

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

ELEMENT 87. (PRELIMINARY PAPER)¹

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The search for element 87, which was undertaken in this Laboratory a number of years ago, was confined in its earlier stages to minerals rich in the rarer alkalis. This procedure was adopted by other investigators,² and as the chemist is aware it did not lead to successful results. Allison and Murphy³ announced the detection of element 87 by a method which they termed *optico-magnetic* and for which they claimed an extremely high sensitivity. Soluble extracts from lepidolite and pollucite, prepared in this Laboratory, were sent to Dr. Allison for examination, and he reported that some of them contained comparatively high quantities of element 87. However, chemical and optical tests to which these preparations were subsequently subjected failed to reveal the presence of the missing element.⁴ This led us to the conclusion that the element in question is either absent in the minerals investigated or present in quantities so small as to warrant the search for other sources. As a basis for the work the following assumptions were formulated. (a) The element will chemically resemble its immediate congeners, at least in a general way. (b) The primary spectral lines of the element will lie in the infra-red range. This will make its spectroscopic identification impossible or doubtful until reasonably high concentrations of the element are obtained. (c) The element is not radioactive, or extremely feebly so, otherwise it would have hitherto been discovered. However, the element, if existent, may be an inactive residue from the disintegration of radioactive elements of existing series or of series long extinct.

With these assumptions in view samarskite was investigated. The particular sample used was rich in uranium, and it contained also rubidium and cesium in addition to the numerous other elements commonly present in minerals of this type.

Ten kilograms of finely ground samarskite was heated in a stream of dry

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² Baxter, *THIS JOURNAL*, **37**, 286 (1915); Dennis and Wyckoff, *ibid.*, **42**, 985 (1920); Bainbridge, *Phys. Rev.*, **34**, 752 (1929); and others.

³ Allison and Murphy, *ibid.*, **35**, 285 (1930).

⁴ Investigations in this Laboratory with the Allison-Murphy apparatus disclosed the fact that solutions of stannic chloride and rhenium chloride gave minima which were coincident with those obtained for element 87 in a solution of "crude cesium chloride" supplied to us by Dr. Allison. It is obvious that there is a possibility for the formation of the monovalent complex ions SnCl_3^+ and ReCl^+ which will approximate in weight the probable atomic weight of ekacesium.

hydrogen chloride at a temperature of about 1000°. The volatile products were converted to sulfates, and upon spectroscopic examination were found to contain potassium and rubidium; the lines of cesium were doubtful because of spectral interferences. The soluble sulfates were extracted with water, and to the solution ammonium hydroxide was added to slight excess. The precipitate, mainly hydrated ferric oxide, was removed by filtration, ignited and washed with hot water. The washings were added to the ammoniacal filtrate and the whole was evaporated to dryness and heated gently to decompose ammonium salts. The residue from this operation gave a strong spectroscopic test for all the alkali elements in addition to other elements in lesser quantities. It was dissolved in water and subjected to crystallization until eight fractions were obtained. Perchloric acid was added to the most soluble fraction. The precipitate, which showed a high concentration of potassium, rubidium and cesium, was converted to sulfate, aluminum sulfate was added and the alkalies, which were obtained as alums, were fractionated by crystallization. The least soluble alum, upon spectroscopic examination, was found to be low in potassium and high in cesium. It was ignited gently and subjected to x-ray spectrographic tests for the presence of element 87.

The x-ray spectrograph used in connection with this work was a Siegbahn vacuum apparatus of high dispersion.⁵ Suitable lines of element 87 were derived from the well-known Moseley diagram.⁶ They are as follows

$$\begin{aligned} M_{\alpha_1} &= 4.517 \text{ \AA.} \\ L_{\alpha_1} &= 1.026 \text{ \AA.} \\ L_{\alpha_2} &= 1.038 \text{ \AA.} \\ L_{\beta_1} &= 0.853 \text{ \AA.} \\ L_{\gamma} &= 0.944 \text{ \AA.} \end{aligned}$$

When the sample was subjected to excitation, all of the lines just enumerated were observed. Other suitable lines were not used because of serious interferences. The L_{α_1} line is overlapped by the W L_{γ_4} and Au $L_{\beta_{10}}$. However, the absence of tungsten and gold in the sample was proved by a subsequent x-ray spectrographic test dependent upon the non-appearance of stronger lines of these elements. A possible interference with the L_{β_1} line may be caused by the second order K_{β_2} line of tin, where $\lambda = 0.425 \text{ \AA.}$ While this is improbable because of the voltage used (28–30 k. v.), additional precaution was taken and the absence of tin in the sample was established by the absence of lines in other ranges.

Of the various lines L_{β_1} was measured accurately and its value was found to be 852.4 X.U.⁷

⁵ For the use of this apparatus we are greatly indebted to Professor F. K. Richtmyer of the Department of Physics.

⁶ See *Phil. Mag.*, [6] **26**, 1024 (1913); *ibid.*, **27**, 703 (1914); Siegbahn, "The Spectroscopy of x-Rays," Oxford Univ. Press, London, 1925, p. 112.

⁷ This was carried out by M. T. Jones of the Department of Physics.

The evidence thus obtained leads us to conclude that element 87 occurs in samarskite. Furthermore, this element yields a chloride volatilizable at 1000° , and its alum is the least soluble in the alkali series. A name for the element will not be announced until additional confirmatory data are obtained.

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NOTES

Objections to a Proof of Molecular Asymmetry of Optically Active Phenylaminoacetic Acid.—In a recent paper¹ G. L. Clark and G. R. Yohe have given what purports to be "a proof of molecular asymmetry in optically active phenylaminoacetic acid." It is the purpose of the present note to point out that the molecular asymmetry of this compound, however likely it may be, by no means follows from the arguments or evidence adduced in the above paper.

The procedure employed by Clark and Yohe is the following. Using the density and x-ray data, they first decide that crystalline *l*-phenylaminoacetic acid is orthorhombic and contains four molecules in the unit of structure. They then remark: "These considerations alone would narrow down the possible space groups to the following: C_{2v}^1 , C_{2v}^2 , C_{2v}^3 , C_{2v}^4 , C_{2v}^5 , C_{2v}^6 , C_{2v}^7 , C_{2v}^8 , C_{2v}^9 , C_{2v}^{10} , Q^1 , Q^2 , Q^3 , Q^4 ." x-Ray data are then examined with reference to the abnormal spacing requirements of the space groups in this list, and all of these particular space groups eliminated except C_{2v}^5 . "The conclusion is, therefore, that *l*-phenylaminoacetic acid belongs to space group C_{2v}^5 , which by its purely geometric derivation demands four asymmetric molecules per unit cell" (there are four equivalent positions in the general case in C_{2v}^5 and there are no special cases of equivalent positions); "Thus the classical theories of van't Hoff and Le Bel are confirmed, for here an examination has been made of an optically active substance, and the space group of the crystal requires that the molecule be asymmetric."

The main error in the above argument is the initial restriction of the possible space groups to the fourteen listed. The datum, four molecules in an orthorhombic unit, leaves for consideration not fourteen but fifty-six space groups, *i. e.*, all of the orthorhombic space groups except C_{2v}^{19} , Q_h^{24} and Q_h^{27} ; for all orthorhombic space groups except these three afford one or more ways of arranging four molecules in a unit provided the molecules are not assumed to be asymmetric.² Thus, although their investiga-

¹ G. L. Clark and G. R. Yohe, *THIS JOURNAL*, **51**, 2796 (1929).

² For example in the space group C_{2v}^{11} , 4 equivalent molecules possessing a plane of symmetry can be placed at $(u, 0, v)$, $(\bar{u}, 0, v)$, $(\frac{1}{2} + u, \frac{1}{2}, v)$, $(\frac{1}{2} - u, \frac{1}{2}, v)$ or again at $(0, u, v)$, $(0, \bar{u}, v)$, $(\frac{1}{2}, \frac{1}{2} + u, v)$, $(\frac{1}{2}, \frac{1}{2} - u, v)$; in the same space group equivalent molecules possessing a digonal axis can be placed at $(\frac{1}{2}, \frac{1}{2}, u)$, $(\frac{3}{2}, \frac{3}{2}, u)$, $(\frac{1}{2}, \frac{3}{2}, u)$,