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OBSERVATIONS ON THE RARE EARTHS. VIII.

THE SEPARATION OF YTTRIUM FROM ERBIUM; THE RATIO $Er_2O_3 : 2ErCl_3$.[1]

BY EDWARD WICHERS, B. S. HOPKINS AND C. W. BALKE.

Received May 27, 1918.

Introductory.

In undertaking the work summarized in this paper, two purposes were entertained. The first was to make a comparative study of several methods which have been used in the separation of yttrium and erbium. The second was to apply the oxide-chloride ratio to erbium material obtained in a high degree of purity by methods employed in the first part of the investigation.

Comparative Study of Methods for Purifying Erbium.

By means of the fractional crystallization of the bromates it is possible to effect a fairly rapid concentration of material which contains erbium and yttrium but is free from other rare earth elements. The material used in the work described in the succeeding paragraphs was so obtained. The original source and the history of the material to this point is described in a publication by Engle and Balke.[2] The greater part of the

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[1] Part of a thesis submitted by Edward Wichers to the Graduate School of the University of Illinois as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] THIS JOURNAL, 39, 53 (1917).

material had a mean atomic weight of 108.5, which is equivalent to about 25% erbium. Neither the original material, nor any part of it, subsequently obtained, showed the presence of any rare earth elements, except yttrium and erbium.

An attempt was made to effect a separation of the 25% material on the basis of the behavior of yttrium and erbium oxalates in dil. sulfuric acid as described by Wirth.[1] No separation was observed.

Drossbach[2] reports a strikingly rapid separation on digesting neutral chloride solution with oxide of the same composition. The authors applied this method on material of atomic weight 104. The yttrium and erbium fractions had atomic weights of 95.9 and 110.6, respectively. These results, while showing a good separation, are not nearly equal to those claimed by Drossbach. James and Willand[3] recommend fractional precipitation with potassium cobalticyanide. Some trouble was experienced in the manipulation of this method, which was apparently due to persistent supersaturation of the rare earth cobalticyanide. Starting with material of atomic weight 108.5, 11 fractions were obtained, the first and last of atomic weights 123.0 and 89.2, respectively.

Fractional precipitation by sodium nitrite has been used, with somewhat varying methods, by several workers. The method used here is described by Hopkins and Balke.[4] Two series were run. In the first, material of atomic weight 108.5 was used and 14 fractions were obtained. The first series of figures gives the per cent. of the original weight of oxide recovered in each fraction. The second series gives the atomic weights of the fractions.

Fraction 1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.
3.0	6.7	6.0	4.0	7.5	9.0	12.4	8.5	14.0	11.7	11.0	5.0	1.5	1.2
129.4	126.7	126.1	126.0	120.5	119.5	115.3	110.1	104.8	97.8	93.0	90.6	89.6	90.4

Since the separation was slow in the earlier fractions, it was decided to divide the second series into less fractions. The material from fractions 1 to 6 of the first series was used, the mean atomic weight of which was 123.7. The data are given as before.

Per cent. of total..................	19.0	24.9	22.1	15.0	15.4	3.6
Atomic weight.....................	142.9	140.2	128.8	..	..	91.3

The method most used by the early workers was the fractional de-

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[1] *Z. anorg. Chem.*, **76**, 174 (1912).

[2] *Ber.*, **35**, 2826 (1902).

[3] THIS JOURNAL, **38**, 1198 and 1497 (1916).

[4] *Ibid.*, **38**, 2332 (1916).

composition of the nitrates by fusion, originated by Berlin.[1] This method was used on some of the material of atomic weight 108.5. When the atomic weights were determined Fraction A had been carried through 3 fusions, Fraction B through 4, and Fractions C, D, E and F through 5 fusions. The results were as follows:

Fraction.	A.	B.	C.	D.	E.	F.
Atomic weight..................	159.3	141.4	119.7	118.1	102.6	91.9

These results indicate that the classic nitrate fusion furnishes a method for separating erbium and yttrium, which is more efficient than any of the other methods proposed for the purpose. Whether it would completely free either of the elements from the other is not shown by these data. The fact that it has been used in nearly every atomic weight study of erbium recommends it for the purification of this element, at least.

Study of the Ratio $Er_2O_3:2ErCl_3$.

The present value for the atomic weight of erbium was determined by Hofmann by the synthesis of the sulfate from the oxide. His material was probably the purest obtained up to that time. Work done in this laboratory has raised serious objections to the oxide-sulfate ratio, however, and it was deemed advisable to study the applicability of the oxide-chloride ratio previously used here for yttrium and dysprosium. It was thought possible that light might be thrown upon the value of the ratio and the general tendency it exhibits to give higher results than are obtained by other ratios.

The material used was a number of fractions from a bromate series consisting of erbium and yttrium and far removed from fractions showing holmium on the one hand, and thulium on the other. This material was then further purified by running it for some time as a nitrate fusion series. The series was run in 6 to 8 fractions through 32 operations. The atomic weights of all the fractions except the second and third were determined by the permanganate titration method of Gibbs.[2] The results were as follows:

32 H.	32 I.	32 K.	32 L.	32 M.	32 N.	32 O.	32 P.
166.31	..	..	166.17	164.68	163.75	154.63	119.90

The permanganate titration method does not give accurate absolute values for the atomic weights, but does give good relative values. It may then be concluded from the above data that Fractions H to L had very nearly the same composition and were approaching pure erbium. An attempt was made to detect yttrium by means of the arc spectrum, but this could not be accomplished with the apparatus at hand. The

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[1] *Forhandl. Scand. Naturf.* 8 Mode, Kjobenhavn, 448 (1860); see also Bahr and Bunsen, *Ann.*, **137**, 1 (1866).

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

fractionation was carried through two more operations and the first 3 fractions were used.

The methods for preparing pure reagents and for converting the erbium oxide to anhydrous erbium chloride were the same in all essentials as have been described in previous papers. One point of variation in the behavior of erbium compounds from those of yttrium and dysprosium was noted. In weighing erbium chloride, some difficulty was experienced which was apparently due to hygroscopicity. This had not been observed with yttrium or dysprosium chloride.

The erbium oxide used was prepared by the ignition of erbium oxalate, after careful purification from base elements. The ignition was carried out in a platinum crucible in an electrically heated crucible furnace. The temperature and duration of ignition varied somewhat on different samples and this was done deliberately when it became suspected that this variation affected the weight of the oxide and consequently the ratio of oxide to chloride. Table I shows the tabulated data for the determinations.

TABLE I.

Detn. No.	Fraction.	Hours at 775–785°.	Hours at 875–885°.	Wt. of Er_2O_3 *in vacuo.*	Wt. of $ErCl_3$ *in vacuo.*	Ratio.	Atomic weight.
1........	34 M	8	...	0.86002	1.22899	0.70027	168.47
2........	34 M (1)	12	...	0.72202	1.03068	0.70053	168.70
3........	34 M	6	1	0.48901	0.69805	0.70054	168.71
4........	34 M (2)	6	1	0.48259	0.68876	0.70067	168.84
5........	34 L	10	1	0.50624	0.72285	0.70034	168.54
6........	....	..	...	...	...	...	..
7........	34 M (3 & 4)	7	3.5	0.81944	1.17074	0.69994	168.16
8........	34 L (5)	14	5	0.24325	0.34762	0.69976	168.00

A number in parenthesis after the fraction number indicates the determination in which the same material was previously used. No. 6 was lost because the chloride was found to be basic after the fusion. Numbers 7 and 8 show the effect of the prolonged ignition at 875–885° and suggested the possibility that some carbon dioxide was rigorously held by the ignited oxide. Accordingly, direct tests for carbon dioxide were made. This was done by the use of a set of absorption bulbs filled with lime water attached to the end of the reaction train. During the solution of the oxide and for some time afterward a current of air free from carbon dioxide was passed through the train. A definite reaction for carbon dioxide was obtained in the two trials made. This retention of carbon dioxide by oxalate ignited to oxide was subsequently found to be the case for dysprosium also.[1]

Hofmann[2] states that erbium oxalate is almost completely decomposed at 575° and that it is completely decomposed at 845°. From

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

[2] *Ber.*, 43, 2631 (1910).

these data it would seem that the ignition of the oxalate in the earlier determinations, and certainly in No. 7, should have been sufficient to give a complete decomposition to oxide. Hofmann does not state how the oxide for his oxide-sulfate ratio was prepared, but from his attention to the decomposition of the oxalate in this same paper it may be inferred that the oxide was prepared by the ignition of the oxalate. If erbium oxalate is not completely decomposed at 845°, or even by heating at 875–885° for 3 or 4 hours, Hofmann's oxide-sulfate ratio, and with it the present accepted atomic weight of erbium, is immediately thrown open to question. It is evident that until the possibility of preparing erbium oxide of the definite composition Er_2O_3 is fully established, no ratio in which the oxide is one term can be reliable. Work on the preparation of pure erbium oxide will be resumed as soon as circumstances permit.

Summary.

1. A comparative study was made of the newer methods proposed for the separation of erbium and yttrium. The cobalticyanide and nitrite precipitation methods were found to give good results. The latter was the more efficient and practicable.

2. The classic nitrate fusion method was found to give results far superior to the other methods which were studied.

3. Erbium material of a very high purity was prepared by the nitrate fusion method.

4. The ratio of erbium oxide to erbium chloride was determined in 7 analyses. The ratio was found to vary with the temperature and length of time of ignition of the oxide.

5. Erbium oxide, prepared by the ignition of the oxalate and ignited for several hours at nearly 800° and two hours at nearly 900° was found to retain appreciable amounts of carbon dioxide. This is contrary to Hofmann's results and consequently brings into dispute the present accepted value for the atomic weight of erbium.

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THE PREPARATION AND PROPERTIES OF YTTRIUM MIXED METAL.

BY J. F. G. HICKS.[1]

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I. Object of and Reasons for the Investigation.

On account of the meagreness of the work done,[2] because the metal has never been obtained in other than powder form, and because of the

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[1] Abstracted from thesis submitted to the Graduate School of the University of Illinois, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Other investigators mention isolation of yttrium (pure metal), but only as