

freezing point, both of which results confirm views held or conclusions arrived at by others.

4. It has then been proved that the preparation of absolute sulphuric acid may rightly be based on the minimum specific electrical conductivity or on the maximum freezing point.

5. It has been shown that for the analysis of 95 per cent. or more concentrated sulphuric acid, the electrical conductivity yields results whose error never seriously exceeds 0.01 per cent., and is generally less.

6. There has been arranged a table of specific electrical conductivities of sulphuric acid which may be used for analytical purposes.

Further work on the conductivity and other physical properties of sulphuric acid is now in progress. It is also hoped that sulphur trioxide may be more fully investigated both as to physical and chemical properties.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

DERIVATIVES OF COMPLEX INORGANIC ACIDS;¹ ALUMINICO-TUNGSTATES AND ALUMINICO-PHOSPHOTUNGSTATES.

By LLOYD C. DANIELS.

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Some years ago Balke and Smith² described an ammonium and a silver ammonium aluminico-tungstate, $3(\text{NH}_4)_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{WO}_3 \cdot 4\text{H}_2\text{O}$ and $11\text{Ag}_2\text{O} \cdot 21(\text{NH}_4)_2\text{O} \cdot 4\text{Al}_2\text{O}_3 \cdot 36\text{WO}_3$, in which the ratio of aluminum oxide to tungstic trioxide was 1:9. It seemed well to prepare other salts to learn whether this ratio was preserved in a series of such derivatives.

It was also desired to isolate the free aluminico-tungstic acid. A solution of it was, indeed, obtained, but upon evaporation, even at room temperature, decomposition occurred. When the solution was neutralized with ammonium hydroxide, a salt identical with that from which the acid was liberated, reappeared.

Aluminico-tungstic acid reacted acid to methyl orange, and in the cold displaced carbon dioxide from solutions of sodium bicarbonate. It is soluble in 50 per cent. or stronger alcohol, but on standing in such a solution the tungstic acid, or part of it, is reduced, a blue solution, but no precipitation, resulting. This acid was prepared by the method employed by Wolcott Gibbs and later workers, in liberating free complex inorganic acids; *i. e.*, by treating the mercurous salt with a little less than the amount of hydrochloric acid required to precipitate all of the mercury

¹ From the author's thesis for the Ph.D degree.

² THIS JOURNAL, 25, 1220.

as mercurous chloride, shaking well, and filtering off the mercurous chloride, and the excess of the mercurous complex salts.

Having established the stability of the ratio Al_2O_3 to 9WO_3 in several salts, the introduction of pentoxides into the complex was made, obtaining new complexes.

The analysis of complex inorganic salts has always been a matter of great difficulty. It will be noticed how often dry gas methods were used in this study to decompose the compounds. This was because they were much simpler on account of not requiring the admixture of large quantities of foreign matter. Tungsten compounds almost always require repeated fusions for complete decomposition, and sometimes a second repetition of a fusion with carbonate or acid sulphate is not enough. The greatest difficulty arising in the dry gas decompositions was the adherence of the residue to the glaze of the porcelain boat. This could usually be avoided by keeping down the temperature of the furnace to as low a point as possible. When any of the gaseous products of the decomposition were to be caught for analysis, as, for instance, the arsenious chloride in the arsenic compounds, the anterior end of the combustion tube was bent into a U, with a bulb at the bottom and one at the anterior side of the U.

Experimental Part.

Copper Aluminico-Tungstate, $2\text{CuO} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{WO}_3 \cdot 16\frac{1}{2}\text{H}_2\text{O}$.—This salt was made in two ways: by adding to a 10 per cent. solution of copper sulphate, a concentrated solution of ammonium aluminico-tungstate, and by precipitating the cupric oxide from an ammoniacal solution with ammonium aluminico-tungstate, $3(\text{NH}_4)_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{WO}_3$.

In the first case, a slimy, "bird's-egg blue" sediment forms at the bottom of the vessel. If the copper sulphate solution be diluted about six times, no precipitate, or very little precipitate, is formed. One or two drops of concentrated hydrochloric acid are sufficient to prevent precipitation, and acid of that strength even redissolves the precipitate on warming. This acid solution is, however, not of such a deep blue as the copper sulphate solution from which it was made, but has an extremely pale blue tint. If the copper sulphate solution be warmed before precipitating, the copper salt formed is of much darker blue and is flocculent in appearance. Filtering this off while hot, more of the pale blue sediment separates from the filtrate on cooling. All attempts to get the salt crystalline by slow evaporation resulted in the separation of the pale blue sediment. Whether precipitated hot or cold, the copper compound, on filtering off and drying in a vacuum desiccator, becomes an indigo-colored powder which dissolves in large amounts of water, and separates out in the pale blue form if evaporated slowly, or as the darker blue floccules upon evaporation on a water-bath.

An ammoniacal solution of cupric oxide on addition of ammonium aluminico-tungstate solution gives a dark blue flocculent precipitate indistinguishable by color from the precipitate formed in hot copper sulphate solutions. This precipitate is preserved in very dilute solutions. Filtered off, washed with (1 to 3) ammonia, and dried, it is of the same color as the copper compound from a copper sulphate solution. It also shows the same reactions on dissolving in much water and evaporating slowly, or rapidly, as mentioned above. The precipitate made in this way, washed with ammonia, and dried in a vacuum-desiccator, was analyzed as follows:

One gram of the sample was dissolved in water to which a little sulphuric acid had been added, and a stream of hydrogen sulphide passed through the solution, until all the copper was precipitated. For fear a little tungsten might precipitate with the copper sulphide, it was re-dissolved in hydrochloric acid, the hydrogen sulphide boiled off and the solution made slightly ammoniacal, and hydrogen sulphide again passed through until the copper was all down. This cupric sulphide was washed with water containing ammonium sulphide and ammonia. It was dried, separated from the filter, the latter burned in a weighed crucible into which the cupric sulphide was then placed, and ignited to cupric oxide. A drop of nitric acid was added after cooling, and the residual cupric oxide again ignited and weighed.

The filtrate from the first cupric sulphide precipitation was evaporated in a platinum crucible and fused with acid sodium sulphate, the fused mass being extracted with hot (1 to 5) nitric acid to which a little hydrochloric acid was added. The filtrate from the tungsten trioxide so formed was analyzed, as usual, for aluminium. The alumina was fused with sodium bisulphate to remove any tungsten trioxide adhering to it. It was then reprecipitated and reweighed.

A half gram of the substance heated on a weighed watch-glass to 200° in an air-bath gave the water content.

A portion, tested in a quantitative way for ammonia, showed none.

Calculated: 2CuO , 6.01; Al_2O_3 , 3.86 ; 9WO_3 , 78.94; $16\frac{1}{2}\text{H}_2\text{O}$, 11.19.

Found: 2CuO , 6.07; Al_2O_3 , 3.80, 3.82; 9WO_3 , 78.74; $16\frac{1}{2}\text{H}_2\text{O}$, 11.39.

WO_3 is by difference.

Barium Aluminico-Tungstate, $8\text{BaO}.\text{Al}_2\text{O}_3.9\text{WO}_3.7\text{H}_2\text{O}$.—This compound is a white powder precipitated from barium chloride solution by ammonium aluminico-tungstate. It is so insoluble that dilute sulphuric acid gives but a very slight precipitate in the filtrate from it. It is not, however, precipitated from a solution of barium chloride containing more than traces of hydrochloric acid, but acids do not dissolve it after drying. The dried powder is somewhat decomposed on boiling

ten or fifteen minutes with concentrated hydrochloric acid, nitric acid or aqua regia.

Complete decomposition of this compound for analysis proved difficult. Three successive fusions with sodium and potassium carbonate mixture failed to remove the tungstic acid completely, and an accidental test of one of the filtrates from the barium carbonate showed the presence of barium in considerable quantity.

Abandoning the alkaline fusion, an effort was made to separate the barium as barium sulphate, by fusing with sodium acid sulphate and leaching with dilute acid to remove aluminium, and then with ammonia to remove tungsten trioxide. This also proved fruitless, since two fusions failed to remove as much as half of the tungstic acid. Alumina also remained in the barium sulphate.

Next, it was sought to remove the tungstic acid by dry hydrochloric acid gas, and it was found that heating to a red heat in the gas does remove a large part of the tungstic acid, but not enough to give anything like quantitative results. By first reducing in dry hydrogen, and then passing dry chlorine at a low temperature over the boat, the tungsten is removed as oxychloride with ease and almost quantitatively, in one operation. One repetition of this treatment leaves a pure white barium chloride alumina mixture in the boat, and if it has not been heated to too high a temperature the boat will not be stained. The barium chloride may then be leached out with water and the alumina weighed. On fusing the alumina with sodium bisulphate, no traces of tungstic acid were found. Barium sulphate was also absent.

It was also observed that hydrogen sulphide passed over the barium aluminico-tungstate in a boat, in a combustion tube heated very gently, converts the tungsten trioxide to tungsten trisulphide, or partly to a lower sulphide depending on the temperature. The contents of the boat treated with dilute hydrochloric acid yield barium chloride free from alumina, and almost free from tungsten trioxide, the traces of the latter being removed by evaporating with hydrochloric acid and taking up with the same dilute acid. The tungsten sulphide is removed from the alumina by an ammonium sulphide solution. This did not give very good results for alumina, but checked well with the method mentioned above for barium.

Calculated: 8BaO , 34.64 ; Al_2O_3 , 2.89 ; 9WO_3 , 58.87 ; $7\text{H}_2\text{O}$, 3.56

Found: 8BaO , 34.80, 34.76; Al_2O_3 , 2.82, 2.73; 9WO_3 , 58.77, 58.90; $7\text{H}_2\text{O}$, 3.61

WO_3 is by difference. The first results are by the first method, the second by the second.

Mercurous Aluminico-Tungstate, $5\text{Hg}_2\text{O}.\text{Al}_2\text{O}_3.9\text{WO}_3$. — When precipitated in the cold, this is a very pale yellow precipitate of a flocculent nature, much like silver bromide. It darkens somewhat on boiling,

and becomes a powder with the lemon-yellow color of tungsten trioxide on drying. It is much more soluble in water than the barium salt, but is not prevented from being precipitated by the presence of a considerable amount of nitric acid. It is not redissolved to any considerable extent by the addition of 3 cc. of concentrated nitric acid to 50 cc. of the supernatant liquor. It is, however, soluble in (1 to 5) nitric acid.

The mercurous oxide in this compound was determined by precipitation as mercurous chloride from a sulphuric acid solution. The precipitate was dried at 105° to 110° , and weighed on a tared filter. The mercury and water were driven off together at a low red heat, and the value of mercurous oxide subtracted from the loss in weight gave the water content. The alumina was determined as in the copper salt.

Calculated: $5\text{Hg}_2\text{O}$, 48.35 ; Al_2O_3 , 2.95 ; 9WO_3 , 48.40

Found: $5\text{Hg}_2\text{O}$, 48.42, 48.38; Al_2O_3 , 2.82, 2.80; 9WO_3 , 48.76, 48.82

WO_3 is by difference.

Zinc Aluminico-Tungstate, $1\frac{1}{2}\text{ZnO} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{WO}_3 \cdot 8\text{H}_2\text{O}$; $\text{ZnO} \cdot \text{Al}_2\text{O}_3 \cdot 9\text{WO}_3 \cdot 20\text{H}_2\text{O}$.—In a solution of zinc oxide in ammonia a solution of ammonium aluminico-tungstate produces a fine white powdery precipitate. This is soluble in much water free from ammonia, and evaporation, slow or rapid, yields a light flocculent residue. The precipitate is immediately soluble in extremely dilute mineral acids or acetic acid. In hot concentrated mineral acids it dissolves to a light yellow solution which deposits tungstic acid on boiling awhile or upon standing in the cold. While attempting to dry on a water-bath, the mass was melted to a yellowish white oil, a white residue floating on its surface. On continued heating on the bath the oil dried up to a vitreous mass, easily friable. On treating this mass with water, the white portion remained undissolved, while the glassy portion went into solution in very little water. The white residue, filtered off, proved to be nearly pure zinc oxide, while the same yellow oil as before, but no more zinc oxide, separated out.

Zinc sulphate solution, even saturated, gives no precipitate with ammonium aluminico-tungstate unless ammonia be added. But a very concentrated zinc chloride solution on treatment with a concentrated solution of ammonium aluminico-tungstate leads to the separation of a yellow oil which settles and soon solidifies at the bottom of the vessel in an amorphous mass. Pouring off the excess of zinc chloride and rinsing quickly with a little water two or three times, the residue is dissolved in a little water. It appears to be in every way like the soluble zinc salt obtained by the other method. Analysis proved this to be the case, but it was difficult to remove all of the zinc chloride and still have enough of the aluminico-tungstate to work with.

The zinc was determined both in the soluble and insoluble compounds

by precipitation from acetic acid solutions with hydrogen sulphide. The zinc sulphide was pure white, and contained no sulphides of tungsten, though the solution took on a distinct bluish tint, showing partial reduction of the tungsten trioxide. The other constituents were determined as in the analysis of the copper compound.

INSOLUBLE COMPOUND.

	Mol. wt.	Calc.	Found.	
1½ ZnO.....	122	4.97	5.09	5.11
1 Al ₂ O ₃	102	4.13	4.10	4.04
9 WO ₃	2088	85.05	84.85
8 H ₂ O.....	144	5.87	5.96
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2455				

SOLUBLE COMPOUND.

	Mol. wt.	Calc.	Found.		
			I.	Ia.	II.
1 ZnO.....	81.4	3.09	3.20	3.14	3.28
1 Al ₂ O ₃	102	3.88	3.92	3.95	3.83
9 WO ₃	2088	79.36	79.37
20 H ₂ O.....	360	13.68	13.51
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2631					

The results in column II are from the sample made from zinc chloride. It did not have the same water content as the other sample, but the zinc oxide and alumina contents are calculated up to this water content. Both these samples were merely air-dried. The sample II gave a distinct test for chlorine.

Ammonium Aluminico-Phosphotungstate, $9(\text{NH}_4)_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{P}_2\text{O}_5 \cdot 9\text{WO}_3 \cdot 13\text{H}_2\text{O}$.—When a concentrated solution of orthophosphoric acid, or a solution of ammonium phosphate, containing excess of ammonia, is added to a solution of ammonium aluminico-tungstate, a white powder separates and the solution becomes slightly yellow in color. The white powder is an ammonium aluminico-phosphotungstate and can be purified by solution in a large quantity of water. It is more soluble in hot than in cold water, but the difference is not great. After separation from solution it redissolves with some difficulty, requiring long boiling and more than enough water to make a saturated solution; nevertheless, it dissolves completely.

The mother liquor from which this compound separates probably contains one or more other aluminico-phosphotungstates since qualitative tests show the presence of the three constituents, but no definite compound could be obtained from it by slow evaporation. If phosphoric acid is used, the liquor is acid after the white powder has deposited. More of the white powder may be obtained on the addition of ammonia

in excess. Silver nitrate added to the liquor, in an attempt to free it from excess of phosphoric acid, and to learn if some recrystallizable silver salt or salts could be obtained, precipitated almost the entire mass, and attempts to dissolve out and recrystallize were not successful. The whole precipitate was soluble in ammonia.

The ammonium aluminico-phosphotungstate obtained above was recrystallized and gave the following tests:

With silver nitrate, a yellow precipitate, soluble in ammonia, insoluble in acetic acid, but soluble in dilute nitric acid. This precipitate was too nearly insoluble in water to allow of crystallization, and attempts to crystallize it from ammoniacal solution gave negative results. Direct sunlight darkens it slowly to a deep brown. An analysis of it is appended.

With copper sulphate, an apple-green precipitate, becoming pale blue on heating, or when the precipitation occurs in hot solution. Deep blue precipitate from ammoniacal solution, insoluble in large excess of ammonia. Both are soluble in dilute nitric acid.

Barium, calcium, zinc and cadmium salts give white powdery precipitates, soluble in dilute acid.

Analysis: The ammonium oxide and water were determined as usual. The compound heated to incipient redness in a boat, in a stream of hydrogen sulphide, carrying vapors of carbon bisulphide from having been passed over the surface of cold carbon bisulphide in a flask, gave all the tungsten as sulphide, and the alumina and phosphoric acid were dissolved out with acid. It is notable that the alumina here is soluble in moderately dilute hydrochloric acid, whereas it dissolved little, or not at all, in the case of the aluminico-tungstates, showing that the acid must be in direct union with the alumina in the complex, or that it is in such close contact that on separation of tungstic acid it goes into combination. The alumina and phosphoric acid were separated by molybdate solution in one-half of the solution, and the phosphoric acid determined as magnesium pyrophosphate. To the other half of the solution a little disodium phosphate and acetic acid and sodium acetate were added, and the aluminium phosphate filtered, washed with acetic acid, and weighed as aluminium phosphate.

	Mol. wt.	Calc.	Found.	
9 (NH ₄) ₂ O.....	468	13.14	13.30	13.24
2 Al ₂ O ₃	204	5.72	5.58	5.62
4 P ₂ O ₅	568	15.95	15.66	15.73
9 WO ₃	2688	58.62	59.07	59.02
13 H ₂ O.....	234	6.57	6.39	(6.39)
WO ₃ is by difference.				

Silver Aluminico-Phosphotungstate, $4Ag_2O.2Al_2O_3.4P_2O_5.9WO_3.6H_2O$.—The silver was determined by precipitating from dilute nitric acid solu-

tion with hydrochloric acid, and the alumina and phosphoric acid as in the ammonium salt, after passing hydrogen sulphide over the compound resting in a boat.

	Mol. wt.	Calc.	Found.
4 Ag ₂ O.....	928	23.70	23.82
2 Al ₂ O ₃	204	5.21	5.06
4 P ₂ O ₅	568	14.50	14.29
9 WO ₃	2088	53.33	53.67
6 H ₂ O.....	128	2.26	3.20

Barium Aluminico-Phosphotungstate, $4\text{BaO} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{P}_2\text{O}_5 \cdot 9\text{WO}_3 \cdot 3\text{H}_2\text{O}$.—

This is a powdery white precipitate formed on adding barium chloride solution in excess to a solution of the ammonium salt of the complex. It is very slightly soluble in water, but very dilute hydrochloric or nitric acid dissolves it immediately, even after drying. The sample used for analysis was washed well with ammonium chloride solution to remove any basic barium salt that came down with it, and then with water. The barium oxide was determined once by direct precipitation as sulphate from an acid solution of the complex salt, and, on the other two occasions, in the acid solution resulting from the separation of the tungsten trioxide, as tungsten sulphide, as in the ammonium and silver salts. The alumina and phosphoric acid were determined as in the ammonium salt of the complex.

		Found.			
	Mol. wt.	Calc.	I.	II.	
4 BaO.....	564	16.02	16.28	15.98	15.90
2 Al ₂ O ₃	204	5.86	5.79	5.93
4 P ₂ O ₅	568	16.03	15.91	15.88
9 WO ₃	2088	60.56	60.75	60.72 (by diff.)
3 H ₂ O.....	54	1.55 1.67
3478					

Zinc Aluminico-Phosphotungstate, $5\text{ZnO} \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{P}_2\text{O}_5 \cdot 9\text{WO}_3 \cdot 11\text{H}_2\text{O}$.

—This salt is a white powdery precipitate, soluble in dilute acids and in a large quantity of concentrated ammonia when ammonium chloride is present. From this solution, by spontaneous evaporation in the air, hard, semi-transparent scales deposit. The zinc was determined as sulphide in acetic acid solution of the complex and then converted into oxide with dilute nitric acid. It was contaminated with some tungstic acid which separated on evaporation in the crucible, so after baking it was taken up with strong nitric acid and a drop of hydrochloric acid, and diluted with two volumes of water. The tungstic acid having been filtered off, the solution was again evaporated, the residue ignited, and the zinc oxide weighed. The alumina and phosphoric oxide were determined as in the analysis of the ammonium salt.

		Found.			
	Mol. wt.	Calc.			
5 ZnO.....	406	11.72	11.85 and 11.91, avg. 11.88
2 Al ₂ O ₃	204	5.89	5.80	5.88	
4 P ₂ O ₅	568	16.40	16.25	16.30	
9 WO ₃	2088	60.27	60.28	60.15	
11 H ₂ O.....	198	5.71	5.79
		3464			

Ammonium Aluminico-Arseno-Tungstate, $6(NH_4)_2O \cdot 2Al_2O_3 \cdot 3As_2O_5 \cdot 18WO_3 \cdot 14H_2O$.—This compound was made in two very different ways, but only the sample from the second method was analyzed. What is said of solubility and qualitative reactions, however, fully applies to both. No difference between them could be discovered.

The first method was in every way like that by which the phospho-complex was made, *i. e.*, adding arsenic acid or ammonium arsenate to a solution of ammonium aluminico-tungstate. The resulting compound was indistinguishable from the phospho-compound in appearance, in sparing solubility and in qualitative reactions.

The second method consisted in boiling a solution of ammonium para-tungstate with a semi-solution of aluminium arsenate in ammonia, adding more ammonia, from time to time, to replace that distilled off. The boiling was kept up for several days, when the filtrate was evaporated until the complex separated in the form of a white powder. Since the resulting compound so closely resembled the phospho-complex, it was supposed that it would have a formula resembling that body, *viz.*, $X(NH_4)_2O \cdot 2Al_2O_3 \cdot 4As_2O_5 \cdot 9WO_3$. Analysis showed a different result, the compound resembling the antimonio-complex, even to the ammonium oxide content.

It was analyzed by passing hydrochloric acid gas over a sample heated in a combustion tube, and catching the arsenic chloride in water in a triple U-tube, which was formed by bending the anterior end of the combustion tube. After the arsenic chloride solution was washed out of the tube the boat was replaced in it, and hydrogen gas was led over it while heating to a low red heat. The hydrogen was interrupted when the boat contents were quite red, and chlorine gas was then passed through, carrying out the tungsten as tungsten oxychloride at a low temperature. The reduction in hydrogen was repeated when no more tungsten oxychloride would come over, and chlorine again passed over the reduced material. This was repeated until no more oxychloride could be obtained. The residue in the boat was weighed as alumina.

The arsenic was determined by oxidizing the arsenious chloride solution with bromine, nearly neutralizing with ammonia and heating to about 90° till the excess of bromine was removed, and then precipitating with a magnesia mixture. Considerable tungstic acid was carried over with the arsenic, but this is no detriment to the method, as was shown by

Gooch and Gibbs in their work on arseno-tungstates and arseno-molybdates.

	Mol. wt.	Calc.	Found.
6 (NH ₄) ₂ O.....	312	5.54	5.68
2 Al ₂ O ₃	204	3.61	3.55
3 As ₂ O ₅	690	12.23	12.08
18 WO ₃	4176	74.12	74.09
14 H ₂ O.....	252	4.47	4.61
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WO₃ is by difference.

Barium Aluminico-Arseno-Tungstate, $4\text{BaO} \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{As}_2\text{O}_5 \cdot 18\text{WO}_3 \cdot 12\text{H}_2\text{O}$.—This salt resembles the barium aluminico-phosphotungstate so closely that it is not to be distinguished by tests which do not decompose the compound. Its solubility is about the same as the phospho compound.

The barium was determined in the solution after the arsenic had been removed by passing dry hydrochloric acid gas over the compound in the boat, and the tungsten had been converted to sulphide by passing hydrogen sulphide over the residue. The alumina and arsenic pentoxide were determined as in the ammonium salt.

	Mol. wt.	Calc.	Found.	
4 BaO.....	564	9.71	9.83	9.80
2 Al ₂ O ₃	204	3.49	3.45	3.41
3 As ₂ O ₅	690	11.79	11.62	11.67
18 WO ₃	4176	71.39	7.49 (diff.)	71.51 (diff.)
12 H ₂ O.....	216	3.70		3.61.

Cadmium Aluminico-Arseno-Tungstate, $4\text{CdO} \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{As}_2\text{O}_5 \cdot 18\text{WO}_3 \cdot 12\text{H}_2\text{O}$.—A white, powdery precipitate, soluble in dilute mineral acids and in a strong ammonia solution. From the ammonia solution it separates in long needles on slow evaporation. These needles were analyzed as follows:

The cadmium was precipitated as sulphide from the dilute hydrochloric acid solution of the complex, washed with hydrogen sulphide water, then with ammonium sulphide water, with alcohol, ether, carbon bisulphide, ether, and alcohol in succession, and weighed on a tared filter. The arsenic oxide and alumina were determined as in the ammonium compound.

	Mol. wt.	Calc.	Found.	
4 CdO.....	512	9.00	8.88	9.07
2 Al ₂ O ₃	204	3.58	3.50	3.43
3 As ₂ O ₅	690	12.11	12.10	12.01
18 WO ₃	4176	73.29	73.50	73.76 (diff.)
17 H ₂ O.....	116	2.05	1.98	

Ammonium Aluminico-Antimonio-Tungstate, $6(\text{NH}_4)_2\text{O} \cdot 2\text{Al}_2\text{O}_3 \cdot 3\text{Sb}_2\text{O}_5 \cdot 18\text{WO}_3 \cdot 17\text{H}_2\text{O}$.—This compound was made in two ways: Antimony pentoxide (made by heating antimonious oxide with nitric acid) was boiled up with a solution of ammonium aluminico-tungstate until no further solution of the antimonious oxide took place. Evaporation of the filtrate from this gave an oily compound which, on further evaporation and drying, became a shellac-like gum, indistinguishable in appearance from ammonium aluminico-tungstate. It, however, contained both alumina and antimony pentoxide.

Hoping to get a compound more like the phosphoric acid complex, ortho-antimonic acid (made by treating antimony pentachloride with water) was boiled in the same way as the antimony pentoxide, but the result was the same.

The gum-like mass gave no indication of being other than a single compound.

It gave precipitates with silver nitrate, mercurous nitrate, and copper sulphate of the same colors as the precipitates obtained with the phospho-complex, but of much darker shades, so that the copper precipitate was of a navy-blue color, and the yellow of the mercurous compound was tinged with red. The barium precipitate had a faint yellow tinge.

This compound did not react well with hydrogen sulphide gas, at least not at a temperature so low that there was no danger of reducing the tungsten sulphide with hydrogen from hydrogen sulphide decomposition. Therefore a weighed quantity was mixed with a large quantity of dehydrated sodium thiosulphate in a porcelain crucible, a layer of pure sulphur spread over the mixture, and the crucible heated till its contents became viscous. This fusion was kept up for an hour, sulphur being added from time to time as it burned off. The contents leached out with dilute sulphuric acid, filtered and treated with ammonia, gave a white precipitate of aluminium hydroxide free from tungstic acid. The antimony pentasulphide and tungsten sulphide were separated by oxidizing with nitric acid, evaporating to dryness, taking up with cold (1 to 1) hydrochloric acid, filtering off the tungstic acid, when the antimony was determined as antimony trisulphide, after partially neutralizing the hydrochloric acid with ammonia.

Water and ammonia were determined in the customary way.

	Mol. wt.	Calc.	Found.	
6 $(\text{NH}_4)_2\text{O}$	312	5.23	5.17
2 Al_2O_3	204	3.42	3.47	3.49
3 Sb_2O_5	960	16.11	16.01	15.97
18 WO_3	4176	70.09	70.27
17 H_2O	306	5.13	5.06

Silver Aluminico-Antimonio-Tungstate, $6Ag_2O \cdot 2Al_2O_3 \cdot 3Sb_2O_5 \cdot 18WO_3 \cdot 12H_2O$.—This deep yellow precipitate is soluble in ammonia, but requires nitric acid (1 : 10) to dissolve it. On drying, it becomes brownish yellow in color. Slow evaporation of the ammoniacal solution does not give a crystalline product, for the salt separates in floccules.

The silver was determined once by precipitation from nitric acid solution as silver chloride and again by separation as silver sulphide from the antimonie sulphide and tungsten sulphide gotten by the sodium thiosulphate fusion, then determining it as silver chloride from a nitric acid solution. The antimonie and tungstic sulphides were washed out from the silver sulphide with ammonia and yellow ammonium sulphide, and determined as in the ammonium compound.

	Mol. wt.	Calc.	Found.	
6 Ag_2O	1302	20.04	19.92	19.89
2 Al_2O_3	204	2.94	2.85	3.02
3 Sb_2O_5	960	13.81	13.99	14.05
18 WO_3	4176	60.10	60.25	60.02
12 H_2O	216	3.11	3.00	
	6948			

Barium Aluminico-Antimonio-Tungstate, $5BaO \cdot 2Al_2O_3 \cdot 3Sb_2O_5 \cdot 18WO_3 \cdot 6H_2O$.—This precipitate was a white powder, somewhat insoluble in dilute hydrochloric acid. It turned slightly yellow and almost fused on drying on the water bath, finally becoming a yellowish white, semi-transparent, easily friable mass. It was reduced to a powder and the drying continued on the bath. The barium was determined as sulphate by taking up the fusion in sodium thiosulphate with ammonia and ammonium sulphide, and adding a little ammonium sulphate to make sure all the barium was precipitated. The alumina was dissolved away from the precipitate with dilute hydrochloric acid. The barium sulphate was reweighed, after fusion with alkali carbonate, and reprecipitation, but the same result was obtained. Alumina and antimony pentoxide were determined as in the ammonium compound.

	Mol. wt	Calc.	Found.	
5 BaO	686	11.12%	11.12	11.29
2 Al_2O_3	204	3.30	3.21	3.26
3 Sb_2O_5	960	15.59	15.40	15.48
18 WO_3	4176	67.68	68.07	67.77
6 H_2O	144	2.33	2.20	