CONTRIBUTION TO THE CHEMISTRY OF PHOSPHOMOLYBDIC ACIDS, PHOSPHOTUNGSTIC ACIDS, AND ALLIED SUBSTANCES.

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INTRODUCTION.

Phosphomolybdic and phosphotungstic acids have long been used in biological chemistry. The ordinary complex acids of commerce are common reagents for proteins, amino-acids, alkaloids, and other organic bases, while the specially prepared solutions of Folín and Denis have in recent years been used for the colorimetric determination of uric acid, adrenalin, phenol, sugar, etc. The chemistry of the complex acids is, however, little understood.

Having had frequent occasion to use the complex acids both as protein precipitants and as color reagents, the writer was led...
to study certain phases of the chemistry of these compounds. With no intention of going into the field of the pure inorganic chemistry of these compounds, attention was confined at first to the color reaction of the Folin-Denis reagents with uric acid, and to the preparation of the ordinary phosphotungstic acid. As the investigation progressed, however, it was found desirable to extend the study so as to cover all the complex phospho-acids of molybdenum and tungsten.

The literature of the complex acids is voluminous and confusing. With the aid of the color reactions which lend themselves to qualitative differentiation as well as to quantitative estimation of the different complex acids, the writer was able to survey the field in a way that was scarcely possible before, and has arrived at a conclusion regarding the present status of our knowledge of the complex acids.

HISTORICAL.

Gmelin discovered that phosphoric acid formed a yellow precipitate in acid solution with ammonium molybdate. The precipitate contained so little phosphorus that he regarded it as unessential. Sonnenschein showed that phosphoric acid was an integral part of the precipitate and suggested its use for the quantitative determination of phosphoric acid. Debray prepared the free phosphomolybdic acid by digesting the yellow precipitate with aqua regia. The ratio of \( P_2O_5 \) to \( MoO_3 \) in the yellow precipitate and acid was according to Debray as 1:20, and according to Rammelsberg, 1:22. But the unanimous conclusion of Finkener, Pemberton, von der Pfordten, Gibbs (1881-82 a), and Hundeshagen that the compound contained 1 \( P_2O_5 \) to 24 \( MoO_3 \) is now generally accepted.

Scheibler in 1872 described two complex acids of tungsten. He boiled sodium acid tungstate (\( Na_8H_3W_3O_{18} + 12 H_2O \)) and half its weight of phosphoric acid, and obtained a crystalline compound of the composition \( Na_8H_11P_2W_6O_{33} + 13 H_2O \). From this he prepared the barium compound which on decomposition (with sulfuric acid) gave a free acid \( H_{18}PW_{19}O_{58} + 18 H_2O \). Using a slightly different procedure, he obtained another acid of the composition \( H_{18}PW_{19}O_{58} + 8 H_2O \). He published no analyses, and he assigned the formulas to his compounds with reservation. There is no doubt that the work of Scheibler possesses only historical value.

Later Gibbs (1880-81 a) took up the study of the complex acids. He boiled 24 mols of \( Na_8WO_4 + 2 H_2O \) with 2 mols of \( Na_8HPO_4 \) and acidified the mixture with nitric acid. The complex acid was precipitated with mercurous nitrate, and the mercurous phosphotungstate was decomposed with hydrochloric acid. The free acid thus obtained contained 1 \( P_2O_5; 24 WO_3 \). Sprenger, Kehrmann and Freinkel (1891), and Brandhorst and
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Kraut obtained the same compound by slightly different methods and all their analytical results showed that the ratio $P_2O_5:WO_3$ was as 1:24.

Besides the compounds containing 1 $P_2O_5$ to 24 $MO_3$ ($M = W$ or $Mo$) Gibbs (1880-81 a, b) reported others with the ratio $P_2O_5:MO_3$ as 1:22, 1:20, 1:18, and 1:16. These compounds were obtained only in the form of salts. The conditions under which they were formed were not well defined, and he believed that it was almost impossible to predict what complex would be formed under exactly similar conditions. He stated repeatedly that the compounds were “only to be distinguished by analysis,” and he also admitted that some of his compounds could not be re-crystallized and that consequently their absolute purity could not be guaranteed. Neither was the method of phosphate determination then available entirely adequate for his problem, and among other sources of error need be mentioned only the circumstance that he had to apply at times to his phosphoric acid determination a correction of 8 per cent, a magnitude as large as the difference between the $P_2O_5$ contents of the 1:24 and 1:22, or between the 1:20 and the 1:18 compounds. In view of all these facts, much of his work is of doubtful significance.

Péchard also reported a number of phosphotungstic acids other than the 1:24 acid. He mixed theoretical quantities of $m$-tungstic acid and phosphoric acid, and claimed to have obtained acids with the ratio $P_2O_5:WO_3$ as 1:20, 1:16, and 1:12. He did not state his method of analysis, and, as far as can be judged from his published figures, duplicate analyses differing among themselves by 5 per cent or more, there is no convincing evidence that his compounds had the composition he assigned to them.

In 1887 Kehrmann prepared a new phosphotungstic acid by boiling 1 mol of sodium tungstate with 4 mols of phosphoric acid. A set of peculiar circumstances led him to assign to his compound a formula with the ratio $P_2O_5:WO_3$ as 1:16. As a result of further research, he corrected his mistake a few years later (1892) and concluded that his compound really contained 1 $P_2O_5$ to 18 $WO_3$. In collaboration with Böhm (1894 a, b) he succeeded in isolating the corresponding molybdenum compound from the mother liquor of the barium salt of the 1:24 acid by salting out with $NH_4Cl$. The ammonium salt crystallized out from the solution as orange-red prisms. The free acid was obtained by treating the potassium salt with theoretical quantity of sulfuric acid and precipitating the potassium sulfate with alcohol and ether. He also observed that the 1:24 phosphomolybdic acid was transformed into the 1:18 acid by free phosphoric acid on long standing, but no method for the preparation of the 1:18 compound was given. (Finkener had previously observed some sodium salt containing 1 $P_2O_5$ to $MO_3$, but, as he did not mention any detail, the discovery of the 1:18 acid is to be attributed to Kehrmann.)

Kehrmann and his collaborators observed that the 1:24 and 1:18 phosphotungstic acids were converted by carbonates into new complexes containing respectively 1 $P_2O_5$ to 22 $WO_3$, and 1 $P_2O_5$ to 17 $WO_3$. These complex salts corresponded to hypothetical acids of the composition $7H_2O\cdot P_2O_5\cdot 22WO_3$ and $5H_2O\cdot P_2O_5\cdot 17WO_3$, but when the salts were boiled with mineral acid the original 1:24 and 1:18 acids were regenerated.
Kehrmann and Freinkel (1892) claimed to have prepared the acid containing 1 \( \text{P}_2\text{O}_5 \) to 21 \( \text{WO}_3 \) which was formed from the 1:22 salt simultaneously with the regeneration of the 1:24 acid. This finding the writer has not been able to confirm.

Compounds containing much smaller amounts of \( \text{WO}_3 \) or \( \text{MoO}_3 \) are also known. Thus the 1 \( \text{P}_2\text{O}_5 \):15 \( \text{MoO}_3 \) compound was reported by Rammelsberg; the 1 \( \text{P}_2\text{O}_5 \):5 \( \text{MoO}_3 \) compound by Rammelsberg, Zenker, Debray, Wernke, and Friedheim; the 1 \( \text{P}_2\text{O}_5 \):4 \( \text{MoO}_3 \) and 1 \( \text{P}_2\text{O}_5 \):2 \( \text{MoO}_3 \) by Friedheim; the 1 \( \text{P}_2\text{O}_5 \):7 \( \text{WO}_3 \) by Gibbs (1880–81 b) and Kehrmann (1892). All these compounds, if they exist at all, are formed either from the higher acids by decomposition with insufficient alkali or from the molybdate and tungstate with insufficient acid. They have been prepared only in the form of salts, as they are converted by mineral acid into the 1:24 or the 1:18 acid.

The Present Status.

The complex phospho-compounds of molybdenum and tungsten fall into two well defined groups:

**Group I.**—This group includes the complexes containing 1 \( \text{P}_2\text{O}_5 \) to 24 \( \text{MO}_3 \) and 1 \( \text{P}_2\text{O}_5 \) to 18 \( \text{NO}_3 \) (\( M = \text{W} \) or \( \text{Mo} \)). They can exist either as free acids or as salts. They are all colored, with the exception of the 1:24 tungsten compound. They are very sensitive to reduction, and precipitable with pyridine in dilute solutions. They are converted by alkali into compounds of Group II.

**Group II.**—This group includes a number of salts with different \( \text{P}_2\text{O}_5 \):\( \text{MO}_3 \) ratios. They exist only in the form of salts, being converted by mineral acids into compounds of Group I. They are all white or colorless. They are not sensitive to reduction, and are not precipitable with pyridine in dilute solutions.

Compounds of Group II are not complex acids, and they have therefore received little attention in this research.

The properties and reactions which have been found useful in distinguishing the complex acids are shown in Table I.

The terms phosphotungstic acid and phosphomolybdic acid are used loosely to represent different compounds. The ordinary acids have been called phosphoduopectungstic and phospho-duopecimolybdic acids, and the acids discovered by Kehrmann were named phospholuteotungstic and phospholuteomolybdic acids, indicating the yellow color of these compounds. It seems desirable to have a system of nomenclature of these complex.
TABLE I.

Properties and Reactions of Complex Acids.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>W 1:18</th>
<th>W 1:24</th>
<th>Mo 1:18</th>
<th>Mo 1:24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Lemon-yellow</td>
<td>Colorless</td>
<td>Bright yellow</td>
<td>Orange</td>
</tr>
<tr>
<td>NH₄ salt</td>
<td>Soluble</td>
<td>Insoluble</td>
<td>Soluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>With uric acid</td>
<td>Blue coloration in alkaline solution</td>
<td>Brown coloration in acid; blue in NaOH (but not in Na₂CO₃) solution, fading rapidly</td>
<td>Blue coloration in alkaline solution</td>
<td>Blue coloration in alkaline or in acid solution with the complex in excess; violet with uric acid in excess</td>
</tr>
<tr>
<td>With SO₂</td>
<td>Blue coloration growing slowly in acid. Only a trace of color in alkaline solution</td>
<td>Almost no reaction. Very faint violet coloration</td>
<td>Blue coloration in alkaline or neutral solution</td>
<td>Blue coloration in alkaline solution with the complex in excess; lavender-blue with SO₂ in excess</td>
</tr>
<tr>
<td>With ferrous salt</td>
<td>Blue in alkaline. Almost none in acid solution</td>
<td>Brown in acid, blue in alkaline solution, fading rapidly</td>
<td>Blue in alkaline as well as in acid solution</td>
<td>Blue in alkaline as well as in acid solution with the complex in excess; lavender-blue with the ferrous salt in excess</td>
</tr>
</tbody>
</table>
compounds based on their composition rather than on their properties. The ratio \( P_2O_5: MO_3 \) or simply \( P_2: M \) is better suited than the ratio \( P: M \) for this purpose, because there are compounds containing 1 \( P_2O_5 \) to an odd number of \( MO_3 \), in which case the ratio \( P: M \) would have a fractional value. Greek numerals might be used, but it is by far simpler to insert an arabic numeral after the word “phospho,” the numeral denoting the number of \( MO_3 \) to 1 \( P_2O_5 \). Thus, the ordinary acid of molybdenum would be phospho-24-molybdic acid, Kehrmann’s tungstic acid would be phospho-18-tungstic acid, the salt obtained from this by the action of carbonate would be phospho-17-tungstate, etc.

**Conditions of Formation of the Complex Acids.**

The formation of the complex acids depends on four factors: (1) acidity or hydrogen ion concentration; (2) concentration of phosphoric acid; (3) concentration of tungstic acid or molybdic acid; and (4) temperature.

Acidity is the most important factor. A definite hydrogen ion concentration is apparently required to condense the simple tungstic acid or molybdic acid into a complex structure which then combines with phosphoric acid. A higher acidity is required to form \((MO_3)_{24}\) than \((MO_3)_{18}\), and for the molybdenum compound than for the corresponding tungsten compound. The concentration of tungstic or molybdic acid and that of phosphoric acid exert their effects in accordance with the mass action, but they are relatively unimportant. Boiling temperature is required to form the complex acids of the 1:18 series, but the 1:24 acids are formed even at ordinary temperatures.

The acidity of a mixture of sodium molybdate and phosphoric acid is not enough to form any complex acid (Group I). Whatever proportion of the two compounds is used, the solution contains only colorless complex molybdate (Group II), even after long boiling. Addition of hydrochloric acid to an equimolar mixture of \( Na_9MoO_4 \) and \( H_3PO_4 \) in an amount equivalent to the quantity of \( Na_9MoO_4 \) used, produces a mixture of the 1:18 and the 1:24 acid. The yield in the latter compound increases with increasing acidity.
The acidity of a mixture of 1 mol of Na₂WO₂H₂O with 4 mols of H₃PO₄ suffices to transform all the tungstate into the 1:18 acid, but none of the 1:24 acid is formed. But if hydrochloric acid is added, the 1:24 acid will be formed almost to the exclusion of the 1:18 acid. The colorless complex tungstates are formed only when the solution is alkaline or weakly acid (in the presence of acetate).

Theoretically a mixture of tungstate or molybdate and phosphoric acid contains all the possible complexes, and the equilibrium can be displaced in one direction or another by suitable means. Thus the molybdenum compounds are very susceptible to transformation. A little ammonium chloride added to a solution of phospho-18-molybdic acid will cause the formation of the ordinary yellow precipitate in the course of time at room temperature, and rapidly at higher temperatures. The tungsten compounds are, however, more stable, and a solution of ammonium phospho-18-tungstic acid may be heated to 60–70°C. without danger of transformation.

Preparation of the Complex Acids.

The methods which have been employed for the preparation of complex acids of the 1:24 series consist in the double decomposition of the mercurous salt by hydrochloric acid, of the barium salt by sulfuric acid, or in the digestion of the ammonium salt with aqua regia. All these methods are at best very tedious. Drechsel suggested the use of ether for extracting the complex acid from an aqueous solution. This procedure simplified the preparation very materially. But the method, whether in Drechsel's original form or as modified by Winterstein, gives not a pure acid but a mixture. The ether extraction, as far as the writer is aware, has been used only for the preparation of the phospho-24-tungstic acid, although Drechsel stated that it could be used for the corresponding molybdenum compound. As a matter of fact, the great solubility in ether is a property common to all complex acids; and they can all be almost quantitatively extracted with ether from strongly acidified solutions.

Kehrmann obtained the phospho-18-tungstic acid by digesting the ammonium salt with aqua regia, and explicit directions were
given. The exact method for the corresponding molybdenum compound was not worked out.

From the study on the formation of the different complex acids and the recognition of their solubility in ether, simple methods have resulted for the preparation of pure complex acids.

*Phospho-24-Molybdenic Acid.*

Dissolve 100 gm. of Na₂MoO₄·2 H₂O in 200 cc. of H₂O. Add 10 cc. of H₃PO₄ (85 per cent) and then 100 cc. of concentrated HCl. Transfer to a 1,000 cc. separatory funnel, add 150 cc. of ether, and shake. Cool under the tap. After standing for 10 to 15 minutes, three layers should be formed. Transfer the lowest layer, which contains nearly all the complex acid, to another funnel. Add 100 cc. of H₂O and shake. Then add 50 cc. of concentrated HCl and some more ether and shake again. Cool. The lowest layer is again transferred to another funnel and washed once more. Transfer the ethereal solution, which should be perfectly clear, to a beaker, add 25 cc. of H₂O and a few drops of concentrated HNO₃ and evaporate on the water bath with occasional stirring until crystals begin to form on the surface. Allow to cool slowly. Yellow octahedra of the composition 3 H₂O·P₂O₅·24 MoO₃ + 59 H₂O are obtained.

*Phospho-18-Molybdenic Acid.*

Dissolve 100 gm. of Na₂MoO₄·2 H₂O in about 450 cc. of H₂O, add 15 cc. of 85 per cent H₃PO₄ and 80 cc. of concentrated HCl. Boil for 8 hours with return condenser. Cool. Stir in 100 gm. of powdered NH₄Cl. The crystalline precipitate, after settling, is filtered on a Buchner funnel, and sucked as dry as possible. Redissolve the precipitate in an equal weight of water. A part of the precipitate (NH₄-phospho-24-molybdate) remains undissolved. Filter through hardened paper. To the perfectly clear solution add enough solid NH₄Cl to make a 20 per cent solution. If the solution is not stirred at all, the NH₄-phospho-18-molybdate will replace the NH₄Cl in situ and larger crystals are formed in this way than when the solution is stirred. After standing 4 to 8 hours the crystals are transferred to a Buchner funnel and sucked as dry as possible. Redissolve in just enough water and evaporate at a low temperature (40°C.) in a vacuum, until crystals begin to form. (The solution cannot be evaporated with the aid of a free flame or even on the steam bath because the ammonium salt is transformed into the insoluble yellow precipitate of the 1:24 series even at 60-70°C.) Allow to cool slowly to 5-6°C. Transfer the crystals to a Buchner funnel, and suck as dry as possible. The suction is discon

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1 If the solution turns brown or green in the course of evaporation more HNO₃ should be added.
tinued and the crystals are covered with a liberal quantity of dry ether. Stir to insure mixing, and, after a few minutes, such as dry as possible. The crystals are then spread on a watch-glass and will be completely dry in an hour or so. The quick drying is necessary, as the product will be contaminated by some yellow precipitate formed from the mother liquor on slow drying. Orange crystals of the composition $3\text{(NH}_3\text{)}\text{P}_2\text{O}_7\cdot 18\text{MoO}_3\cdot 11\text{H}_2\text{O}$ are obtained. They should give a perfectly clear solution in water.

The free phospho-18-molybdic acid can be prepared as follows:

Dissolve 50 gm. of the ammonium salt in 100 cc. of $\text{H}_2\text{O}$, add 60 cc. of concentrated $\text{HCl}$, and extract with ether in a separatory funnel. Cool. The lowest layer is transferred to another funnel. Add 100 cc. of $\text{H}_2\text{O}$ and shake; then add 60 cc. of concentrated $\text{HCl}$ and some more ether, and shake again. Repeat the washing once more. Transfer the ethereal solution to a tall beaker, add 40 cc. of $\text{H}_2\text{O}$, and blow off the ether by means of compressed air. Allow the solution to evaporate over $\text{H}_2\text{SO}_4$. (Like the ammonium salt the free 1:18 acid is transformed into the 1:24 acid at high temperatures.) Orange prisms of the composition $3\text{(NH}_3\text{)}_2\text{P}_1\text{O}_7\cdot 18\text{MoO}_3\cdot 11\text{H}_2\text{O}$ are obtained. The solution should give no precipitate with $\text{NH}_3\text{Cl}$. Phospho-24-Tungstic Acid.

This acid is the chief ingredient of the commercial phospho-tungstic acid which is never pure. The Kahlbaum and Merck products contain about 10 per cent of the phospho-18-tungstic acid. To prepare pure phospho-24-tungstic acid proceed as follows:

Dissolve 100 gm. of $\text{Na}_4\text{WO}_4\cdot 2\text{H}_2\text{O}$ in about 100 cc. of $\text{H}_2\text{O}$ with the aid of heat. Add 10 cc. of 85 per cent $\text{H}_3\text{PO}_4$ and then 80 cc. of concentrated $\text{HCl}$. Allow to cool. The crystalline precipitate which is gradually formed consists of sodium phospho-24-tungstate but is usually contaminated by traces of acid tungstates. After 4 hours or more, filter on a Buchner funnel and suck as dry as possible. Redissolve the precipitate in 120 cc. of $\text{H}_2\text{O}$, pour the solution into a liter separatory funnel, add about 70 cc. of ether, and then 40 cc. of concentrated $\text{HCl}$. Shake. After standing a few minutes there should be three layers of liquid. The lowest layer contains nearly all the complex acid. If there are only two layers, more ether should be added and the mixture shaken again. Transfer the lowest layer to another separatory funnel, add about 120 cc. of water and shake vigorously, then some more ether (30 cc.), and finally 40 cc. of concentrated $\text{HCl}$. Shake. After standing, the lowest layer, which should be perfectly clear, is transferred to a beaker. Add 20 cc. of $\text{H}_2\text{O}$ and
evaporate on a steam bath until crystals begin to form on the surface. Colorless octahedra of the composition $3\text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 24\text{WO}_3 \cdot 59\text{H}_2\text{O}$ are obtained.

**Phospho-18-Tungstic Acids.**

While preparing the ammonium salt of the acid in the uric acid reagent of Folin and Denis it was observed that the crystals first deposited had a different form from those which were deposited later. The two kinds of crystals differ also in other properties such as solubility, hardness, etc., but above all they differ in their chromogenic value. When equal weights (10 mg.) of them were dissolved in water, an excess of uric acid (5 mg.) was added, and the solution rendered alkaline with sodium carbonate (5 cc. of 20 per cent solution), the color (in 50 cc.) produced by the form first deposited was about 30 per cent stronger than that produced by the other form. Since analysis later showed that the stronger form contained a smaller per cent of tungsten it must be concluded that they were two different chemical individuals. As they both contain 1 $\text{P}_2\text{O}_5$ to 18 $\text{WO}_3$, they are both phospho-18-tungstic acids. For convenience the stronger form will be designated as A, and the weaker form B. The B form has been identified with the leuteophosphotungstic acid of Kehrmann, but the A form is hitherto unknown. The exact relation between the two forms has not been determined, but as there is clearly the possibility of isomerism their properties, preparation, and analysis will be described in detail.

To 200 gm. of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ dissolved in a liter of water 280 gm. of 85 per cent phosphoric acid were added. The mixture was boiled for 8 hours under return condenser. Toward the end of the boiling the liquid was allowed to concentrate to a volume of about a liter. A few drops of

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2 It must be pointed out that Kehrmann (1887) in his early study of the phosphotungstic acids had observed different crystalline forms of the yellow potassium salt which he prepared. He believed that there were three compounds represented by short prisms (lemon-yellow), monoclinic octahedra (pale yellow), and small needles (yellowish white), and these forms were designated by him as A, B, and C. The C form was deposited first, then followed the other two. However, he studied only the prismatic form A, of which he made some crystallographic measurements, but in his later work he did not refer to these findings.
bromine water were added to decolorize the solution, which turned to pure yellow. After cooling, about 200 gm. of powdered NH₄Cl were stirred in. The crystalline precipitate was filtered by suction, redissolved in water, and reprecipitated with solid NH₄Cl. This process was repeated twice. The precipitate was then dissolved in about 600 cc. of luke warm water (about 50°C.) and the solution allowed to stand in a warm room (37°C.). After a few days the A crystals (2 to 3 mm.) were deposited in characteristic form, unmixed by any of the other kind. When the deposit ceased to grow, the mother liquor was decanted into another beaker. The A crystals were washed with ice-cold water and recrystallized five times from water.

Fig. 1. A. Ammonium A-phospho-18-tungstate. Hexagonal prism truncated by two rhombohedra. The narrow faces are usually not developed.
B. Ammonium B-phospho-18-tungstate. Rhomboidal plate with truncated edges (not shown).

If the solution is somewhat colored, due to reduction of the complex acids by organic dusts, as is usually the case, the crystals of the A form will be much darker than those of the B form. Sometimes the former is almost black, whereas the latter is only faintly green. It is therefore possible to separate the two forms mechanically by means of forceps.
Chemistry of Acids

After another week or so the B crystals were formed. When the deposit apparently ceased to grow, it was separated from the mother liquor, dissolved in water, and allowed to recrystallize. The crystals were divided into three crops, the first and last were put aside for other use, while the middle crop was recrystallized four times. Large crystals (1 to 2 cm. long) were obtained.

The preparations were air-dried. Ground samples were used for analysis. Neither preparation gave test for chloride, showing that they were completely freed from the mother liquor which contained a large excess of phosphoric acid.

The yield in the A form was about 30 gm., representing about 20 per cent of the tungstate used.

The method of analysis used embodies certain improvements upon the older procedure. It is at once simple and accurate, and believed to be generally applicable to the analysis of complex phospho-compounds of tungsten and allied elements. The ammonium salt lends itself especially well to analysis, because of the ease with which the non-volatile constituents can be determined.

The method is as follows:

1. Determination of $P_2O_5$.

The $P_2O_5$ must be determined in the unignited sample, because some of it is always lost during ignition. 2.5 to 3 gm. of the substance are dissolved in about 25 cc. of warm $H_2O$, 25 to 30 cc. of a 10 per cent solution of sodium hydroxide are added, and the mixture is heated to boiling until the precipitate which is first formed has entirely redissolved. Continue the heating at a slightly reduced temperature for 20 minutes longer. By this process the complex acid is completely decomposed into phosphate and tungstate. Fusion with $Na_2CO_3$ as recommended in the literature was never found necessary. After cooling, add 5 to 6 gm. of ammonium chloride. When it has dissolved, add slowly 10 to 15 cc. of magnesia mixture (55 gm. of $MgCl_2\cdot 6H_2O$, 140 gm. of $NH_4Cl$, and 350

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4 The method for $P_2O_5$ in phosphomolybdic acids is much simpler. The preliminary boiling with NaOH is not necessary, since the complex molybdenum compounds are decomposed by excess of concentrated ammonia even at room temperature. Incidentally the contamination by silica from glass is practically eliminated and the double precipitation of the magnesium ammonium phosphate may be omitted.

5 See, for example, Scott, W. W., Standard methods of chemical analysis, New York, 3rd edition, 1018, 482.
cc. of concentrated NH₄OH to the liter), and then one-fourth volume of strong ammonia. After 4 hours the precipitate is filtered and washed with 1:4 ammonia. The precipitate is always contaminated by a considerable amount of silica dissolved from the beaker by the alkali and by a trace of tungstate. To remove these the precipitate is ignited, whereby the silica and tungstic acid are rendered insoluble. If the precipitate is merely redissolved in HCl without ignition, as is recommended in the literature, the impurities are only partly removed. Digest the ignited precipitate with 15 cc. of 2N HCl for an hour at 80-90°C. with occasional stirring. Filter off the silica on a small filter paper (1½ inches diameter) and wash with ten 5 cc. portions of 0.5 N HCl. Add to the filtrate and washings 5 cc. of magnesia mixture and then very slowly 25 cc. of concentrated ammonia. The precipitate which is now pure magnesium ammonium phosphate is filtered after 4 hours, washed with 1:4 ammonia until free from chloride, ignited with the usual precautions, and weighed. As the amount of phosphate determined is only about 0.1 gm. and the quantity of reagents used is considerable, it is important to make a blank determination and make the correction, if any, accordingly.

2. Determination of WO₃.—Many previous investigators determined the WO₃ in phosphotungstic acids by the difference between the combined oxide (WO₃ + P₂O₅) and the phosphoric anhydride. The combined oxide was determined by igniting the ammonium phosphotungstate or the mercurous phosphotungstate obtained by precipitating with mercurous nitrate. It was pointed out by Barber that the ignition residue always weighed less than the theoretical sum of P₂O₅ and WO₃, using compounds of known composition, and he attributed this discrepancy to the partial reduction of WO₃ to some lower oxide. As a matter of fact experiments made by the writer showed that it was not due to this cause, although a trace of tungsten was almost always reduced, imparting a bluish color to the trioxide. When the ignition residue was dissolved in alkali and the P₂O₅ in it determined, the figure obtained was always lower than the true P₂O₅ content of the unignited substance, the difference amounting to 7 to 15 per cent of the P₂O₅ content. It was clear that some P₂O₅ was lost during ignition, and this probably accounted for the discrepancy which Barber had observed.

To determine WO₃ by difference, it is therefore necessary to determine the P₂O₅ in the ignited residue. Accordingly the determination of WO₃ is carried out as follows:
2.5 to 3 gm. of the substance are ignited in a platinum crucible placed inside a porcelain crucible which is heated to bright redness until the residue shows no appreciable loss of weight on successive weighings. The residue is then dissolved in 25 to 30 cc. of a 10 per cent solution of sodium hydroxide and the $\text{PO}_4$ in it determined as described above.

3. Determination of Ammonia and Water — The ammonia is determined by distillation and titration in the usual manner, and calculated as $(\text{NH}_4)_2\text{O}$. The total water is determined by difference.

The results of the analyses representing two preparations each of A and B are shown in Table II and summarized in Table III. A and B forms must therefore have respectively the formulas

$$3 (\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 18 \text{WO}_3 + 16 \text{H}_2\text{O}$$

and

$$3 (\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 18 \text{WO}_3 + 11 \text{H}_2\text{O}$$

Excepting the number of molecules of $\text{H}_2\text{O}$ which may be in error by unity, the composition of the compounds as given is beyond any doubt.

The two forms thus differ only in the water content, and the anhydrous forms would have the same composition if the water is all “water of crystallization.” There is then the possibility of isomerism and polymerism. But some of the water may be “water of constitution” and an anhydride relation may exist between the two forms.

The free acids of both forms are conveniently prepared from the corresponding ammonium salt by the ether extraction method, although they can also be obtained by digesting the salts with aqua regia.

A-Acid.—

Dissolve 10 gm. of salt in 25 cc. of water. Add 15 cc. of concentrated $\text{HCl}$ and an excess (10 cc.) of ether and shake. Transfer the lowest layer to another separatory funnel, add 10 cc. of water, and shake; and then 6 cc. of concentrated $\text{HCl}$ and some more ether and shake again. Transfer the ethereal solution to a beaker, add 5 cc. of water, and evaporate on the water bath until crystals begin to form on the surface. The crystallized acid has the composition $\text{P}_2\text{O}_5 \cdot 18 \text{WO}_3 \cdot 38 \text{H}_2\text{O}$.

---

6 This is true also for the formulas of other compounds given in this paper.
TABLE II.
Analyses of Ammonium Salts of Phospho-1% Tungstic Acids.

### 1. P$_2$O$_5$

<table>
<thead>
<tr>
<th>Preparation No.</th>
<th>Form A</th>
<th></th>
<th>Form B</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight of sample</td>
<td>Mg$_3$P$_2$O$_7$</td>
<td>P$_2$O$_5$</td>
<td>Weight of sample</td>
</tr>
<tr>
<td></td>
<td>gm.</td>
<td>gm.</td>
<td>per cent</td>
<td>gm.</td>
</tr>
<tr>
<td>I</td>
<td>3.0769</td>
<td>0.1431</td>
<td>2.963</td>
<td>3.1564</td>
</tr>
<tr>
<td></td>
<td>2.8336</td>
<td>0.1319</td>
<td>2.972</td>
<td>2.6205</td>
</tr>
<tr>
<td>II</td>
<td>3.0538</td>
<td>0.1430</td>
<td>2.990</td>
<td>2.5099</td>
</tr>
<tr>
<td></td>
<td>2.5458</td>
<td>0.1184</td>
<td>2.970</td>
<td>2.7979</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td></td>
<td>2.974</td>
<td></td>
</tr>
</tbody>
</table>

### 2. WO$_3$

<table>
<thead>
<tr>
<th>Form A</th>
<th>Form B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of sample</td>
<td>Weight of residue</td>
</tr>
<tr>
<td>gm.</td>
<td>gm.</td>
</tr>
<tr>
<td>I</td>
<td>2.4787</td>
</tr>
<tr>
<td>II</td>
<td>3.5249</td>
</tr>
<tr>
<td>Average</td>
<td></td>
</tr>
</tbody>
</table>

### 3. (NH$_4$)$_3$O

<table>
<thead>
<tr>
<th>Form A</th>
<th>Form B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of sample</td>
<td>0.1 N HCl neutralised</td>
</tr>
<tr>
<td>gm.</td>
<td>cc.</td>
</tr>
<tr>
<td>I</td>
<td>1.1320</td>
</tr>
<tr>
<td>II</td>
<td>1.2464</td>
</tr>
<tr>
<td>Average</td>
<td></td>
</tr>
</tbody>
</table>

TABLE III.
Composition of Ammonium Phospho-1% Tungstates.

<table>
<thead>
<tr>
<th>Per cent</th>
<th>P$_2$O$_5$</th>
<th>WO$_3$</th>
<th>(NH$_4$)$_3$O</th>
<th>H$_2$O (by difference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.974</td>
<td>87.595</td>
<td>3.266</td>
<td>6.165</td>
</tr>
<tr>
<td>B</td>
<td>3.055</td>
<td>89.425</td>
<td>3.370</td>
<td>4.150</td>
</tr>
</tbody>
</table>

| Ratio | A | 18.03 | 2.999 | 16.35 |
| B | 1 | 17.93 | 3.012 | 10.72 |
Dissolve 10 gm. of salt in 15 cc. of water. Add 10 cc. of concentrated HCl and extract with 10 cc. of ether. Then proceed as described for the A-acid. The crystallized B-acid has the composition $\text{P}_2\text{O}_5 \cdot 18\ \text{WO}_3 \cdot 40\ \text{H}_2\text{O}$.

The physical properties of the two forms of ammonium phospho-18-tungstate are shown in Table IV.

TABLE IV.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility.</td>
<td>51° gm. in 100 gm. $\text{H}_2\text{O}$</td>
<td>122° gm. in 100 gm. $\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Strength.</td>
<td>Tough</td>
<td>Brittle</td>
</tr>
<tr>
<td>Color.</td>
<td>Lemon-yellow</td>
<td>Pale yellow</td>
</tr>
<tr>
<td>Deliquescence.</td>
<td>Does not lose water of crystallization easily.</td>
<td>Loses water of crystallization easily and crumbles into powder.</td>
</tr>
<tr>
<td>Crystallographic properties.†</td>
<td>Uniaxial. Simple hexagonal prism terminated by two rhombohedra, one of which, probably the unit form, is more strongly developed (Fig. 1). Habit: radial groups consisting of needles elongated in the direction of vertical axis. The second rhombohedron is usually not developed and the crystal then bears a superficial resemblance to a duodecahedron. Optical character, negative.</td>
<td>Biaxial. Probably triclinic. Habit: thin rhombooidal plates with truncated edges (Fig. 1). In one crystal studied the axial plane makes an angle of 70° with one edge and 4° with the other. With the plate lying flat the interference figure shows one axis well within the field. The angle $E$ is estimated as 30°. Optical character, positive.</td>
</tr>
</tbody>
</table>

* Approximately.
† The writer is indebted to Professor C. H. Warren of the Massachusetts Institute of Technology for these observations.

Chemically the two forms are similar. They are both reducible by uric acid in alkaline solution, but the colors produced differ in quality as well as in intensity. For the same weight of $\text{WO}_3$ the A form gives about 30 per cent more color than the B form.
The color of the A form has a tint of green, that of B form, violet. The A form is more sensitive to reduction.

The comparison of the chromogenic values was made as follows:

To 1 cc. of 1 per cent solution of the ammonium salt in a 50 cc. volumetric flask were added, in the order given, 10 cc. of water, 5 cc. of 0.1 per cent uric acid solution (made by dissolving 0.1 gm. of uric acid and 0.1 gm. of lithium carbonate in 100 cc. of H₂O), 0.5 cc. of 5 per cent sodium cyanide, and finally 5 cc. of 20 per cent sodium carbonate solution. The cyanide was used to retard the fading, and it did not affect the relative color values. The color solution was diluted to volume and read in a 50 mm. Duboscq colorimeter. The ratio of the color intensities was

\[
\frac{10 \text{ mg. } \text{NH}_4 - \text{A-salt}}{10 \text{ mg. } \text{NH}_4 - \text{B-salt}} = \frac{25.4}{20} = 1.27
\]

or in terms of the anhydrous salts

\[
A = 1.3B
\]

Two 1 cc. portions of the uric acid solution used in the preceding experiment were measured into two 100 cc. flasks. To one were added 10 cc. of 1 per cent solution of the A-salt, and to the other, the B-salt. 10 cc. of 20 per cent sodium carbonate solution were then added to each flask. The color solutions were diluted to volume and read. The ratio of the color intensities was

\[
\frac{A}{B} = \frac{25.6}{20} = 1.28
\]

### TABLE V.

<table>
<thead>
<tr>
<th></th>
<th>P₂O₅</th>
<th>WO₃</th>
<th>(NH₄)₂O</th>
<th>H₂O (by difference)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>per cent</td>
<td>per cent</td>
<td>per cent</td>
<td>per cent</td>
</tr>
<tr>
<td>I</td>
<td>3.100</td>
<td>86.00</td>
<td>5.642</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>3.095</td>
<td>85.98</td>
<td>5.687</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>3.098</td>
<td>85.99</td>
<td>5.665</td>
<td>5.247</td>
</tr>
</tbody>
</table>

When treated with sodium carbonate or hydroxide in the cold, the two forms of phospho-18-tungstic acid yield the same decomposition product. This consists of small glistening rectangular plates difficultly soluble in carbonate or hydroxide solution. The ammonium salt obtained by using ammonium carbonate is easily purified by recrystallization from water without undergoing any change. Analysis gave the following results (Table V).
The ratios \( \text{P}_2\text{O}_5 : \text{WO}_3 : (\text{NH}_4)_2\text{O} : \text{H}_2\text{O} \) in the salt are as \( 1 : 16.99 : 4.993 : 13.36 \). It must therefore have the formula \( 5 (\text{NH}_4)_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 17 \text{WO}_3 + 13 \text{H}_2\text{O} \).

When the phospho-17-tungstate, whether obtained from the A or the B form, was boiled with hydrochloric acid, the phospho-18-tungstic acid regenerated was exclusively the B form. This was proved by identification of the ammonium salt of the regenerated acid, but it was also easily shown by a simple experiment as follows:

To 1 cc. of 1 per cent solution of the A-salt was added 1 cc. of \( \text{N Na}_2\text{C}_2\text{O}_4 \) solution. After 2 minutes (the decomposition was practically instantaneous) 2 cc. of \( \text{N HCl} \) solution were added and the solution was heated in the boiling water bath for 30 minutes. A similar experiment on the B-salt was made side by side. 1 cc. of 1 per cent solution of ammonium phospho-17-tungstate and 1 cc. of 1 per cent solution of B-salt were also heated each with 1 cc. of \( \text{N HCl} \) in the same bath. After cooling, the chromogenic values were compared as described above. The results follow:

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mg. A-salt decomposed and regenerated</td>
<td>= 9.7 mg. B-salt</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 &quot; B-salt &quot; &quot; &quot; &quot; &quot; &quot; &quot; &quot;</td>
<td>= 9.8 &quot; &quot; &quot; &quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 &quot; colorless salt regenerated</td>
<td>= 9.4 &quot; &quot; &quot; &quot;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Since 10 mg. of the A-salt are equivalent chromogenically to 12.7 mg. of B-salt, it is clear that by the process of decomposition and regeneration the A-salt has been transformed into the B-salt. Incidentally the experiment showed that regeneration was practically complete.

The exact relation between the two forms of phospho-18-tungstic acid, as well as the more general problem of the structure of the complex acids, stands in need of further study. This is, of course, a problem of inorganic rather than of biological chemistry.

**Phosphomolybdictungstic Acids.**

Mixed complex acids containing molybdenum and tungsten both of the 1:18 and of the 1:24 series have been prepared. The methods of their preparation are very similar to those of compounds containing only one metal. Their properties lie between those of the pure molybdenum and pure tungsten compounds and, to be sure, resemble more the pure compound of the
predominant element. Thus, the soluble ammonium salts of the mixed complex acid of the 1:18 series with high content of molybdenum are easily transformed into insoluble salts of the 1:24 series, while those with high tungsten content may be heated to 70°C. without danger of transformation. The sensitivity to reduction of these compounds runs roughly parallel to their molybdenum content, if one uses as a measure of sensitivity the intensity of the color produced from a given weight (20 mg.) of the ammonium salt, with an excess of sodium sulfite (10 cc. of 10 per cent solution).

The number of mixed complex acids must be very large, and here the possibility of isomerism is far greater than in the case of the pure molybdenum or tungsten compound. By using sodium tungstate and molybdate in different molecular ratios, the writer has obtained about twenty ammonium salts of the 1:18 series. When these salts are reduced with reagents which do not affect the pure tungsten compound, the amount of color produced is far more than can be accounted for by the amount of molybdenum in the form of pure molybdenum compound in them. Their reduction products also show a great variation in color whereas the pure molybdenum and pure tungsten compounds give colors which are only slightly different from each other. The color changes from bluish green to violet as the proportion of tungsten is increased. The preparations showed no change by recrystallization from luke warm water. They must therefore be either different chemical individuals or mixtures of two adjacent members of the series; for example, \(3H_2O\cdotP_2O_5\cdot10WO_3\cdot8MoO_3\) and \(3H_2O\cdotP_2O_5\cdot9WO_3\cdot9MoO_3\). These compounds would be not only isomorphous but all their properties would be so similar that their separation is practically impossible. A few compounds of the 1:24 series have also been obtained which likewise give different colors on reduction.

The mixed complex acids of the 1:24 series are of no particular interest, and it suffices to mention here that they were prepared from mixtures of tungstate and molybdate by essentially the same methods as described for pure acids of the 1:24 series.

The mixed complex acids of the 1:18 series, on the other hand, count among its members the chief component of the phenol reagent of Folin and Denis, and it is of practical impor-
tance to know the conditions of their formation. These have been found as follows:

1. In the absence of a strong acid (hydrochloric) the complex formed is one with high tungsten content (not very sensitive to reduction), no matter how much molybdate may be used. It appears that under this circumstance the MoO₃ is not sufficiently condensed to form a long chain; the excess MoO₃ remains in the form of colorless compounds of Group II.

2. A strong acid (hydrochloric) must be used in order to incorporate all the molybdate used in the complex. The greater the proportion of molybdenum used in the mixture, the larger is the amount of acid required.

3. In the presence of molybdate a considerable amount of strong acid may be used without the formation of the complexes of the 1:24 series. However, when too much strong acid is used the 1:24 complexes are formed with corresponding decrease in the yield of the 1:18 complexes.

Since the 1:18 complexes are the desired components of the phenol reagent, the condition should be so adjusted as to obtain the maximum yield of those products. The following method, which gives a solution identical with the "phenol reagent" of Folin and Denis, prepared according to the latest direction, is intended to illustrate the preparation of mixed complex acids of 1:18 series.

Dissolve 100 gm. of Na₂WO₄·2 H₂O and 25 gm. of Na₂MoO₄·2 H₂O in 700 cc. of H₂O. Add 50 cc. of 85 per cent H₃PO₄ and 100 cc. of concentrated HCl. Boil with return condenser for 8 hours. The resulting solution contains mixed acids of the 1:18 series with a bare trace of the acids of the 1:24 series, and may be diluted for use as a phenol reagent.

To prepare the pure 1:18 mixed acid proceed as follows:

Saturate the cooled solution with solid ammonium chloride. Filter the crystalline precipitate on a Buchner funnel. Redissolve in 150 cc. of warm water, and remove the insoluble yellow residue by filtration through hard-ened filter paper. Add to the clear filtrate an equal volume of concentrated HCl, extract with ether, and proceed as described under the preparation of the phospho-18-molybdate acid. The mixed acids of the 1:18 series suffer transformation at high temperatures to the 1:24 acid, and the solution should be evaporated at room temperature, preferably over H₂SO₄.
If only the ammonium salt is desired, it may be salted out with NH₄Cl from the clear solution and recrystallized from warm water. The free acid should give no precipitate (amorphous) with ammonium chloride, and the ammonium salt should give a perfectly clear solution.

Analysis of the ammonium salt, which was chloride-free, gave the following results (Table VI).

<table>
<thead>
<tr>
<th>Per cent</th>
<th>P₂O₅</th>
<th>WO₃</th>
<th>MoO₃</th>
<th>(NH₄)₂O</th>
<th>H₂O (by difference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.327</td>
<td>73.57</td>
<td>15.10</td>
<td>3.690</td>
<td>4.313</td>
<td></td>
</tr>
<tr>
<td>Ratio</td>
<td>1</td>
<td>13.55</td>
<td>4.48</td>
<td>3.060</td>
<td>10.24</td>
</tr>
</tbody>
</table>

The P₂O₅, the combined oxides, and the (NH₄)₂O were determined as described under the phospho-18-tungstic acids; the molybdenum was separated from the tungsten by the tartaric acid method of Rose, and determined directly. It will be noted that the ratio

\[
\frac{WO_3 + MoO_3}{P_2O_5} = 18.03
\]

showing that the compounds belong to the 1:18 series. The sample analyzed was clearly not a chemical individual, but a mixture of

\[3 (NH_4)_2O \cdot P_2O_5 \cdot 13 WO_3 \cdot 5 MoO_3 \cdot 10 H_2O\]

and

\[3 (NH_4)_2O \cdot P_2O_5 \cdot 14 WO_3 \cdot 4 MoO_3 \cdot 10 H_2O\]

It is to be noted also that the ratio MoO₃:WO₃ in the complex is about the same as the ratio of the molybdate to the tungstate used in the preparation, and it seems that individual mixed acids can be obtained by starting with molybdate and tungstate in ratios of integers which give a sum of 18.

**Reduction of the Complex Acids.**

The phosphotungstic and phosphomolybdic acids are very sensitive to reduction, remarkably so in comparison with the corresponding simple acids. The complex acids are, indeed, akin to chromic acid in their power of oxidation and in their
The complex acids yield on moderate reduction highly colored compounds which resemble the corresponding unreduced compounds in all respects except that of color. Thus, the reduced phospho-24-molybdic and phospho-24-tungstic acids form difficultly soluble ammonium salts. The salts of the reduced phospho-18-molybdic and phospho-18-tungstic acids are soluble, but they can be salted out with ammonium chloride. All are precipitable with pyridine in acid solution and all are extractable with ether. The methods described for the isolation and purification of the unreduced compounds are also applicable to the reduced compounds.

The complex acids arranged in the order of increasing sensitivity to reduction are as follows:

1. Phospho-24-tungstic acid.
2. B-Phospho-18-tungstic acid.
4. Phospho-24-molybdic acid.

The last two acids react with a variety of mild reducing agents in acid as well as in alkaline solution, while the first three are reduced only when the solution is rendered alkaline. The sensitivity to reduction runs parallel with the color of the compound, and this parallelism holds also for the mixed complex acids.

The salient feature of the reduction of the complex acids is that the sensitivity is localized in one or two atoms of the metal in the 1:18 series, and probably the same number in the 1:24 series. This view finds support in the fact that complex salts of the 1:17 and 1:22 series formed respectively from the 1:18 and 1:24 acids with the loss of one and two atoms of the metal are totally inert.

Mild reducing agents (ferrous salt, sulfite, uric acid, etc.) affect only the sensitive atoms, and the resulting products are still complex acids. But if the reduction is carried further, for example, by means of an excess of zinc and hydrochloric acid,
the complex structure is disintegrated and all the atoms of the metal originally in the complex can be reduced just as those in the simple acids would be under the same circumstance. The disintegration of the complex is shown by the fact that pyridine no longer produces a precipitate and that after reoxidation the simple tungstic acid or molybdic acid can be seen suspended.

The reduced complex acids are readily restored to the original by oxidation, for example with bromine water. This shows that none of the atoms of the metal is detached from the complex. Consequently the exact composition of the reduced compounds has to be inferred from their oxidation-reduction equivalent, because the difference is too small to be determined with certainty by direct analysis. The oxidation-reduction equivalent was determined by titration of the reduced compound with potassium permanganate and by comparison of the maximum color produced by a given amount of the complex (in the presence of an excess of reducing agent) with that produced by a given amount of the reducing agent (in the presence of an excess of the complex acid). This latter method is applicable, of course, only when the colors produced are the same and are not interfered with by the products of the reaction. The data on the oxidation-reduction equivalents have been obtained mainly from the study of the molybdenum compound.

Just as molybdenum and tungsten trioxides yield on reduction a number of lower oxides, so also do the complex acids give rise to new complexes containing different lower oxides. The exact compounds formed depend on the nature and amount of the reducing agent, and on whether the solution is acid or alkaline. Thus uric acid reduces in acid solution the phospho-24-tungstic acid, forming a brown-colored complex, but if the solution is rendered alkaline by sodium hydroxide the compound formed is blue in color. The phospho-24-molybdic acid gives a lavender-blue compound with excess of the reducing agent and a greenish blue compound when the complex acid is in excess. It is of course a matter of common observation that different polyphenols and other substances which react with the "uric acid reagent" and the "phenol reagent" usually produce colors of different shade which cannot be wholly accounted for by the color of the oxidation products of phenols.
No attempt was made in this research to prepare all the possible complexes containing lower oxides of tungsten and molybdenum. But a few of them have been obtained in pure state to indicate the possibility of others.

Phospho-18-molybdic acid is reduced with the loss of 1, 2, or 3 atoms of oxygen. The ammonium salts corresponding to these stages have been obtained pure. The tungsten compounds undergo reoxidation rapidly when removed from the reducing medium. They could doubtless be prepared pure in a non-oxidizing atmosphere, but this experiment has not been undertaken. From their analogy with the molybdenum compounds, however, their composition may be inferred.

Complex compounds formed from the 1:24 acid by the loss of only 2 and 4 atoms of oxygen have been obtained, but the possibility of others is of course not excluded. Here again, the reduced phospho-24-tungstic acids show such a tendency to be reoxidized that one has to be content with drawing conclusions by analogy with the molybdenum compound.

The formulas of the reduced complex acids of the 1:18 series, as inferred from their oxidation-reduction equivalents, may be represented as follows:

\[
\begin{align*}
(a) & \quad 3 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 17 \text{MO}_3 \cdot \text{MO}_2 \\
& \quad 3 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 16 \text{MO}_3 \cdot 3 \text{M}_2\text{O}_5 \\
(b) & \quad 3 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 16 \text{MO}_3 \cdot 2 \text{MO}_2 \\
& \quad 3 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 14 \text{MO}_3 \cdot 2 \text{M}_2\text{O}_5 \\
& \quad 3 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 15 \text{MO}_3 \cdot 3 \text{MO}_2 \cdot 3 \text{M}_2\text{O}_5 \\
(c) & \quad 3 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 15 \text{MO}_3 \cdot 3 \text{MO}_2 \\
& \quad 3 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 12 \text{MO}_3 \cdot 3 \text{M}_2\text{O}_5 \\
& \quad 3 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 14 \text{MO}_3 \cdot 2 \text{MO}_2 \cdot 3 \text{M}_2\text{O}_5 \\
& \quad 3 \text{H}_2\text{O} \cdot \text{P}_2\text{O}_5 \cdot 13 \text{MO}_3 \cdot 2 \text{MO}_2 \cdot 3 \text{M}_2\text{O}_5
\end{align*}
\]

It should be noted that it is not a matter of indifference whether, for instance, the compound (a) has the first or the second formula. The first contains one tetravalent atom, and the second, two pentavalent atoms of the metal. It is quite conceivable that the molybdenum or tungsten atoms of different valency are responsible for different shades of color of the reduced complex acids as they are in the simple lower oxides. The gradual increase
in the intensity of the blue color obtained in uric acid determinations may be explained by the conversion of $\text{MO}_2\text{MO}_3$ into $\text{M}_2\text{O}_5$ in the complex or vice versa. It is easy to understand why different shades of color are produced with the same complex acid under different conditions of reduction, especially in the case of the phenol reagent, for here the number of possible structures corresponding to the loss of the same number of oxygen atoms is greatly increased.

**Reduction Experiments.**

*Reduction of Phospho-18-Tungstic Acids by Uric Acid.*—Two color solutions representing the maximum color obtainable respectively from 10 mg. of $\text{NH}_4\text{A-phospho-18-tungstate}$ and 0.3 mg. of uric acid were prepared as follows: (1) 10 cc. of 1 per cent uric acid solution (made by dissolving 1 gm. of uric acid and 1 gm. of Li$_2$CO$_3$ in 100 cc. of H$_2$O) + 2 cc. of 10 per cent Na$_2$SO$_3$ + 1 cc. of 5 per cent NaCN + 1 cc. of 1 per cent $\text{NH}_4\text{A-phospho-18-tungstate}$ + 1 cc. of 20 per cent Na$_2$CO$_3$, and water to a volume of 50 cc. (2) 1 cc. of 0.03 per cent uric acid solution + 2 cc. of 10 per cent Na$_2$SO$_3$ + 1 cc. of 5 per cent NaCN + 10 cc. of 20 per cent Na$_2$CO$_3$ + 10 cc. of 1 per cent $\text{NH}_4\text{A-phospho-18-tungstate}$, and water to a volume of 50 cc.

The Na$_2$SO$_3$ and NaCN together retarded the fading, but did not intensify the color as NaCN alone would, and in this case unequally. The ratio of the color intensities was

\[
\frac{10 \text{ mg. } \text{A}}{0.3 \text{ mg. uric acid}} = \frac{22.7}{20}
\]

or

\[
10 \text{ mg. } \text{A} = 0.34 \text{ mg. uric acid}
\]

A similar experiment with $\text{NH}_4\text{B-phospho-18-tungstate}$ gave

\[
10 \text{ mg. } \text{B} = 0.32 \text{ mg. uric acid}
\]

Since the A form contains 87.6 per cent WO$_3$, and the B form 89.4 per cent WO$_3$, it follows that 18.6 WO$_3 \approx 1$ uric acid for the A form and 20.2 WO$_3 \approx 1$ uric acid for the B form. Considering the inequality of conditions of the color solutions, it may be concluded that 18 WO$_3 \approx 1$ uric acid or 3 H$_2$O·P$_2$O$_7$·18 WO$_3 \approx 1$ uric acid for either form of the complex acid.

*Reduction of Phospho-18-Tungstic Acids in Alkaline Solution by Ferrous Sulfate.*—1 cc. of freshly prepared 0.005 N solution of ferrous ammonium sulfate in 0.2 N H$_2$SO$_4$ was transferred by means of an Ostwald pipette to a 50 cc. volumetric flask. 2 cc. of 5 per cent solution of B-phospho-18-tungstic acid were added, followed by 10 cc. of 20 per cent sodium carbonate solution. 1 cc. of 1 per cent solution of ammonium B-phospho-18-
tungstate was placed in another 50 cc. flask, 5 cc. of the ferrous sulfate solution were added, and diluted with 20 cc. of water, followed immediately by 10 cc. of carbonate solution. Both flasks were then diluted to the mark and mixed. The first solution was not diluted with water before the addition of the carbonate, because the dilute ferrous sulfate solution could not be diluted with water without undergoing considerable oxidation. The dilution was necessary in the second solution to avoid precipitation of the colored compound together with the ferric hydroxide.

The second solution was centrifuged to remove the ferric hydroxide. (Filtration could not be used, because filter paper would absorb some of the blue color.) The solutions were read in a Duboscq colorimeter. The ratio of the color intensities was

\[
\frac{\text{1st solution}}{\text{2nd solution}} = \frac{23}{20}
\]

Now since preliminary experiments had shown that the colors obtained in the first and second flasks were the maximum colors obtainable respectively from 1 cc. of 0.005 N ferrous salt, and 1 cc. of 1 per cent complex salt, and since the latter contained 89.4 per cent of \(\text{WO}_3\), it follows that 1 cc. of 0.005 N ferrous salt \(\approx \frac{23}{20} \times 0.00894 \approx 0.0103\) gm. \(\text{WO}_3\). Whence

\[
8.85 \text{WO}_3 \approx \text{Fe}.
\]

A similar experiment with the A form gave

\[
\frac{1 \text{ cc. of 0.005 ferrous salt}}{1 \text{ cc. of 1 per cent complex salt}} = \frac{23.6}{20}
\]

Since the ammonium salt of the A-acid contained 87.6 per cent of \(\text{WO}_3\), it followed that 1 cc. of 0.005 N ferrous salt \(\approx \frac{23.6}{20} \times 0.00876 \approx 0.0104\) gm. of \(\text{WO}_3\). Whence 8.90 \(\text{WO}_3 \approx \text{Fe}.
\]

In either case the ratio \(\text{WO}_3:\text{Fe}\) was close enough to 9:1 to justify the conclusion that 3 \(\text{H}_2\text{O}-\text{P}_2\text{O}_7\cdot18 \text{WO}_3\) loses 1 atom of oxygen when reduced by ferrous salt in alkaline solution.\(^7\)

Comparison of the Colors Obtained by Reduction with Uric Acid and with Ferrous Salt.—1 cc. of freshly prepared 0.01 N solution of ferrous ammonium sulfate in 0.2 N \(\text{H}_2\text{SO}_4\) was placed in a 100 cc. volumetric flask. In another flask was placed 1 cc. of 0.1 per cent solution (= 1 mg.) of uric acid dissolved with the aid of lithium carbonate. To each flask were then added 2

\(^7\) Sometimes the ferric hydroxide remained in colloidal solution, in which case the experiment was of course discarded. At other times the two color solutions did not match well and slightly different readings may be obtained by different observers. This does not, however, alter the conclusion already reached.
cc. of a 10 per cent solution of B-phospho-18-tungstic acid, followed by 20 cc. of 20 per cent sodium carbonate solution. The solutions were diluted to the mark, mixed, and read in a Duboscq colorimeter. The ratio of the color intensities was

\[
\frac{1 \text{ mg. uric acid}}{1 \text{ cc. 0.01 N ferrous salt}} = \frac{23.8}{20} = 1.19
\]

The experiment was repeated using the A form with the same result. If 1 molecule of uric acid was oxidized by 1 atom of oxygen, the 0.1 per cent solution was exactly 0.0119 N. It is therefore to be concluded that 1 molecule of uric acid reacts with 1 molecule of 3 H₂O·P₂O₅·18 WO₃, confirming the results already obtained in the two previous experiments.

When the methods employed in the above experiments were applied to the corresponding molybdenum compound, the results obtained were not rational, probably because different reduction products were formed. This was to be expected from the much greater susceptibility to reduction of the molybdenum as compared with the tungsten compound. But another possible reason was that the molybdenum compound was also more readily decomposed by alkali, so that a part of it may be decomposed instead of being reduced.

Preparation of Ammonium Salts of Reduced Complex Acids: 3 (NH₄)₂O·P₂O₅·17 MoO₃·MoO₃·H₂O.—The phospho-18-molybdic acid is reduced only with the loss of 1 atom of oxygen by ferrous salt in acid solution. The reduction is an incomplete reaction and a large excess of the reducing agent must be used to prepare the reduced compound.

10 gm. of ammonium phospho 18 molybdate and 25 gm. of ferrous sulfate were dissolved together in 60 cc. of 10 per cent sulfuric acid. When all the solid substances had dissolved, 12 gm. of ammonium chloride were stirred in. Immediately a black crystalline precipitate was formed which after standing 10 minutes was filtered on a small Buchner funnel and washed with 20 per cent ammonium chloride solution until free from iron. The precipitate was redissolved in 50 cc. of warm water and evaporated at 60°C. until crystals began to form on the surface and allowed to cool slowly. Black crystals. It lost 12.50 per cent of its weight on gentle ignition. By calculation (on the basis of 1 P₂O₅ to 18 MoO₃ in the residue) 1 gm. of the substance = 0.8295 gm. of MoO₃. 14.30 cc. of 0.01 N permanganate were required to titrate 0.2206 gm. of the substance. Whence 18 Mo = O.

The corresponding tungsten compound could be prepared by reduction with slight excess of Zn and hydrochloric acid in the cold, but, as already mentioned, it could not be easily purified.
Chemistry of Acids

\[3 \text{(NH}_4\text{)}_2\text{O}_7\text{P}_2\text{O}_{16} \text{MoO}_3 \text{+ MoO}_3 \text{+ H}_2\text{O} = 10 \text{ gm. of the orange molybdenum salt were dissolved in 50 cc. of H}_2\text{O, and 5 cc. of 40 per cent HI and 5 gm. of NaHSO}_3 \text{ were added. The mixture was allowed to stand 24 hours. 10 gm. of solid NH}_4\text{Cl were stirred in. After a few minutes the crystalline precipitate was filtered on a Buchner funnel, washed with 20 per cent NH}_4\text{Cl solution until free from sulfate, and finally once with ice-cold 5 per cent NH}_4\text{Cl solution, and sucked as dry as possible. The product was recrystallized from warm water. Black crystals. It lost 21.45 per cent of its weight on ignition. By calculation 1 gm. of the substance = 0.7447 gm. of MoO}_3. \text{ 0.2595 gm. of the substance required 14.46 cc. of 0.02 N KMnO}_4 \text{ to discharge the blue color. Whence 18 Mo } \approx 20.\]

\[3 \text{(NH}_4\text{)}_2\text{O}_7\text{P}_2\text{O}_{16} \text{MoO}_3 \text{+ H}_2\text{O} = 10 \text{ gm. of the orange salt were dissolved in 50 cc. of H}_2\text{O, 5 cc. of 40 per cent HI were added, and a current of H}_2\text{S was passed into the solution until the latter was saturated. After 24 hours the solution was filtered to remove the sulfur. The filtrate was treated with 10 gm. of solid ammonium chloride. The crystalline precipitate was filtered and washed with 20 per cent NH}_4\text{Cl solution until free from iodide. The product was recrystallized once from warm water. Black crystals, with violet reflex. The preparation lost 18.65 per cent of its weight on ignition. By calculation 1 gm. of the substance = 0.7713 gm. of MoO}_3. \text{ 22.90 cc. of 0.02 N permanganate were required to titrate 0.2615 gm. of the substance. Whence 18 MoO}_3 \approx 30.\]

\[3 \text{(NH}_4\text{)}_2\text{O}_7\text{P}_2\text{O}_{16} \text{MoO}_3 \text{+ H}_2\text{O} = 10 \text{ gm. of phospho-24-molybdic acid were dissolved in 50 cc. of H}_2\text{O, 5 cc. of 40 per cent HI and 5 gm. of NaHSO}_3 \text{ were added. When all the sulfite had dissolved, 10 gm. of NH}_4\text{Cl were stirred in. The amorphous precipitate was filtered, washed with NH}_4\text{Cl solution until free from sulfate, and finally once with water. Blue powder. It lost 11.07 per cent of its weight on ignition. By calculation 1 gm. of the substance was equivalent to 0.8541 gm. of MoO}_3. \text{ 0.3268 gm. of the substance suspended in water required 15.05 cc. of 0.02 N KMnO}_4 \text{ for the titration. Whence 24 MoO}_3 \approx 20.\]

\[3 \text{(NH}_4\text{)}_2\text{O}_7\text{P}_2\text{O}_{16} \text{MoO}_3 \text{+ H}_2\text{O} = 10 \text{ gm. in the above experiment the reacting mixture was allowed to stand 24 hours, the reduction would proceed further. The resulting product was quite soluble and was separated from the solution by saturation with NH}_4\text{Cl. A deposit of black precipitate was formed on standing. It was filtered, washed with 20 per cent NH}_4\text{Cl solution until free from sulfate, and finally once with water. The preparation lost 15.55 per cent of its weight on ignition. By calculation 1 gm. of the substance was equivalent to 0.8110 gm. of MoO}_3. \text{ 0.2668 gm. required 24.85 cc. of 0.02 N KMnO}_4 \text{ for titration. Whence 24 MoO}_3 \approx 40.\]

**Application of Complex Acids in Analytical Chemistry.**

Phosphomolybdic and phosphotungstic acids have been used largely in organic analysis. The readiness with which the complex acids undergo reduction and the intensity of the color of the
The complex acid solution should of course give no color when rendered alkaline. Sometimes the complex acid solution assumes a greenish tint due to some reduction by organic dust. This is of no practical consequence, but it can be removed by a few drops of bromine water. The excess of the bromine should of course be boiled off.

1. *Detection of Copper.*—Cuprous copper reduces the complex acid. The color of the reduction product is so intense that one part of Cu in 5,000,000 parts of water gives an unmistakable test. It is at least 50 times as sensitive as the ferrocyanide reaction. To apply the test to cupric copper proceed as follows:

To the copper solution add a few drops of 5 per cent potassium cyanide solution, acidify with HCl, followed by a few drops of the solution of the complex acid ("phenol reagent"). Mix. If more than a trace of copper is present the solution will become blue at once. But if only a trace of copper is present, the blue color will be obscured by the yellow color of the complex acid. Render the solution alkaline with saturated sodium carbonate solution, whereupon the unreduced yellow complex acid is transformed into a colorless salt. If copper is present the solution will now be blue.

The complex acids react also with ferrous salts, hydrogen sulfide, hydrogen iodide, sulfur dioxide, stannous chloride, etc., and its usefulness for the detection as well as for the colorimetric determination of these substances is apparent.

2. *Detection of Phosphoric Acid.*—Hydrogen iodide reduces phosphomolybdic acids but not simple molybdic acid in the cold. Since the phospho-24-molybdic acid is formed from phosphoric acid and molybdic acid even in the cold, the presence of phosphoric acid can be tested with the aid of hydrogen iodide. The test may be made as follows:

---

8 Arsenomolybdic acids probably react like phosphomolybdic acids.
To the solution to be tested, add 1 to 2 cc. of 2 per cent pure ammonium molybdate solution, then 2 to 3 cc. of 10 per cent potassium iodide solution, 1 cc. of 10 per cent NaHSO₃ solution, and finally 1 to 2 cc. of concentrated HCl. Mix the solution and allow to stand. The color develops slowly when the amount of phosphoric acid present is small, but the solution will assume a greenish tint after 10 or 20 minutes even when only a trace of phosphoric acid is present. The bisulfite destroys the iodine liberated and hastens the reaction, but it imparts to the solution a yellow color and tends to obscure the blue color of the reduced phospho-24-molybdic acid. Render the solution alkaline with saturated sodium carbonate solution. The yellow color will now disappear and a pure blue color will be obtained. One part of phosphorus in 1,000,000 parts of water gives unmistakable test. It is well to carry a blank to insure that the reagents used are free from phosphoric acid.

3. Colorimetric Determination of Phosphoric Acid.—The qualitative reaction for phosphoric acid can be made the basis of a colorimetric method for the determination of that substance. The writer expects to apply the method to biological fluids and to describe the details elsewhere. The provisional procedure may be given as follows:

To the unknown solution containing 0.1 to 0.2 mg. of P in a volume of about 5 cc. add 5 cc. of each of the following solutions: 10 per cent sodium bisulfite, 10 per cent potassium iodide, 2 per cent ammonium molybdate, and 1:1 HCl. Add the same solutions to 5 cc. of standard phosphate solution containing 0.15 mg. of P. Mix. Cover the flasks (graduated at 50 cc.) with watch-glasses and allow to stand for 2 hours. Then add to each flask 10 cc. of 20 per cent sodium carbonate solution, shake to hasten the escape of CO₂, dilute volume, mix, and compare the color values in a colorimeter (Duboscq). The color developed at the end of 2 hours is not the maximum, but it is sharply proportionate to the amount of phosphoric acid within the range from 0.1 to 0.22 mg. of P.

4. Indicator in Oxidation-Reduction Titrations.—An inside indicator for oxidation-reduction titrations is a long felt want in analytical chemistry. The advantages of the dichromate solution are offset by the inconvenience of the outside indicator. If to a ferrous salt solution a few drops of the mixed complex acid solution are added, the solution will be colored blue until all the ferrous iron is oxidized. Unfortunately the green color of the chromium salt tends to obscure the end-point, and satisfactory results can be obtained only when the amount of chromium involved is small (about 30 cc. of 0.02 N bichromate solution),
and then it is also necessary to have a blank by the side for comparison.

If no colored compound is produced in the oxidation-reduction reaction, the end-point is then very sharp. This is the case when a ferrous solution is titrated with a solution of hydrogen peroxide. The following experiment may be cited.

20 cc. of 0.05 N ferrous ammonium sulfate (in 10 per cent H₂SO₄) solution were measured into an Erlenmeyer flask, and three drops of the complex acid solution were added. An approximately N/15 solution of hydrogen peroxide was then run into the iron solution until all the blue had disappeared and a pure yellow color (due to complex acid) was obtained. 29.98 cc. of H₂O₂ were used. 30 cc. of the same solution required exactly 20 cc. of standard 0.05 N KMnO₄ solution for the titration. In this experiment a solution of ferrous salt previously titrated with a slight excess of H₂O₂ was placed by the side for comparison when the end-point was approached.

Hydrogen peroxide does not of course keep well enough to be depended upon for constant use, unless it is standardized with KMnO₄ whenever used. The writer offers the suggestion only to indicate the possibility of this novel use of the complex acid.

SUMMARY.

1. There are two series of complex phospho-acids of molybdenum and tungsten. In one series the ratio P₂O₅ : MO₃ is as 1:18; in the other, as 1:24. The “uric acid reagent” and “phenol reagent” of Folin and Denis contain acids of the former series.

2. Distinguishing reactions for the different complex acids are given.

3. Conditions of the formation of complex acids have been studied, and simple methods for the preparation of all the complex acids have been worked out.

4. Two phospho-18-tungstic acids, possibly isomeric forms, have been prepared.

5. A large number of complex acids containing both molybdenum and tungsten are shown to exist, and the method of their preparation is illustrated by an example.

6. Complex acids give on moderate reduction a number of new complex acids containing lower oxides of molybdenum and tungsten. The possibility of isomerism in these compounds is discussed.
7. New applications of the complex acids in analytical chemistry are illustrated by their use for the detection of minute quantities of copper and of phosphoric acid, for the colorimetric determination of phosphoric acid, and by their use as inside indicator for oxidation-reduction titrations.

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CORRECTION.

On page 215, Vol. XLIII, No. 1, August, 1920, lines 20 and 21, the formula $3 \left(\text{NH}_4\right)\text{O} \cdot \text{P}_2\text{O}_5 \cdot 17 \text{MoO}_3 \cdot \text{MoO}_2 + \text{H}_2\text{O}$ should read $3 \left(\text{NH}_4\right)\text{O} \cdot 
\text{P}_2\text{O}_5 \cdot 17 \text{MoO}_3 \cdot \text{MoO}_2 + \text{n H}_2\text{O}$. The formulas on page 216 of the same volume should be similarly corrected.