TABLE III.

Series No.	$HClO_4$.	$Hg_2(ClO_4)_2$.	$E_{obs.}$[1]	E_0 (volt).
1	0.0817	0.002750	0.77770	0.78960
		0.001375	0.76880	0.78960
			Av.,	0.78960
2	0.0817	0.000550	0.75685	0.78945
		0.000275	0.74795	0.78945
			Av.,	0.78945
3	0.0236	0.000550	0.79200	0.79270
		0.000275	0.78315	0.79275
			Av.,	0.79273
4	0.0118	0.0001062	0.78893	0.79293
		0.0000531	0.78000	0.79290
			Av.,	0.79292
5	0.0059	0.0001062	0.80588	0.79220
		0.0000531	0.79700	0.79220
			Av.,	0.79220
Average of Series 3, 4, and 5				0.7926

Conclusions.

(1) The fair agreement of the E_0 values, with the exception of those with 0.0817 M $HClO_4$, seem to justify the adoption for dilute solutions of the rule, proposed by Adams and Rosenstein with reference to the degree of dissociation of bi-univalent salts.

(2) The best value for the potential of the mercurous electrode is —0.7928 v. (av. of Series 3 and 4).

(3) From the e. m. f. measurements of concentration cells no regular deviations from the theoretical value were observed, from which it may be concluded that there is no appreciable dissociation, of Hg_2^{++} into Hg^+ even in very dilute solutions with reference both to the perchloric acid (0.0059 M) and to the mercurous perchlorate (0.0000531 M).

Finally, I wish to express my indebtedness, for many helpful suggestions, to Professor G. N. Lewis and Doctor E. Q. Adams.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ARIZONA.]

THE VANADATES OF BERYLLIUM.

BY PAUL H. M.-P. BRINTON.

Received September 8, 1916.

In the course of a general study of vanadates Berzelius[2] prepared what he describes as a yellow, neutral, difficultly soluble, and pulverulent

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[1] Averages of $E_{obs.}$ of Table II.

[2] *Pogg. Ann.*, **22**, 58 (1831).

salt, by the addition of ammonium vanadate to a solution of a beryllium salt. He made no analysis of the substance, and assigned no formula. The only other mention of any vanadate of beryllium is made by Tanatar and Kurovski,[1] who by the action of sodium vanadate on beryllium chloride solution obtained a yellow amorphous precipitate which contained 47.28% of V_2O_5. Another precipitate obtained by using beryllium, nitrate in place of the chloride contained 25.4% V_2O_5 and 46.3% BeO; differing from the one before mentioned in being of somewhat lighter color. The compositions of these substances are said to correspond to formulas of the following types: $x\mathrm{BeCl_2}.y\mathrm{Be_3(VO_4)_2}.z\mathrm{BeO}$ and $x\mathrm{Be(NO_3)_2}.y\mathrm{Be_3(VO_4)_2}.z\mathrm{BeO}$.

During the progress of an investigation[2] of certain general properties of beryllium salts, opportunity was offered for some study of the vanadates of beryllium, and the results of these experiments are here recorded.

A solution of ammonium vanadate, made by dissolving vanadium pentoxide in concentrated ammonium hydroxide and evaporating to small bulk, was added to a dilute solution of beryllium nitrate. The latter was, of course, acid in reaction, owing to hydrolysis, and there was no precipitate on mixing the two solutions. Ammonium hydroxide was added drop by drop until a yellow precipitate formed, and this increased with every drop of the hydroxide. The precipitate, after drying for a week over sulfuric acid in partial vacuum, was analyzed by methods which will be discussed later. The results led to a formula approximately expressed by $4\mathrm{BeO}.\mathrm{V_2O_5}.6\mathrm{H_2O}$. Subsequent trials in which the conditions of precipitation were varied gave precipitates in which the ratio $\mathrm{BeO}/\mathrm{V_2O_5}$ went to about 4.3, while the molecules of water varied from 3.1 to 9.7. It is evident that the products of such precipitations are simply basic mixtures of variable proportions, and do not represent pure compounds.

The ratio 4 for $\mathrm{BeO}/\mathrm{V_2O_5}$ differs considerably from that of Tanatar and Kurovski, who obtained a figure of about 13. If they precipitated in the presence of an excess of beryllium salt the variance is easily explained, for my investigations have shown that the ratio of base to acid in such cases can go as high as 60 : 1—in fact, there is no limit to the basicity under these conditions. If the precipitates were obtained in the presence of excess of vanadate the matter is not so easily explained, but in this event it is probable that the difference in composition is due to varying degrees of washing. It was found that the washings from the yellow precipitates, although apparently colorless, none the less contained notable quantities of the vanadate which gave a very distinct yellow color upon concentration by evaporation. From this it is easy to see how the mixtures could become more basic by long-continued washing.

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[1] *J. Russ. Phys.-Chem. Soc.*, 41, 813 (1909).

[2] This investigation will be the subject of a later paper.

It was evident that a normal beryllium vanadate was not to be obtained by precipitation with a soluble vanadate, so other means were tried for the preparation of such a compound. With the idea of obtaining an orthovanadate, beryllium hydroxide and vanadium pentoxide were taken in the molecular ratio of 3 : 1. A little of this mixture was boiled with water for an hour, and the yellow solution was filtered from the undissolved residue. Upon cooling the clear yellow filtrate became turbid. Set to evaporate on the water bath, the solution again became clear, and when considerably concentrated it still remained clear after standing in the cold overnight. Evaporation was continued until a deep orange-red, syrupy liquid was obtained, and this, after standing in the cold for two days, set to a solid mass of fascicular crystals. Upon repeating the above experiment with larger quantities of material—6 g. of the mixed oxides, boiled with three successive liters of water—and evaporating to about 40 cc., it took nine days before any separation of crystals took place. At the end of that period the whole had set to a mass of dark yellow crystals, which seemed to get a little darker on standing. The mass was so hard that it was difficult to scratch out a sample with a knife, and it evidently consisted of crystals of two colors, yellow and brown. Upon adding alcohol to some of the crystal mixture the whole surface was converted to a uniform yellow crystal mass.

A rough preliminary analysis of a small portion of the heterogeneous mass indicated that there was probably present a normal metavanadate instead of an orthovanadate, and this metavanadate had either three or four molecules of water of crystallization, as well as a slight excess of beryllium oxide. The analysis was not regarded as very reliable, and it is not worthy of record. It suggested two points, however: that equimolecular weights of the two oxides should be taken to boil together, as that since alcohol was capable of transforming the surface of the heterogeneous mass to fine, yellow crystals, it might be able to precipitate out these yellow crystals from the concentrated syrupy liquid, and these crystals might then be free from basicity.

Equimolecular proportions of beryllium hydroxide and vanadium pentoxide were boiled with water as before, the yellow liquid freed from insoluble residue by filtration, and evaporated to an orange-red syrup. This hot syrup was then poured into a large volume of 95% alcohol. A copious separation of lemon-yellow particles immediately occurred, and after standing twelve hours a thick layer of yellow crystals had settled to the bottom of the dish. Under the microscope the crystals appeared as perfectly homogeneous, yellow, waxy plates. Later attempts in which alcohol was added to a more dilute solution furnished larger crystals of more definite form, and it could then be seen that there were really two sets of crystals; the main mass consisting of particles of about

0.25 mm. average diameter; but scattered among these were a few little flat, tabular crystals, the largest of which did not exceed 0.05 mm. in width or length. These surely did not make up as much as 1% of the total mass. The main crystals are evidently isometric, being cubes modified by an octohedron. The polar angle gives a value of 54° 46′, the theoretical value being 54° 44′. The cube face in contact with the glass does not show the octohedral modifications. The upper horizontal face is, in nearly all cases, characterized by a quadrangular embayment, or negative development. This feature being developed on only one face of the cube suggests a tetragonal habit, but the values given above for the polar angle seem to prove conclusively that the crystals are isometric. The embayments, then, would appear to result from physical position only, and not from any crystallographic consideration. Thin fragments of these crystals do not polarize light, but the larger tabular crystals, found scattered among the large ones, do polarize light, and seem to show an orthorhombic habit. One of these little crystals was mounted on the goniometer, but, although six faces in the prismatic zone gave signals, they were too irregular to yield satisfactory measurements. For the crystallographic measurements, which were made with a two-circle Goldschmidt goniometer, I am indebted to Prof. F. N. Guild, of the University of Arizona.

Whether or not these very small crystals were the same in substance as the larger ones cannot be said. Making up as small a percentage of the whole as they did, it is certain that they could not have very much effect on the analytical results, and it was physically impossible to isolate enough of the little particles to make an independent analysis of them.

Several batches of the yellow crystals were made at different times, and the following analyses were made on three different lots. The results show clearly that the salt is a normal beryllium metavanadate tetrahydrate, a compound which has not heretofore been prepared.

$Be(VO_3)_2.4H_2O$.

	Calculated.	Found.		
BeO	9.00	8.44	9.74	9.18
V_2O_5	65.22	66.60	65.38	66.86
4 H_2O	25.78	24.96	24.88	23.96

The material represented by the first analysis was crystallized from water, the other two by precipitation with alcohol. The amounts used for analysis in the first two samples were small, and in view of the somewhat unsatisfactory method of separation used, the results are perhaps as concordant as might be expected. The third analysis was made on a good-sized sample, and is in all respects the most reliable. The ratio of BeO : V_2O_5 in this analysis is 1 : 1.002, and this may be taken as conclusive proof that we are dealing with a normal metavanadate of beryllium, with four molecules of crystal water, though a little of the latter is evidently lost with comparative ease.

Some difficulty was experienced in finding a method suitable for the exact, quantitative separation of beryllium and vanadium in the scheme for analysis. Attempts to remove the vanadium first, as lead vanadate, were unsuccessful, for it seemed that a concentration of acetic acid sufficient to prevent the co-precipitation of beryllium caused incompleteness in the precipitation of lead vanadate. The method finally adopted was essentially that of Noyes, Bray and Spear.[1] It was, however, necessary to redissolve the first precipitate of basic beryllium carbonate in nitric acid, and to repeat the precipitation under pressure. Occluded sodium salts were removed by again dissolving the basic carbonate in nitric acid, and making final precipitation with ammonium hydroxide. After ignition and weighing, the residue was dissolved in sulfuric acid, and the traces of vanadium determined by titration with permanganate, after reduction by sulfur dioxide. The final filtrate from the beryllium precipitation was treated with sulfuric acid, evaporated to fumes, diluted, reduced by sulfur dioxide, and titrated with potassium permanganate for the determination of the main portion of the vanadium. It should be mentioned that this filtrate was warmed for an hour before the sulfuric acid was added. This treatment usually caused a slight separation of beryllium hydroxide, which was filtered off and added to the main portion. This little precipitate seemed pure white, but if it did contain any vanadium compound this would be corrected for by the determination of the vanadium in the ignited beryllium oxide. The percentage of water of crystallization was taken by difference, having first made sure that there was no alcohol of crystallization.

The approximate solubility of the beryllium metavanadate tetrahydrate was determined by agitation of the fine crystals in a sealed test tube for five days, in a thermostat at 25°. In the filtrate the vanadium was determined by titration, and the solubility thus calculated was found to be one part per thousand of water at this temperature. In hot water the crystals are readily soluble, and on cooling there is a strong tendency toward supersaturation. In pyridine the solubility seems to be of the same order as that in water. The crystals are practically insoluble in chloroform, ether, and absolute alcohol.

The specific gravity of the metavanadate, determined by suspension in methylene iodide diluted with benzene, was found to be 2.273.

The crystals lose water slowly, but continuously, over sulfuric acid, but no definite end point of dehydration could be obtained.

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[1] THIS JOURNAL, 30, 481 (1908).

Summary.

It has been shown that basic mixtures, and not chemical compounds, are obtained by the addition of soluble vanadates to solutions of beryllium salts.

A new compound, beryllium metavanadate tetrahydrate, has been prepared, and its properties described.

TUCSON, ARIZ.

THE ARSENATES OF LEAD.

[SECOND PAPER.]

EQUILIBRIUM IN THE SYSTEM PbO, As_2O_5, H_2O.

BY C. C. MCDONNELL AND C. M. SMITH.

Received October 4, 1916.

In a preceding article[1] we showed that trilead arsenate, although spoken of freely in the literature, is not so easily produced as is ordinarily believed. Double decomposition between soluble lead salts and soluble arsenates rarely gives a product of theoretical composition, and the action of excess ammonia on dilead arsenate leads to the formation of a basic compound, as was first recorded by Tartar and Robinson.[2] These facts suggested that trilead arsenate is relatively unstable and capable of existing only under very limited conditions. In order to clear up this point the following phase rule study was undertaken.

The three component system PbO, As_2O_5 and H_2O can easily be investigated as far as mono- and dilead arsenates are concerned, but the system as such cannot be followed beyond dilead arsenate, owing to the insolubility of lead hydroxide. This necessitates the use of some other base to produce alkalinity. Ammonia seemed particularly suitable for this purpose, since it is easily prepared free from carbon dioxide, has practically no solvent action on lead compounds, and does not form double salts under conditions such as obtained in these experiments. Then, too, it is of especial interest since its action on dilead arsenate has long been considered the best means of producing trilead arsenate, as first stated by Berzelius.[3]

The use of ammonia in such a system introduces a fourth component, but by keeping its concentration constant one degree of freedom is destroyed, and the system will behave like a three-component one. (Owing to the low concentrations employed, we are justified in the assumption that the volume changes were nil or insignificant.)

The experiments were carried out in the following manner: Pure ammonia water was prepared (by distilling concentrated C. P. ammonia water over barium hydroxide to remove CO_2, and absorbing the evolved

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[1] THIS JOURNAL, 38, 2027 (1916).

[2] *Ibid.*, 36, 1848 (1914).

[3] *Ann. chim. phys.*, [2] 11, 229 (1819).