[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF ILLINOIS, AND SLOANE LABORATORY, YALE UNIVERSITY]

OBSERVATIONS ON THE RARE EARTHS. XV. A SEARCH FOR ELEMENT SIXTY-ONE

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It was first shown by the work of Moseley[2] that an element, whose atomic number, 61, places it between neodymium and samarium, is missing.

Eder[3] had postulated the existence of "eurosamarium," basing his evidence on spectroscopic data. As the name indicates, he placed it between samarium and europium. Kiess,[4] working on the infra-red spectra of the cerium group elements, found a number of lines common to both neodymium and samarium, and suggested that these may be due to the presence of the missing element.

The purpose of this investigation was to find definite proof of the existence of the element. Although the results were negative, it is felt that a brief description of materials and methods may be of value, particularly to those who may continue the search.

Materials

The element may be expected to be associated with neodymium and samarium and to be concentrated in the intermediate fractions obtained in the separation of these two earths by fractional crystallization. The materials were pure neodymium oxide, pure samarium oxide, and the oxides of intermediate fractions prepared at the University of Illinois. The pure neodymium and samarium oxides which were used in the spectroscopic tests were from the same material as that supplied to the Bureau of Standards[4] for their study of the infra-red spectra, and were known to be of a high degree of purity. The oxides of intermediate fractions used for X-ray analysis were taken from a series obtained from "Welsbach residues" and from a gadolinite series. In each case neodymium-rich and samarium-rich samples were tested. An intermediate fraction from a fergusonite series was also examined.

Arc Spectrum

Corroboration of the work of Kiess[4] was found in the examination of a small region of the ultra-violet spectrum. Five lines, 3305.8 Å., 3329.1 Å., 3342.5 Å., 3378.0 Å., and 3379.2 Å., were found, common to pure neodymium and samarium and to the intermediate fractions. It is not thought that these lines are due to either of the two elements, because they were very faint in the spectra of the pure materials and somewhat more intense in the spectra of the mixtures. The second order spectrum of the

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[1] National Research Fellow in Chemistry.

[2] Moseley, *Phil. Mag.*, **26**, 1024 (1913); **27**, 703 (1914).

[3] Eder, *Sitzber. K. Akad. Wiss. Wien*, **126**, IIa, 473 (1917).

[4] Kiess, *Bur. Standards Sci. Paper*, **18**, 201 (1922).

6.4 meter grating spectrograph at Sloane Laboratory was used for this work.

X-Ray Absorption Spectrum

Since definite proof of the existence of the element could best be found by X-ray methods of analysis, they were applied to the problem. The measurement of the secondary radiation was not attempted because of the relatively feeble spectrum obtained. The absorption method as given by de Broglie[5] and the standard primary-emission method were both used.

For the former method the X rays from a Coolidge tube were passed through a 0.4mm. layer of rare earth oxide, placed in front of the slit, to a calcite crystal, and the spectrum was recorded on a photographic plate. The K absorption limit of samarium was found very easily, but when a mixture of samarium and neodymium containing about 5% of the latter was examined, no neodymium absorption was recorded on the plate. The method was abandoned as inadequate, because the element might be expected to be present in smaller percentages.

Primary-Emission Spectrum

The usual technique was followed in photographing the primary-emission spectrum and therefore a detailed description of procedure and apparatus need not be given. It may be well, however, to record a few details of construction of the X-ray tube. A gas tube with water-cooled anode and cathode was used. The anode was made removable by means of a ground-glass joint. The rare earth oxide under examination was fused by means of a copper arc to a perforated copper plate, which was screwed to the anode. A target, prepared in this manner and filed down smooth, could be run for 20 hours or more without renewal, and was found to be much superior to one prepared by rubbing the oxide onto a roughened surface in the usual manner. A mica window, 0.02 mm. thick, was used when the L series was photographed. The tube was evacuated by a Langmuir diffusion pump and a Hyvac forepump. The source of energy was the high voltage apparatus at Sloane Laboratory. It consists of a motor-generator set (500 cycles), transformer and kenetrons.

It was found impracticable to run the tube at a voltage that was high enough to excite the K radiation of the missing element. The high energy input into the tube caused such intense local heating on the target that the surface became badly pitted; powdered oxide was blown off instantly.

The L series could be photographed successfully. Data on a typical exposure are as follows: e.m.f., 30,000 volts; current, 6 m.a.; time, 10 hours; crystal turned over 20′ of arc.

A series of tests made on artificial mixtures of neodymium and samarium

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[5] de Broglie, *Compt. rend.*, **158**, 1493 (1914).

showed that 0.1% of an impurity may thus be detected with certainty. It may therefore be concluded that the element, if present, existed in smaller amounts.

Work on the problem is being continued.

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Summary

1. Spectroscopic evidence indicates that an element, probably number 61, may be associated with neodymium and samarium.

2. X-ray analysis of samples from different sources has so far given no evidence of the presence of this element.

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A STATEMENT OF THE THIRD LAW OF THERMODYNAMICS

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Lewis and Gibson[1] state the third law of thermodynamics as follows: "If the entropy of each element in some crystalline form be taken as zero at the absolute zero, the entropy of any pure crystal at the absolute zero is zero, and the entropy of any other substance is greater than zero." The essential features of this view are embodied in the more comprehensive statement of Lewis and Randall:[2] "Every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances." In seeking the theoretical basis of the law as stated above, Lewis and Gibson conclude that the entropy of a system in any state is associated with the randomness of that state, and that perfect crystals at the absolute zero lack any sort of randomness, while non-crystalline substances possess it. Some of the questions arising from these considerations have been experimentally investigated by Gibson, Parks and Latimer,[3] and by Gibson and Giauque.[4] The results obtained in their researches make it appear very probable that the entropy of supercooled liquids at the absolute zero is in fact greater, as predicted by Lewis and Gibson, than that of the corresponding crystalline substances. That the correct ex-

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[1] Lewis and Gibson, This Journal, **42**, 1529 (1920).

[2] Lewis and Randall, "Thermodynamics, and the Free Energy of Chemical Substances," McGraw-Hill Book Company, New York, **1923**.

[3] Gibson, Parks and Latimer, This Journal, **42**, 1542 (1920).

[4] Gibson and Giauque, *ibid.*, **45**, 93 (1923).