

double fluoride can thus be avoided and the operation carried out in small volume. The precipitation of the arsenic sulfide is complete and rapid in the cold.

PHILADELPHIA, PENNSYLVANIA.

[CONTRIBUTION FROM THE BUREAU OF STANDARDS, U. S. DEPARTMENT OF COMMERCE.]

THE CO-PRECIPITATION OF VANADIC ACID WITH AMMONIUM PHOSPHOMOLYBDATE.¹

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Received October 6, 1921.

1. Introduction.

In 1912 there was developed in this laboratory a method for the determination of vanadium in which this element was separated from other materials by co-precipitation with ammonium phosphomolybdate. In the paper³ describing this method no details of the mechanism of this reaction were given. The purpose of the present paper is to discuss an investigation of the mechanism of the co-precipitation of vanadic acid with the ammonium phosphomolybdate in order to define better the conditions upon which the success of the procedure as an analytical method depends and, incidentally, to throw light upon the formation of vanado-phosphomolybdates and to indicate that a simple relation exists among the many members of this class of so-called "complexes."

The method, as published, is in brief outline as follows. The hot nitric acid solution containing the vanadium as vanadic acid is nearly neutralized with ammonium hydroxide, and phosphorus (as sodium phosphate) is added in an amount at least ten times that of the vanadium suspected to be present. The phosphorus is then precipitated as ammonium phosphomolybdate and the resulting precipitate is washed with ammonium hydrogen sulfate solution. Finally, the vanadium is determined by dissolving the precipitate in conc. sulfuric acid, reducing with hydrogen peroxide, and titrating with permanganate. Except for the changes of conditions made necessary in order to study the problem advantageously, this general method was adhered to in all the experiments that follow.

2. Preliminary Study.

It was mentioned in the former paper that the color of the ammonium

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² The experimental work reported in this paper was carried out in 1912. Publication of the results has been delayed on account of the resignation of the authors since that time.

³ "A Rapid Method for the Determination of Vanadium in Steels, Ores, etc., based on its Quantitative Inclusion by the Phosphomolybdate Precipitate." *Bur. Standards, Tech. Paper*, 8. J. R. Cain and J. C. Hostetter, *J. Ind. Eng. Chem.*, 4, 250 (1912).

phosphomolybdate containing vanadium varies with the ratio of phosphomolybdate to vanadic acid (or, more conveniently expressed, of phosphorus to vanadium) at the time of precipitation. With small amounts of phosphorus and large amounts of vanadium the color of the resulting precipitate is deep orange or even dark red, while with greater quantities of phosphorus (with the same amount of vanadium) the precipitate approaches yellow as the limiting color. It was at first thought that this lighter color was due merely to a mixture of an ammonium vanado-phosphomolybdate with pure ammonium phosphomolybdate and, accordingly, experiments were made in order to determine which one of the numerous vanado-phosphomolybdates was present. This preliminary test consisted of a precipitation of the same quantities of phosphomolybdate in the presence of varied amounts of ammonium vanadate. If but one ammonium vanado-phosphomolybdate were formed under these conditions the precipitates formed from all solutions containing more than the required amount of vanadium would have the same color. Instead of possessing one color, however, the successive precipitates showed a progressive change from the very light orange of the one formed in the presence of little vanadium to the deep orange of that containing most vanadium. This made it evident that the resulting precipitate is not of constant composition, *i. e.*, it is not a chemical compound as the term is commonly used. Because of the indication afforded by this preliminary test it was decided to study the phenomenon quantitatively.

3. Quantitative Study.

A. Reagents.

The following solutions were prepared.

Sodium Phosphate Solution.—This was made up to contain about 124 g. of sodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, per liter of solution. It was standardized (1) by evaporating known volumes to dryness and igniting the residue to sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$, and (2) by precipitating as ammonium magnesium phosphate, and weighing finally as magnesium pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$. The value of 1 cc. of the solution was found to be by (1), 11.53 and by (2), 11.52 mg. of phosphorus.

Ammonium Metavanadate Solution was so prepared that 1 cc. was approximately equal to 0.5 mg. of vanadium. This solution was frequently standardized by titration with permanganate after reduction with hydrogen sulfide, sulfur dioxide, or hydrogen peroxide.⁴

Potassium Permanganate Solution was 0.01 *N*, and was standardized against sodium oxalate.

Molybdate Reagent was made up according to Blair.⁵

Ammonium Molybdate Solution contained 60 g. of the salt per liter.

⁴ "The Reduction of Vanadic Acid in Concentrated Sulfuric Acid Solution by Hydrogen Peroxide and by Persulfates." J. R. Cain and J. C. Hostetter, *THIS JOURNAL*, 34, 274 (1912).

⁵ Blair, "The Chemical Analysis of Iron," 8th ed., p. 62.

B. The Ratio of Vanadium to Phosphorus in the Solid Phase.

Series One. Vanadium Constant, Phosphorus Varied.—A study of the ratio of phosphorus to vanadium in the solid phases, when constant amounts of vanadium and varied amounts of phosphorus are present, was carried out as follows. Equal volumes of the ammonium vanadate solution were measured into flasks; ammonium nitrate in definite amounts and sodium phosphate solution in gradually increased quantities were then added to the contents of the successive flasks. The different solutions were made up to equal volumes with water and then, after adjusting the temperature, the phosphorus was precipitated by molybdate reagent. The temperature of the phosphorus-vanadium solution could easily be adjusted so that after the addition of molybdate reagent the final temperature was approximately 65°. The phosphomolybdate was allowed to settle out and the amount of vanadium which was carried down was determined, as mentioned above, by reducing with hydrogen peroxide and titrating with permanganate. Other details are given in the tables.

TABLE I.
PRECIPITATION OF VANADIUM. VANADIUM CONSTANT; PHOSPHORUS VARIED.
Temp., 65°. 5 g. of Ammonium Nitrate Used in All Experiments.

Vanadium present. Mg.	Total volume. Cc.	Phosphorus added. Mg.	Vanadium pptd. Mg.	Phosphorus added. Mg.	Vanadium pptd. Mg.
With 50 g. of Molybdate Reagent.					
			20.1 mg. of Vanadium present; 100 cc. of Molybdate reagent; 190 cc. Total Volume.		
4.66	108.7	2.30	1.40	5.18	6.18
		4.60	2.41	5.76	6.01
		9.21	3.47	11.52	10.2
		11.52	3.82	17.26	10.2
		17.28	4.32	23.04	14.5
		23.04	4.70	28.8	15.0
		34.56	4.63	34.6	16.6
		40.32	4.72	40.3	16.4
10.05	120	2.30	2.96	46.1	17.8
		5.76	4.97	51.9	17.8
		11.52	7.23	57.6	19.5
		17.28	8.53	63.3	19.3
		23.04	9.24	69.0	19.8
With 100 g. of Molybdate Reagent.					
10.05	170	25.31	9.05	74.8	19.1
		28.80	9.32	80.6	18.6
		31.10	9.24	92.1	19.3
		34.56	9.54	97.9	19.9
		36.90	9.39	103.7	18.8
		40.32	9.70	115.2	20.5
		42.7	9.44	161.3	20.8
		46.1	9.87		
		51.9	10.2		
		69.1	10.2		

After completing a series in this manner other series were run similarly but with different initial amounts of vanadium. The data so obtained are given in Table I, and shown graphically in Fig. 1.

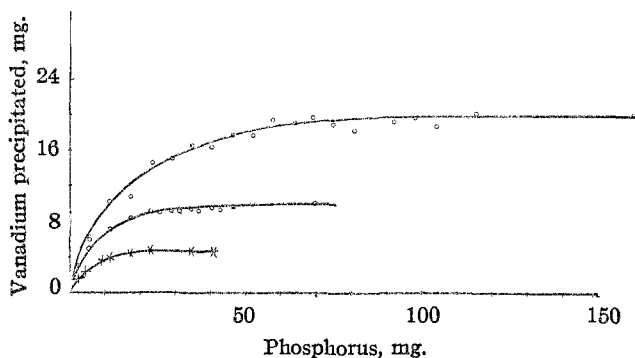


Fig. 1.

Inspection of these curves shows that under the conditions that obtain here complete precipitation is brought about by an amount of phosphorus approximately 5 times that of the vanadium. This ratio of 5:1 is only half of that which was used in the investigation described in the first paper, but the larger excess was thought to be necessary in order to insure complete precipitation under the somewhat different conditions there employed. An excess of precipitant seems to eliminate irregularities in the amount of vanadium precipitated, which sometimes occur under different conditions of temperature, acidity and especially of agitation during the actual precipitation. Thus, shaking the precipitating solution on a mechanical shaker causes less co-precipitation of vanadium than when the reagents are merely mixed and the precipitate is allowed to form and settle. This, however, is true only when the amount of phosphorus is far too low for complete precipitation. Since, in the series that follow, the amount of phosphorus was always less than that required for complete precipitation, the precipitates were allowed to settle on standing rather than shaken out on a machine.

The curves of Series 1 follow, within the experimental error, the equation $V/P = BC^m$, in which V/P is the ratio of vanadium to phosphorus in the solid phase, C the concentration of vanadium remaining in the solution, and B and m are constants. Expressing C in mg. of vanadium in 100 cc. of solution, the equation is $V/P = 0.38 C^{0.47}$. Further discussion of these curves and of the above equation will be taken up later.

Series Two. Phosphorus Constant, Vanadium Varied.—In this series, equal amounts of phosphorus were precipitated in the presence of gradually increasing quantities of vanadium. The same conditions of precipitation obtain here as for Series One except that with the higher vana-

dium concentrations the flask was shaken until an actual separation of the solid phase took place, after which the rest of the precipitate separated on long standing.

The results obtained are given in Table II and shown in Fig. 2. A comparison of the curve with the curves of Series 1 shows that they are very similar in general character,

TABLE II.

PRECIPITATION OF VANADIUM. PHOSPHORUS CONSTANT; VANADIUM VARIED.

23.4 mg. of Phosphorus, 20 g. of Ammonium Nitrate, 50 cc. of Molybdate Reagent and Total Volume of 250 cc. in All Experiments. Room Temperature.

Total vanadium. Mg.	Vanadium pptd. Mg.
4.66	4.70
10.0	9.24
20.0	15.1
25.0	19.1
50.0	29.0
100	35.3
150	41.3
200	42.0

Closer study, however, reveals the fact that when the ratio of vanadium to phosphorus becomes very high the curve of Series 2 does not rise as rapidly as would be expected.

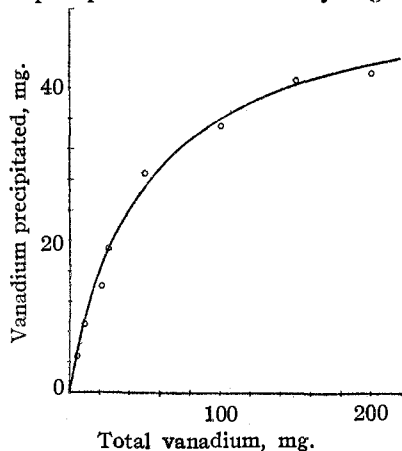


Fig. 2.

This is in accord with the well-known fact that ammonium phosphomolybdate is not precipitated at all in the presence of an exceedingly high concentration of vanadic acid. This unfortunate condition makes it impossible to extend the curve further, and hence limits the application of this method as applied to the preparation of ammonium vanado-phosphomolybdates.

It is essential to note that the color of the precipitates secured along this curve varies gradually from a light orange to a very dark orange.

This increase in color is continuous and is likewise parallel to the increasing vanadium content. Another interesting fact is that the color of the highest member of this series is very nearly that of the lowest member of a series of ammonium vanado-phosphomolybdates prepared in another manner by William Blum,⁶ specimens of which he has very kindly placed at our disposal. In color, Blum's series ran through combinations

⁶ Blum, THIS JOURNAL, 30, 1860 (1908).

of orange, red, and brown up to the highest member, which was black. Combining these two series we have then a perfect continuity in the colors possessed by the numerous ammonium vanado-phosphomolybdates. At one end of the complete series is ammonium phosphomolybdate with the ratio of vanadium to phosphorus equal to zero and at the other end ammonium phosphovanadate with this ratio relatively large. Extending from ammonium phosphomolybdate toward the other limiting compound there is probably a series of *solid solutions*, in which the relative quantities

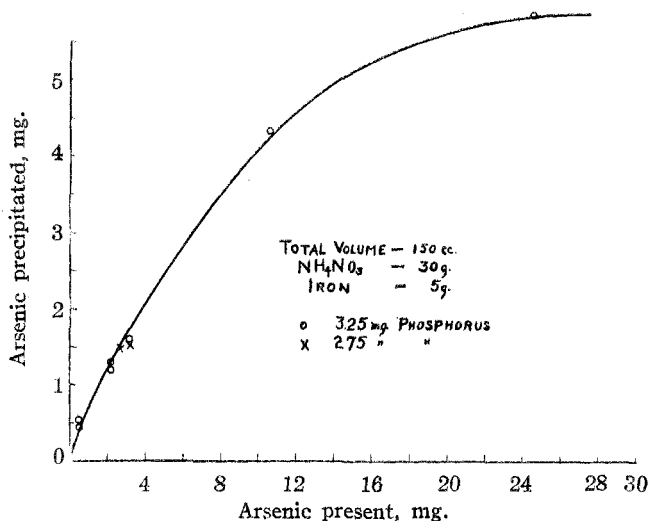


Fig. 3.

of the components can vary continuously within certain limits. This point will be referred to later.

The Co-precipitation of Arsenic with Ammonium Phosphomolybdate.—For purposes of comparison we may here insert an account of an investigation by Frank and Hinrichsen⁷ on the co-precipitation of arsenic with ammonium phosphomolybdate. The similarity between their results for arsenic and ours for vanadium is very striking. Their most complete series of experiments corresponds to that just described, namely, precipitation of arsenic with fixed concentration of phosphorus. Their results, plotted in Fig. 3, are quite comparable with those for vanadium plotted in Fig. 2. It is evident that the mechanism of the reaction in the case of arsenic is the same as that for vanadium.

Series Three. Effect of Dilution.—In this series the only condition that was varied was the concentration of the reacting substances at the time of precipitation. The total volume of the system was increased by steps from about 100 cc. to 1000 cc. The data are given in Table III and plotted in Fig. 4.

⁷ Frank and Hinrichsen, *Stahl u. Eisen*, **28**, 295 (1908).

TABLE III.

PRECIPITATION OF VANADIUM. EFFECT OF DILUTION AND OF AMMONIUM NITRATE CONCENTRATION.

Temp., 85°. 10.05 mg. of Vanadium, 23.04 mg. of Phosphorus, and 50 cc. of Molybdate.

Reagents Used in All Experiments.

Ammonium nitrate. G.	Total volume. Cc.	Vanadium pptd. Mg.
	108	9.24
	170	8.20
	200	6.42
5.0	400	4.40
	600	3.09
	800	2.23
	1000	1.71
100.0	1000	8.94

Effect of Ammonium Nitrate.—In connection with the results obtained upon the effect of dilution on the amount of vanadium carried down it

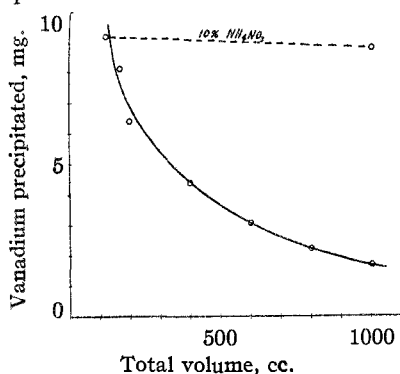


Fig. 4.

was suspected that ammonium nitrate was an essential factor in the co-precipitation. Accordingly, the precipitation of the most highly diluted system (1000 cc. in volume) was repeated with the addition of 100 g. of solid ammonium nitrate. The result was, within the experimental error, identical with that obtained when the total volume was but 100 cc. This confirmed what had been empirically established before, that ammonium nitrate counteracts the influence of dilution on the co-precipitation of the vanadic acid. The theoretical significance of this will be discussed later.

An identical effect with ammonium nitrate was observed by Frank and Hinrichsen on the co-precipitation of arsenic by ammonium phosphomolybdate. In their experiments they used 20 or 30 g. of nitrate in 150 cc. and found that the co-precipitation of arsenic was favored by the addition of this salt.

Series Four. Effect of Temperature.—The results given in Table IV show that the maximum co-precipitation occurs within the range 40°–50°. The exact curve (Fig. 5) is difficult to reproduce but each set of

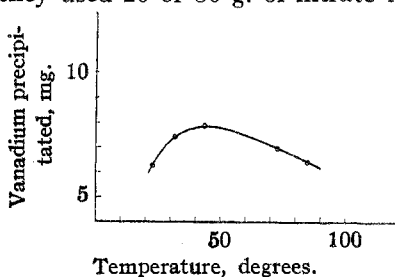


Fig. 5.

results exhibited a maximum in this region. These results are in partial accord with those of Brearley and Ibbotson⁸ who found more vanadium precipitated at the higher than at the lower temperatures. These data are not in accord with their assertion, however, that phosphomolybdates precipitated in the cold are free from vanadium, a result that is possible only under limiting conditions, as is evident from the data already presented.

TABLE IV.

PRECIPITATION OF VANADIUM. EFFECT OF TEMPERATURE.

10.05 mg. of Vanadium; 23.0 mg. of Phosphorus; 5 g. of Ammonium Nitrate; 50 cc. of Molybdate Reagent; Total Volume, 120 cc.

Temp. °C.	Vanadium pptd. Mg.
23	6.23
32	7.43
44	7.88
74	6.92
85	6.45

Series Five. Effect of Acidity.—The effect of acidity on the co-precipitation was studied by adding standardized nitric acid in gradually increased volumes to a succession of mixtures of otherwise neutral solutions of sodium phosphate, ammonium vanadate and nitrate. The precipitant was an ammonium molybdate solution prepared from the crystallized salt. The data given in Table V and presented graphically in Fig. 6 show that the maximum co-precipitation takes place in a nitric acid concentration of approximately 2 *N*. In practice this concentration is

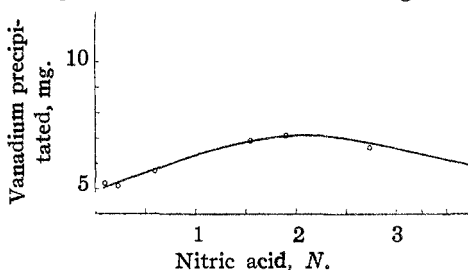


Fig. 6.

TABLE V.

EFFECT OF ACIDITY.

10.05 mg. of Vanadium; 23 mg. of Phosphorus; 2.5 g. of Molybdic Acid; 5 g. of Ammonium Nitrate; Total Volume, 170 cc. Temp., 65°.

Nitric acid. <i>N</i> .	Vanadium pptd. Mg.
0.12	5.2
0.24	5.1
0.60	5.7
1.55	6.9
1.90	7.1
2.73	6.6
3.75	5.9

⁸ Brearley and Ibbotson, "The Analysis of Steel-works Materials," 1902, pp. 164-166.

roughly secured by adding to the nearly neutral solution, containing the vanadium and phosphorus, an equal volume of the molybdate reagent as ordinarily made.

4. Discussion of Results.

A study of the curves in Series 1, 2 and 3 clearly indicates that (1) the curve showing the relation of phosphorus to vanadium in the solid phase is *logarithmic* and not linear as would be expected if the precipitate were a chemical compound; (2) with a given amount of phosphorus the amount of vanadium in the precipitate depends upon the *concentration of vanadium* initially present. The co-precipitation of the phosphorus and vanadium might be referred to as (1) an occlusion, (2) an absorption, (3) an adsorption, or (4) a partition effect. Without attempting to decide which term best describes the known facts, we shall merely call attention to the well-known fact that when any substance distributes itself between two solvents X and Y, the concentrations of the dissolved substance in the two solvents being C_X and C_Y respectively and the molecular weight of the dissolved substance in the solvent X being 20 times the molecular weight in the solvent Y, then the ratio C_X/C_Y^n is constant. Now, as shown above, the equation $V/P = 0.38 C^{0.47}$ satisfactorily represents the curves of Series 1. In this equation C is the concentration of vanadium remaining in the solution, and if the precipitate be thought of as a *solid solution* of the vanadium compound in the phosphorus compound, V/P is for practical purposes the concentration of vanadium in the solid solution. That is, $C_X/C_Y^{0.47} = 0.38$, and therefore the phenomena with which we are dealing may be described as a case of the distribution or partition of a solute (the vanadium compound) between two solvents one of which is a liquid and the other a solid. The exponent 0.47 is nearly equal to $1/2$ and hence the molecular weight of the compound when dissolved in X (*i. e.*, in solid solution) would be half as great as its molecular weight in Y (*i. e.*, in aqueous solution). Whether or not this viewpoint is the correct one can be determined only by further experimentation, but for convenience we shall refer to the phenomena as a partition effect.

Inasmuch as we are dealing then with a partition effect it is evident that the precipitation of vanadic acid by ammonium phosphomolybdate is never complete. However, we can make the residual quantity just as small as we like by a process analogous to that of extraction with immiscible solvents. If the amount of vanadium is small we can secure all but the merest trace by making the quantity of precipitant sufficiently great. When the vanadium content is high, more thorough separation is obtained by precipitating several times with smaller portions of phosphomolybdate. If conditions are carefully adjusted and the ratio of phosphorus to vanadium is at least 10, only negligible traces of vanadium will remain in the solution when precipitating from 1 to 10 mg. of this element.

The effect of ammonium nitrate upon the partition—increasing the amount of vanadic acid carried down—may perhaps be a consequence of a repressing effect upon the dissociation of the vanadium complex co-precipitated. This would be in exact accord with what has been shown by Richards on the occlusion of ferric sulfate by barium sulfate;⁹ by Richards, McClaffrey, and Bisbee, on the occlusion of magnesium oxalate by calcium oxalate;¹⁰ and by Baxter on the occlusion of molybdic acid and ammonium molybdate by ammonium phosphomolybdate,¹¹—namely, that co-precipitation in these cases is the distribution of an undissociated substance between the solution and the nascent solid. Any condition, therefore, which tends to decrease the concentration of the undissociated portion,—for instance, dilution,—tends to decrease the amount of this substance co-precipitated, and conversely.

Vanado-phosphomolybdates in General.—Taking up the subject of ammonium vanado-phosphomolybdates in general one cannot but wonder at the large number of these “compounds” that have been described. It is merely necessary to emphasize that no less than 27 of them are mentioned in Gmelin-Kraut¹² in addition to those (8 in number) subsequently prepared by Blum. We will note further that Toggenburg¹³ found certain of his “compounds” underwent changes in composition when recrystallized.

It is difficult to believe that all of the combinations between these components that have been described are true chemical compounds. The large number of these “compounds” described in the literature is, in itself, a reason for considering them other than chemical compounds and suggests that they are related in some simple manner. That such a relation exists between the many members in this and in other series of salts of similar complex inorganic acids has already been suggested by Wherry.¹⁴ From a study of the optical properties¹⁵ of the series of vanado-phosphomolybdates prepared by Blum he concluded that “it is surely not permissible to call them chemical compounds,” and “that they are but a step removed from the so-called ‘adsorption-compounds’ of colloid-chemistry.” His conclusion is in harmony with the conclusions of this paper, since the relation between adsorption and occlusion is very close. That

⁹ Richards, *Z. anorg. chem.*, **23**, 383 (1900).

¹⁰ Richards, McClaffrey and Bisbee, *Z. anorg. chem.*, **28**, 71 (1901).

¹¹ Baxter, *Am. Chem. J.*, **28**, 298 (1902).

¹² Gmelin-Kraut, “Handbuch der anorganischen Chemie,” 7th ed., III, 2, pp. 205-211.

¹³ *Dissertation*, Bern, 1902, pp. 22 and 29.

¹⁴ Wherry, *J. Franklin Inst.*, **169**, 487 (1910).

¹⁵ Some of the solids prepared in the course of this investigation were very kindly examined microscopically by Mr. A. A. Klein. Time was not available for the preparation of more suitable specimens, however, and accordingly the results obtained were not conclusive. The authors wish to express here their appreciation of Mr. Klein's interest in the matter.

these complex salts are indeed intimately related to "adsorption-compounds" is evident from the similarity between the equation representing the occlusion of vanadic acid and that of the "adsorption isotherm."

Having indicated, therefore, that many of the "ammonium vanado-phosphomolybdates" are probably solid solutions it is an easy task to account for their number. They may be considered as points on the curve showing the amount of vanadium occluded by a fixed amount of phosphorus in the presence of increasing amounts of vanadium. This curve is that of Series 2 and its extension. When viewed from this standpoint, one cannot but wonder that many more "compounds" have not been described, inasmuch as there is an infinite number of possible combinations.

The fact that Toggenburg found his salts to change composition on recrystallization is clearly accounted for by the partition effect already shown. It is, in fact, to be expected. If a solid separates from a solution of one of these salts it must bring about a partition of material between the solid and the solution, causing thereby a progressive change in composition of the solid. The composition of the solid phase would also depend upon the concentration of the solution (Series 3) and upon other conditions such as temperature (Series 4). Only under limiting conditions, therefore, would the solid phase be identical with that of the original salt.

5. Summary.

1. The co-precipitation of vanadic acid with ammonium phosphomolybdate may be explained as a phenomenon resulting from a partition of the vanadic acid in some undissociated form between the solution and the solid phase.

2. The maximum absorption by the solid phase occurs at a temperature of 40° to 50° and in a nitric acid concentration of 2 N.

3. The effect of dilution in lowering the amount of occlusion is a direct result of the partition law and can be minimized by the presence of ammonium nitrate, the latter probably tending to repress the dissociation of the vanadium complex which is occluded.

4. The ammonium vanado-phosphomolybdates are probably a series of solid solutions the end members of which may be ammonium phosphomolybdate and ammonium phosphovanadate; the exact relations can be established only by a thorough investigation of the appropriate systems.

Acknowledgment of helpful suggestions and criticism should here be made to Dr. William Blum of the Bureau of Standards and to Dr. L. H. Adams of the Geophysical Laboratory.

WASHINGTON, D. C.