

ART. VIII.—*Contributions to Chemistry from the Laboratory of the Lawrence Scientific School*; by WOLCOTT GIBBS, M.D., Rumford Professor in Harvard University.—No. 2.

§ 1.

On the separation of chromium from aluminum, iron, manganese, cobalt, nickel, zinc and magnesium.—Sesquioxyd of chromium in an alkaline solution is readily oxydized to chromic acid by means of chlorine, bromine or deutoxyd of lead. When chlorine or bromine are employed as oxydizing agents, the alkaline solution may be neutralized by acetic acid, after the oxydation is complete, and the chromic acid may then be precipitated by acetate of barium, when the solution is free from sulphuric acid, and directly weighed in the form of chromate of barium. In place of free alkali it will be found in practice very much more convenient to employ acetate of sodium or potassium. When a solution of sesquioxyd of chromium is rendered nearly neutral by a solution of carbonate of sodium, and acetate of sodium is added in excess, a current of chlorine gas, or a solution of chlorine water, readily converts the whole of the chromium present into chromic acid, especially when the solution is hot, and when it is kept nearly neutral by occasional addition of carbonate of sodium. The excess of chlorine is easily expelled by boiling,

²⁰ Of course; for in this oil the density is the same. See our article, this Journal, 1864, xxxvii, 51, $\delta=0$.

²¹ Malgré la différence des lois que suivent les forces attractives dans ce cas et celui des grandes masses planétaires, nous avons vu se produire, en petit, une représentation frappante de la plupart des phénomènes de configuration relatifs aux corps célestes.

after which, in the presence of bases not precipitated by ammonia, the chromic acid may be precipitated by acetate of lead, or acetate of barium, and weighed in the form of chromate, provided, of course, that no sulphuric acid is present. When sulphate and chromate of barium are thrown down together, the chromic acid may be reduced to sesquioxyd by boiling with concentrated chlorhydric acid and alcohol, after which the barium may be precipitated by sulphuric acid, and the sesquioxyd of chromium thrown down in the filtrate by boiling with ammonia in the usual manner. As the reduction of chromate of barium by means of chlorhydric acid and alcohol does not take place very readily, it is better to boil the chromate with an excess of carbonate of potassium or sodium, to filter off the carbonate of barium, and determine the chromic acid by means of nitrate of suboxyd of mercury, or by reduction to oxyd of chromium and precipitation with ammonia in the usual manner.

When aluminum and iron are to be separated from chromium by this process, the two oxyds may be precipitated together by simply boiling, the solution after the complete oxydation of the chromium to chromic acid, in the presence of excess of acetate of sodium. It is more convenient and equally accurate to neutralize the solution with ammonia, separate the alumina and sesquioxyd of iron by filtration, and determine the chromium in the filtrate by reduction and precipitation with ammonia.

When the oxyds of calcium, magnesium, zinc, nickel, cobalt and manganese are present in a solution containing sesquioxyd of chromium, it is best to oxydize the chromium to chromic acid as above, and then to precipitate with acetate of lead or barium.

I have stated in a former paper that chromic iron ore may be completely resolved by fusion with fluohydrate of fluorid of potassium. In this and in all similar applications of the fluohydrate, it is best to evaporate the finely pulverized mineral to dryness with a concentrated solution of the salt. On subsequently heating to low redness, the resolution of the mineral is effected with the utmost ease, a portion of the chromium being usually oxydized to chromic acid by the oxygen of the air. After expelling the fluorine by heating the fused mass with sulphuric acid, the remaining mass may be treated with acetate of sodium and chlorine in the manner already pointed out, the iron and aluminum separated by boiling, and the chromic and sulphuric acids precipitated by acetate of barium, after which the chromium may be determined as above.

In precipitating chromic acid by means of nitrate of suboxyd of mercury, hot solutions must not be employed, as a small portion of chromic acid is always reduced to sesquioxyd of chromium. The precipitated chromate should be allowed to

stand some hours before filtering. In general, the precipitation by acetate of lead or acetate of barium is to be preferred even when the resulting chromate is to be weighed as such.

§ 2.

On the employment of acetate of sodium for the separation of iron and aluminum from other bases.—The facility with which iron and aluminum are precipitated from neutral solutions of the sesquioxys, by boiling with acetate of potassium or sodium, has led to frequent analytical applications, though the method is not so generally employed as it deserves. Mr. C. F. Atkinson has devoted much time to a careful study of the subject, and has arrived at the following results, which appear to me worthy of attention. The sesquioxys of iron and aluminum may be perfectly separated from the protoxys of manganese, cobalt, nickel, zinc, magnesium and calcium, and from sesquioxyd of uranium, by boiling the neutral or nearly neutral solutions with acetate of sodium, provided that the following precautions are observed. The solutions from which the sesquioxys are to be precipitated must be dilute: half a liter of the solution should not contain more than one gram of either sesquioxyd or of the two when both are present. The quantity of acetate of sodium should be sufficient to convert by double decomposition all the bases present into neutral acetates. The acetate should be added to the metallic solution when cold and the whole should then be heated together and boiled for a short time. It is not necessary to filter upon a water-bath funnel, but the beaker containing the solution should be kept nearly at the boiling point during filtration, and a ribbed filter should be employed. In all cases it is best to add a few drops of free acetic acid to the solution, to prevent the formation of basic acetates of the protoxys. This is especially necessary in separating iron and aluminum from zinc and nickel.

Finally, it is best, whenever it is possible, to have all the bases present in the form of chlorids. The iron and alumina upon the filter in the form of basic acetates must, whenever an absolutely complete separation is necessary, be redissolved in chlorhydric acid and again precipitated by boiling with the acetate after rendering the solutions nearly neutral by means of carbonate of sodium. In this manner only is it possible to separate the last traces of the stronger bases. Finally, the basic salts of the iron and aluminum, after washing, must be redissolved in chlorhydric acid, and precipitated by boiling with ammonia in the usual manner, to free them completely from alkali. The precaution of a second treatment with acetate of sodium is more necessary with alumina than with sesquioxyd of iron alone. It is scarcely worth the trouble in the separation of iron from calcium and magnesium.

According to my own observations, the sesquioxys of iron and aluminum cannot be separated from sesquioxyd of chromium by boiling with acetate of sodium, although the last mentioned oxyd is not precipitated when alone in solution. In this case it is necessary to oxydize the chromium to chromic acid by chlorine in the manner already pointed out.

§ 3.

On the separation of manganese from cobalt, nickel and zinc.—Schiel's method of separating manganese from the alkaline earths by adding acetate of sodium to the mixed solutions, heating the liquid gently and then passing chlorine through it so as to convert the manganese into a hydrate of the sesquioxyd, is better than that formerly given by myself in which peroxyd of lead is used as the oxydizing agent. With respect to Schiel's method, however, it must be remarked that it cannot be employed to separate manganese from nickel or cobalt, because both of these metals are converted into higher oxyds under the same circumstances. Nickel may, as Popp has recently shown, be completely precipitated as a deep blue hyperoxyd, while as I have myself observed, cobalt is also oxydized, though not precipitated, unless the solution is boiled with an alkaline carbonate. In separating manganese from zinc, calcium or magnesium, I have repeatedly found that a second treatment is necessary in order to obtain a perfect separation. This second treatment may be neglected in separating manganese from calcium and magnesium, but not in separating it from zinc, although the addition of a few drops of free acetic acid renders the process more exact.

Though the method of separating manganese from other bases by means of peroxyd of lead, which I formerly proposed, will hardly be used in future, now that we are in possession of more convenient processes, it will still be of some interest to chemists to know the precise nature of the insoluble black compound which is formed when peroxyd of lead, PbO_2 , is digested or boiled with an excess of a solution of chlorid or nitrate of manganese and afterward thoroughly washed. An analysis of this body, made some years since in my laboratory by my lamented friend and former pupil, Mr. Theodore Parkman, gave the following results:

			Anhydrous.	Theory.
Manganese,	-	-	35.10	37.96
Lead,	-	-	32.49	35.13
Oxygen,	-	-	24.87	26.90
Water,	-	-	7.52
			100.00	100.00

Neglecting the water, which may have been, in part at least, mechanically combined, and which amounts to between three

and four equivalents, we have the formula, $\text{MnO}_2 + 4\text{PbO}_2$, as the simplest expression of the results of the analysis.

A simple and perfectly satisfactory process for separating manganese from cobalt, nickel, and zinc, is the following: To the neutral or nearly neutral solution of the chlorids, acetate of sodium is to be added in excess together with a few drops of free acetic acid. The solution is then to be boiled, and a rapid current of sulphydric acid gas passed through it while boiling and continued for half an hour. Every trace of cobalt, nickel and zinc, is precipitated in the form of sulphid, while the whole of the manganese remains in solution. The precipitate is to be thrown upon a ribbed filter and quickly washed with cold water saturated with sulphydric acid gas. It is easily washed, and though the sulphids of cobalt and nickel precipitated in this manner are far more easily oxydized than when precipitated by boiling sulphid of sodium from boiling solutions, they will be found to present no difficulty as regards oxydation upon the filter. Manganese may then be determined in the filtrate by boiling with chlorhydric acid and precipitating in the usual manner with carbonate of sodium. The mixed sulphids upon the filter, supposing for the sake of generality that all three are present, are to be dissolved in chlorhydric acid and the metals converted into double cyanids by means of an excess of cyanid of potassium, after which the zinc may be precipitated by means of sulphid of sodium, as recommended by Wöhler.

When perfectly pure cyanid of potassium is not at hand, the following process will be found particularly convenient. Acetate of sodium is to be added to the solution of the mixed chlorids, after which the vapor of cyanhydric acid generated in a flask from sulphuric acid and ferrocyanid of potassium is to be passed directly into the solution. Cyanid of zinc is immediately precipitated more or less completely as a perfectly white powder. A solution of sulphid of sodium is then to be added as long as a precipitate is formed, after which the sulphid of zinc is to be separated by filtration. Cobalt and nickel remain in solution as double cyanids. The same process may be used to separate manganese from cobalt and nickel, sulphid of sodium throwing down under these circumstances a pure flesh red precipitate. It is easy to see that zinc and manganese together may be separated from cobalt and nickel by the same process and at one operation. No cyanid of manganese appears to be formed when cyanhydric acid is passed into a solution containing a salt of manganese, acetic acid, and acetate of sodium.

I have stated in a former paper^a that the sulphids of nickel and cobalt are thrown down from boiling solutions by a boiling solution of sulphid of sodium in an insoluble form, so that in

^a This Journal, March, 1864.

fact even strong chlorhydric acid scarcely exerts upon them an appreciable action. This process has been applied to the separation of cobalt and nickel from zinc and manganese by my excellent assistant, Mr. Maurice Perkins, and gives results which are very satisfactory, especially for qualitative purposes, the sulphids of manganese and zinc precipitated under the same circumstances being readily soluble, even in dilute acid. The process is now substituted in this laboratory for that given in most of the recent works on qualitative analysis, and has been repeatedly tested with satisfactory results.

§ 4.

On the separation of cobalt from nickel.—A method of separating these metals, given some years since by Liebig,⁴ consists in boiling the mixed double cyanids of nickel and potassium and cobalt and potassium with oxyd of mercury. Oxyd of nickel is precipitated, while an equivalent quantity of mercury is dissolved as cyanid. The method certainly gives good results but is not free from objection. Long boiling is necessary before the precipitation is complete, and it is difficult to prevent "bumping" during ebullition. The excess of oxyd of mercury must be separated from the oxyd of nickel by a special operation, and the nickel afterwards again precipitated by caustic alkali.

These inconveniences may be completely avoided by employing, instead of the oxyd alone, a solution of the oxyd in the cyanid of mercury. When this solution is added to a hot solution of the double cyanid of nickel and potassium, the whole of the nickel is immediately thrown down as a pale green hydrate of the protoxyd. Under the same circumstances cobalt is not precipitated from the double cyanid of cobalt and potassium. Mr. W. N. Hill, who has repeatedly employed this method and carefully tested it, has found that the separation effected is complete. No cobalt can be detected in the precipitated oxyd of nickel by the blowpipe, nor can nickel be detected in the cobalt (finally separated as oxyd) by Plattner's process with the gold bead. The solution of oxyd of mercury is easily obtained by boiling the oxyd with a strong solution of the cyanid, and filtering. According to Kühn⁵ the cyanid formed in this manner has the formula $\text{HgCy} + 3\text{HgO}$. The hydrated oxyd of nickel precipitated may be filtered off, washed, dried, ignited and weighed. The cobalt is more readily and conveniently determined by difference, when, as is always possible, the two metals have been weighed together as sulphates. I am not prepared to say that this modification of Liebig's method of separating nickel and cobalt gives better results than Stromeyer's process by

⁴ Ann. der Chemie und Pharmacie, lxxv, 244.

⁵ Berzelius, Lehrbuch der Chemie, iii, 872.

means of nitrite of potassium, but it is at least very much more convenient and requires much less time. The complete precipitation of cobalt in the form of $\text{Co}_2\text{O}_3 \cdot 2\text{NO}_3 + 3\text{KONO}_3$ usually requires at least forty-eight hours, and rarely succeeds perfectly except in experienced hands.

§ 5.

On the separation of uranium from zinc, cobalt and nickel.—The method which I have given above for the separation of manganese from cobalt, zinc, and nickel, by precipitating the sulphids of the three last named metals, by means of sulphydric acid gas, from a boiling solution of the acetates, may be also used, according to the carefully conducted experiments of Mr. Perkins, for the separation of uranium from the same metals. The process is in all respects the same, and requires, therefore, no further description. It will be found much simpler and more convenient than that described by Rose, by means of carbonate of barium.

§ 6.

On the electrolytic precipitation of copper and nickel as a method of analysis.—The precipitation of copper by zinc, in a platinum vessel, with the precautions recommended by Fresenius, leaves nothing to be desired, so far as accuracy, ease and rapidity of execution are concerned. The method labors, however, under a single disadvantage: the introduction of zinc renders it difficult, or at least inconvenient, to determine with accuracy other elements which may be present with the copper. It has occurred to me that this difficulty might be overcome, the principle of the method being still retained, by precipitating the copper by electrolysis with a separate rheomotor. The following numerical results, which are due to Mr. E. V. M'Candless, will satisfactorily show the advantages of the method for the particular cases in which it is desirable to employ it. The copper was, in each case, in the form of sulphate; the deposition took place in a small platinum capsule, which was made to form the negative electrode of a Bunsen's battery of one or two cells, in rather feeble action. The positive electrode consisted of a stout platinum wire, plunged into the surface of the solution of copper at its center. The following table gives the results obtained in the analysis of pure sulphate of copper:

Number.	Salt taken.	Copper found.	Percentage.
I.	1.2375	0.3145	25.41
II.	0.4235	0.1075	25.38
III.	1.0640	0.2705	25.42
IV.	1.3580	0.3440	25.33
V.	0.5665	0.1450	25.59
VI.	0.4735	0.1205	25.48

In seven determinations of copper in the alloy of copper and nickel employed by the government for small coins, the following results were obtained :

Number.	Weight of alloy.	Copper.	Percentage.
I.	0.4160	0.3640	87.50
II.	0.6180	0.5410	87.54
III.	0.4600	0.4090	88.91
IV.	0.5120	0.4481	87.51
V.	0.4220	0.3693	87.51
VI.	0.2525	0.2225	88.11
VII.	0.3705	0.3255	87.85

The percentage of copper required by the formula CuO , $\text{SO}_3 + 5\text{HO}$ is 25.42, while the government standard alloy of nickel and copper contains 87.50 per cent of copper. The time required for precipitation varied from one to three hours, the separation of the last traces of copper being in each case determined by testing a drop of the liquid upon a porcelain plate with sulphuretted hydrogen water. The copper, after precipitation, was washed with distilled water, dried in vacuo over sulphuric acid, and weighed with the platinum vessel. The only precaution necessary is to regulate the strength of the current so that the copper may be precipitated as a compact and bright metallic coating, and to dry as quickly as possible. When the copper is thrown down in a spongy condition, it not only oxidizes rapidly, but it is impossible to wash out the last traces of foreign matter contained in the solution. This is well shown by number III and number VI of the second series, in both of which cases the copper was precipitated too rapidly. The solution from which the copper has been deposited contains the other elements present in the original substance. It may be easily poured off without loss, and the washings added.

It appears at least probable that nickel may be determined by electrolysis in the same manner as copper, the solution employed being the ammoniacal sulphate with excess of free ammonia. Mr. M'Candless obtained in two determinations in a commercial sample 91.26 and 91.60 per cent nickel. In both cases the nickel was thrown down completely as a bright coherent metallic coating upon the platinum.

Cambridge, Oct. 1st, 1864.