

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

## A Revision of the Atomic Weight of Europium. The Analysis of Europous Chloride

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Through the very great kindness of Dr. Herbert N. McCoy we have been able to examine a sample of europium material purified as already described by Dr. McCoy,<sup>2</sup> and in that paper are given the preliminary results of four analyses by us of europous chloride, yielding the atomic weight 151.95. From our final results we find the value 151.96.

According to the spectroscopic report by Dr. King<sup>2</sup> no other rare earths could be detected in this sample except neodymium and that only to the extent of 0.001% or less. Barium and calcium, however, were present in traces. The original oxalate (190 g.) was converted to oxide by careful ignition to redness in a platinum boat contained in a quartz muffle. The oxide was dissolved in redistilled nitric acid in platinum and the nitrate was subjected to fractional crystallization from concentrated nitric acid. The head fraction (I) received three crystallizations, a second fraction (II), obtained from the mother liquors, received four. The remaining mother liquors were combined and used in preliminary experiments (III).

Samples I and II of nitrate were twice precipitated as oxalate in the presence of 0.5 normal nitric acid, with the use of oxalic acid which had been crystallized from dilute nitric acid and from water. After each precipitation the oxalate was converted to oxide by ignition as before. Then the oxide was dissolved in redistilled hydrochloric acid in quartz and the europic chloride was fractionally crystallized in platinum from a solution saturated at 0° with hydrogen chloride. Sample Ia, the head fraction, received three crystallizations as chloride; Sample Ib, the second fraction, and Sample Ic, the third, each received four crystallizations. Sample II of chloride, made from Sample II of nitrate, was twice crystallized in quartz. Barium and calcium could not be detected spectroscopically in the chloride samples.

Sample III of nitrate was once precipitated as oxalate. The oxalate was ignited and the resulting oxide was dissolved in hydrochloric acid

and once crystallized as chloride. This material was used only in preliminary experiments (III).

In order that melting might be avoided during the drying of the chloride the transition temperature was determined approximately with a portion of Sample III. This appeared to be in the neighborhood of 95°.

We first attempted to prepare anhydrous europic chloride by dehydration in a current of dry hydrogen chloride. The first stage in the dehydration began at about 80° and the temperature was not allowed to rise above the inversion temperature until water evolution had nearly ceased. The temperature was then allowed to rise very slowly. Water was given off continuously with a pronounced step at about 170° and a final step at 210°. After dehydration the salt was maintained at 300–350° for some time.

Salt thus prepared was yellow, and yielded a clear solution, but on standing the solution became turbid. This appears to be due to thermal decomposition during the drying of europic chloride with the formation of europous chloride. On standing in air the neutral aqueous solution of the latter becomes oxidized and therefore basic. In one experiment the basic salt was dissolved in nitric acid and the chlorine determined as silver chloride. The percentage of chlorine found, 41.16, is slightly lower than that to be expected from our final value for the atomic weight of europium, 41.18. Only in one instance, when the europic chloride had not been heated above 130° in the drying process, was a permanently clear solution of europic chloride obtained. For our purpose this was of no practical advantage for at 130° the salt still retains moisture.

If the salt is eventually fused in dry hydrogen chloride a dark green crystalline mass is obtained which, as is to be expected, gives a turbid solution. (Urbain and Bourion made a similar observation.<sup>3</sup>) When the fusion was carried out in a platinum boat several hundredths of a gram of platinum was removed from the boat and appeared as a spongy mass in the solution of the salt. The salt had the same appearance and behavior when fused in a quartz boat, but it seemed on the whole

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(2) McCoy, *THIS JOURNAL*, **59**, 1131 (1937).

(3) Urbain and Bourion, *Compt. rend.*, **153**, 1155 (1911).

wiser to avoid the use of platinum as a receptacle during the drying. A weighed sample of salt, dried and fused as above in a quartz boat, was dissolved, the solution was clarified with nitric acid, and the chlorine was determined as silver chloride. The percentage of chlorine found was 40.29. In another similar experiment, where the salt was fused at the lowest possible temperature, the percentage of chlorine was even lower, 40.21.

In order to prevent the decomposition of the trichloride, in two experiments the salt was dried and fused in an atmosphere of chlorine and hydrogen chloride. The percentages of chlorine found in the salt, 40.37 and 40.45, are not much higher than when the fusion atmosphere was hydrogen chloride alone. No improvement was effected by drying the salt at 300° in an atmosphere of chlorine and hydrogen chloride. In one experiment the percentage of chlorine found was 41.16, a value identical with that obtained under the same conditions but without chlorine in the drying atmosphere.

Since hydrated salts which have been dried without fusion are likely to retain traces of moisture and since halogens are more apt to be retained by halides than the corresponding halogen hydrides, we next turned to the possibility of preparing the dichloride by heating and fusing the salt in an atmosphere of hydrogen and hydrogen chloride. When the anhydrous trichloride is heated to 400° the original yellow color begins to change to white. (Urbain and Bourion state that reduction begins at 275°.<sup>3</sup>) At higher temperatures the change is more rapid until finally the unfused material is apparently pure white. Fusion yields a light amber liquid which fluoresces green, and upon cooling a white solid with a bluish cast. The blue is apparently due to fluorescence for the salt gives a pronounced blue when exposed to ultraviolet light. McCoy has already noticed that the hydrated dichloride fluoresces blue (*loc. cit.*, p. 1132). In a preliminary experiment the percentage of chlorine was found to be 31.82, which is identical with that predicted from our final atomic weight. More careful experiments with the dichloride showed that salt dried and fused in hydrogen and hydrogen chloride is of constant composition, independent of deliberate variations in the period of heating and fusion. It therefore seems legitimate to assume that we were dealing with a substance of definite formula, europous chloride. (Urbain and Bourion

state that europous chloride is not further reducible.<sup>3</sup>)

Material was prepared for the final experiments as follows. Contained in a weighed quartz boat placed in a quartz tube the crystallized trichloride was dehydrated gradually by efflorescence first at 80–90°, then at about 170° both in an atmosphere of dry hydrogen and hydrogen chloride (1 to 1). The temperature was then raised slowly until the salt had become white and finally had fused. After solidification the hydrogen and hydrogen chloride were swept out with dry nitrogen and this in turn with dry air. By means of a Richards bottling system the boat was transferred to the weighing bottle in which it originally had been weighed, and after coming to the temperature of the balance room the system was reweighed. Since in one experiment the weight of the salt increased only 0.05 mg. in twelve hours and in another 0.04 mg. in thirty-six hours, oxidation of the salt in dry air is evidently so slow as to be negligible.

In order to prevent the precipitation of basic salt by oxidation, the dichloride was dissolved in water containing a small excess of nitric acid. The original green solution gradually lost its color completely. When this had occurred the chloride was precipitated with a solution of a weighed nearly equivalent amount of pure silver and the end-point was found by the equal opalescence method with a nephelometer. The final end-points were observed after a period of several months' standing.

Gases were purified and dried by conventional methods except that the final drying of the hydrogen chloride and hydrogen was effected over freshly fused calcium chloride chilled with solid carbon dioxide and alcohol.<sup>4</sup> This seemed desirable since at ordinary temperatures concentrated sulfuric acid leaves sufficient water in the gas to condense at -78°.

Some of the silver was purified by precipitation as chloride, crystallization as nitrate, precipitation with ammonium formate, and electrolytic transport through a concentrated silver nitrate solution with a dissolving anode followed by fusion on lime in hydrogen. The remainder was purified chiefly by three or four repetitions of the electrolytic purification. This material when examined spectroscopically seemed to be identical with earlier specimens of pure metal prepared

(4) Cf. Baxter and Behrens, *THIS JOURNAL*, 54, 600 (1932).

THE ATOMIC WEIGHT OF EUROPIUM							
Analysis	Sample of $\text{EuCl}_2$	$\text{EuCl}_2$ in vacuum, g.	Ag in vacuum, g.	Ag added, g.	Corrected wt. of Ag in vacuum, g.	Ratio $\text{EuCl}_2 : 2\text{Ag}$	At. wt. Eu
6	II	2.37130	2.29621	-0.00060	2.29561	1.032971	151.960
7	II	3.08194	2.98294	+ .00060	2.98354	1.032981	151.962
11	Ib	2.81858	2.72892	- .00045	2.72847	1.033026	151.972
12	Ic	4.88934	4.73360	- .00020	4.73340	1.032945	151.954
13	Ib	4.71094	4.56063	- .00010	4.56053	1.032981	151.962
14	Ib	4.76278	4.61072	- .00015	4.61057	1.033013	151.969
15	Ia	4.18924	4.05527	+ .00010	4.05537	1.033011	151.968
16	Ia	2.96223	2.86786	- .00020	2.86766	1.032978	151.961
Average						1.032988	151.963

for atomic weight comparison in this Laboratory.<sup>5</sup>

The quartz boats were resistant to attack by the fused salt. One boat with its weighing bottle changed in weight only 0.01 mg. in two experiments, the other 0.29 mg. in eight experiments.

All weighings were made by substitution, in the case of the boat and weighing bottle with the use of a similar counterpoise. For the purpose of correcting for the buoyancy of the air, the density of freshly fused europous chloride was found by displacement of xylene in a special pycnometer.<sup>6</sup> The weight of xylene, of specific gravity 0.8505<sup>30,34</sup>, displaced by 2.965 g. of europous chloride at 30.34° was 0.5192. The density of europous chloride is therefore 4.86<sup>30</sup>. In another experiment made by Mr. Wallace M. Kelley 9.4437 g. of europous chloride at 25° displaced 1.6577 g. of xylene, of specific gravity 0.8550<sup>35</sup>, where the specific gravity of europous chloride is 4.87<sup>25</sup>. On either basis the vacuum correction per gram of europous chloride is +0.102 mg. A vacuum correction for silver of -0.031 mg. per gram also was applied.

Urbain and Lacombe<sup>7</sup> by the determination of europic oxide and water in the hydrated sulfate

found the atomic weight 151.96. Jantsch<sup>8</sup> from the percentage of europic oxide in the hydrated sulfate found 152.04. Hopkins and Meyers<sup>9</sup> dehydrated europic chloride in hydrogen chloride and finally fused the chloride in a quartz flask. Since our experiments indicate that fusion in hydrogen chloride leads to decomposition, it is not surprising that their result, 152.30, is higher than ours.

Aston's isotopic composition<sup>10</sup> is  $\text{Eu}^{151}$  50.6%,  $\text{Eu}^{153}$  49.4%. With a packing fraction of  $-4 \times 10^{-4}$  and conversion factor 1.00027 the atomic weight is 151.89. Our value for the atomic weight, with the same values of packing fraction and conversion factor, corresponds to 47% of  $\text{Eu}^{151}$  and 53% of  $\text{Eu}^{153}$ .

### Summary

1. Europic chloride is found to be unstable at its fusion point.
2. The preparation of anhydrous europous chloride is described.
3. The atomic weight of europium is found, by analysis of europous chloride, to be 151.96.
4. The density of europous chloride is found to be 4.87<sup>25-30</sup>.

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(5) Baxter, *THIS JOURNAL*, **44**, 591 (1922).

(6) Baxter and Hines, *Am. Chem. J.*, **31**, 220 (1904).

(7) Urbain and Lacombe, *Compt. rend.*, **138**, 627 (1904).

(8) Jantsch, *ibid.*, **146**, 473 (1908).

(9) Hopkins and Meyers, *THIS JOURNAL*, **57**, 241 (1935).

(10) Aston, *Proc. Roy. Soc. (London)*, **A146**, 46 (1934).