

is the formation of the acetic acid group. Cross¹ and Bevan call attention to this fact and point out that the formation of pentosans and acetic acid "increases, *pari passu*, with age, which is in accordance with the view of a common origin." The mechanism of this transformation is not yet fully explained; it seems, however, to be primarily a process of dehydration.

The various substances into which woody fiber may be resolved by hydrolysis have led many to believe that we are dealing with more or less of a mechanical mixture—a substratum of cellulose overlaid with "incrusting substances." This view, however, is no longer tenable. The cellulose, pentosans, lignin and acetic acid obtained from cane-fiber are all hydration products, which, in the parent substances, are intimately combined. While, therefore, a study of the groups split off by hydrolysis is our chiefest aid in investigating the problems of constitution, the mistake must not be committed of regarding the products obtained by chemical treatment as absolutely identical with fiber constituents.

A study of the progressive changes, which the fiber of sugar-cane undergoes during its period of growth, is at present being conducted, and it is hoped that the results of the work will throw additional light upon the theoretical and practical questions involved.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,
NO. 83.]

OBSERVATIONS ON THE METALLIC ACIDS.²

BY ROY D. HALL.

Received July 26, 1904.

THE results presented here constitute a very brief chapter in a much larger investigation which has been in progress for some time and which will be published in full in due course. The observations, while preliminary in character, possess distinct value in various lines which the larger research has taken and along which it has been and will continue to be carried in the future.

The starting-out material for the columbic and tantalic oxides was columbite from Haddam, Conn., and from South Dakota.

The Haddam mineral was very iridescent, lamellar and brittle.

¹ Cross and Bevan's "Cellulose," page 192.

² From the author's thesis for the Ph.D. degree.

It gave a brown-colored powder, inclined to red. Its specific gravity was found to be 5.75 at 4° C. Upon analysis it showed:

| | Per cent. | Per cent. |
|---|-----------|-----------|
| Ta ₂ O ₅ + Cb ₂ O ₅ | 79.75 | 79.49 |
| WO ₃ + SnO ₂ | 0.32 | 0.32 |
| Fe ₂ O ₃ | 15.11 | 15.09 |
| U ₃ O ₈ | 0.23 | 0.24 |
| MnO | 6.69 | 5.83 |

Five kilograms of this substance were reduced to a powder fine enough to pass through a 120-mesh sieve. It was decomposed by the method first suggested by Wolcott Gibbs.¹ The fusions were made fine and treated with two to three times their weight of concentrated sulphuric acid, and heated until the excess of acid had been expelled.

On extracting the mass with boiling water the oxides of columbium and tantalum remained insoluble, with the oxides of silicon, titanium, tungsten, tin and any lead sulphate which had been formed by the action of the acids on the lead vessels. They were washed until the washings no longer gave a precipitate with ammonium hydroxide, and were then covered with a concentrated solution of yellow ammonium sulphide and allowed to stand for several days.

It was supposed that by this treatment all of the tin and tungsten would be removed, while the iron and manganese would be changed to sulphides, which could be dissolved out with dilute sulphuric acid. The residue would then consist only of the oxides of silicon, titanium, columbium and tantalum, and lead sulphate.

Accordingly, the residual oxides were dissolved in hydrofluoric acid and the lead sulphate filtered out. The hydrochloric acid solution was made of such a concentration that on the addition of its equivalent of potassium fluoride most of the tantalum and silicon fluorides separated as double fluorides. These were filtered out and dried. The filtrate was evaporated in large dishes of hard rubber over a water-bath, a slight excess of potassium fluoride being added. When more of the needles of potassium tantalum fluoride separated they were added to the first crop.

The remaining double fluorides were taken out in two fractions, the first consisting largely of potassium columbium oxyfluoride,

¹ *Am. J. Sci.*, 37, 357 (1864).

while the second contained the same salt, together with the excess of potassium fluoride. The weights of the fractions were :

| | Kilos. |
|---|--------|
| K ₂ TaF ₇ + K ₂ SiF ₆ | 1.250 |
| K ₂ CbOF ₅ | 1.800 |
| K ₂ CbOF ₅ + KF | 1.325 |
| Total | 4.375 |

After recrystallizing about 100 grams of the middle portion four times, its solution gave a precipitate with hydrogen sulphide, which was found to consist largely of tin sulphide.

A solution of the salt was brought to boiling and saturated with hydrogen sulphide, then filtered and the filtrate tested by diluting and again passing in hydrogen sulphide, with negative results. Upon evaporation of the filtrate to crystallization and analyzing a portion of the crystals obtained, the resulting columbic oxide stained the platinum crucible. Upon taking the crystals up in water and passing in hydrogen sulphide, more tin sulphide was precipitated. It was found impossible to remove all of the tin with hydrogen sulphide even upon crystallizing five times, taking up the crystallizations in water and passing hydrogen sulphide through the solution each time.

The salt remaining after the above treatment was crystallized twice and analyzed.

(1) 0.5508 gram gave 0.2522 gram Cb₂O₅, and 0.3288 gram K₂SO₄, giving an atomic weight of 93.4 for columbium.

(2) 0.5105 gram gave 0.2342 gram Cb₂O₅, and 0.3044 gram K₂SO₄, or an atomic weight of columbium of 93.8.

In both cases the platinum crucible used for the ignition of the oxide was stained.

Most analysts have deemed the mere washing of the oxides of columbium and tantalum with yellow ammonium sulphite sufficient to eliminate the tin and tungsten, but the experience recorded above proves the opposite. Earlier work in this laboratory¹ along this same line demonstrated that prolonged treatment with ammonium sulphide led to the solution of considerable quantities of the oxides of columbium and tantalum, but, despite this fact, it was determined to pursue the last course; consequently, the well-washed oxides from 500 grams of the double fluorides were di-

¹ This Journal, 18, 38.

gested with yellow ammonium sulphide on a water-bath for twenty-four hours, the ammonium sulphide solution decanted, and a fresh portion added. This was repeated four times. The several portions of the ammonium sulphide solutions, when acidified with hydrochloric acid, yielded precipitates, which, filtered, ignited and then reduced in hydrogen, gave more than a gram of metallic tin, the hydrochloric acid solution of which reduced a mercuric chloride solution, gave purple of Cassius with a solution of gold chloride and a brown-black sulphide, soluble in yellow ammonium sulphide.

The part insoluble in hydrochloric acid was ignited, fused with potassium bisulphate and extracted with boiling water. Upon digestion of the hydroxide thus obtained with ammonium hydroxide a large amount dissolved. After filtering, the filtrate gave a precipitate with acids, but was white, not yellow, and did not become yellow after long boiling. There was every evidence that the precipitated tungstic acid contained columbic acid and that, on digesting the mixed hydroxides with ammonium hydroxide, a complex acid had been formed. Long boiling with strong acid was required to precipitate all of the oxide from this solution.

These oxides were filtered out and, after ignition, were fused with sodium carbonate. Upon taking up in water, the sodium carbonate was nearly insoluble in the excess of alkali and could be filtered out. The addition of acid to the filtrate gave a yellow precipitate which answered to all the tests for tungstic oxide.

That part which was insoluble in ammonium hydroxide was also fused with sodium carbonate and likewise found to contain both columbic and tungstic oxides. This would indicate that a separation of the mixed hydroxides of columbium and tungsten by digestion with ammonium hydroxide is impossible.

These experiences, just outlined, confirm the statement of H. Rose, that the oxides of tin and tungsten could not be removed by digestion with ammonium sulphide, so recourse was had to the method adopted by him, namely, fusion with sodium carbonate and sulphur.

The fusions were made in a porcelain crucible at a temperature below that at which sodium carbonate would melt.

Upon extracting with water, the columbic oxide remained in-

soluble as an acid sodium salt; the tin and tungsten going into solution were filtered off.

The acid sodium salt was ignited and changed to the oxide by fusion with potassium bisulphate and extracting with boiling water to remove the sodium and potassium sulphates. A portion of the oxide tested for tin and tungsten by a second fusion with sodium carbonate and sulphur failed to show their presence.

There is no doubt but that one can never be certain of the complete elimination of tin and tungsten from columbium and tantalum oxides unless the last procedure has been scrupulously followed.

The columbic oxide, being thus freed from two of its frequent associates, was changed to potassium columbium oxyfluoride and the latter recrystallized twice, the first portions alone being taken. Each time the dried crystals were taken up in water and boiled a slight residue separated; this was tantalum. In order to remove all of the latter the double fluoride was heated to 150° - 175° in an air-bath, when, on dissolving, a considerable residue remained. Upon repeating this twice a tantalum-free preparation was obtained. It weighed about 150 grams.

Another question which constantly obtruded itself was—Is there any titanium in this sample of columbium? Marignac confessed that the columbic oxide used by him was not free from titanium and, further, that he knew of no method by which the latter could be entirely removed. The hydrogen peroxide test for titanous acid was used by Weller in the quantitative estimation of this substance. He employed it to estimate titanium in the presence of zirconium and suggested that it might answer equally well in the presence of columbium, but failed to test the suggestion. Osborne used the method, working in chloride solutions.

As the reaction is not delicate in the presence of fluorides, the solution was changed to chloride in the following way: A portion of the double fluoride was decomposed with sulphuric acid, the oxide well washed, then boiled for a few minutes with concentrated hydrochloric acid, after which it was soluble on diluting or in water. On adding hydrogen peroxide to this solution the color characteristic of titanium appeared.

Another crystallization of the potassium columbium oxyfluoride was made, only the first fraction being taken. It was well washed

and tested for titanium, but showed its presence in amount nearly equal to that in the first sample. The failure to reduce the amount of titanium, shown in successive crystallization, made it evident that this impurity could not be completely eliminated from columbium by a limited number of crystallizations.

The columbium potassium oxyfluoride was next changed to the normal double fluoride and this crystallized in the hope that, not being isomorphous with potassium titanium fluoride, it might separate free from that impurity. Four crystallizations were made from a fairly concentrated hydrofluoric acid solution, when some of the salt was converted into chloride and tested with hydrogen peroxide. Titanium was found, but the amount had decreased by one-half.

The columbium was again changed to oxyfluoride by crystallizing twice from water, the mother-liquors discarded and the crystals dried in an air-bath at 150° . They were analyzed according to the method used by Marignac.

0.5684 gram of salt gave 0.2659 gram of oxide and 0.3485 gram of K_2SO_4 , showing an atomic weight for columbium of 92.8.

It seemed advisable now to ascertain the delicacy of the hydrogen peroxide test for titanium, together with the effect of the presence of various substances on its delicacy.

Accordingly, 0.1017 gram of potassium titanium fluoride, containing 0.03356 gram of oxide, was converted into sulphate and made up to 100 cc. One cc. contained 0.00003356 gram TiO_2 . One-tenth of this solution or 0.000003356 gram TiO_2 gave the color with hydrogen peroxide when made up to 50 cc. in a Nessler tube of one-inch diameter.

The most dilute standard solution which could well be used for comparison work would be 2 cc. of the above in 50 cc., or 0.00067 gram TiO_2 in 50 cc., each cubic centimeter containing 0.000013 gram TiO_2 . With such a solution the successive comparisons against an unknown did not vary over 2 cc., or 0.000026 gram of TiO_2 . This agrees fairly well with that found by Weller, who gave the limit of the method as 0.1 mg. in 1 cc.

A solution of potassium titanium fluoride, containing 0.00128 gram of TiO_2 , developed a color with hydrogen peroxide equal in intensity to that given by 0.000318 gram in sulphate solution,

or a loss of color due to the presence of fluoride of about three-fourths.

It was observed that the intensity of the color given by hydrogen peroxide with titanium was much lessened by the presence of citric acid, but was not noticeably affected by oxalic or tartaric acid. This behavior, therefore, would permit of the use of the oxalate or binoxalate solution of tantalum and columbium in the making of the tests for titanium, as the moist hydroxides of tantalum and columbium, as well as that of titanium, are readily soluble in potassium binoxalate to stable solutions. When, therefore, 0.5 gram of potassium tantalum fluoride was decomposed by acid, and the hydroxide dissolved in potassium binoxalate, it showed no color with hydrogen peroxide. Upon the addition of 0.00015 gram of TiO_2 , a color was produced which was equaled by that of a solution containing 0.000147 gram of titanic oxide, showing that tantalum does not interfere with the color test for titanium in potassium binoxalate solution. The percentage of titanic oxide in the potassium columbium oxyfluoride was determined by destroying the fluoride and dissolving in potassium binoxalate. The tin- and tungsten-free sample, after two crystallizations, showed oxide of titanium to be about 0.5 per cent. of the total oxide; after the four crystallizations from hydrofluoric acid the amount was reduced to 0.25 per cent.

As previously remarked, the question of the complete removal of the last traces of titanium from columbium preparations has long been unanswered.

Krüss and Nilson claimed that by prolonged boiling of the solutions of potassium columbium oxyfluoride, replacing the water lost by evaporation, an insoluble acid salt was produced which contained no titanium. This procedure was adopted, the oxide set free from the salt, dissolved in hydrochloric acid and tested with hydrogen peroxide. 0.032 gram showed the presence of 0.00015 gram of titanium dioxide, or 0.05 per cent., the best that had yet been obtained.

It had been noticed by Smith¹ that sulphur monochloride dissolved the oxides of columbium, tantalum and titanium, in the first two cases forming crystalline bodies and with the oxide of titanium a liquid. It was hoped that by a further study of this

¹ *J. Am. Chem. Soc.*, 20, 289.

reaction a method might be found which would eliminate the traces of titanium from the columbium.

Oxide of titanium, heated in a sealed tube with sulphur monochloride at 200° for several hours, went into solution, and when the contents of the tube were transferred to a distilling bulb the titanium was volatilized with the sulphur monochloride, probably as the tetrachloride. Oxide of columbium, under the same conditions, went into solution in the sulphur monochloride and separated from it on cooling in transparent yellow prisms, of what was later found to be the pentachloride. On transferring to a distilling bulb the sulphur monochloride could be distilled off and then the columbium chloride distilled over into the stem of the distilling bulb, sealed off and analyzed.

The chloride of columbium came over between 220 and 235° . Prepared in this way, it was difficult to free from sulphur monochloride. After several failures a sample was obtained containing only a small amount of sulphur and analyzing as follows:

0.4400 gram gave 0.2160 gram Cb_2O_5 and 1.1380 grams AgCl , or 0.2815 gram Cl .

0.5395 gram gave 0.2690 gram Cb_2O_5 and 0.0195 gram BaSO_4 , or 0.0027 gram S .

| | Calculated for CbCl_5 . | Found. | |
|-------------------------------|----------------------------------|--------|------|
| Cb | 34.62 | 34.7 | |
| Cl | 65.38 | 64.0 | |
| S | | 0.5 | |
| | 100.00 | 99.2 | |
| Cb_2O_5 | 49.35 | 49.8 | 49.1 |

The analysis was made by decomposing the sample with dilute ammonia water, evaporating to small bulk and filtering off the columbic hydroxide after neutralizing the excess of ammonia with nitric acid. The chlorine was determined in the filtrate. The second sample was decomposed with water and the sulphur oxidized with bromine water, and the filtered hydroxide was washed with dilute ammonium hydroxide to remove all the sulphuric acid. Any oxide of columbium adhering to the glass was dissolved off with potassium binoxalate, or by boiling with concentrated hydrochloric acid and again precipitated by ammonium hydroxide.

In order to see if titanium could be removed from columbium

by means of sulphur monochloride, 1.1 grams of columbic oxide, containing 0.25 per cent. of oxide of titanium, were heated with sulphur monochloride in a sealed tube for fourteen hours.

The contents of the tube were transferred to a distilling bulb and distilled. The sulphur monochloride and the oxide carried with it were decomposed by ammonia water and the ignited oxide tested for titanium. 0.0955 gram obtained was found to contain 0.00066 gram of titanitic acid, or 0.7 per cent.

The sublimed crystals of columbic chloride were changed to oxide and 0.4295 gram found to contain 0.00075 gram of TiO_2 , or 0.18 per cent., showing only a slight improvement.

The desire to prepare the chloride of columbium free from oxychloride and sulphur monochloride led to an attempt to change the oxide to chloride by heating in a current of sulphur monochloride, and distilling the resulting chloride in a current of chlorine.

Under these conditions the ignited oxide was rapidly changed to chloride at a moderate temperature and with a small amount of sulphur monochloride. Oxychloride was at first formed, but this changed rapidly in the sulphur monochloride vapors to chloride. On cutting out the sulphur monochloride and substituting a current of dry chlorine gas the columbium pentachloride could be distilled and freed from sulphur, as the following analyses show:

(1) 0.6290 gram $CbCl_5$ gave 0.3105 gram Cb_2O_5 ; 1.6590 grams $AgCl$, or 0.2178 gram Cb and 0.4101 gram Cl .

(2) 0.4084 gram $CbCl_5$ gave 0.2021 gram Cb_2O_5 ; 1.0788 grams $AgCl$, or 0.1418 gram Cb and 0.2658 gram Cl .

| | Calculated. | Found. | |
|-----------------|-------------|--------|--------|
| | | I. | II. |
| Cl | 65.38 | 65.20 | 65.33 |
| Cb | 34.62 | 34.63 | 34.71 |
| | 100.00 | 99.83 | 100.04 |
| Cb_2O_5 | 49.35 | 49.26 | 49.49 |

The silver chloride obtained was perfectly white and showed no trace of sulphide.

The chloride of tantalum was prepared in a similar way, because of its higher boiling-point it is easier to free from sulphur monochloride than is columbium chloride.

It was obtained in nearly white crystals, fusing to a light yellow oil. It was analyzed by decomposing in dilute ammonia, allowing to stand twenty-four hours, then adding nitric acid in slight excess, which caused the tantalic hydroxide to separate in flocks and filter readily. The chlorine was determined in the filtrate.

1.4684 grams of $TaCl_5$ gave 0.9085 gram Ta_2O_5 ; 2.9215 grams $AgCl$, or 0.7454 gram Ta and 0.7228 gram Cl.

| | Calculated. | Found. |
|-----------------|-------------|--------|
| Ta..... | 50.76 | 50.77 |
| Cl..... | 49.24 | 49.22 |
| | <hr/> | <hr/> |
| | 100.00 | 99.99 |
| Ta_2O_5 | 61.86 | 61.87 |

The ease with which these two difficultly reducible oxides were changed to chlorides in a current of sulphur monochloride vapor led to a series of qualitative experiments to see what oxides could be so changed and if certain quantitative separation might not be effected by the use of sulphur monochloride; also, if various minerals might not be readily decomposed by means of it.

It was found that the oxides of titanium, aluminum, and iron, besides those of columbium and tantalum, were readily changed to volatile chlorides at a moderate temperature.

Oxides of tungsten, vanadium and molybdenum were changed to volatile oxychlorides.

Oxides of zirconium and tin were changed to volatile chlorides, but exposure to a temperature approaching the softening-point of glass for a considerable time was required for complete transformation.

Oxides of boron and silicon were not affected, while chromic oxide was changed to the slightly volatile violet chloride. Oxides of manganese, sodium and those oxides forming non-volatile chlorides were changed to chlorides, the latter remaining in the boat and being soluble in water.

Some of the columbite from the Black Hills, S. D., was readily decomposed, the tantalum, columbium and iron being volatilized and leaving manganese chloride sufficient in weight to give 13 per cent. MnO ; that obtained in the analysis was 12.92 per cent.

Chromite was changed to volatile ferric chloride and the violet

chromium chloride, which, calculated to oxide with the gangue, gave 46 per cent. remaining in the boat.

The titanium in rutile was completely expelled and the iron and titanium in ilmenite were driven out, leaving a white residue. All of the titanitic oxide was volatilized from a mixture of titanitic and silicic acids.

The use of sulphur monochloride affords an excellent and convenient method of preparing the anhydrous chloride of many of the elements. It offers a means of separating those forming volatile chlorides from those forming non-volatile chlorides. It also affords an excellent means of decomposing some of the most refractory minerals.

However, the removal of the titanium had not yet been accomplished. Recalling a statement of Demarçay¹ that columbium is completely precipitated from the solution of its oxyfluoride by exactly neutralizing with ammonium hydroxide and then boiling, while titanium, under similar conditions, was not precipitated, the suggestion was tested.

The hydroxide thus precipitated was dissolved in hydrofluoric acid and the operation repeated.

0.1473 gram of this oxide in hydrochloric acid solution showed no yellow with hydrogen peroxide, while the addition of 0.00003 gram of titanitic acid gave the characteristic color for titanium. The amount of titanium present, therefore, was materially less than 0.02 per cent.

When the precipitation was made from a boiling solution, some titanium was brought down with the columbium hydroxide. Four precipitations made in this way, starting with oxyfluoride containing 0.5 per cent. of titanium oxide, gave a product which still had 0.1 per cent. of titanium. Further precipitations in boiling solutions failed to diminish the quantity, while four precipitations in the cold, throwing out each time from one-half to three-fourths of the columbium present, yielded columbic oxide perfectly free from titanium. At least, the most searching tests for it failed to reveal it.

In the course of the present study occasion was taken to make a series of comparative qualitative tests with the double fluorides of titanium, zirconium, columbium and tantalum. The results are exhibited in the appended table.

¹ *Compt. Rend.*, 100, 740.

Potassium titanium fluoride is much less soluble in a solution containing potassium iodide than in water. The crystals separating from such a solution carry down a large amount of potassium iodide. Thus 1.5 grams of potassium titanium fluoride were dissolved in 37.5 cc. of water, and to this solution were added 112.5 cc. of a cold saturated solution of potassium iodide. The liquid was boiled and became clear. On cooling, a mass of feathery crystals separated. These were freed from mixture by means of a filter-pump, pressed between filter-paper and analyzed.

0.8408 gram of substance gave 0.1273 gram of silver iodide, or 0.0899 gram of potassium iodide, and 0.2320 gram of titanous oxide, or 0.6960 gram of K_2TiF_6 .

| | Per cent. |
|------------------|---------------------|
| K_2TiF_6 | 82.8 |
| KI | 10.6 |
| H_2O | 6.6 (by difference) |

Potassium bromide showed a similar action. The potassium titanium fluoride which separated carried with it about 10 per cent. of potassium bromide.

These two halides showed a like behavior when their solutions were added to the solution of potassium zirconium fluoride.

The potassium columbium oxyfluoride proved less soluble in solutions of the alkaline halides than in water, while in the solution of potassium tantalum fluoride precipitates were produced by potassium iodide, bromide and chloride.

Solutions of the double fluorides of titanium, zirconium, columbium and tantalum were not affected by potassium bromate, chlorate, perchlorate, dichromate, sodium metaphosphate, sodium pyrophosphate, ammonium sulphate, silver nitrate, mercuric chloride, ammonium oxalate, oxalic, acetic, fumaric, maleic, formic, salicylic, succinic and benzoic acids, α -nitroso- β -naphthol in 50 per cent. acetic acid, sodium molybdate and sodium tungstate.

| Reagents. | Titanium. Solution : 5 grams of pure K_2TiF_6 in 400 cc. of water. | Zirconium. Solution : 10 grams of K_2ZrF_6 in 500 cc. of water. | Columbium. Solution : 10 grams of $2KF.CbOF_3$ in 500 cc. of water. | Tantalum. Solution : 1 gram of K_2TaF_7 in 150 cc. of water. |
|-------------------------|--|---|--|---|
| NaOH. | Complete precipitation. | Complete precipitation. | Precipitate, nearly all soluble in slight excess of reagent. Large excess causes separation of crystals of sodium columbate. | Slight permanent precipitate, not soluble in excess. Crystals separate on standing. |
| $KHCO_3$. | No precipitate in the cold ; incomplete on boiling. | No precipitate. | Precipitate soluble in excess on standing. | |
| Na_2CO_3 . | Precipitation complete. | Precipitation slow, but complete. | Precipitation complete. Nearly all soluble in slight excess. Same as NaOH. | Precipitation after long standing. |
| $(NH_4)_2CO_3$. | No precipitate in the cold. Slight precipitation after twenty-four hours. | No precipitate. | Precipitate soluble in excess. | Heavy precipitate. |
| $BaCO_3$ (emulsion). | Precipitation complete in the cold. | Precipitation nearly complete in the cold. | Precipitation nearly complete in the cold after twenty-four hours. | Little reaction in the cold. Precipitation complete on boiling. |
| KCN. | Precipitation complete. | Precipitation complete. | Heavy white precipitate. | Precipitation complete. |
| KCNS. | A crystalline precipitate on using a concentrated solution of the reagent. | Ditto. | Slight precipitate with concentrated reagent. | Slight precipitate. |
| $K_4Fe(CN)_6$. | | Slight white precipitate. | Yellow precipitate, separating slowly. | A yellow precipitate, forming slowly. |
| $K_3Fe(CN)_6$. | Crystalline precipitate. | Few granular crystals separated. | No precipitate. | No precipitate. |

| | Titanium. Solution : 5 grams of pure K_2TiF_6 in 400 cc. of water. | Zirconium. Solution : 10 grams of K_2ZrF_6 in 500 cc. of water. | Columbium. Solution : 10 grams of $2KF.CbOF_3$ in 500 cc. of water. | Tantalum. Solution : 1 gram of K_2TaF_7 in 150 cc. of water. |
|---------------------------|---|---|---|--|
| Reagents. K_2CrO_4 . | Almost complete precipita- tion. Insoluble in water. | White precipitate. In- complete. Insoluble in water. | Complete precipitation. | Complete precipitation. |
| KIO_3 . | Precipitation complete with an excess of the reagent upon boiling vigorously. | Precipitation complete on boiling. | An equal volume of hot sat- urated solution of the re- agent gave no precipitate. Partial precipitation after long boiling. | No precipitate. |
| Na_2HPO_4 . | Complete precipitation. | Complete precipitat'n. | No precipitation. | No precipitation. |
| Na_2SO_3 . | Precipitate; not complete on boiling. Does not occur in acid solution. | Slow precipitation; al- most complete in twenty-four hours. | Complete precipitation in neutral solution. | Precipitation exceedingly slow. |
| $Na_2S_2O_3$. | Slight precipitate. Forms slowly. | Precipitation slight. | | Slight precipitate. |
| K_2SO_4 . | No change. | No change. | No change. | A very heavy precipitate with a cold saturated solution of the reagent. Soluble on warming. |
| H_2SO_2 . | Yellow color. | A light yellow colored precipitate slowly separated. | Slight precipitate after long standing. | Heavy precipitate after standing some time. |
| $Pb(C_2H_3O_2)_2$. | Heavy precipitate. in nitric acid. | Soluble | Heavy precipitate. | Ditto. |
| | | | Ditto. | Ditto. |

| Reagents. | Titanium. Solution : 5 grams of pure K_2TiF_6 in 400 cc. of water. | Zirconium. Solution : 10 grams of K_2ZrF_6 in 500 cc. of water. | Columbium. Solution : 10 grams of $2KPa.CbOF_3$ in 500 cc. of water. | Tantalum. Solution : 1 gram of K_2TaF_7 in 150 cc. of water. |
|-----------------------|---|--|---|--|
| $BaCl_2$. | Slight precipitate, becoming heavy and flocculent on boiling. Soluble in acids. | Precipitate; soluble in hydrochloric acid. | Slight precipitate after long standing. | Heavy precipitate after standing some time. |
| Alcohol. | An equal volume of 95 per cent. alcohol precipitated nearly all of the double fluoride. | Crystalline precipitate; soluble on warming. | An equal volume of 95 per cent. gave a heavy gelatinous precipitate. | No precipitate. |
| $NaC_2H_3O_2$. | Precipitation almost complete on boiling. | Precipitation not complete. | Precipitation complete in the cold. | A heavy white precipitate, nearly complete on boiling. |
| NH_4 — Fumarate. | Precipitation on boiling. | Ditto. | Precipitation complete on boiling. | Precipitation complete on long boiling. |
| NH_4 —Maleate. | Precipitation on boiling. | Ditto. | Ditto. | Ditto. |
| NH_4 —Formate. | Slow precipitation. Nearly complete on boiling. | Incomplete precipitation on boiling. | Precipitation complete on boiling. | Precipitation complete on long boiling. |
| NH_4 —Citrate. | No precipitate; excess of ammonium hydroxide does not cause precipitation. | Ditto. | Ditto. | No precipitate; ammonium hydroxide slowly precipitates on boiling. |
| Malic acid. | No precipitate, until after the addition of a large excess of ammonium hydroxide. | No precipitation. Subsequent addition of ammonium hydroxide has no effect. | No precipitation. Partial precipitation by an excess of ammonium hydroxide. | No precipitate. Ammonium hydroxide in the cold has no effect, but precipitation occurs on boiling. |

| Reagents. | Titanium. Solution : 5 grams of pure K_2TiF_6 in 400 cc. of water. | Zirconium. Solution : 10 grams of K_2ZrF_6 in 500 cc. of water. | Columbium. Solution : 10 grams of $2KF.CbOF_3$ in 500 cc. of water. | Tantalum. Solution : 1 gram of K_2TaF_7 in 150 cc. of water. |
|------------------------|--|--|--|---|
| Na—Benzoate. | Precipitation not complete on boiling. | No precipitation. Subsequent addition of ammonium hydroxide has no effect. | Precipitation complete on boiling. | Slight precipitate. |
| Tartaric acid. | No precipitate. Prevents precipitation by ammonium hydroxide. | Ditto. | Precipitation in presence of excess of ammonium hydroxide after long boiling. | Slowly precipitated on boiling in the presence of ammonium hydroxide. |
| Zn + HCl. | Sea-green color. | No color. | Green-brown, passing into deep brown. | No color. |
| H_2O_2 . | Deep yellow color. | No color. | No color. | No color. |
| Solution of gall nuts. | Neutral solution. No precipitate, red color. Yellow color in presence of a little hydrochloric acid. | Slight white precipitate in acid solution. | No precipitate; reddish color. On the addition of hydrochloric acid and the application of heat the color fades and a brick-red precipitate is produced. | Faint yellow color. Ammonia gives a brown color. |