

tions, the atomic weight of silver was taken as 107.93, and of chlorine as 35.473<sup>1</sup>.

THE RATIO OF INDIUM TRIBROMIDE TO SILVER BROMIDE.

The indium tribromide was made by heating metallic indium in a current of carbon dioxide gas containing bromine. The carbon dioxide was passed through a gas wash bottle that contained bromine and the indium was converted into the tribromide in the apparatus already described under the preparation of the trichloride. Indium tribromide is a white substance that sublimes easily. The ratio of indium tribromide to silver bromide was ascertained in the manner directly analogous to that described under the ratio of indium trichloride to silver chloride. In the calculation of results, the atomic weight of bromine was taken as 79.953<sup>2</sup>.

	Grams InBr <sub>3</sub> .	Grams AgBr.	Atomic Weight of Indium.
7	2.73494	4.34550	114.89
8	7.69880	12.23341	114.86
9	6.27450	9.96917	114.89
10	5.36642	8.52741	114.85
11	5.16112	8.20128	114.85
12	4.98336	7.92009	114.81
			Average, 114.86

SUMMARY.

Because of the unavoidable errors in the precipitation and weighing of the silver chloride due to the solubility of that substance<sup>3</sup>, the results obtained for the ratio of indium tribromide to silver bromide were probably more accurate than those from the ratio of indium trichloride to silver chloride. The averages of the two ratios, however, give closely agreeing values, 114.88 and 114.86. On the basis of these results the author would recommend as the atomic weight of indium the value

114.9.

In conclusion, the author takes this opportunity to express his thanks to Professor L. M. Dennis, who suggested the subject, and to Dr. A. W. Browne and Dr. W. C. Geer, for valuable assistance during the course of the investigation.

CORNELL UNIVERSITY, JANUARY, 1907.

## A NEW METHOD FOR THE SEPARATION OF THE YTTRIUM EARTHS.

BY C. JAMES.

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In working up a specimen of gadolinite for the rare earths, the remarkable fact was noted that the filtrate, after the beryllium separation

<sup>1</sup> This Journal, 28, 7, (1906).

<sup>2</sup> Baxter, this Journal, 28, 1335 (1906).

<sup>3</sup> Richards, Proc. Am. Acad. Arts and Sci., 29, 71 (1893); and Richards and Wells, Carnegie Institution Public. (Washington) April (1905).

by ammonium carbonate, contained a small quantity of rare earth oxalate; and that the nitrates obtained therefrom gave absorption bands which were very intense for erbium, while the holmium and dysprosium bands had grown very faint. The insoluble oxalates, which had been previously removed in the usual manner, after conversion into the nitrates presented the ordinary absorption spectrum of erbium, holmium and dysprosium, etc.

It was at once apparent that either erbium oxalate was more soluble in beryllium oxalate or else traces of the rare earth oxalates had been thrown down by the ammonium hydroxide, redissolved in ammonium carbonate and fractionated by means of heat. On boiling some of the oxalate material with a very concentrated solution of beryllium oxalate; it was found that the filtrate contained no erbium. The only alternative was that the fractionation was due to the ammonium carbonate.

#### METHOD OF SEPARATION.

Having determined by further experiment that the yttrium group oxalates were very soluble in ammonium carbonate, a careful search for the conditions bearing upon the separation was made, and the following method of procedure was found to give the best results.

The oxalates, freed from those earths giving insoluble double sodium sulphates, are treated with a solution of ammonium carbonate made by saturating a diluted (1-4) solution of ammonium hydroxide with the solid salt. The whole is then well stirred and the beaker placed in a water-bath when on warming it enters into solution forming a reddish yellow liquid. The temperature of the bath is then raised to boiling when a precipitate soon appears. This is filtered off and the filtrate again treated in the same manner and some five fractions are thus obtained of approximately equal size.

Usually after the first two fractions have been taken the liquid rapidly loses carbon dioxide; although sometimes the ammonium carbonate begins to decompose even before the first precipitate forms.

The oxalates should be fresh and moist so as to easily mix up, and not contain more than traces of the cerium metals; for otherwise complete solution will not be obtained.

After a little practice one is able to add just about the right amount of ammonium carbonate to dissolve the mixed oxalates and thus avoid waste of this rather expensive reagent.

#### RESULT OF FRACTIONATION.

Fraction I soon formed and consisted of a crystalline powder with a faint pink tinge. One portion on igniting gave a yellow oxide and another on treatment with hydrochloric acid dissolved entirely with strong effervescence. The solution gave faint traces of the bands of didymium. The holmium and dysprosium bands were stronger than the erbium, but

all the bands were weaker; showing a great increase in the percentage of yttrium. This first fraction consisted simply of carbonates.

Fraction II appeared to be similar to Fraction I, except that it possessed more of a pink color. The oxide was yellow and the original precipitate was again entirely soluble in hydrochloric acid. The solution gave no didymium absorption bands while those of holmium, dysprosium and erbium were stronger; and when compared with a solution of the gadolinite oxides, it was seen that holmium and dysprosium had increased and erbium decreased in intensity.

Fraction III took longer to form, was heavier, of a rose color and was not entirely soluble in hydrochloric acid; so at this stage oxalates were being precipitated also. On ignition it gave a yellowish oxide and the absorption bands of the solution were very much the same as the original material.

Fraction IV took a considerable time to deposit and was of a salmon color. On heating it gave a light colored oxide with a faint yellow tinge, which on dissolving in nitric acid gave a very intense erbium spectrum, that of holmium and dysprosium had become weak.

Fraction V, obtained by evaporation to dryness and calcining, gave a very dense oxide of a pink color. It was soluble in strong nitric acid after heating for some time on the water-bath; giving a fine rose-colored solution presenting an intense erbium spectrum; holmium and dysprosium being very weak. This last fraction was converted into the oxalate and again submitted to fractionation.

Fraction (*a*) colored rose,

(*b*) salmon.

(*c*) a very delicate salmon.

The resulting oxide had a rose color, which on being treated with nitric acid, gave a very concentrated solution with only faint bands of holmium and dysprosium.

Fraction (*d*) evaporated to dryness and ignited gave a white oxide with a pink tinge. This fraction was practically free from holmium and dysprosium. It gave erbium bands, also a thulium band in the red and contained a fair amount of ytterbium and some thorium. It will be seen by the above that the earths separate in the following order:—Cerium group,—Yttrium, Terbium—Dysprosium, Holmium—Erbium—Thulium—Ytterbium.

Yttrium oxide was separated from the first fractions by the method of Muthmann & Rölig<sup>1</sup>, as follows:—The precipitate, consisting chiefly of carbonate of yttrium, was ignited, dissolved in nitric acid, the concentrated solution boiled and a thick cream of magnesium oxide added until the liquid no longer gave absorption bands of holmium, dysprosium and erbium. This well known method gives excellent results, although Den-

<sup>1</sup> Ber. 31, 1718.

nis and Dales<sup>1</sup> were not successful in getting good separations by its aid. Their trouble undoubtedly lay in the fact that they employed the chlorides instead of the nitrates as recommended by Muthmann & Rölig. While this method separates erbium, holmium and dysprosium from yttrium, terbium clings and so for the final purification the chromate method of Muthmann & Böhm<sup>2</sup> was employed and a pure white yttria was easily obtained.

The material separated from the major portion of the yttria by the above methods was again converted into oxalates and fractionated from ammonium carbonate solution.

It is always advisable to first treat the oxides from minerals very rich in yttria by the above methods in order to remove the excess of this earth before proceeding with the fractionation.

It will be seen that the "oxalocarbonate" method gives excellent results, the separation especially of pure erbium from holmium, dysprosium and terbium being accomplished in a much shorter time than by any other known method. The fractionation of holmium, dysprosium and terbium is much slower than that of erbium, thulium and ytterbium, the two last being found in the most soluble fractions.

Another advantage of this procedure lies in the fact that the last fraction is evaporated to dryness and so no soluble elements are washed away, as is the case when dilute solutions are employed.

This method has also been applied to some monazite residues which were on hand and which were rich in terbium, holmium and dysprosium and contained besides some erbium, yttrium and traces of samarium and gadolinium. As before the oxalates were very soluble and gave dense precipitates, but the separation was not so immediate and complete as in the case of the gadolinite oxalates. The color of the oxides varied from orange-brown to nearly white, the latter coming from the most soluble portion.

In all of these separations it is highly important that in comparing fractions by the absorption spectrum the same acid be used as solvent for otherwise erroneous conclusions may be reached, owing to the spectra varying in different compounds.

#### COMPLEXITY OF ERBIUM<sup>3</sup>.

One of the interesting and important results of this method of separation is the fact that the material known as erbium is in all possibility complex as was found to be the case with didymium. Differences in the

<sup>1</sup> This Journal, 24, 428.

<sup>2</sup> Ber., 33, 47, and Chem. News, 81, 161.

<sup>3</sup> While this article was in press the announcement of C. Auer v. Welsbach, Monatsheft, 27, 935-45, of the presence of a new element, Er,  $\gamma$ , which is undoubtedly the same as here noted, has been called to my attention.

absorption spectra of erbium from different sources are noticeable and while it is too early to give any detailed description of the changes observed it does seem well to call the attention of chemists, working on the rare earths, to this peculiarity in the hope that it may be confirmed and the separation made.

A considerable amount of gadolinite and xenotime is now being worked up and separated for purposes of future research.

In conclusion I wish to thank Professor Charles L. Parsons for advice and the interest he is taking in the work; and acknowledge my indebtedness to the Welsbach Light Company for raw material received through the courtesy of Dr. H. S. Miner.

NEW HAMPSHIRE COLLEGE.  
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[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY  
OF THE UNIVERSITY OF CHICAGO.]

## ON AMORPHOUS SULPHUR: STUDY OF THE TWO FORMS OF LIQUID SULPHUR AS DYNAMIC ISOMERS.<sup>1</sup>

BY CHARLES MACDONALD CARSON.

Received December 22, 1907.

In their first paper on amorphous sulphur it was shown by Smith and Holmes<sup>2</sup> that the freezing point of liquid sulphur is depressed below  $119.25^{\circ}$  to various extents and that the depressions are quantitatively in the direct ratio of the proportions of amorphous sulphur obtained by chilling the specimens immediately after the temperature of freezing has been read. In their second paper<sup>3</sup> it was shown that there are two forms of liquid sulphur,  $S_{\lambda}$  and  $S_{\mu}$ , of which the former is pale yellow and mobile and the latter is brown and viscous. These forms are miscible and exist in equilibrium with one another in proportions depending upon the temperature. It was shown that these two forms have different curves of solubility in solvents like triphenylmethane and that melted sulphur shows a very marked minimum of dilatation at  $160^{\circ}$ . It was suggested that the thermal effect and sudden increase in viscosity which occur just above this temperature were probably due to the separation of a new phase consisting of a liquid, the viscosity of which is due to increased proportions of  $S_{\mu}$ . The third<sup>4</sup> paper by the same observers dealt with the influence of foreign substances on the results of super-

<sup>1</sup> Read in abstract by Prof. Smith before the American Chemical Society at Ithaca, June 30, 1906. A paper with this title and embodying the conclusions reached in this paper is published in collaboration with Prof. Alexander Smith in the *Zeitschrift für Physikalische Chemie*, 57, 685.

<sup>2</sup> *Zeit. Phys. Chem*, 42, 469 (1903).

<sup>3</sup> Smith, Holmes and Hall, this Journal, 27, 797 (1905). *Zeit. phys. Chem.*, 52, 602 (1905).

<sup>4</sup> This Journal 27, 979 (1905). *Zeit. Phys. Chem.*, 54, 257 (1906).