

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

OBSERVATIONS ON THE RARE EARTHS. IX. THE ATOMIC WEIGHT OF YTTRIUM.

[THIRD PAPER.]

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The investigation described in this paper is a continuation of the researches on yttrium, carried on in this laboratory. This paper, however, describes only the most recent attempt to obtain a correct value for the atomic weight of this element.

A paper by Egan and Balke¹ on the preliminary purification of the yttrium material used in this investigation and giving also trial attempts of the determination of its atomic weight appeared in 1913. Since then and up to the time when the second paper² appeared in 1916 more work was done on the further purification of the yttrium material then on hand and a rather exhaustive study was made of the various methods used in determining its atomic weight. Since a full and complete account of the history of the atomic-weight determination of yttrium was given in the second paper, this will not be repeated here.

The purpose of the present investigation was to study more fully the chloride-silver ratio of this element. Egan and Balke studied this ratio in a preliminary way, but due to lack of time rather incomplete results were obtained. This ratio has been found to give encouraging results with dysprosium³ and also with samarium.⁴ Since dysprosium approaches yttrium more nearly in properties than it does many of the other rare earths, it seemed quite probable that the same ratio might succeed with the latter element. The material used in this investigation was purified by the sodium nitrite precipitation method. This work was done by Hopkins and Balke as described in their paper of 1916.

Preparation of Reagents Used in the Atomic-Weight Determinations.

Water, Nitric Acid, Hydrochloric Acid, Oxalic Acid and Silver were all prepared by the methods described in the paper on dysprosium.⁵ The first three reagents were always prepared just before use and the last two were part of the stock prepared during the summer of 1916.

Preparation of Yttrium Chloride.

The yttrium oxalate, the first step in the purification of the precipitate from the sodium nitrite, was ignited to the oxide in platinum and dissolved in redistilled nitric acid. The solution was filtered and diluted to two

¹ THIS JOURNAL, 35, 365 (1913).

² Hopkins and Balke, *Ibid.*, 38, 2332 (1916).

³ H. C. Kremers, B. S. Hopkins and E. W. Engle, *Ibid.*, 40, 598 (1918).

⁴ A. W. Owens, Doctor's Thesis, University of Illinois, 1918.

⁵ THIS JOURNAL, 40, 598 (1918).

liters with conductivity water in a 4-liter Jena glass flask. Freshly distilled ammonia gas was passed over the solution and the flask gently shaken. In this manner a very flocculent precipitate was obtained which settled very rapidly and could be washed several times by decantation. The washed hydroxide was then dissolved in redistilled nitric acid, diluted and heated nearly to boiling. A hot dilute solution of pure oxalic acid was then slowly added and during the addition of the acid the solution of yttrium nitrate was shaken constantly. The very crystalline precipitate thus obtained was easily washed first by decantation and lastly on a small Büchner funnel. The oxalate was dried and ignited. Two more alternate purifications were given as described above, always ending with the ignited oxide. The final oxide was then moistened with water and pure hydrogen chloride gas passed in until it had dissolved. After filtering, the yttrium chloride was stored in a quartz flask.

The Ratio, Yttrium Chloride to Silver.

Since the same apparatus was used and the method of procedure was similar to that used before in this laboratory only changes in manipulation will be mentioned.

A portion of the yttrium chloride solution was introduced into the weighed quartz reaction flask and the latter attached to the purification train. The dehydration, fusion and weighing were carried out as described in former papers.

The previous attempts in this laboratory to precipitate all the chlorine from a solution of yttrium chloride were unsuccessful,¹ due to the fact as now seems probable, that the solutions had not reached equilibrium when the final tests were made. Later work with dysprosium and samarium chlorides revealed the fact that very dilute solutions and thorough shaking were important factors in reaching the desired equilibrium. Consequently in the present investigation much more dilute solutions were used and the addition of silver nitrate was made very slowly and with constant and long-continued shaking. Much greater difficulty was encountered in obtaining an equilibrium in the case of yttrium than with either dysprosium or samarium chlorides. Finally the following procedure was adopted and proved to give a satisfactory end-point: The anhydrous yttrium chloride after being weighed was dissolved in a small amount of water in the 25 cc. quartz reaction flask and the solution transferred to a 5-liter glass stoppered resistance glass bottle. This solution was diluted to two liters and mixed with an equal volume of silver nitrate solution which contained the calculated amount of silver. The latter solution was added slowly while the former was being thoroughly agitated. The stopper was then wired in and the bottle placed immediately on a shaking machine and

¹ THIS JOURNAL, 35, 373 (1913).

shaken for at least 12 hours. After allowing the precipitate to settle for several hours, portions of the clear liquor were tested in the nephelometer for an excess of either chloride or silver ions. Additions of a standard solution of either silver nitrate or sodium chloride were made until equivalence was obtained. After the addition of standard solutions the bottle was again shaken for several hours before again being tested. All work involving the silver reactions was carried out in a dark room in which no other work was being done.

The weights used were carefully standardized to 0.01 mg. All weighings were made by the method of substitution and corrected to vacuum standard. The specific gravity of the weights was taken as 8.4, that of yttrium chloride as 2.8, and that of silver as 10.53. The atomic weight of silver was taken as 107.88 and that of chlorine as 35.46. The following values were obtained for this ratio and the consequent atomic weight:

No.	Sample.	Wt. of YCl ₃ .	Wt. of Ag.	Ratio—YCl ₃ : 3Ag.	At. wt.
1.....	O ₄₋₆	3.31143	5.47636	60.468	89.32
2.....	O ₄₋₆	2.31979	3.83587	60.476	89.34
3.....	O ₄₋₆	2.26815	3.75045	60.477	89.35
4.....	O ₄₋₆	2.29376	3.79302	60.473	89.33
5.....	T ₁₁	2.00731	3.31977	60.465	89.31
6.....	R ₄	1.97610	3.26827	60.463	89.30
7.....	R ₄	2.17949	3.60389	60.476	89.34

Mean, 89.33

The material O₄₋₆ was of the sample prepared in the former investigation of Hopkins and Balke, and is described in Table VII of that paper. Three determinations by the oxide to chloride ratio were made from this sample by the above authors. Sample R₄ was also used in determinations Nos. 6 and 7 described in Table VIII of the above mentioned paper.

In all of the above samples a very faint holmium line could be detected in the absorption spectrum of a 5 cm. layer of the concentrated solution. No other absorption lines could be detected in the visible portion of the spectrum. A comparison of this holmium line with that of a standard holmium solution indicated that the amount of holmium present in the yttrium material was not over 0.005%. This would have no appreciable effect upon the atomic weight. In comparing the standard holmium solution with the solutions of yttrium salts it was assumed that the intensity of the absorption lines of holmium would not be effected by the great excess of yttrium in the latter solutions. This assumption seems to be justifiable by the striking dissimilarity of the absorption spectra of solutions of salts of the two metals.

The results obtained by the use of the oxide-chloride ratio gave values for the atomic weight of yttrium lying between 88.80 and 89.06, the mean of 7 determinations being 88.91. It is the opinion of the authors of this

paper that the results obtained by the chloride to silver ratio are more reliable than those obtained in former investigations by the oxide to chloride ratio in spite of the fact that they are farther from the accepted value. It has been found in this laboratory that some carbonate was still present in the oxides of erbium¹ and dysprosium² when ignited at 850° in platinum for several hours. This would tend to give high results in the oxide to chloride ratio. No attempt is made, however, to explain the reason of the higher results obtained in the present work over those obtained by the oxide to chloride ratio in the investigation of 1916.

Summary.

1. The chloride to silver ratio has been successfully tried on yttrium. The value 89.33 was obtained as the mean of 7 determinations.

2. The results obtained by the chloride to silver ratio seem more reliable than those obtained by the oxide to chloride ratio in a former investigation.

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ON THE DETERMINATION OF BOILING POINTS OF SOLUTIONS.

By F. G. COTTRELL.

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The method and apparatus here described were devised some 9 years ago and used with very satisfactory results in the undergraduate laboratory courses which the writer was then conducting in the University of California. It was the intention to subject them to a more rigorous test as regarded the ultimate accuracy attainable before publishing, but upon the author's leaving the University for the Government service a year later this program was interrupted.

A couple of years later Prof. E. W. Washburn kindly interested himself in the method and by adopting and further developing it incidentally to his own researches on the constitution of solutions, furnished the lacking data. At his request, the present account was prepared in March, 1913, to accompany his article and is now published in that connection³ in the hope it will not only serve as a preface to his more important work on fundamental questions but also make the apparatus available in its simplest form for everyday use and be suggestive to others who may find opportunity to further develop and perfect it for still higher orders of accuracy.

The boiling-point determination for a pure liquid has always been one of the most accurate of temperature measurements, at the same time

¹ THIS JOURNAL, 40, 1618 (1918).

² *Ibid.*, 40, 609 (1918).

³ Washburn and Read, THIS JOURNAL, 41, 729 (1919).