

tracted along with lead. Repeated crystallization will entirely remove the yellow color of the lead thiocyanate. It requires only a trace of bismuth in the solution to give a decided yellow cast to the precipitate, yet a considerable quantity is necessary before enough bismuth is present to appear as a residue when dissolved in boiling water.

Lead thiocyanate is white when pure but is readily contaminated by the presence of foreign salts, especially bismuth, in the solution from which it is precipitated. It is entirely soluble in hot water crystallizing out unchanged on cooling, and can be purified by repeated crystallization. Basic lead thiocyanate can not be prepared by boiling the normal salt with water, but must be prepared from a solution of a basic salt such as the acetate.

UNIVERSITY OF WISCONSIN,  
MADISON, WISCONSIN.

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### AMMONIUM VANADICOPHOSPHOTUNGSTATE.

BY EDGAR F. SMITH AND FRANZ F. EXNER.

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During the summer months of 1901 large quantities of wolframite were examined by us for the purpose of ascertaining just what minute constituents were present in it, which might possibly contaminate the tungstic acid derived from this source. That such impurities existed in tungstic acid seemed very probable as the numerous attempts to fix the atomic weight of tungsten, by reduction of the oxide in hydrogen and subsequent oxidation of the tungsten metal, gave unsatisfactory results. The difference between the maximum and minimum values seemed too great to be attributed entirely to the inefficiency of the method so it was determined to seek for impurities, some hint as to the nature of which it was thought could be best realized by taking into study large quantities of the starting-material—wolframite, from Lawrence County, South Dakota.

The finely divided material was decomposed by prolonged digestion with aqua regia. The hydrated tungstic acid, after filtration and thorough washing, was digested with ammonia water.

This solution gave on evaporation large yields of ammonium paratungstate, which after two or three recrystallizations was perfectly white in color. Portions of the same were ignited to trioxide and the latter digested with a 2 per cent. sodium carbonate solution, after the manner of Taylor,<sup>1</sup> when the white residue observed by him remained. It showed the presence of iron, manganese and tungstic acid. Portions of the same ammonium paratungstate were recrystallized ten times from water, the first portions only being used. The tungsten trioxide from the tenth crystallization, when digested with sodium carbonate, left a white residue in which iron, manganese and tungsten were found as before. This proves that mere crystallization, although repeated many times, fails to eliminate this peculiar compound, noticed by Taylor, which most probably has contaminated all tungstic acid derived from wolframite. It could easily occasion the peculiar rise and fall observed in the many atomic weight determinations made during the last fifty years. We shall, however, refrain from further comment on this point, as the purification of tungstic acid is still under investigation in this laboratory.

Those persons who have made ammonium paratungstate from wolframite have surely noticed the dark color of the mother liquor from the salt. In our work the concentration of the mother liquors was continued until their color was black. The ammonium paratungstate was placed to one side, the mother liquors alone being watched. They became very heavy with increased concentration until finally, after great reduction in volume, greenish yellow masses separated, in which brownish octahedral crystals were found. In the filtrate from the greenish masses additional octahedral forms, now perfectly black in color, separated. The greenish material was removed with difficulty from these crystals. But eventually we discovered that if the dark-colored solutions of the octahedral forms were boiled with pure precipitated calcium carbonate the contaminations of the octahedral substance were entirely eliminated and that the concentrated liquids now yielded brilliant black and quite large octahedra. A half pound of these forms was obtained from the wolframite from Dakota and also from impure ammonium paratungstate made from Connecticut

<sup>1</sup> Thesis for Ph.D., 1901.

wolframite. This compound puzzled us. It showed the presence of ammonia, water and tungstic acid, with a small amount of iron and manganese. That it contained ammonia and tungstic acid and did not give these up when boiled with calcium carbonate, suggested the advisability of boiling aqueous solutions of ammonium paratungstate and ammonium metatungstate with calcium carbonate. The tungstic acid in each case was quantitatively precipitated (or nearly so). Ammonium molybdate also surrendered its molybdic acid content completely to the same reagent.

The question then arose why does not the black, octahedral substance yield its tungstic acid content under similar treatment? Ammonium paratungstate and ammonium metatungstate, when heated with acids, yield tungstic acid. The octahedral compound was boiled for six hours with concentrated hydrochloric acid and three hours more with aqua regia, but tungstic acid did not separate. Evidently the tungstic acid in it was held in a peculiarly combined condition. Boiling with ammonia water caused no change. Fusion with sodium carbonate decomposed the compound. The cold fusion showed a slight bluish tinge, indicating manganese, and on dissolving it in water a slight amount of iron and manganese oxides remained (about 1.20 per cent.). The alkaline aqueous solution, when warmed with hydrochloric acid, gave a precipitate of tungstic acid, which soon acquired a deep orange color. When the black crystals were decomposed with acid potassium sulphate, the cold fusion showed a rosin-like appearance. It dissolved partly in water. The aqueous solution was reddish yellow in color, while the residue was white. The solution, acid in reaction, when acted upon by hydrogen sulphide became amethystine in color; the same coloration was noticed when portions of the solution were saturated with sulphur dioxide. The mystery increased.

A reaction frequently used in this laboratory in the past in the purification of tungstic acid, to expel molybdic acid, was now tried; *viz*: the black crystals were ignited in a crucible, and after reduction to powder, were exposed in a porcelain boat to dry hydrochloric acid gas, when to our amazement a brown-colored liquid appeared in the anterior portion of the tube. On drying, this became greenish blue in color. The acid water in the receiver

showed a faint blue tinge which upon concentration of the solution became more intense, indicating *the presence of vanadium*, which was definitely established by the hydrogen peroxide test as well as by other reactions. Thus, vanadium, a hitherto unsuspected impurity in tungstic acid, was found. But, it might fairly be asked, is it probable that this element exists in ammonium paratungstate? A portion of the latter, perfectly white in color after four recrystallizations from water, was examined and it disclosed vanadium!

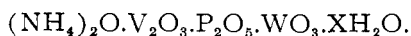
Returning to the black salt it may well be asked why did the sulphuric acid solutions mentioned above take on an amethystine color when they were exposed to the action of hydrogen sulphide and of sulphur dioxide? Surely the presence of small amounts of tungstic acid could not cause this behavior, for ammonium vanadotungstate, prepared according to the recommendation of Dr. Wolcott Gibbs, showed a red or reddish yellow colored solution and gave the blue color characteristic of vanadium when reduced with hydrogen sulphide or sulphur dioxide, after the removal of the major portion of the tungstic acid. How was the peculiar color of the vanadium solution we were studying to be explained? Upon adding ammonium phosphate to ammonium vanadate containing ammonium tungstate, all in aqueous solution, then acidulating with sulphuric acid and reducing the liquid with hydrogen sulphide or sulphur dioxide, an amethystine red color will be produced and not a trace of the blue, always given by vanadium. So at last the abnormal behavior of the latter in the presence of well known reducing agents could be explained. It was due to the presence of phosphoric acid. When some of the black crystals were dissolved in water, and nitric acid and ammonium molybdate added to this solution, the familiar yellow ammonium phosphomolybdate revealed itself.

The puzzle was now solved. The black octahedral salt contained ammonia, water, tungsten, vanadium and phosphorus, with traces of iron and manganese. It was concluded that we had in hand an ammonium phospho-vanado-tungstate. The literature on "complex inorganic acids" gave us no information upon derivatives of this constitution. Assuming that the salt was of this class we employed for its analysis the method of Wolcott Gibbs and also

a method by the same chemist, modified by Friedheim, for vanado-tungstates, but to our surprise both failed, because of the presence of phosphoric acid, so that it was necessary to devise a new method which will be described later elsewhere. It will suffice for the present to mention that success in the analysis was finally reached, and the results are accordingly given as follows :

	Per cent.	Per cent.
$(\text{NH}_4)_2\text{O}$ .....	5.40	5.27
$\text{H}_2\text{O}$ .....	11.85	12.25
$\text{WO}_3$ .....	75.94	75.71
$\text{P}_2\text{O}_5$ .....	0.99	0.94
$\text{V}_2\text{O}_3$ .....	4.03	4.01
$\text{Fe}_2\text{O}_3$ .....	1.19	1.07
$\text{MnO}$ .....	0.04	0.05
	99.44	99.30

Ammonium phospho-vanadates and vanado-tungstates are yellowish red to red in color in aqueous solution. On boiling ammonium tungstate, vanadate and phosphate together, deep red colored solutions resulted. Consequently we were at a loss to account for the brownish black to black color of the aqueous solution of our new salt until after considerable experimenting it was discovered that by the use of vanadium trioxide ( $\text{V}_2\text{O}_3$ ) with ammonium phosphate and ammonium tungstate black colored solutions were obtained, from which octahedral forms crystallized, containing ammonia, water, tungstic acid, vanadium trioxide and phosphorus pentoxide. Regarding the iron and manganese as adventitious substances and deducting them the percentages of the remaining constituents were about identical with those obtained from a salt which was later prepared as indicated immediately above. The new compound, isolated from the mother-liquors of ammonium paratungstate, is a representative of a new group of derivatives. It may be termed ammonium vanadicophosphotungstate,



It suggested the possibility of forming vanadophosphotungstates, vanadoarsenotungstates, vanadovanadotungstates, etc., etc. Thirteen such complex bodies have been made and remade. Their analyses are most satisfactory. They will be described later by Mr. Allen Rogers, who is now occupied with their investigation.

It is needless to add that molybdic acid may be substituted for tungstic acid in all these bodies, and very likely columbic and tantallic oxides may be introduced for vanadic, arsenic and phosphoric oxides, and also with them, thus opening up a new and extensive class or group of acids which we hope to study as time permits.

UNIVERSITY OF PENNSYLVANIA.

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### A NEW QUALITATIVE TEST FOR COBALT.

BY J. L. DANZIGER.

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THE following test, if carried out properly, will serve to detect the presence of cobalt, in a solution containing 1 part of cobalt, in 500,000 parts of water, provided the solution is colorless or but slightly colored, which can readily be obtained by dilution.

To about 5 cc. of the solution, acid with hydrochloric acid, in a test-tube, there is added solid ammonium thioacetate,  $\text{CH}_3\text{COSNH}_4$ , a few drops of stannous chloride solution, and an equal volume of amyl alcohol, or a mixture of acetone and ether or of alcohol and ether; the whole is well shaken and allowed to separate. If any cobalt is present, the upper layer will be colored blue, the intensity of the color depending on the amount of cobalt present. Solid ammonium thioacetate is added to prevent dilution of the solution, since water destroys the blue color. Stannous chloride is added to reduce any iron present, since ferric iron gives a deep red coloration, as with ammonium thiocyanate. Amyl alcohol, a mixture of acetone and ether or of alcohol and ether, is added to diminish the dissociation and extract the color produced by the undissociated cobalt salt. Amyl alcohol was found to be the most efficient, but is objectionable on account of its disagreeable odor.

In order to ascertain to what compound the color was due, a large amount was prepared by the addition of a saturated solution of ammonium thioacetate to a saturated solution of cobalt chloride, the solution extracted with a mixture of acetone and ether, and the ethereal solution evaporated.