The formulas deduced from the preceding figures of analysis are imposing and appear rather improbable, so that, for the present, they can be cmitted, as the introduction of other dioxides is projected. Efforts, too, are being made to find other means of arriving at the molecular magnitudes of these bodies.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 78.]

DERIVATIVES OF COMPLEX INORGANIC ACIDS.

[FOURTH PAPER.]

BY ALLEN ROGERS AND EDGAR F. SMITH.

Received September 25, 1903.

IT may be observed that in those bodies containing vanadium but two oxides of the latter element appear—the trioxide and pentoxide. No derivatives of vanadicotungstic acid ($H_2O.V_2O_3WO_3$) have yet been prepared. In the classification of Wolcott Gibbs they are lacking. Further, the question had arisen whether by reduction of vanadic acid with hydrochloric acid the resulting oxide was really not the same as that produced on reducing vanadic acid with sulphur dioxide. If the stages of reduction were identical, then the hydroxides corresponding to these oxides—V_2O_5 and V_2O_4—if combined with tungstic acid, would yield one and the same complex acid. As will be seen, the products were dissimilar.

AMMONIUM VANADICO-TUNGSTATE,

$3(NH_4)_2O.V_2O_3.8WO_3.10H_2O$.

Thirty grams of ammonium paratungstate were boiled for six hours, when 6 grams of vanadium trioxide were introduced and the boiling continued for two hours longer. The filtered solution was reduced to a small volume and allowed to crystallize. Frequently, ammonium tungstate separated first and mixed with the vanadico-tungstate derivative. The crystals were treated several times with ice-water, which did not dissolve the ammonium tungstate, and, on evaporating the solution, ammonium vanadico-tungstate crystallized out in thin crusts, very soluble in water, but insoluble in organic solvents. The addition of nitric acid to the salt solution changed the color from black to yellow, and tungsten trioxide separated. Hydrochloric acid caused a slight deposition of trioxide. Mercurous nitrate produced an olive-green colored precipitate, insoluble in boiling water, but dissolving upon the addition of a few drops of nitric acid. The silver salt was olive-green in color and only partially soluble in boiling water. Mercuric chloride and copper sulphate produced no precipitates in the neutral aqueous solution of the salt. Ammoniacal cadmium chloride and ammoniacal cobalt nitrate produced precipitates which were insoluble in water. They dissolved on the addition of a few drops of nitric or hydrochloric acid, with the deposition of tungsten trioxide. The barium salt was insoluble in boiling water.

In analyzing the salt, the Gibbs method, modified by Friedheim,[1] was adopted.

		Found.		
	Theory.	I. Per cent.	II. Per cent.	III. Per cent.
$(NH_4)_2O$	6.66	6.56	6.56	6.52
V_2O_3	6.40	6.44	6.39	5.91
WO_3	79.24	79.24	79.26	79.76
H_2O	7.70	7.79	7.79	7.81

AMMONIUM VANADOSO-TUNGSTATE,

$5(NH_4)_2O.2V_2O_4.14WO_3.13H_2O$.

Ammonium vanadate, in the presence of sulphuric acid, was reduced with sulphur dioxide and the solution precipitated with ammonium hydroxide. The resulting body, after washing, was added to a boiling solution of ammonium paratungstate. After filtering and evaporating to a small volume, black, well-defined, octahedral crystals separated. These proved to be very soluble in water. Nitric acid changed the color of the black solution to yellow *without,* however, *the separation of tungsten trioxide.* Hydrochloric acid does not change the color of the solution in the cold and only very slowly on boiling. No deposition of trioxide occurred. The mercurous salt was insoluble in pure water, but dissolved on the addition of a little nitric acid. The lead salt behaved in the same way. Mercuric chloride, cadmium chloride and copper sulphate were without action. The last two salts, in ammoniacal solution, did precipitate insoluble compounds, that

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[1] *Ber. d. chem. Ges.*, **23**, 353 (1890).

acids dissolved. Ammoniacal cobalt nitrate behaved in the same way. The barium salt, emerald-green in color and insoluble in water, dissolved on the addition of a few drops of acid.

Analysis:

		Found.		
	Theory.	I. Per cent.	II. Per cent.	III. Per cent.
$(NH_4)_2O$	6.38	6.47	6.29	6.33
V_2O_4	8.15	8.30	8.28	...
WO_3	79.72	79.27	79.56	80.43
H_2O	5.75	5.96	5.87	...

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DERIVATIVES OF COMPLEX INORGANIC ACIDS.

[FIFTH PAPER.]

BY CLARENCE W. BALKE AND EDGAR F. SMITH.

Received September 25, 1903.

FIFTY years ago Struve made double molybdates, which he believed were analogous to the alums. Wolcott Gibbs showed that the products of Struve's efforts were salts of "complex inorganic acids," in which the various sesquioxides, together with molybdenum trioxide, constituted the several anions in union with protoxides—cathions. It was Struve's intention to prepare analogous tungstates. He never described any of these and, in order to complete certain gaps in a line of inquiry, upon which we have been engaged, we undertook the preparation of compounds following the general types

$$R_2O.\ x\ Al_2O_3\ \ y\ WO_3.$$
$$R_2O.\ x\ Fe_2O_3\ \ y\ WO_3.$$
$$R_2O.\ x\ Cr_2O_3\ \ y\ WO_3.$$
$$R_2O.\ x\ Ni_2O_3.\ \ y\ WO_3.$$
$$R_2O.\ x\ Mn_2O_3.\ \ y\ WO_3.$$
$$R_2O.\ x\ Bi_2O_3\ \ y\ WO_3,\ \text{etc.}$$

All of these have been made. In this communication, however, we shall only describe those derivatives in which aluminum and bismuth oxide are present. The remaining bodies will be