ART. XXXI.—*Contributions to Chemistry from the Laboratory of the Lawrence Scientific School;* by WOLCOTT GIBBS, M.D., Rumford Professor in Harvard University.—No. I.

1. *On the relations of hyposulphite of soda to certain metallic oxyds.*

THE employment of hyposulphite of soda as an analytical reagent was first suggested by Himly,[1] who in a short paper, intended only as a preliminary notice, pointed out the relations of this salt to solutions of arsenic, antimony, copper and platinum, and suggested its use as a general reagent in place of sulphydric acid. Himly's paper attracted little attention and was soon forgotten. The subject was again taken up at about the same time by Vohl[2] and Slater[3] who appear to have been unacquainted with Himly's results. Vohl's investigation embraces the action of the hyposulphite upon solutions of arsenic, antimony, tin, copper, mercury, silver, gold, platinum, lead, bismuth, and cadmium. Slater studied the action of the salt upon solutions of chromium in the form of chromic acid, arsenic, antimony, copper, bismuth, lead, and mercury, as well as upon ferridcyanid, ferrocyanid, and cyanid of potassium, and upon sulphocyanid of iron and hypermanganate of potash. The results obtained by these chemists differ in some particulars, especially as regards copper and lead. More recently Chancel[4] has employed the hyposulphite for the separation of alumina from iron, and Stro-

[1] Annalen der Chemie und Pharmacie, xliii, 150. [2] The same, xcvi, 237.
[3] Chemical Gazette, 1855, 369. [4] Comptes Rendus, xlvi, 987.

meyer[5] has extended the same process to the separation of iron from titanic acid and zirconia. Other analytical applications of the hyposulphite have been made in which the salt is employed either as a solvent or in volumetric processes: these do not require notice in this place. The following observations on the behavior of the hyposulphite toward certain metallic salts are interesting from a purely chemical rather than from an analytical point of view.

Nickel.—When a neutral solution of sulphate, chlorid or nitrate of nickel is boiled with a solution of hyposulphite of soda, a black precipitate of sulphid of nickel is thrown down, and after very long boiling the precipitation is complete and the solution is free from nickel. If the solution of nickel be previously acidulated by the addition of a drop or two of acetic acid the precipitation is more rapid. It is very difficult to determine the exact point at which the solution ceases to contain nickel; the boiling must usually be continued for several hours. When chlorhydric acid is added to the mixed solutions of nickel salts and hyposulphite, no precipitate is produced on boiling: in this case nickel behaves like iron and the other metals of the same group: in the cases first mentioned its analogies are with copper. The presence of free ammonia does not prevent the precipitation of sulphid of nickel but the action goes on very slowly. Rammelsberg[6] long since observed that a solution of hyposulphite of nickel is partially decomposed by evaporation, and that the dry mass on heating yields a yellow sulphid of nickel: the same is true of a mixed solution containing sulphate of nickel and hyposulphite of soda.

The formation of sulphid of nickel, which takes place slowly in solutions evaporating or boiling under ordinary atmospheric pressure, is facilitated in an extraordinary degree by heating in closed tubes to a temperature of 120° C. Ordinary combustion tubes answer the purpose very well: the tube is first closed at one end and then drawn out near the other end to a narrow neck. The solution of nickel is introduced by a long funnel together with the solution of hyposulphite which should be in excess and concentrated. After sealing the tube before the blast-lamp it is to be heated in an air-bath and kept for half an hour at a temperature of about 120° C. Every trace of nickel is thrown down in the form of sulphid mixed with free sulphur: the tube may then be opened at the point, the liquid allowed to flow into a beaker, the tube cut across and the sulphid of nickel washed out. It may be thrown on a filter and washed with boiling water without oxydizing in the smallest degree. The equation representing this reaction appears to be

$$NiCl + 2NaO,S_2O_2 = NiS + NaCl + NaO,S_3O_5.$$

[5] Ann. der Chem. und Pharm., cxiii, 127.

[6] Pogg. Ann., lvi, 295.

This process answers extremely well for the analysis of nickel salts and gives more accurate results than the precipitation of the nickel as oxyd by caustic potash: it also requires less time since the sulphid may be washed with the greatest ease. On the other hand, as I shall show, it is of very limited application as a means of separating nickel from other metals. The sulphid of nickel precipitated by heating with solution of hyposulphite of soda appears black at first, but after ignition has a dark bronze yellow color. It is unchangeable in the air, and may be boiled with strong chlorhydric acid without being sensibly attacked. Strong sulphuric acid exerts no action upon it: nitric acid oxydizes it to sulphate of nickel. It may be heated in a covered porcelain crucible without oxydation, but by roasting in a current of air is converted into a basic sulphate. For quantitative purposes it is best, after washing and drying the sulphid, to burn it with the filter in a porcelain crucible so as to convert it into basic sulphate, to add to this a few drops of sulphuric acid, evaporate to dryness and gently ignite the resulting neutral sulphate, from the weight of which the nickel may be calculated. The sulphate must be completely soluble in hot water. Rose has shown that the sulphate may be completely converted into oxyd by strong ignition.[7]

Cobalt.—The relations of cobalt to hyposulphite of soda are almost identical with those of nickel; the only marked difference consists in the much greater difficulty with which cobalt is precipitated. In fact a complete precipitation under the ordinary atmospheric pressure is almost impossible. In a sealed tube, at a temperature of 120° C., the precipitation is complete in an hour at farthest. The sulphid is black, and is almost if not quite as insoluble in acids as the sulphid of nickel; it may be washed upon a filter with boiling water, and does not oxydize in the air. When heated to redness in contact with air it is readily oxydized to sulphate of cobalt, which is not basic unless the temperature is very high. In all cases, however, it is best to treat the roasted sulphid with a few drops of sulphuric acid, evaporate and ignite gently. The cobalt may then be calculated from the weight of the sulphate. Cobalt may be easily determined quantitatively in soluble neutral salts by this process; as in the case of nickel, however, the hyposulphite of soda serves to separate cobalt from other metals only in a very limited number of cases. Nickel and cobalt are completely precipitated together as sulphids by hyposulphite of soda at 120° C.: it is best to weigh them together as sulphates and then determine the cobalt by Stromeyer's method as modified by Dr. Genth[8] and myself; the nickel is then found by simply subtracting the weight of the sulphate of cobalt from that of the mixed sulphates.

[7] Pogg. Ann., cx, 132.

[8] This Journal, [2], vol. xxiv, p. 86.

Iron.—A solution of peroxyd of iron becomes of a deep violet color upon the addition of hyposulphite of soda; after a short time the color disappears and the iron is reduced to protoxyd. According to Fordos[9] and Gélis, the reaction which takes place in this case is represented by the equation

$$Fe_2Cl_3 + 2NaO.S_2O_2 = NaCl + 2FeCl + NaO,S_4O_5.$$

A solution of a protosalt of iron may be boiled or evaporated with hyposulphite of soda without undergoing any perceptible change. When, however, the two solutions are heated together for an hour or more to a temperature of 130°–140° C., the hyposulphite of soda being in excess, the whole of the iron is thrown down as a black sulphid, which is not oxydized by exposure to the air, and is not sensibly dissolved by strong chlorhydric acid. Nitric acid readily oxydizes it; dilute sulphuric acid has no sensible action. The complete precipitation of iron as sulphid under these circumstances requires a longer time and a higher temperature than that of either cobalt or nickel: the sulphid is the protosulphid, FeS, and is readily oxydized to sesquioxyd by ignition in a current of air. When sesquioxyd of iron, which has been strongly ignited so as to be with difficulty soluble in acids, is mixed with an excess of dry hyposulphite of soda and heated to redness, a black sulphid is formed which is readily soluble in chlorhydric acid with evolution of sulphydric acid gas. Nickel and cobalt give insoluble sulphids under the same circumstances, nevertheless I have not found it possible to separate iron quantitatively from either of the other two metals by this process. From what has already been stated it will also be evident that heating with solutions of the hyposulphite also fails to separate iron from cobalt and nickel.

Alumina.—A dilute solution of alumina, according to Chancel, is completely precipitated by long boiling with hyposulphite of soda, as a hydrate which is easily washed. The reaction is here expressed by the equation

$$Al_2O_3,3SO_3 + 3NaO,S_2O_2 + 3HO = Al_2O_3,3HO + 3NaO,SO_3 + 3SO_2 + 3S.$$

The boiling must be continued until the whole of the sulphurous acid is expelled. Chancel applies this reaction to the quantitative separation of alumina from iron, but I have always found that the complete precipitation of the alumina is, to say the least, extremely difficult. This may be due to the formation of a sulphite which is not decomposed by boiling. When a solution of alum is heated to 120° C. with a strong solution of hyposulphite of soda the whole of the alumina is precipitated after a short time, as a hydrate mixed with sulphur. The precipitate is white and of a peculiar semi-gelatinous character; it is more easily washed than the ordinary hydrate thrown down by ammonia. It

[9] Ann. de Chimie et de Physique, viii, 351.

is almost completely insoluble in cold and strong chlorhydric acid but is slowly dissolved by boiling. Dilute sulphuric acid has no action upon it: strong sulphuric acid and nitro-muriatic acid dissolve it with difficulty.

Zinc.—When solutions of sulphate of zinc and hyposulphite of soda are heated together in a closed tube to 120° C.–140° C., the zinc is partially precipitated as a yellowish white powder, which is a mixture of sulphid of zinc and free sulphur. A large quantity of zinc remains in solution.

Manganese.—Sulphate of manganese and hyposulphite of soda may be heated together to 120° C. without any apparent action. When however iron is present, the precipitated sulphid of iron always contains manganese which cannot be separated from it by acids.

The insolubility of the sulphids of cobalt and nickel when precipitated in the manner above described at high temperatures led me to examine the behavior of the sulphids when precipitated under ordinary atmospheric pressure from boiling solutions. When a boiling solution of sulphid of sodium is added to a boiling solution of sulphate of nickel or cobalt, the sulphids are completely precipitated in such a state of aggregation that they may be thrown upon a filter, washed with boiling water, and dried in the air without the least oxydation. It is well before filtering to render the liquid slightly acid so as to avoid free sulphid of sodium; acetic acid answers best for this purpose. The sulphid of nickel or cobalt, or the mixed sulphids, may be converted into sulphates and weighed as such.

2. *On the determination of nitrogen by weight.*

Bunsen[10] has given a method of analyzing nitrates and nitrites which renders it possible to determine all the constituents of the salt in a single analysis. This method consists essentially in igniting the salt in an atmosphere of nitrogen gas, absorbing the oxygen evolved by metallic copper, and collecting the water in a chlorid of calcium tube. The nitrogen in the salt is given by the loss of weight in the apparatus.

In those analyses of nitrates or nitrites in which it is only desired to determine the nitrogen, the following process may be employed with advantage. A hard glass tube, about six inches in length, is sealed at one end, and its volume determined by filling it with mercury and pouring this into a graduated vessel. The tube is to be carefully dried and weighed with a good cork: it is then to be filled with finely divided metallic copper, prepared by reduction of the oxyd, so as to enable the operator to judge of the quantity necessary. The salt to be analyzed is then weighed and mixed with the metallic copper, either in a

[10] Ann. der Chemie und Pharmacie, lxxii, 40.

mortar or with a mixing wire in the tube, and the tube with its contents and cork is again weighed. The weight of the copper employed is thus known and its volume may then be found by dividing this weight by the density of metallic copper. A weighed chlorid of calcium tube is then adjusted as in organic analysis, and the combustion tube is heated in the usual manner. When the combustion is finished, the open end of the chlorid of calcium tube is sealed with the blowpipe flame and the combustion tube allowed to become perfectly cold. The chlorid tube is then removed and weighed, and the combustion tube also weighed with its cork. The increase in weight of the chlorid of calcium tube gives the amount of moisture in the copper and the water in the salt analyzed. The loss of weight in the combustion tube gives the nitrogen in the salt after correction for the oxygen in the tube, for the moisture in the copper, and for the water in the salt. The correction for the oxygen in the combustion tube absorbed by the copper is easily found, with a sufficiently close approximation, by subtracting the volume of the copper from that of the tube, finding the weight of the residual air, taking one-fifth of this as oxygen, and considering the whole of this oxygen as absorbed by the copper. A piece of asbestos may be placed between the copper and the cork with advantage, but this renders an additional correction necessary. Two analyses were executed by this method. In the first a sample of pure saltpetre gave 13·86 per cent nitrogen; the formula KO, NO_5 requires 13·86 per cent. In the second a specimen of the commercial salt gave 13·7 per cent nitrogen, while the same salt analyzed by Simpson's method, in which the volume of the nitrogen is determined, also gave 13·7 per cent. The whole analysis, with the weighings, may easily be executed in an hour and a half by a single person. It is easy to see that this method applies to all inorganic nitrates and nitrites, whether hydrous or anhydrous, but that it can not be employed in the case of organic or ammoniacal salts. In the analysis of inorganic nitrates or nitrites by Simpson's method, it is not necessary to use oxyd of mercury to prevent the formation of deutoxyd of nitrogen. In all such cases it will be found sufficient to mix the salt with pure metallic copper. In this manner the dimensions of the combustion tube may be greatly diminished. I have also found it advantageous to pump out the air from the combustion tube by a small hand air-pump before disengaging carbonic acid from the carbonate of manganese. By alternately pumping and filling the tube with carbonic acid the air may be completely expelled before the combustion commences. It is also better to draw the tube out before a Bunsen's gas-blast, as it is difficult to make a cork and india-rubber connector perfectly tight. With a little practice the drawing out is easily effected

even with the hardest combustion tubes. Where many nitrogen determinations are made it will be found convenient to employ printed forms for logarithmic calculation, the logarithmic constants of reduction being printed upon the form itself in their proper places.[11]

3. *On the separation of Cerium from Didymium and Lanthanum.*

The methods which have been recently proposed for the separation of cerium from lanthanum and didymium are familiar to chemists, and do not require recapitulation in this place. They all depend, like the older methods, upon the oxydation of cerium to a sesquioxyd or to Ce_3O_4, and upon the formation of insoluble basic salts of the sesquioxyd. No one of these methods effects a complete or quantitative separation, though all afford means of obtaining salts of cerium in a state of chemical purity. The following observations upon this subject are believed to be new. When a salt of cerium, lanthanum, and didymium is boiled with dilute nitric acid, and peroxyd of lead added to the solution, the cerium is quickly, and under some circumstances completely, oxydized, the solution becoming more or less deeply orange-yellow. This process affords an extremely simple and delicate test for cerium; it succeeds with all the salts which are soluble in nitric acid, though of course when the mixed oxalates are tested the oxalic acid is oxydized to carbonic acid before the characteristic cerium-yellow appears. For the purpose of testing it is sufficient to dissolve the salt to be examined in nitric acid diluted with its own volume of water, to add a small quantity of pure peroxyd of lead and boil for a few minutes, when the smallest trace of cerium can be detected by the yellow color of the solution. The reaction is here exactly analogous to that of nitric acid and peroxyd of lead with solutions of manganese, which last is oxydized, not as Crum supposed, to hypermanganic acid, but, as Rose has shown, to sesquioxyd.

When a solution containing a salt of cerium dissolved in strong nitric acid is boiled for a short time with a large excess of peroxyd of lead, oxygen gas is copiously evolved, and at the same time the sesquioxyd of cerium formed at first is completely reduced to protoxyd, the solution becoming perfectly colorless. The remarkable reaction which occurs in this case appears to be connected with the formation of nitrate of lead, since, when the solution of protoxyd of cerium contains a large excess of this salt the cerium is not peroxydized by boiling with nitric acid and the peroxyd. Solutions of cerium salts are also oxydized by boiling with peroxyd of lead and dilute sulphuric acid, but

[11] Such printed forms may be had from the publishers of this Journal at an almost nominal price.

the protoxyd of cerium in the nearly insoluble double sulphate of soda and the cerium metals is only partially oxydized by heating with strong sulphuric acid and peroxyd of lead although oxygen is freely evolved.

A solution of hypermanganate of potash has no immediate action upon a solution of protoxyd of cerium either in nitric or in sulphuric acid, the violet color remaining unchanged even in a hot solution. On boiling for some time, however, the color changes slowly, the solution gradually becomes yellow and a brown flocky precipitate is thrown down, which consists of hydrate of sesquioxyd of manganese.

According to Stapff, a solution of hypermanganate of potash is immediately decolorized by a solution of the sulphate of potassium and protoxyd of cerium in chlorhydric acid, but after some time chlorine is evolved and the sesquioxyd of cerium found is reduced to protoxyd. It is clear that in this case the oxydizing agent is chlorine. The further investigation of this subject was committed to Dr. T. M. Drown, who has obtained the following results.

When a solution of cerium, didymium, and lanthanum, is treated with nitric acid and peroxyd of lead in the manner pointed out above, the deep orange colored liquid evaporated to dryness, and heated for a short time to a temperature sufficiently high to expel a portion of the acid, it will be found that boiling water acidulated with nitric acid dissolves only the salts of lanthanum and didymium, leaving the whole of the cerium in the form of basic nitrate, insoluble in water. The insoluble matter is to be filtered off and thoroughly washed. A current of sulphydric acid gas passed into the filtrate removes the lead, after which the lanthanum and didymium may be precipitated together as oxalates, which if the process has been carefully performed, are perfectly free from cerium. The mass on the filter is readily dissolved by fuming nitric acid. Sulphydric acid is then to be passed through the solution sufficiently diluted with water until the lead is completely precipitated. The cerium may then be thrown down by oxalic acid, ignited and weighed as $Ce_3 O_4$, or as sulphate. In this manner Dr. Drown obtained in four analyses of the same salt

DiO and LnO = 24·84, 25·31, 25·54, 24·65 per cent.

Nitrate of protoxyd of cerium obtained by this process gives, when tested by the spectroscope with transmitted light, even in very thick layers, a scarcely perceptible indication of didymium. I may here mention that Gladstone's lines furnish, with proper care, the most delicate test for the presence of didymium which we possess. It is only necessary to transmit the light through very thick layers of liquid and to employ a condensing lens so

as to throw the transmitted light directly upon the slit of the spectroscope.

4. *On the separation and estimation of cerium.*

The precipitation of cerium in the form of oxalate from a slightly acid solution is unquestionably the most satisfactory method of separating the oxyd. The estimation of the oxalate upon a weighed filter is accompanied with the usual trouble and loss of time in perfectly drying the filter before and after collecting the precipitate upon it. By the following mode of proceeding, these difficulties may be easily and completely avoided. The solution of cerium, (I understand here the usual mixture of cerium, lanthanum and didymium,) when neutral, is to be rendered slightly acid by sulphuric or chlorhydric acid and then largely diluted with water. Half a litre of water for every estimated gramme of oxyd is a good working proportion. The solution is then to be boiled and a hot solution of oxalic acid or oxalate of ammonia added. On cooling, especially when the solution has been well stirred with a glass rod, or shaken, the oxalate separates in large crystalline grains of a pale rose-violet color. The precipitate is to be filtered off and well washed with boiling water, the washing being extremely easy in consequence of the coarse granular character of the precipitate. The filter is then to be pierced and the oxalate carefully washed down into a crucible, after which the water in the crucible may easily be removed by evaporation and the oxalate dried at a temperature of 100° C. The equivalents of lanthanum and didymium are so near to that of cerium that no very sensible error is committed by considering the mixed oxalates as consisting simply of $CeO\,C_2O_3+3$ aqs. In mineral analyses in which the relative quantity of oxygen in the acids and bases must be determined with accuracy, it may be desirable to ascertain the quantity of oxalic acid in a weighed portion of the oxalates by combustion with oxyd of copper. From this the acid in the entire precipitate may be found, and the oxygen in the three bases will then be one-third of the oxygen in the acid.

5. *On the quantitative separation of cerium from yttrium, aluminum, glucinum, manganese, iron and uranium.*

The relations of the three metallic oxyds of the cerium group to sulphate of potash have long been familiar to chemists, and have furnished methods of separation from other oxyds which are still in use. In examining this subject I have found that sulphate of soda possesses great advantages over sulphate of potash, the double sulphates of sodium and the protoxyds of cerium, lanthanum and didymium, being absolutely insoluble in a saturated solution of sulphate of soda. On the other hand, the

double sulphates of sodium and glucinum, aluminum, yttrium, protoxyd of iron, and sesquioxyd of uranium, are readily soluble in sulphate of soda and may easily be washed out from the highly crystalline insoluble double sulphates of the cerium group. In the analysis of minerals in which cerium occurs with one or more of the other oxyds, the following method may be employed with great advantage. The oxyds are to be brought into the form of sulphates, dissolved in the smallest quantity of water, and a saturated solution of sulphate of soda added, together with a sufficient quantity of the dry sulphate in powder, to saturate the water of solution. It is most advantageous to use hot solutions. The insoluble double sulphates of soda and the cerium metals separate immediately, as a white, highly crystalline powder, which is to be brought upon a filter and thoroughly washed with a hot saturated solution of sulphate of soda. After washing, the double sulphates upon the filter are to be dissolved in hot dilute chlorhydric acid, the solution largely diluted with water, and the cerium metals precipitated by oxalate of ammonia, in the manner already pointed out (4). From the filtrate, the oxyds of the yttrium group may be precipitated at once by oxalate of ammonia, after peroxydizing the iron by means of chlorine water, and rendering the solution slightly acid with chlorhydric or sulphuric acid. The only precaution to be taken in this process is to reduce the iron completely to the form of protosulphate before precipitating the cerium with sulphate of soda. This is best accomplished by means of a current of sulphydric acid gas passed into the hot solution. The precipitated sulphates always contain iron when this precaution has been neglected. This iron is easily detected in the filtrate from the oxalates, and may be precipitated by ammonia and added to that obtained from the main solution.

6. *On the employment of fluohydrate of fluorid of potassium in analysis.*

The facility with which the double fluorid of titanium and potassium, or fluotitanate of potassium, separates in a crystalline state from hot aqueous solutions, on cooling, suggested to Wöhler the best method at present known for obtaining pure titanic acid. In Wöhler's process, rutile or titaniferous iron is fused with an excess of carbonate of potash, the fused mass treated with water, which leaves the greater part of the iron undissolved and the filtrate saturated with fluohydric acid. By recrystallization the fluotitanate TiF_2 KF, or perhaps more correctly, Ti_2F_4, 2KF, may be obtained in white, scaly crystals, resembling boric acid; from this salt pure titanic acid is easily obtained by precipitation with ammonia. Marignac modified this process very advantageously in the treatment of zircon to obtain pure zirconic

acid. The zircon was fused with fluohydrate of fluorid of potassium directly. In this manner a perfect resolution of the mineral was easily obtained; the fluozirconate of potassium was then dissolved out from the insoluble fluosilicate by hot water, acidulated with fluohydric acid. The observations of Wöhler and Marignac suggested to me a further extension of the same process, the general result of the investigation being that fluohydrate of fluorid of potassium or sodium may be employed with great advantage in resolving minerals containing metallic oxyds of the types RO_2 and R_2O_3. The special results are as follows.

Glucinum.—Glucina, purified from iron and aluminum by the usual methods, is to be fused with twice its weight of fluohydrate of fluorid of potassium, and the fused mass treated with boiling water, to which a small quantity of fluohydric acid has been added. On filtering a notable quantity of the insoluble fluorid of aluminum and potassium almost always remains upon the filter, even when the separation from glucinum has been carefully executed, by means of carbonate of ammonia. The filtrate, on cooling, deposits colorless transparent crusts of the double fluorid of glucinum and potassium which are easily purified by recrystallization. This method affords the simplest—I am almost disposed to say the only—method of obtaining a chemically pure salt of glucinum. The double salt is apt to contain an excess of fluorid of potassium. To obtain it perfectly pure for analysis, Mr. J. C. Newbery fused the fluohydrate of potassium with an excess of glucina. The salt as thus obtained gave him

	Calculated.	Found.
Glucinum, - - - -	5·74	5·70
Potassium, - - - -	47·73	47·76
Fluorine, - - - -	46·53	46·50
	100·00	99·96

which corresponds precisely with the formula G_2F_3+3KF, if glucinum be taken as 7, or with $GF+KF$, if glucinum be taken as 4·66. In this analysis the fluorine was estimated by the loss. Berzelius gives the formula G_2F_3+3KF. Glucina may be obtained directly from beryl, as Mr. Newbery[12] has found, by fusing the finely pulverized mineral with fluohydrate of potassium, dissolving out the soluble double fluorid of glucinum and potassium, and purifying by recrystallization. As, however, beryl contains only 13 or 14 per cent of glucinum, this process is not economical. It is better to separate the other oxyds as far as possible by the ordinary methods and then to purify the crude glucina by the process above pointed out. It is perhaps worthy of notice that while almost all proto- and sesquioxyds give insol-

[12] Prof. Joy had already remarked that beryl may be completely resolved by fusion with fluorid of potassium. See this Journal for July, 1863.

uble double salts with fluorid of potassium, the fluorid of glucinum behaves like a bifluorid, so as to suggest that glucina may possibly be GO_2 instead of GO or G_2O_3. Ammonia precipitates glucina directly from the solution of the double fluorid. When a solution of fluorid of sodium is added to one of aluminum and glucinum, the whole of the aluminum is thrown down in the form of cryolite, Al_2F_3, 3NaF, while the glucinum remains in solution. It is probable that this method will give accurate quantitative results.

Hyponiobic acid.—I am indebted to the kindness of Prof. B. Silliman, Jr., for a liberal supply of columbite from Middletown, Connecticut. Mr. F. W. Tustin has found that the finely pulverized mineral treated with a solution of three times its weight of fluohydrate of potassium is almost completely resolved during the mere process of evaporation to dryness. The dry white powder thus obtained by fusion in a platinum crucible gives a beautiful rose-colored mass which is easily separated from the crucible, and which in a moist atmosphere falls to a crystalline powder. On boiling with water acidulated with fluohydric acid a clear solution is obtained, from which, on cooling, hypo-fluoniobate of potassium separates in colorless crystals. By repeated crystallization, the salt may be obtained free from iron and manganese, but containing an excess of fluorid of potassium. It is better, however, to pass a current of sulphydric acid gas through the solution to remove traces of tin and tungsten and reduce the iron to proto-fluorid and afterward to evaporate and crystallize.

When the object in view is simply to prepare perfectly pure hypo-fluoniobate of potassium, it is better to fuse one part by weight of columbite with two of fluohydrate of potassium. The fused mass has then a greenish tint. It must be rubbed to very fine powder before boiling with water acidulated with fluohydric acid. After passing sulphydric acid gas through the solution and filtering, the hypo-fluoniobate crystallizes in colorless acicular crystals which must be purified by repeated crystallization. The salt is much more soluble in hot than in cold water. In this process a considerable quantity of fluosilicate of potassium, fluorid of calcium, quartz, and other impurities, usually remain upon the filter, with the sulphids of tin and tungsten. The difficulty in this process consists in separating the iron, when, as in the mineral columbite, this is present in comparatively large quantity. In this case very large platinum or silver vessels and numerous recrystallizations become necessary. It is better, therefore, in preparing large quantities of pure hyponiobic acid to fuse with fluohydrate of potassium, dissolve the fused mass in water as before, and filter to separate quartz, fluosilicate of potassium and fluorid of calcium, evaporate the solution to dryness and heat with pure sulphuric acid until the whole of the fluorine

is expelled. By diluting with water and boiling, the whole of the hyponiobic acid is precipitated. If after the precipitation rochelle salt is added, and the whole is boiled, the hyponiobic acid will be almost completely free from iron, manganese, tungsten and tin. After thorough washing, it may be again fused with fluohydrate of potassium, and the double fluorid obtained perfectly pure by recrystallization.

Chromic iron ore.—Mr. P. C. Dubois has found that the finely pulverized ore may be completely resolved by fusing it at a red heat for ten or fifteen minutes over a blast lamp with four or five times its weight of fluohydrate of potassium. The fused mass has a clear green color. By treating this with sulphuric acid until the whole of the fluorine is expelled, and then adding water, the chromium iron and aluminum are completely dissolved as sesquisalts. Perhaps the easiest method of separation is the following. To the solution an excess of caustic soda is added, after which, without filtering, chlorine gas is to be passed through until the sesquioxyd of chromium is converted into chromic acid. The solution is then to be heated to expel excess of chlorine, nitric acid added in slight excess, and the sesquioxyd of iron and alumina precipitated by ammonia. To the filtrate, acetic acid is to be added in small excess, after which the chromic and sulphuric acids may be precipitated together by acetate of lead. The precipitate after washing is to be boiled with chlorhydric acid and alcohol, the lead separated as chlorid and the chromium determined in the usual manner as sesquioxyd. This method gives a complete separation, even when magnesia and nickel are present in the ore.

Tinstone.—Mr. J. W. B. Hallett has found that tinstone is very easily resolved by fusion with three or four times its weight of fluohydrate of potassium. The mineral must be finely pulverized. The fused mass may be treated directly in the crucible with sulphuric acid to expel fluorine, after which, by adding water, filtering and boiling the filtrate, the whole of the tin may be thrown down as stannic acid, which is to be separated from traces of iron in the usual manner. This method of resolving the ore of tin is very much more convenient than fusion with caustic alkalies, or with sulphur and carbonate of soda.

From what has been said it will appear that fluohydrate of potassium possesses peculiar advantages in resolving those minerals which contain metallic acids of the type RO_2 or hyponiobic acid. The salt is easily prepared in a state of purity and may be preserved in vessels of lead or of vulcanized india-rubber or gutta-percha.

Cambridge, Mass., Jan. 18th, 1864.