guarded against and the proper conditions carefully observed, however, if accurate results are to be obtained. Further reduction of the tetravalent vanadium to trivalent (Reaction 2) does not take place appreciably in solutions in which the concentrations of hydrogen and iodide ion are kept low, but it is possible by making these two factors favorable to effect a complete reduction of tetravalent to trivalent vanadium.[1] Naturally, pentavalent vanadium can be reduced to trivalent by the use of high concentrations of acid and iodide,[2] but the evidence does not justify the assumption that the tetravalent condition is not reached as an intermediate stage. The conditions or effecting a quantitative reduction must be more sharply defined than in the case of hydrobromic acid, but there seems to be no evidence that the mechanism of the reaction is different from that occurring in the case of the other halogen acids.

Summary.

(1) The reaction between vanadic acid and hydriodic acid at room temperature and at considerable dilution has been investigated. Within the limits of concentration covered by this investigation the reaction results in the formation of tetravalent vanadium, and not trivalent. This is contrary to the observations of Ditz and Bardach. A probable source of error in the results of Ditz and Bardach has been pointed out.

(2) The mechanism of the reactions between vanadic acid and the halogen acids, and the influence of various factors upon the equilibrium, has been discussed.

CHARLOTTESVILLE, VA.

ANALYSIS OF CERTAIN TUNGSTEN DERIVATIVES.

BY ORLAND R. SWEENEY.

The analysis of "complex inorganic acids" and their salt derivatives has been a subject of interest to analysts. Peculiar difficulties have been frequently encountered, and the impression exists that none of the methods proposed for the various separations are satisfactory. In passing, it may be observed that these doubts are particularly strong in connection with the separation of phosphoric and vanadic acids from molybdic and tungstic acids. In this laboratory where, for many years, "complexes" have received attention, numerous opportunities have arisen to test the proposals made from time to time, and as it was given me to inquire more closely

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[1] Gooch and Curtis, *Am. J. Sci.*, [4] 17, 41 (1904); Friedheim and Euler, *Ber.*, 28, 2067 (1895); Edgar, *Am. J. Sci.*, [4] 27, 174 (1908).

[2] Gooch and Curtis, *Am. J. Sci.*, [4] 17, 41 (1904); Friedheim and Euler, *Ber.*, 28, 2067 (1895).

into some of these problems, I submit personal experiences with certain of these derivatives. I tried first of all to separate arsenic from tungstic acid; the acids being in the form of their sodium salts. Since arsenic acid may be completely volatilized from its salts, if the latter are exposed, at a comparatively low heat, to the action of dry hydrogen chloride gas, it seemed that in a mixture of sodium pyroarsenate and sodium tungstate this course would lead to a prompt and complete elimination of the arsenic acid. Accordingly weighed portions of sodium arsenate and sodium tungstate were exposed in a boat, to a stream of hot hydrogen chloride. The tungstate was immediately attacked, giving variously colored products, depending upon the temperature. It was found, however, that the arsenic, in the presence of the tungstate, was completely expelled only with great difficulty.

Numerous experiments were made to determine the temperature at which a complete separation could be effected. The results showed that the temperature at which it was practical to remove the arsenic acid was dangerously near the point at which the tungstic acid began to volatilize.

Since only a small amount of the tungstic acid volatilized at 300° (measured by a thermometer lying at the side of the combustion tube), it was thought best to collect the portion which volatilized, rather than try to regulate the temperature in such a manner as to completely prevent it. By working in this way the arsenic acid was fully removed to a suitable receiver in four hours. The contents of the combustion tube were rinsed into an evaporating dish with dilute ammonia and evaporated to dryness on the water bath. The residue was then digested with 1 : 1 nitric acid, while small quantities of hydrochloric acid were added from time to time. When all action had ceased the watch-glass cover was rinsed off, and the liquid was evaporated. The residue was moistened with nitric acid and evaporated several times to remove all chlorine. The residue, consisting of tungsten trioxide and sodium nitrate, was dissolved in sodium hydroxide, diluted and filtered. A few drops of methyl orange were added, and the solution was just neutralized with nitric acid. It was then boiled, cooled, and the tungstic acid precipitated with mercurous nitrate. After standing four hours it was filtered, washed with 2% mercurous nitrate, and ignited and weighed as tungsten trioxide.

The method of evaporating with nitric acid, and then filtering out the tungsten trioxide, always gave low results. The procedure described —which is really an adaptation of Smith and Exner's method of getting pure tungsten trioxide—gave splendid results. In operating with a "complex" salt, such as sodium arsenio-tungstate, a weighed portion was brushed into a small tube, open at both ends, and distributed by rolling and tapping. This tube was then placed in a combustion tube and exposed to a stream of dry hydrogen chloride for about an hour. The

temperature, as measured by a thermometer lying at the side of the combustion tube, was about 200°. Since, however, the temperature within the tube varied somewhat with the construction of the apparatus, the proper temperature was ascertained by turning the flames gradually higher until the tungstic acid began to volatilize, and condense on the tube, over the sample; a few degrees lower than this seemed to be the proper temperature to use. With this point determined, the wing-top burners were left permanently adjusted, the gas being regulated at the gascock.

After an hour the apparatus was cooled, the inner tube removed, the sample moistened with water, the tube replaced, and the gas passed for one-half hour longer. This precaution was repeated three times.

Then the receiver was disconnected and the contents of the combustion tube were rinsed into it after first withdrawing the inner tube. A second receiver was put in place, the sample again moistened and the operation repeated. Should the contents of the second receiver show the presence of arsenic when treated with hydrogen sulfide, the treatment must be repeated. The following results were obtained:

Sample of arsenio-tungstate.	Percentage As_2O_5.	Percentage WO_3.
0.1028 g.	11.63	71.01
0.1550 g.	11.57	70.83
0.2858 g.	11.77	70.88
0.2090 g.	.....	71.10
0.1409 g.	11.93	70.76
0.2788 g.	11.93	70.91

The method is then satisfactory and does not require a longer time for its execution than many other procedures in general use.

My next thought was to treat an antimonio-tungstate precisely as had been done with the arsenio-tungstate. The following data proved the concordance of results obtained by the method:

Samples.	Percentage Sb_2O_5.	Percentage WO_3.
0.1462 g.	66.87	16.07
0.0799 g.	66.84	16.02
0.1090 g.	66.81	15.96
0.1811 g.	.....	15.90
0.1582 g.	66.85	15.86
0.3040 g.	67.01	16.05

I had the following experience with a sodium vanadio-tungstate: When the dry hydrogen chloride was passed, the vanadium volatilized as a red vapor, condensing to a reddish brown liquid (the oxychloride). The residue was, however, soon reduced to a brownish mass no longer attacked, but on introducing chlorine gas along with the hydrogen chloride the vanadic acid was quite rapidly and completely expelled.[1]

[1] McAdam, *J. Am. Chem. Soc.*, 32, 1603 (1910).

In most satisfactory separations I employed a form of the apparatus pictured in the sketch.
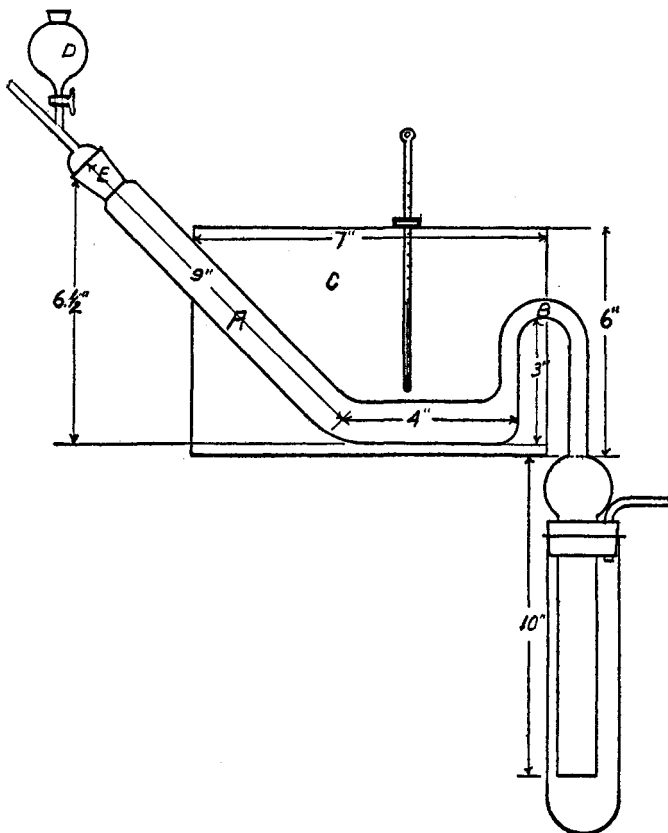
The tube was made in one piece as shown. It consisted of one-inch soft glass tubing, A, to which was sealed a one-half inch exit tube, B. To the exit tube a calcium chloride tube was sealed; this prevented the water from being drawn back into the hot tube. The receiver was a large test tube. A tin box, C, served as an oven. It was provided with a thermometer. By sealing on D, a small separatory funnel, the sample could be moistened without "breaking" the ground-glass joint E. The dimensions should be about as given. Such a piece is easily cleaned, and the vanadium will not diffuse back to the joint. After it is once started it requires no attention.

Chlorine was generated by dropping hydrochloric acid upon potassium permanganate. Hydrogen chloride was generated in the usual manner. The mixed gases were passed through two wash bottles containing sulfuric acid.

In the actual working, weighed portions of the vanadio-tungstate were introduced into the tube by means of a piece of glazed paper.   On passing hydrogen chloride, containing a small amount of chlorine, the sample was attacked with the formation of the customary reddish brown volatile liquid.   After a time a gentle heat was applied to the oven, and the temperature was gradually increased until it reached 200°.   A green residue, soluble in water, after evaporation becomes again volatile in hydrogen chloride.   If the vanadium condenses in the neck of the tube it should be allowed to distil off slowly in the stream of hot hydrogen chloride.

After about an hour the reduction tube was cooled, and 5 cc. of a 10% sodium hydroxide solution were added.[1]   On evaporating in a stream of the gases it was again heated, for one-half hour, at 200°.   It was then alternately moistened with water and treated with the gas mixture until the red vanadium oxychloride no longer appeared in the cool portion of the exit tube.   The rear end of the tube was then rinsed out, a second receiver put in place, and the operation repeated.

The appearance of the red film proved to be a very delicate test for vanadium.   When it no longer showed it was always found that the vanadic acid had been completely expelled.   The precaution of an extra treatment was, however, observed.

The tungsten was removed from the tube with ammonium hydroxide, and then determined as described under arsenic.

Various methods for estimating the vanadic acid were studied, and it was finally decided that the volumetric method, using potassium permanganate, was best suited to the conditions presented by the hydrogen chloride method.

Experiments were made to prove that there was no loss on evaporating a strong hydrochloric acid solution of vanadium.   Such a solution was evaporated, in a retort, the distillate was collected and failed to show the slightest color with hydrogen peroxide.

In the determination of the vanadic acid which had been volatilized, and which it was proposed to estimate with potassium permanganate, I proceeded as follows: The receiver, contents, and exit tube, were rinsed into an evaporating dish, 5 cc. of concentrated sulfuric acid were added, and the solution concentrated, as far as possible, on the water bath.   It was then heated, over a low flame, until white fumes of sulfuric acid came off.   The contents of the dish were next rinsed into an Erlenmeyer flask, diluted to two hundred cc., heated to boiling, and a stream of sulfur dioxide passed in to completely reduce the vanadium to the vanadyl salt.

[1] This was necessary since the vanadio-tungstic acid contained no sodium or potassium, and, for that reason, a soluble residue resulted on treating with hydrogen chloride.

The boiling was continued and a stream of carbon dioxide was passed to expel the excess of sulfur dioxide, after which the solution was titrated, while still hot, with potassium permanganate, previously standardized with pure vanadium pentoxide, which had been reduced in the same manner.

The following results were obtained:

Vanadio-tungstic acid.	Percentage V_2O_5.	Percentage WO_3.
0.2204 g.	. . . . .	65.47
0.3396 g.	. . . . .	65.31
0.3227 g.	16.17	. . . . .
0.3022 g.	15.92	65.35
0.3127 g.	15.90	. . . . .
0.2460 g.	15.95	65.20
0.2487 g.	15.95	65.38
0.1848 g.	16.09	65.39

This method is so satisfactory that I prefer it to the others. The temperature is easily regulated; cooling can be quickly effected by removing the oven; the danger of loss from creeping is slight, and the volatile constituent is more quickly removed.

The methods mentioned above, for the separation of arsenic, antimonic and vanadic acids from tungstic acid seem to me superior to those ordinarily employed, hence I offer them in the hope that they may be of service to others who are called upon to work with similar combinations.

In this connection, I desire to record a further experience with certain "complexes." It will be recalled that Balke and Smith made the potassium, ammonium and strontium salts of a bismuthico-tungstic acid. These salts had the general formula 3 M'_2O, 2 Bi_2O_3, 11 WO_3 + xH_2O.[1]

I prepared the potassium salt and from it obtained the mercurous salt, light yellow in color, well defined and very stable. Its analysis gave the ratio

$$3 \ Hg_2O, \ 2 \ Bi_2O_3, \ 11 \ WO_3, \ 15 \ H_2O.$$
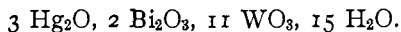
A portion of this salt was covered with water and hydrochloric acid added in an amount insufficient to decompose the whole of it. After several hours' contact in the cold, with occasional shaking, the residue was filtered out. The aqueous filtrate was evaporated under reduced pressure and at a low temperature. A greenish oil separated when the water was nearly removed. Finally, hydrochloric acid vapors began to appear. Then, the greenish yellow solid was permitted to dry out in a desiccator over solid sodium hydroxide until the odor of hydrogen chloride was no longer perceptible. From an analysis, I at first thought that the hydrogen chloride had taken the place of the water of crystallization; later behavior seemed to indicate, however, that the acid had replaced the mercury oxide, and that the new substance had a composition corresponding to the formula

[1] THIS JOURNAL, 25, 1233 (1903).

6 HCl, 2 Bi$_2$O$_3$, 11 WO$_3$. This is questionable and purely speculative. A new study of the compound is now in progress.

PHILADELPHIA, PA.

NEW DERIVATIVES OF TUNGSTEN.

BY J. BENNETT HILL.

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As early as 1859, Blomstrand[1] reported a series of compounds of molybdenum derived from the dihalides MoCl$_2$ and MoBr$_2$. These dihalides had been obtained by repeated volatilization of the trihalides in a current of carbon idoxide. The nonvolatile product was soluble in alkalies and from this solution hydrates of the type Mo$_3$Cl$_4$(OH)$_2$ were precipitated by weak acids. All of these derivatives were yellow in color. They could be dissolved in strong acids, the nitric acid solutions showing no ionized halogen. The hydrochloric acid solution of the chloromolybdenum hydroxide gave on crystallization, Mo$_3$Cl$_6$.6H$_2$O, and on dilution a pale yellow insoluble compound, Mo$_3$Cl$_6$.3H$_2$O. Mixed halogen derivatives, such as Mo$_3$Cl$_4$Br$_2$.6H$_2$O and Mo$_3$Br$_4$Cl$_2$.6H$_2$O were also obtained. The chemistry and constitution of these compounds was further developed by Atterberg,[2] Liechti and Kempe,[3] Muthmann and Nagel,[4] Rosenheim and Kohn,[5] and Koppel.[6] Muthmann and Nagel determined the molecular weight of molybdenum dichloride dissolved in ethyl alcohol, and found it to correspond to the triple formula Mo$_3$Cl$_6$. Rosenheim and Kohn prepared a compound, Mo$_3$Cl$_6$.HCl.4H$_2$O, by dissolving Mo$_3$Cl$_6$ in strong hydrochloric acid, evaporating on a water bath and allowing the solution to crystallize. The compound consisted of glistening yellow needles, soluble in hydrochloric acid but was hydrolyzed by pure water. Only three-sevenths of the chlorine in the compound were ionized.

In 1909, Chapin[7] described halide bases of tantalum. He prepared these compounds by a method previously used by Chabrie[8] for obtaining what he called the dichloride of tantalum. It consisted in heating the pentachloride with 3% sodium amalgam in a hard glass tube sealed at one end and evacuated by means of a suction pump. Chapin used the pentabromide of tantalum. The reaction mass, taken up with water and

[1] *J. prakt. Chem.*, **77**, 88 (1859).

[2] *Jahresb.*, **1872**, 260.

[3] *Ann.*, **169**, 354 (1873).

[4] *Ber.*, **31**, 2009 (1898).

[5] *Z. anorg. Chem.*, **66**, 1 (1910).

[6] *Ibid.*, **77**, 289 (1912).

[7] THIS JOURNAL, **32**, 323 (1910).

[8] *Compt. rend.*, **144**, 804 (1907).