An Improved Method of Purifying Europium*

BY HERBERT N. McCOY

WITH NOTES BY ARTHUR S. KING ON ITS "SPECTROSCOPIC PURITY," BY LINUS PAULING ON THE "ISOMORPHISM OF EUROPOUS SULFATE WITH STRONTIUM AND BARIUM SULFATES," AND BY G. P. BAXTER AND F. D. TUEMMLER ON THE "ATOMIC WEIGHT OF EUROPIUM"

The method described earlier[1-3] for the separation of europium from other rare earths leads easily to a fairly complete recovery of this element from monazite residues and gives, after a sufficient number of repetitions of the process, substantially pure europium. However, the material obtained after eight or nine successive precipitations as sulfate still contains a few tenths of a per cent. of impurities—principally neodymium, samarium and gadolinium. Doubtless any required degree of purity might be obtained by further repetitions of the process. The method though fast compared with fractional crystallization is rather laborious when the object is the preparation of material spectroscopically free from other rare earths.

The new process here described leaves little to be desired in the matter of speed, convenience and purity of product obtained. It depends upon the fact that a concentrated solution of europous chloride containing up to 30% of other rare earths gives with concentrated hydrochloric acid a crystalline precipitate of europous chloride dihydrate, $EuCl_2 \cdot 2H_2O$. This precipitate is practically free from other rare earths. By aid of this reaction in three days' time 125 g. of exceptionally pure europium oxalate was prepared. The progress of purification is shown by the following observations.

After one precipitation as europous chloride, no absorption bands of the other rare earths could be seen in a 10-cm. layer of the concentrated solution. The rare earths extracted from the filtrate showed strong bands of neodymium and weaker ones of samarium. After a second precipitation the rare earths from the filtrate showed in addition to europium only the strongest bands of neodymium (λ 5205 and λ 5522, and the group at λ 5726 to 5782) and these were very faint. After a third precipitation, europium recovered from the filtrate showed no bands of the other rare earths. The method is therefore very effective in the purification of europium. How effective was shown by an examination of its emission spectrum.

This work was kindly undertaken by Dr. Arthur S. King, who has made exhaustive studies of rare earth spectra.[4]

Dr. King states: "A spectrogram made with the 15 foot [454 cm.] concave grating having 15,000 lines to the inch [2.54 cm.] showed the sample of europium chloride to be of high purity. An examination of the ultraviolet region where many strong lines of gadolinium normally occur showed only faint traces of the strongest of these. One or two of the strongest lines of lanthanum may be present in this region. Barium and calcium are also present."

Following this examination, which showed traces of gadolinium present and probably lanthanum and by inference also some neodymium and samarium, the whole of the material was given two further precipitations (making a total of five) as europous chloride. A new sample in the form of trichloride was examined by Dr. King who reported: "The spectrogram of this new sample made with a normal exposure (for europium) showed no lines of other rare earths. The strongest lines of neodymium, samarium and gadolinium were looked for especially but not found."

"A second spectrogram, so much overexposed as to be useless for europium, showed three or four lines of neodymium, especially the strongest at λ 4303. No samarium or gadolinium lines could be seen on this plate. By comparison with plates exposed similarly and made with europium-neodymium mixtures of known composition, the amount of the latter present in the purest europium was estimated as not more than one in 100,000. Barium and calcium are still present in noticeable amounts."

Experimental Part

The starting material was a rare earth chloride solution of density 1.35. It had been partially purified by three successive precipitations as europous sulfate.[3] About 70% of its rare earth content was europium, the remainder being mostly neodymium, samarium and gadolinium. Four

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* This article consists of four independent papers on closely related subjects. Each supplements the others to round out a research that would have been impossible without coöperation. It is a great pleasure to acknowledge my indebtedness to my collaborators.

(1) McCoy, THIS JOURNAL, **57**, 1756 (1935).

(2) *Ibid.*, **58**, 1577 (1936).

(3) *Ibid.*, 2278 (1936).

(4) King, *Astrophys. J.*, **68**, 194 (1928); **72**, 221 (1930); **74**, 328 (1931); **75**, 40 (1932); **77**, 9 (1933).

hundred ml. of this chloride solution was put in a quart (liter) bottle[5] with a few ml. of concentrated hydrochloric acid and 100 g. of 30-mesh amalgamated C. P. zinc. The bottle, tightly stoppered, was shaken vigorously by hand and from time to time was placed directly before the slit of the spectroscope for the observation of the absorption spectrum of the solution. The latter, nearly colorless at first, turned yellowish and the europium band at λ 5253 gradually faded until after thirty or forty minutes it was no longer visible. All other absorption bands of europium had disappeared also, thus showing complete reduction.[2] The solution was next decanted from the remaining zinc into a second quart bottle in an atmosphere of carbon dioxide. The second bottle was closed by a two-holed stopper carrying a 250-ml. dropping funnel and a capillary outlet for the escape of gas. Concentrated hydrochloric acid was now run in slowly from the dropping funnel, while the contents of the bottle was kept well mixed. When about 200 ml. of acid had been added crystallization of hydrated europous chloride began and reached a maximum with about 500 ml. of acid. Ninety per cent. of the europium present separated out. The somewhat warm mixture was set in a refrigerator for two or three hours. It now consisted of nearly equal parts by volume of pure white crystals with a light blue fluorescence and an almost colorless mother liquor.

In filtering the crystals, which oxidize in air with great ease, a 12-cm. porcelain funnel with cotton filter cloth was used. It was fitted with a cardboard collar extending 12 to 15 cm. above the rim of the funnel. Carbon dioxide was led into the filter and collar in a rapid stream during filtration.[6] The crystals were not washed but were sucked as dry as possible.

With care, very little oxidation occurs. If oxidation takes place the filter cake gets very hot and fumes of hydrogen chloride come off. The cake of europous chloride was dissolved in water and the solution poured into a carbon dioxide filled bottle for repetition of the whole process. The second and following operations went much like the first, excepting that less time was required for the reduction as the material was mostly in the reduced state at the start.

After five repetitions of the process, the final europous solution was oxidized with nitric acid in the presence of sufficient hydrochloric acid to form the trichloride, filtered from a trace of insoluble matter—largely carbon left from the zinc dissolved—and precipitated with a solution of oxalic acid. The yield of oxalate from 400 ml. of original solution was 125 g. This was about half of the rare earth content of the starting material.

Subsequently three further lots of material were refined in this way. Five successive precipitations of each lot as europous chloride yielded a total of about 500 g. of pure europium oxalate.

The preparation of europous chloride dihydrate for analysis and its subsequent weighing was carried out wholly in an atmosphere of carbon dioxide since the substance oxidized rapidly on exposure to air. The chloride was made as already described, and filtered, washed, and weighed in a 130-ml. filtering tube having a coarse fritted glass filter plate.

The apparatus was arranged so that the tube could be kept filled with pure dry carbon dioxide (from "dry ice"). A 10% solution of hydrogen chloride in methyl alcohol, contained in an attached dropping funnel, was used for washing the europous chloride. The alcohol and excess hydrogen chloride were finally removed by a fast stream of carbon dioxide gas while the tube and its contents were gently warmed. When the outflowing gas no longer affected congo paper the material was free from excess acid and was dry.

The outlet of the filtering tube was now closed with a rubber plug and the stopper replaced by a solid rubber stopper. The tube and contents were weighed, the crystals, 1.9165 g., were dissolved in water and made up to 250 ml. Fifty-ml. portions were analyzed for europium and chlorine. The solution was oxidized with nitric acid and the europium precipitated as oxalate, ignited and weighed as oxide. The chloride was determined in a separate portion of solution as silver chloride.

0.3833 g. of substance gave 0.2619 g. of europium oxide and 0.4301 g. of silver chloride. Calcd. for $EuCl_2 \cdot 2H_2O$: Eu, 58.7; Cl, 27.4. Found: Eu, 59.0; Cl, 27.8.

The crystals of europous chloride dihydrate could not be distinguished under the microscope from those of barium chloride dihydrate which are similarly precipitated by hydrochloric acid. The two may be isomorphous.

The carrying down of europous sulfate with barium sulfate[7] and with strontium sulfate[8] suggests that these salts may also be isomorphous. In fact the possible isomorphism of strontium and europium sulfate led Brukl to use the former to carry down the latter in extracting 12 g. of europium from a rare earth mixture by an electrolytic method closely resembling that used by Yntema.[9]

Europous sulfate, like barium and strontium sulfates, is not hydrated and is almost insoluble in water. In acids it is but little soluble except when oxidation occurs. The density of europous sulfate was determined and was found to be still greater than those of barium and strontium sulfates.

These facts made it seem desirable to discover whether isomorphism plays a part in the similarities mentioned. Dr. Linus Pauling of the California Institute of Technology kindly offered to make the examination. As the method used was not well suited to a body so readily oxidized as europous chloride, the determinations were confined to the sulfates.

The density determinations of europous sulfate were made by the use of two auxiliary liquids—tetrachloroethane and benzene. The former led to a value of 4.981 at 25°, the latter to one of 4.989 at 20°.

Report on the X-Ray Study of the Isomorphism of Compounds of Bivalent Europium and Barium

BY LINUS PAULING

The X-ray powder photographs taken during this investigation were prepared with the use of

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[5] Quart milk bottles are admirably suited for this purpose and are superior to any of the usual chemical shapes.

[6] This was supplied by 300 to 400 g. of solid carbon dioxide in a liter flask.

[7] Selwood, THIS JOURNAL, **57**, 1145 (1935).

[8] Brukl, *Angew. Chem.*, **49**, 159 (1936).

[9] Yntema, THIS JOURNAL, **52**, 2782 (1930).

CuK α radiation (λ = 1.539 Å.) filtered through nickel. The camera radius was 5.00 cm. The crystal powder was mounted on the surface of a small glass fiber; a correction for absorption in the sample was applied.

Photographs of barium sulfate, europous sulfate, and a powder formed by precipitation of a solution containing equal mole fractions of europous chloride and barium chloride with sulfuric acid were found to be closely similar in appearance. The barium sulfate photographs could be indexed on the basis of the accepted orthorhombic unit with a_0 = 8.85 Å., b_0 = 5.44 Å., and c_0 = 7.13 Å. The europous sulfate photographs show lines corresponding to an orthorhombic unit with a_0 = 8.46 Å., b_0 = 5.37 Å., and c_0 = 6.90 Å. (all ± 0.02 Å., the errors being larger than usual because of uncertainty in the correction for absorption). The space group criteria for V_h^{16}, with the orientation Pnma as in barium sulfate, are satisfied, and the intensities of corresponding lines on the two photographs are about the same. This indicates strongly that the substances are isomorphous. Verification is provided by the photographs of the powder prepared by simultaneous precipitation of europous sulfate and barium sulfate, which shows instead of the lines of the two substances but a single pattern midway between them, proving that the powder is a solid solution of europous sulfate and barium sulfate.

The density calculated from the X-ray data for europous sulfate, assuming 4 $EuSO_4$ in the unit cell, is 5.22 g./cc., in approximate agreement with the directly determined value 4.99 g./cc.

The lattice constants of europous sulfate are intermediate between those of barium sulfate and those of strontium sulfate, which also has the barium sulfate structure:

	a_0, Å.	b_0, Å.	c_0, Å.
$BaSO_4$	8.85	5.44	7.13
$EuSO_4$	8.46	5.37	6.90
$SrSO_4$	8.36	5.36	6.84

Taking 1.35 Å. as the ionic radius (for coördination number 6) of Ba^{++} and 1.13 Å. as that of Sr^{++}, we interpolate to obtain 1.17 Å. as the ionic radius of Eu^{++}. It may be pointed out that this lies closer to the value for Sr^{++} than to that for Ba^{++}.

These results give a definite answer to the question of the isomorphism of europous sulfate with barium and strontium sulfates. It is thus plain why the last two salts are effective in aiding the precipitation of the first from dilute solutions.

A part of my best europium oxalate amounting to 190 g., essentially free from all rare earth impurities, but still contaminated with traces of calcium and barium, was sent to Dr. Gregory P. Baxter of Harvard University who kindly agreed to undertake a new determination of the atomic weight of europium. A preliminary report of the results obtained follows.

Report by G. P. Baxter and F. D. Tuemmler

A preliminary determination of the atomic weight of europium has been made by analysis of europous chloride. The original oxalate was ignited and after solution in nitric acid the europic nitrate was purified by several crystallizations from concentrated nitric acid. After two precipitations of europic oxalate in the presence of half normal acid, with conversion to oxide, the latter was dissolved in hydrochloric acid and europic chloride purified by crystallization from hydrochloric acid. Spectroscopic examination gave no evidence of the presence of barium or calcium.

Attempts to prepare anhydrous europic chloride by careful dehydration in dry hydrogen chloride even in the presence of high percentages of chlorine were uniformly unsuccessful. The product contained much europous chloride, even when not fused, while fusion accentuated the difficulty.

On the other hand, if the europic chloride is carefully dehydrated and fused in a current of hydrogen chloride and hydrogen, complete reduction to europous chloride is apparently attained, and the fused material remains essentially constant in weight in dry air.

Weighed quantities of europous chloride were dissolved and allowed to oxidize in the air, in the presence of a small excess of nitric acid to prevent the precipitation of basic salt. The solutions were then compared with solutions of weighed nearly equivalent amounts of pure silver by the equal opalescence method. Pending the determination of the density of the anhydrous europous chloride the value 5.00 is assumed for the computation of the vacuum correction. The following table gives the results so far obtained.

THE ATOMIC WEIGHT OF EUROPIUM

$EuCl_2$, g.	Ag, g.	Ratio $EuCl_2$:2Ag	At. wt. Eu
2.37131	2.29571	1.03293	151.95
3.08192	2.98364	1.03294	151.95
2.81855	2.72847	1.03301	151.97
4.88930	4.73350	1.03291	151.95
	Average	1.03295	151.95

Urbain and Lacombe [*Compt. rend.*, **138**, 627 (1904)] found 151.96; Jantsch [*ibid.*, **146,** 473 (1908)], 152.04; Aston [*Proc. Roy. Soc.* (London), **A146,** 46 (1934)] from the isotopic constitution, 151.90; Hopkins and Meyers [THIS JOURNAL, **57,** 241 (1935)], 152.30. The International value has been 152.0 for some time.

Summary

1. A concentrated solution of the chlorides of the rare earths containing 70% or more of europium gives upon reduction of the latter with zinc and treatment with concentrated hydrochloric acid a crystalline precipitate of europous chloride dihydrate, $EuCl_2 \cdot 2H_2O$, practically free from accompanying rare earths.

2. By means of this reaction about 500 g. of europium oxalate has been prepared, the high purity of which is shown by spectrograms by Dr. King.

3. An X-ray examination by Dr. Pauling has established the isomorphism of $EuSO_4$ and $BaSO_4$, and therefore also of $SrSO_4$.

4. Dr. Baxter and Mr. Tuemmler have completed the purification of europium and determined its atomic weight to be 151.95.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

The Raman Spectrum and the Structure of Water

BY PAUL C. CROSS, JOHN BURNHAM AND PHILIP A. LEIGHTON

The tridymite-like structure of ice as regards the distribution of the oxygen atoms appears to be definitely established,[1] and Pauling's[2] explanation of the discrepancy between the third law and statistical entropies in ice leaves little doubt that the hydrogens are unequally spaced between the oxygens. Each four-coördinated oxygen nucleus, at 0°, has bonded at tetrahedral angles four oxygens at d = 2.76 Å., with a proton along each oxygen–oxygen axis; two chemically bonded at d = 0.99 Å. (see section III) and two "hydrogen bonded" at d = 1.77 A. Present theory, as developed by Bernal and Fowler[3] and modified by Katzoff[4] and others, considers liquid water at ordinary temperatures as having essentially a broken down ice structure, with a considerable amount of coördination still persisting through hydrogen bonding which, however, decreases with increasing temperature or addition of electrolytes. Little progress has been made beyond this qualitative picture, and to obtain further evidence on the nature and extent of coördination in water the authors have reinvestigated, using rather high dispersion, the Raman spectrum of water over a wide range of temperatures, of ice at 0°, and of deuterium oxide. The results are treated on the basis of a model consisting of coupled O—H oscillators perturbed by various types of coördination.

An empirical treatment of the perturbation forces leads to an estimate of the intermolecular frequencies which confirms their identification. For earlier measurements and their interpretation we refer to the review and bibliography of Magat[5] and to the recent paper of Hibben.[6]

I. Experimental Data

The Raman spectra were excited by the unreversed 2536.52 Å. line of a mercury–argon discharge lamp and photographed on a quartz spectrograph of 3.5 Å./mm. dispersion at 2650 Å. The water was placed in a fused silica tube of 30 mm. diameter for the work below 100°, while at higher temperatures the high pressures (up to 218 atm. at 375°) necessitated the use of a smaller bore; a 4-mm. tube with 1.1-mm. walls being employed. For frequency measurements each spectrum was partially overlaid with an iron arc spectrum. Wave lengths were corrected to vacuum.

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(1) Barnes, *Proc. Roy. Soc.* (London), **A125**, 670 (1929).

(2) Pauling, THIS JOURNAL, **57**, 2680 (1935).

(3) Bernal and Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

(4) Katzoff, *ibid.*, **2**, 841 (1934).

(5) Magat, *Ann. phys.*, **6**, 108 (1936).

(6) Hibben, *J. Chem. Phys.*, **5**, 166 (1937).