greater or less than that of the element desired; otherwise the separation of one impurity would result in a concentration of the other interfering element in the best fractions. Fractional crystallization of the bromates as recommended by James[4] seemed to be best suited for the preliminary separation of the yttrium group.

The most persistent impurity occurring with holmium is erbium and fractionation of the bromates was employed for separating these two elements and obtaining fractions consisting of holmium and yttrium only. The course of the fractionation was followed by examination of the absorption spectra of the solutions. The most characteristic line in the absorption spectrum of erbium lies at 523. It also happens that neodymium has a strong band in this same region, so that with a small amount of neodymium present it is impossible to determine when the last trace of erbium has been removed. Neodymium concentrates in the least soluble fractions very quickly, but on long continued fractionation it is carried into the yttrium-holmium fractions before the last trace of erbium has been removed. In order to avoid this difficulty and, at the same time, hasten the concentrations it was thought best to split each series into two portions. The A portion consisting of fractions containing neodymium and the B portion consisting of the more soluble fractions which were free from neodymium. As the soluble fractions of the A series became freed from neodymium they were added to the fraction in the B series of equal erbium content. By this means yttrium-holmium fractions could be obtained at the insoluble end of the B series entirely free from neodymium and erbium.

Partial Decomposition of the Nitrates

For the separation of holmium from yttrium most workers recommend a method depending upon differences in basicity, since these two elements vary so widely in this property. It has been shown[5] that partial decompo-

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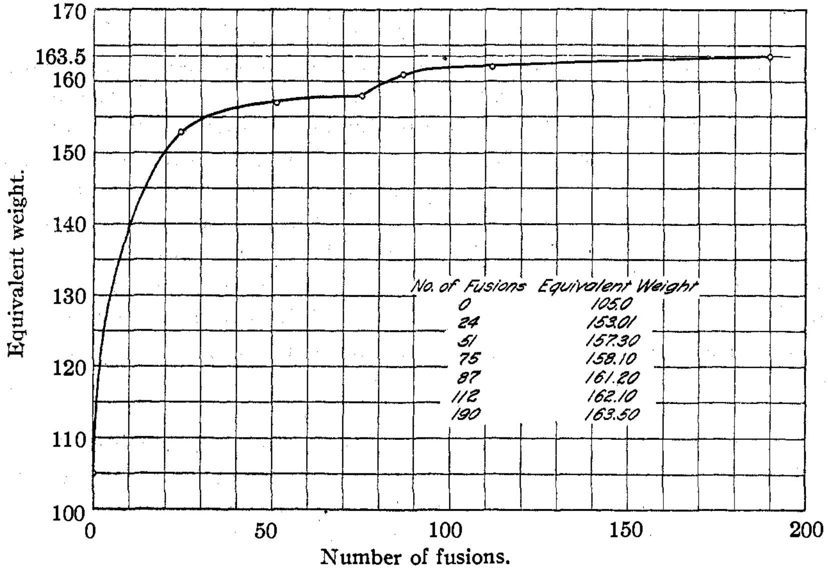
[4] James, THIS JOURNAL, **30**, 182 (1908).

[5] Kremers and Hopkins, *ibid.*, **40**, 598 (1918).

sition of the nitrates of holmium, yttrium and samarium gives a rapid concentration of holmium.

The weight of the mixed holmium and yttrium oxides obtained from the bromate fractionations was 120 g. and the equivalent weights of the various fractions were determined by the Gibbs method[6] and were found to vary from 102.3 to 106.6, corresponding to a holmium content of 18–23%. It was found that the holmium content in a bromate series varied in proportion to the neodymium content. Thus it seems advisable to make only an incomplete separation of the cerium group if the material is being worked for the concentration of dysprosium or holmium. These oxides were dissolved in nitric acid and the solution was evaporated to dryness.



No. of Fusions	Equivalent Weight
0	105.0
24	153.01
51	157.30
75	158.10
87	161.20
112	162.10
190	163.50

Fig. 1.

The mass was then fused until partial decomposition had taken place. The fused mass was cooled and treated with just enough water so that it dissolved to a clear solution on boiling. It was then allowed to cool when the basic nitrate of the least electropositive portion crystallized.

From the determination of the atomic weights of the best holmium fractions during the course of the fusions it was seen that partial decomposition of the nitrates gave a rapid separation of holmium and yttrium until most of the yttrium was removed but the rate of separation rapidly decreased with the increase in the purity of the material. One cause for this is the complete decomposition of the nitrate along the edge of the casserole due to "local action." In order to prevent this, the fusions were

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[6] Gibbs, *Am. Chem. J.*, **15**, 546 (1893).

carried out in an electric furnace where the temperature could be controlled very accurately.

The furnace used was of a special design with inner dimensions 18 × 28 × 56 cm., and provided with a Nichrome heating unit; in it a temperature of 250–255° was constantly maintained. The fractions were evaporated over an open flame until they were just at the point of decomposition. They were transferred, at this time, to the electric furnace for a period of 1.5 to 2 hours depending upon the size and composition of that particular fraction. In Fig. 1 the equivalent weight of the best holmium fraction is plotted against the number of nitrate fusions to which it had been subjected. Fusions 1 to 75 inclusive were those carried out over an open flame. The sharp break in the curve at 75 indicates the increase in the efficiency of separation when the electric-furnace method of temperature control is used.

Determination of Magnetic Susceptibility

One of the chief difficulties in determining the purity of holmium lies in the fact that its physical properties are not well enough established to permit a detection of any impurity by this method. The determination of mean equivalent weight is not applicable as the atomic weights of dysprosium and holmium lie so close to each other that a considerable amount of dysprosium would not appreciably lower the equivalent weight of the mixture. Yntema[7] made a careful study of the absorption spectra of holmium and dysprosium and found that there is no absorption line of dysprosium which does not coincide with an absorption line of holmium. Thus it is impossible to detect the presence of dysprosium in holmium by either of these methods. The arc spectra of holmium and dysprosium are not well enough established to permit a study of the purity by this method.

Urbain[8] has pointed out the application of magnetic susceptibility in following the separation of holmium and dysprosium by combining the measurement of the magnetic susceptibility of the various fractions with the determination of their equivalent weight. From the equivalent weights of the fractions the percentages of holmium may be calculated, and from these data the theoretical magnetic susceptibility of the mixture may be determined. When the susceptibility is plotted against the fraction number, a curve is obtained which should coincide with the experimental curve obtained by a direct determination of the magnetic susceptibility of the fractions. If the experimental curve should lie above the theoretical curve it would indicate the presence of dysprosium in the series.

The equivalent weights were determined by the Gibbs method and the magnetic susceptibilities of the fractions were determined by means of a modified Curie and Chevenaux[9] magnetic balance designed and built in this Laboratory.

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[7] Yntema, This Journal, **45,** 907 (1923).

[8] Urbain, *Compt. rend.*, **150,** 913 (1910).

[9] Curie and Chevenaux, *Phil. Mag.*, **236,** [6] 357 (1910).

The balance (Fig. 2) consisted of a light aluminum arm *a* supported by a constantin torsion wire. From one end of the arm was suspended a small glass tube *t* that contained a weighed amount of the oxide to be analyzed. At the other end of the arm was a pointer *p* that moved over a graduated scale *s* read through a lens *l* in the top of the case. The tube containing the oxide was counterbalanced by means of two riders *r*, that dipped into a vessel of Nujol (purified paraffin oil) in order to damp the swing of the arm. Parallel with the experimental tube was a permanent magnet *m* supported on a brass-lined track. The magnet could be moved back and forth by means of an adjustment screw at the back of the case. The position of the magnet was read by means of the micrometer screw *gs*.

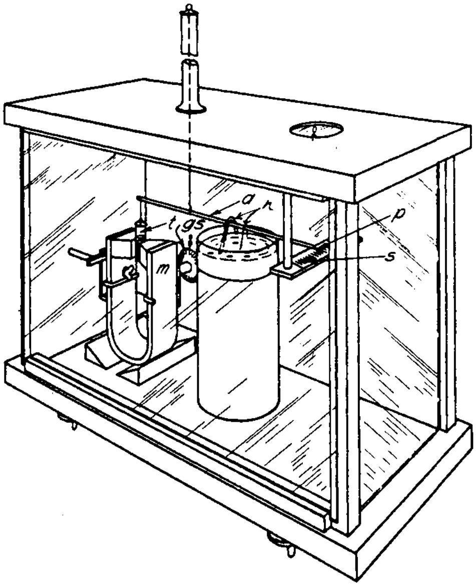

Fig. 2.

In Table I are given the values for the equivalent weight, the calculated susceptibility and the experimentally determined susceptibility from Fractions 15 to 24 from the nitrate fusion series.

It will be noticed that the first three values lie within the limits of experimental error. The value of Fraction 21 is slightly low, presumably due to the presence of a small amount of yttrium in this fraction. The constancy of the atomic weights and the magnetic susceptibility of the first three fractions seems to indicate that no dysprosium is present in these fractions.

TABLE I

VALUES FROM THE NITRATE FUSION SERIES

Fraction	Magnetic susceptibility $\times 10^6$	Magnetic susceptibility calculated	Equivalent weight	Difference
24	224.15	....	163.54	0.0
23	224.90	....	163.48	.0
22	223.90	....	163.50	.0
21	221.29	223.86	163.32	−2.5
20	225.68	222.65	162.65	+3.0
19	229.05	221.28	161.88	+7.7
18	218.74	211.54	156.75	+7.2
17	215.23	205.80	153.89	+9.4
16	187.20	192.88	147.71	+4.3
15	154.15	149.04	129.57	+5.1

Preparation of Materials for Atomic Weight Study

The purification of the reagents used in this investigation was carried out in the same manner as that described in earlier publications from this Laboratory.[10]

The holmium nitrate obtained from Fractions 22, 23 and 24 was purified by alternate precipitations of the oxalate and the hydroxide, the last two precipitations being carried out in conductivity water. The final oxalate obtained from each fraction was dried and ignited to the oxide in a platinum crucible.

Formation of Anhydrous Holmium Chloride

The purified holmium oxide was transferred to a quartz reaction flask and a small quantity of conductivity water was added. A mixture of air and hydrogen chloride was then passed in from the purifying train while the temperature of the flask was maintained at 100°. When the salt began to crystallize, the air was stopped and only hydrogen chloride was passed through. The temperature was kept at this point until the first five molecules of water of crystallization had been driven off. The temperature was then gradually raised to 195° when the last molecule of water of crystallization began to come off, dehydration being complete at 225°. The temperature was slowly raised to 350° and kept at this point for one hour. The current of hydrogen chloride was then stopped and the chloride was fused by means of a Bunsen flame. After the flask had cooled, the hydrogen chloride was replaced by dry air and the flask was removed to the balance case where it was allowed to hang for two hours before being weighed.

The Ratio of Holmium Chloride to Silver

After it had been weighed, the holmium chloride was dissolved in conductivity water and the solution transferred to a 3-liter glass-stoppered Jena glass bottle. Assuming that the atomic weight of holmium is 163.5, a sample of silver was weighed out to within 1 mg. of the calculated amount, dissolved in redistilled nitric acid and slowly added to the chloride solution while the mixture was constantly shaken. The bottle was then placed in a shaking machine in the dark room for five to six hours. After removal of the bottle from the shaker it was allowed to stand for 24 hours and a portion of the solution was tested in the nephelometer for any excess of silver or chloride. Weighed portions of standard solutions of silver nitrate or sodium chloride were then added until the nephelometer test indicated equivalence. After each addition of the standard solution, the bottle was shaken for six hours and allowed to stand for 24 hours before the liquid was tested in the nephelometer again.

In the following tabulated data, the number of the fraction of the nitrate fusion series from which the material was taken is shown together with the weight of the anhydrous chloride, the weight of silver required

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[10] Kremers, Hopkins and Engle, THIS JOURNAL, **40,** 598 (1918).

and the atomic weight of holmium. The number in parentheses indicates the previous determination in which the same sample was used.

The weighings were made by the method of substitution, the tare flask being of quartz and differing in weight from the reaction flask by only a few milligrams. The weights were standardized to 0.01 mg., and weighings were corrected to the vacuum standard.

The following densities were used: holmium trichloride, 3.80; silver, 10.5; platinum weights, 21.5. The atomic weight of silver was taken as 107.88 and that of chlorine as 35.457.

Table II

Atomic Weight of Holmium

Detn.	Fraction	Wt. of anhydrous chloride G.	Wt. of silver G.	Ratio	At. wt. of Holmium
I	24	0.87393	1.04789	0.83399	163.54
II	23	.28290	.33929	.83379	163.48
III	22	.43914	.52663	.83386	163.50
IV	24 (1)	.73784	.88498	.83373	163.46
V	22 (3)	.42703	.51224	.83365	163.43
VI	23 (2)	.26736	.32071	.83365	163.43
					Av. 163.47

Summary

1. Fractionation of the yttrium group bromates from gadolinite and fergusonite yielded holmium and yttrium fractions containing approximately 20% of holmium. It was found that a more efficient separation could be made by splitting the series into fractions containing neodymium but no erbium and those containing erbium but no neodymium.

2. Partial decomposition of the nitrates gave a rapid concentration of holmium material of high holmium content. Decomposition of the nitrates by means of electrical temperature control increased the efficiency of the nitrate fusion separation and made possible the complete separation of holmium from yttrium.

3. A comparison of the magnetic susceptibilities calculated from the equivalent weight with the experimentally determined magnetic susceptibilities showed that three fractions were free from yttrium and dysprosium.

4. The ratio of holmium chloride to silver was determined in six analyses. The value 163.47 was obtained for the atomic weight as the mean of six determinations. This value agrees with the former value of 163.50 assigned to holmium.

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