loss of adsorbed water followed by an abrupt loss of chemically combined water corresponding to one mole per mole of Fe_2O_3. Since the particular structure has been obtained only by hydrolysis of ferric chloride,[14] it would appear that the adsorbed chloride stabilizes the crystal lattice. This is supported by the observation that a preparation containing appreciable adsorbed chloride starts to lose its hydrate water at a temperature 50° higher than does a relatively pure sample. The experimentally determined x-ray diffraction data agree with those calculated on the assumption that the crystals are orthorhombic and have the following lattice constants: a_0 = 5.28 Å.; b_0 = 10.24 Å.; c_0 = 3.34 Å. The density of the compound corresponds to the density calculated from the x-ray data on the assumption that the unit cell contains 2 molecules of $Fe_2O_3 \cdot H_2O$ or 4 molecules of FeOOH.

Since the two well-known monohydrates are α-$Fe_2O_3 \cdot H_2O$ and γ-$Fe_2O_3 \cdot H_2O$, the new monohydrate herein described has been termed β-$Fe_2O_3 \cdot H_2O$.

Summary

The slow hydrolysis of ferric chloride solutions that are not too dilute, yields a yellowish, hydrous precipitate which Böhm believed to be a basic chloride. Evidence obtained by x-ray analysis and isobaric dehydration indicates that this product is a third polymorph of ferric oxide monohydrate. The experimentally determined x-ray diffraction data agree with those calculated on the assumption that the crystals are orthorhombic and have the following lattice constants: a_0 = 5.28 Å.; b_0 = 10.24 Å.; c_0 = 3.34 Å. The compound has been designated β-$Fe_2O_3 \cdot H_2O$ to distinguish it from the well-known α- and γ-$Fe_2O_3 \cdot H_2O$.

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[14] Weiser and Milligan, *J. Phys. Chem.*, **39**, January (1935).

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

Observations on the Rare Earths. XLIII. I. The Atomic Weight of Europium. II. The Specific Gravity of Europium Chloride[1]

BY E. L. MEYERS WITH B. S. HOPKINS

The object of the work described in this paper was to determine the atomic weight of europium by using the chloride-to-silver ratio.

The atomic weight of europium in current use, 152.0,[2] is based on the work of Urbain and Lacombe,[3] and Jantsch[4] on the oxide-to-sulfate ratio. The disadvantages of the oxide-to-sulfate ratio have been discussed critically by Hopkins and Balke,[5] and Brauner and Švagr.[6] Since the atomic weight of europium has never been determined by the chloride-to-silver ratio, and since the difference between the atomic weights of europium and gadolinium is greater than the difference between the atomic weights of any other pair of rare earth elements, it was deemed advisable to redetermine the atomic weight of europium.

Purification of Europium Material

The original source of the europium material was Brazilian monazite. Two different quantities of the material were obtained from the Welsbach Company as the crude rare earth oxides. In both cases the cerium was removed by the permanganate-phosphate[7] method. The cerium free oxides were converted to the double magnesium nitrates and subjected to a series of fractional crystallizations. The samarium–europium–gadolinium[8] rich fractions at the more soluble end of the different series were combined in a new series.

After approximately 1000 fractionations, large amounts of bismuth magnesium nitrate were added for the dual purpose of (a) splitting[9] in between samarium and europium, and (b) increasing the bulk of material. After about 200 more fractionations, the europium–gadolinium fractions were converted to the simple nitrates, bismuth nitrate being used as the separating agent for the elimination of the samarium at the more soluble end of the series. After the removal of the major portion of the samarium by some 150 fractionations, the europium rich–gadolinium poor fractions were reconverted to the double magnesium

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[1] Summary of a thesis presented to the Graduate School of the University of Illinois by E. L. Meyers in partial fulfilment of the requirement for the degree of Doctor of Philosophy.

[2] Report of the Committee on Atomic Weights of the International Union of Chemistry, THIS JOURNAL, **55**, 441 (1933).

[3] Urbain and Lacombe, *Compt. rend.*, **138**, 627 (1904).

[4] Jantsch, *ibid.*, **146**, 473 (1908).

[5] Hopkins and Balke, THIS JOURNAL, **38**, 2334 (1916).

[6] Brauner and Švagr, *Coll. Czecho. Chem. Communications*, **4**, 51 (1932).

[7] Neckers and Kremers, THIS JOURNAL, **50**, 955 (1928).

[8] All the fractionation of the samarium–europium–gadolinium material was carried out in this Laboratory by Drs. L. L. Quill and P. W. Selwood.

[9] This method of splitting in a separator element was probably first used by G. Urbain. He gives an excellent summary of his methods in *Chem. Rev.*, **1**, 155 (1924).

nitrates and fractionated 100 times. The europium rich material was fractionated again as the simple nitrates, and finally as the double magnesium nitrates, each series being recrystallized 150 times.

At the conclusion of this treatment twelve fractions were obtained, numbered Eu-1 to Eu-12. The bismuth was first partially removed from this series by hydrolysis and the remainder removed by precipitation as the sulfide with hydrogen sulfide gas. This procedure was carried out six times to ensure the complete removal of all the bismuth.

These treatments were planned to give europium of high purity. The last impurities to be removed were bismuth, samarium and gadolinium, which were expected to concentrate in the end fractions of the series, leaving the purest europium in the middle fractions.

A sample from each of the twelve fractions was removed for spectrographic examination, using an E_1 Hilger instrument and pure graphite electrodes. The most persistent spectrum lines of samarium were faintly visible in fractions Eu-1-7, those in Eu-7 being barely detectable. Likewise in fractions Eu-11 and 12 the most persistent lines of gadolinium could be discerned very faintly. No bismuth was detected in any of the fractions. Fractions Eu-8, Eu-9 and Eu-10 gave no spectroscopic evidence of the presence of any element except europium. Magnetic susceptibility measurements also indicated exceptional purity. The latter determinations were made by Professor E. H. Williams of the University of Illinois, Department of Physics, whose accurate determinations of these values have been most helpful. His final results have not yet been compiled.

Fraction Eu-8, being considerably larger than the other two fractions, was divided into two portions called Eu-8 and Eu-8a.

Purification of Reagents

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 europium nitrate obtained from fractions Eu-8, Eu-8a, Eu-9 and Eu-10 was purified by alternate precipitations of the oxalate and the hydroxide, all the 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 Europium Chloride[11]

The purified europium oxide was transferred to a quartz reaction flask and was dissolved in redistilled hydrochloric acid and conductivity water. A mixture of nitrogen and hydrogen chloride was then passed in from the purifying train while the temperature of the flask was maintained at 95°. When the salt began to crystallize, the nitrogen was stopped and only hydrogen chloride was passed through the reaction flask. The temperature was raised to 110° and maintained at this point until the first five molecules of water of crystallization had been driven off. The temperature was then gradually raised to 175° 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 nitrogen and this in turn by air. The flask was then removed to the balance case where it was allowed to hang for three hours before being weighed.

The Analysis of Europium Chloride

After it had been weighed, the europium chloride was dissolved in conductivity water and the solution transferred to a 3-liter glass-stoppered Jena glass bottle. The solution was diluted to approximately one liter so that the concentration was less than 0.05 normal. Assuming that the atomic weight of europium was 152.0, a sample of silver was weighed out to within a milligram of the calculated amount, dissolved in redistilled nitric acid with special precautions to avoid loss of spray, and the solution was diluted to a volume of about one liter. The silver solution was then added in small portions with gentle agitation to the chloride solution. The bottle was then placed in a shaking machine in the dark room for six hours. After its removal from the shaker the bottle was allowed to stand for twenty-four hours and a portion of the solution was tested in the nephelometer for any excess of silver or chloride. Weighed portions of hundredth normal 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 twenty-four hours before the solution was tested in the nephelometer again.

In the following tabulated data, the number of the fraction of the series from which the material was taken is shown together with the weight of the anhydrous chloride, the weight of silver required, and the atomic weight of europium. The number in parentheses indicates the previous determination in which the same sample was used.

TABLE I

ATOMIC WEIGHT OF EUROPIUM

Detn.	Fraction number	Anhydrous chloride, g.	Silver, g.	Ratio	At. wt. of europium
I	Eu-8a	1.15506	1.44544	0.79911	152.25
II	Eu-9	0.43279	0.54140	.79939	152.33
III	Eu-10	0.60180	0.75291	.79930	152.31
IV	Eu-8	1.10986	1.38862	.79924	152.29
V	Eu-8a(1)	1.00560	1.25820	.79924	152.29
VI	Eu-10(3)	0.52157	0.65262	.79919	152.27
VII	Eu-8(4)	.90408	1.13104	.79933	152.32
VIII	Eu-9(2)	.33150	0.41472	.79930	152.31
IX	Eu-10(6)	.57944	0.72498	.79925	152.29
X	Eu-8a(7)	.91942	1.15035	.79925	152.29
			Average	.79926	152.30[12]

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

(11) In the preparation of anhydrous rare earth chlorides in this Laboratory we have been following the methods developed by such careful studies as those of Matignon, *Compt. rend.*, **133**, 289 (1901), and Baxter and Chapin, THIS JOURNAL, **33**, 15–19 (1911).

(12) After this manuscript had been delivered to the Editor, Professor Aston's article [*Proc. Roy. Soc.* (London), **A146**, 50 (1934), became available. His value for the atomic weight of europium is 151.90.

All 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. Weighings were made on a balance sensitive to 0.01 mg. with weights which had been carefully standardized and were corrected to the vacuum standard. Electrostatic charges were eliminated by means of thorium oxide in the balance case.

The following densities were used: europium chloride, 4.47; silver, 10.49; platinum weights, 21.5. The atomic weight of silver was taken as 107.88 and that of chlorine as 35.457. The determination of the density of europium chloride is described in a later part of this paper.

II. The Specific Gravity of Europium Chloride

For the purpose of finding the buoyant effect of the air on anhydrous europium chloride in the preceding investigation, a knowledge of the density of this salt was necessary. Since the density of the anhydrous europium chloride is not given in the literature, it was determined by displacement of xylene.

Xylene was fractionally distilled, with rejection of the first and last third of the distillate, although the boiling point was constant within a degree and no solid material was left on evaporation. The specific gravity of the xylene at 35° referred to water at 4° was determined with an Ostwald pycnometer to be 0.8458.

Europium chloride was dehydrated and fused as described in the preceding part of this paper, and was weighed in the pycnometer. The salt was then quickly covered with xylene and placed in a vacuum desiccator in which the pressure was reduced until the xylene boiled gently. As soon as the air had thus been expelled from the salt, the pycnometer was filled with xylene at 35° and carefully weighed, the final weight being the mean of three trials. From the weight of the pycnometer filled with xylene and containing the salt, and the weight similarly determined without the salt, the xylene displaced was found. In Table II are shown the weight of anhydrous chloride, the weight of xylene displaced and the calculated density of anhydrous europium chloride at 35°.

TABLE II

THE DENSITY OF ANHYDROUS EUROPIUM CHLORIDE

Density of xylene d_4^{35} 0.8458

Detn.	$EuCl_3$, g.	Xylene, g.	Density of $EuCl_3$ at 35°/4°
1	0.7142	0.1351	4.472
2	.3111	.0589	4.468
3	.2747	.0520	4.469
4	.1344	.0254	4.476
		Average	4.471

Summary

1. The preparation of anhydrous europium chloride is described.

2. The ratio of europium chloride to silver is found to yield 152.30 with a mean deviation of ±0.018 as the atomic weight of europium. This value is higher by 0.3 unit than the present value assigned to europium.

3. The specific gravity of anhydrous europium chloride at 35° is found by displacement of xylene to be 4.471.

URBANA, ILL. RECEIVED JULY 2, 1934

The Purification and Physical Properties of Organic Compounds. VII. The Effect of Impurities on the Apparent Heat of Fusion

BY EVALD L. SKAU[1]

In usual practice the heat of fusion is not measured directly but is obtained graphically by plotting the heat contents for the solid and for the liquid at various temperatures, extrapolating each to the freezing point, and then finding the difference in their heat contents at that temperature. As was pointed out by Tammann,[2] the heat of fusion so determined is considerably lower if impurities are present in the sample, since the melting then takes place over a temperature range instead of at constant temperature. The heat content for the solid is thus higher than that for the pure substance at all temperatures above the melting point of the eutectic formed between the substance and the impurities, and becomes more and more markedly so as the freezing point is approached. The heat content of the liquid state is on the other hand relatively unaffected by a

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[1] Guggenheim Fellow, Bayerische Akademie der Wissenschaften, Munich, Chemisches Institut der Universität, Frankfurt am Main, and Bureau International des Étalons Physico-chimiques, Brussels.

[2] Tammann, "Krystallisieren und Schmelzen," Leipzig, 1903, p. 14.