

and  $(\text{OH})^-$ . The positively charged hydrogen and potassium combined with the negative oxygens are not ionized, while the negatively charged hydroxyl combined with the predominatingly negatively charged oxygen ionizes. These relations may be shown to hold generally. To go a step farther, and following Werner,<sup>1</sup> it may be stated that compounds of the first order do not ionize, but must go over into compounds of higher orders before ionization may appear.

An attempt is made in this paper to show the method by which the theoretical views of chemical structure based upon the classifications developed with the electron conception of valence may be used in connection with the classification based upon the relations founded on Werner's theory. It is manifestly impossible to enter into a systematic development in detail in a paper such as this. Instead, a few fundamental relations have been chosen and explained by means of typical compounds. A study of Werner's "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie" on the basis of these relationships will show a large number of applications and extensions of these views to related compounds. It is believed that the views developed here and explained in connection with Werner's classifications add certain ideas to the latter, and especially bring out, perhaps in ways not evident before, a connection between the valence structures of inorganic and organic compounds. As a first exposition of these views it is to be expected that uncertainties and questionable points with regard to individual compounds and perhaps to some of the generalizations will appear, but on the whole, the further development of the views outlined appears to promise useful classifications of the compounds of inorganic chemistry as a branch of chemistry in general.

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[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

## A SEARCH FOR AN ALKALI ELEMENT OF HIGHER ATOMIC WEIGHT THAN CESIUM.

By GREGORY PAUL BAXTER.

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Two years ago the writer was fortunate enough to secure a considerable quantity of pollucite, which was obtained in the Paris, Maine, region. The material contained, approximately, 33% of cesium, rubidium and potassium oxides, chiefly cesium oxide, besides about 2% of lithium and sodium oxides. Through the assistance of Mr. C. C. Wallace the bases were extracted from the mineral by fine grinding and digesting with concentrated nitric acid. Treatment of the silicic acid residue with hydrofluoric acid showed that the extraction with nitric acid was very nearly complete.

<sup>1</sup> *Loc. cit.*, p. 89.

The nitric acid extract was evaporated until a very considerable proportion of the cesium nitrate separated as such. From the mother liquor the aluminum was precipitated with an excess of ammonia. The filtrate was then evaporated to dryness, and the residue was freed from ammonium nitrate by ignition. The cesium nitrate was then purified further from sodium nitrate by two crystallizations. The final yield was somewhat over 3.5 kg. of fairly pure cesium nitrate.

With so large a quantity of this rare substance, it seemed well worth while to examine it carefully for the presence of an unknown alkali element of higher atomic weight, although Richards and Archibald<sup>1</sup> have already made such a search, unsuccessfully, with a much smaller quantity of material. Therefore, the whole quantity was subjected to a prolonged fractional crystallization of the nitrate according to the usual plan, since it seemed likely from the solubilities of the nitrates of the alkalis that the nitrate of any alkali metal of higher atomic weight than cesium would be the least soluble of all. After 18 series of crystallizations the least soluble fraction, which contained about 3 g. of cesium nitrate, and the extreme mother liquor, were carefully examined. The mother liquor, besides containing a very large proportion of sodium with much lithium, contained also rubidium, potassium and thallium.<sup>2</sup> Some of these elements may owe their origin in this material to the presence of a small quantity of lepidolite in the pollucite. The quantities of potassium, rubidium and thallium were, however, so small that they could not be detected spectroscopically in the original mineral.

The flame spectrum of the extreme crystal fraction was compared visually with that of one of the large intermediate fractions and no line could be seen in the spectrum of one which was not present also in that of the other. The spark spectrum of these fractions in the visible and ultraviolet regions also was examined by photography with a Féry quartz spectrograph, by placing the chloride between platinum electrodes. Here again, the spectrum was identical with that of one of the intermediate fractions.

Furthermore, the radio-activity of the least soluble fraction was investigated by means of a sensitive, gold-leaf electroscope, and the rate of discharge of the electroscope was found not to be accelerated in the least by the crystals. The same result was obtained with the original pollucite and with the residues obtained from the extreme mother liquor.

Finally the atomic weight of the least soluble fraction was determined through the chloride by Mr. O. J. Stewart.<sup>3</sup> The nitrate was changed

<sup>1</sup> *Proc. Am. Acad.*, 38, 449 (1903).

<sup>2</sup> Both H. L. Wells and T. W. Richards found thallium as an impurity in cesium material. *Proc. Am. Acad.*, 38, 449 (1903).

<sup>3</sup> Mr. Stewart carried out this experiment at the close of two years' continuous experience in the exact analysis of chlorides.

to chloride by several evaporations with an excess of hydrochloric acid in a quartz dish. Then the chloride was twice crystallized from a cold solution by saturating with hydrochloric acid gas, with centrifugal drainage of the crystals in each case. As the purified product weighed less than a gram, only one analysis was made. The salt was fused in an atmosphere of dry hydrochloric acid gas in a platinum boat contained in a quartz tube. It was bottled in the Richards "bottling apparatus" and its weight, in vacuum, was found to be 0.72285 g. After solution in water it was precipitated with an equivalent amount of silver, 0.46336 g. (in vacuum) of the latter substance being found to be necessary. When an excess of silver nitrate was added and the precipitate collected and weighed, 0.61583 g. (fused, in vacuum) of silver chloride was obtained. From the amount of silver necessary, the atomic weight of the specimen is computed to be 132.84 ( $\text{Ag} = 107.880$ ;  $\text{Cl} = 35.457$ ), while the silver chloride corresponds to an atomic weight of 132.79. The average result is 132.82, a value essentially identical with the value chosen by the International Committee upon Atomic Weights, 132.81, which depends chiefly upon the work of Richards and Archibald.

It is certainly obvious that the foregoing experiments give no indication of the existence of an unknown alkali element.

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CAMBRIDGE, MASS.

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## A METHOD OF DETERMINING THE HYDRATES FORMED BY A SALT.

By H. W. FOOTE.

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It is a well-known fact that the addition of sulfuric acid in sufficient quantity to the saturated solution of a hydrated salt with which the acid does not react, will cause the salt to crystallize, either as a lower hydrate or in the anhydrous condition. As an illustration, Taboury<sup>1</sup> has shown recently that beryllium sulfate yields the dihydrate when crystallized from a solution containing two volumes of concentrated sulfuric acid, although the tetrahydrate is the form crystallizing from water. This property of producing a lower hydrate is not peculiar to sulfuric acid alone, for the same effect may be produced by dissolving any other substance, provided it is sufficiently soluble and does not react chemically. Van't Hoff<sup>2</sup> has shown, for instance, that magnesium sulfate crystallizes with only four molecules of water instead of with seven, in the presence of a

<sup>1</sup> *Compt. rend.*, **159**, 180 (1914).

<sup>2</sup> *Sitzungsber. K. Akad. Wiss.* (Berlin), **1899**, 340.