ART. IX.—*Notes on the Platinum Metals, and their Separation from each other;* by M. CAREY LEA, Philadelphia.—Part I.

(I.)

FEW branches of inorganic chemistry present difficulties comparable with those involved in the study and separation of the platinum metals. Their close analogy with each other, and the remarkable manner in which the relations of each to chemical reagents are controlled by the presence of the others, give rise to difficulties in their detection and separation which are only by degrees being surmounted. Much time and unwearied labor on the part of the chemist are required to reach results which when obtained appear insignificant in proportion to the effort which they cost, and it may in fact be said that the platinum metals constitute a chemistry in themselves, governed by special rules and to be studied by special methods. Each step in the simplification of the processes by which the separations are effected, each decisive reaction by which the presence or absence of a member of the group may be certainly inferred, is so much gained toward conquering a complete knowledge of these rare and interesting bodies.

For much the better half of all we know upon this subject, we are indebted to Dr. Claus, whose method of separation I have followed up to a certain point, and then have diverged from it, with I think some advantage. I propose to introduce the use of *oxalic acid*, as an agent in effecting the separation, in the manner which I shall presently describe.

From my friends, Prof. Booth, of the U. S. Mint, and Mr. Garrett, I received the material upon which I have worked. This was Californian osmiridium, which had already undergone a preliminary fusion with nitre and caustic potash.

This material was next boiled with aqua regia to extract all the soluble portions, the residue was then ignited with nitre and caustic soda,[1] the fused mass was heated with water. From the resulting solution small portions of osmite of potash crystallized out. The metallic oxyds were next precipitated, and this precipitate, together with the portions insoluble in water, was boiled again with aqua regia, ignited again, &c. These ignitions, in addition to that which it had undergone before coming into my hands, still left a small portion of unattacked residue.

The boiling with aqua regia was continued for a very long time in order to get rid as thoroughly as possible of the osmic acid; in all, this treatment was extended over two hundred hours. Even this however still left osmium in the solution, in easily recognizable but in comparatively small quantity. The greatest advantage was found throughout the whole of this part of the operation from the use of the blowing apparatus, which I described in a former number of this Journal, and with the aid of which all inconvenience from the fumes of osmic acid was avoided. The apparatus was constantly swept clear by a powerful air-current, and the osmic acid was removed as fast as it volatilized. The treatment which the ore had undergone before it was placed in my hands, had removed the greater part of the osmium; a portion of what remained had separated out as osmite of potash, and it was not deemed worth while to attempt to save the little that remained. It would be easy, however, in operating upon fresh material with the aid of this blowing apparatus, to conduct the osmic fumes through an appropriate reducing agent, and at the same time to sweep out every trace which escaped reduction. As the ignition of the ore with alkaline nitrate and caustic scarcely drives off any osmium, and as almost all inconvenience in manipulating the resulting solutions can be avoided by throwing down the metals with alcohol from

[1] Attention is necessary to the order in which these substances are employed. If the caustic soda is melted first, it attacks the iron vessel strongly and may even go through. If added last, it causes sudden and violent effervescence, with danger of boiling over. Therefore, place the nitre first in the vessel, and when it is fused, add the caustic soda. When a red heat is attained, add the osmiridium by degrees.

the hot alkaline solution, in place of using acid, it is clear that the difficulties arising from the noxious effects of osmic acid can be almost wholly removed from each of the various stages of the process.

A very prolonged treatment with aqua regia was found to have the great advantage of converting nearly the whole of the ruthenium into bichlorid. The separation of ruthenium in this form from the other metals is so easy in comparison with the difficulties presented by the separation of the sesquichlorid, that this advantage cannot be looked upon as other than a very material one.

Salammoniac was next added to the mixed solution in quantity sufficient to saturate it. The sandy crystalline precipitate (A) was thoroughly washed out, first with saturated, and then with dilute salammoniac solution. The saturated solution of ammonium salt carried through with it nearly the whole of the ruthenium as bichlorid (B), the dilute solution was found to contain small quantities of iridium, rhodium, and ruthenium (C).

Over (A), water acidulated with chlorhydric acid was placed, and allowed to stand for some days. This was treated with ammonia and boiled. The precipitate was inconsiderable, and, when treated with chlorhydric acid, furnished green chlorid of osmium, with traces of ruthenium.

In these preliminary steps I have used Claus' process, which undoubtedly offers advantages over any other, and best brings the metals into a convenient state for separation, varying it only by prolonging the treatment with aqua regia, and converting the ruthenium principally into bichlorid instead of sesquichlorid. We have now three portions of material, (A) consisting of iridium salammoniac, containing also ruthenium, osmium, rhodium, and platinum in small quantities. (The ore which I examined contained no palladium, which metal, if present, has always its own peculiar mode of separation, and does not enhance the difficulties of the operation.) (B) containing bichlorid of ruthenium, together with iron in quantity, copper, and other base metals which may be present. Finally, (C) containing chiefly bichlorid of ruthenium, mixed with small quantities of iridium and rhodium.

The next step in the process is to introduce the iridium-salammoniac (A) into a large flask with twenty to twenty-five times its weight of water, and apply heat until the solution is brought to the boiling point; the whole of the iridium-salammoniac should be brought into solution in order that the reduction to be operated may not occupy too long a time, as otherwise the platinum and ruthenium salt, if any be present, might likewise be attacked. Crystals of oxalic acid are thrown in as soon as the solution actually boils, whereupon a lively effervescence

takes place, and the iridium salt is rapidly reduced. As fast as the effervescence subsides, more oxalic acid is added until further additions cease to produce any effect. When this is the case, the liquid is allowed to boil for two or three minutes longer, not more; the heat is to be removed, and the flask plunged into cold water.

By this treatment any platinum present is unaffected. Sal-ammoniac in crystals is added, about half enough to saturate the quantity of water present. The salammoniac may be added immediately before the flask is removed from the fire. After cooling, the solution should be left for a few days in a shallow basin, whereby the platinum salammoniac will separate out as a yellow, a reddish, or even (especially if the quantity of water used was insufficient) as a black crystalline powder, according to the quantity of bichlorid of iridium which it may contain.

The mother water is to be again placed in a flask and boiled with aqua regia. On cooling, the platinum salammoniac crystallizes out, and any traces of rhodium and ruthenium which may be present remain in solution. The iridium salt is to be washed with a mixture of two parts saturated solution of salammoniac and three parts of water, and may then be regarded as pure.

The treatment by oxalic acid, which is now proposed for the first time, affords iridium free from all traces of ruthenium. The detection of very small quantities of ruthenium in presence of much iridium has been hitherto an impossibility, or could only be effected by Claus' method of allowing a small quantity of water acidulated by chlorhydric acid to remain in contact with the iridium salammoniac for some days. The ruthenium salt, by its superior solubility, tended to dissolve first, hence the acidulated water after standing contained ruthenium in larger relative proportion than the original crystals—the ruthenium reactions were more marked, and if it was present and in sufficient quantity, it could be detected by sulphocyanid of potassium, or better, to an experienced eye, by acetate of lead. The objections to this method are sufficiently obvious. I shall presently describe a reaction which will detect ruthenium in the presence of any quantity of iridium, and, scrutinized by that test, the iridium prepared in the manner which I have just described, is free from ruthenium, as well as from the other more easily separable cognate metals.

The treatment of solutions (B) and (C) presents no difficulty. With (B) the best plan is to place the solution aside in a beaker covered with filter paper for some time. Treated in this way the bichlorid gradually crystallizes out, and by recrystallizations may be obtained in a state of perfect purity.

Solution (C) is to be evaporated to dryness and reduced to an impalpable powder. It is then to be thrown upon a filter and

thoroughly washed with a perfectly saturated solution of sal-ammoniac. The bichlorid of ruthenium is thus carried through, with perhaps a trace of sesquichlorid of rhodium, from which, however, it is easily freed by crystallization. From the residue, the sesquichlorid of rhodium and ammonium, $3NH_4Cl, Rh_2Cl_3 + 3HO$, is removed by a dilute solution of salammoniac, perfectly free from the iridium, which is left behind.

In connection with this separation I may make a remark, which, though of special reference to this particular case, is also applicable to all those cases in which the double chlorids of the platinum metals are to be separated by their various solubilities in solution of salammoniac. This most valuable process, in which we are indebted as for so much else, to Claus, whose untiring labors have made him the father of this department of chemistry, requires to be applied with some attention to minutiæ. The crystalline matter must be reduced to the finest powder, and after being thrown upon the filter, it must be washed continuously until the separation is effected. Any interruption of the washing is followed by more or less crystallization of salammoniac through the material which precludes an effectual separation. The same material which in a state of coarse powder will hardly yield up enough $RuCl_3$ to color the salammoniac solution, will, when thoroughly pulverized, give an almost opaque blood-red filtrate.

Solution (C) may be subjected to a different treatment from the foregoing, and oxalic acid may be used to effect the separation. The solution is to be brought to the boiling point and oxalic acid added as long as effervescence is produced. The bichlorid of iridium is thereby reduced, the bichlorid of ruthenium and the sesquichlorid of rhodium are not affected. Salammoniac is then to be dissolved in the solution to thorough saturation. By standing and repose the double chlorid of rhodium and ammonium, $3NH_4Cl, Rh_2Cl_3 + 3HO$, separates out. The solution is then re-oxydized by boiling with aqua regia; by standing for some days in a cool place the iridium-salammoniac crystallizes out, and the supernatant solution contains double chlorid of ammonium and bichlorid of ruthenium which may be rendered pure by several recrystallizations.

For purifying the double chlorid of iridium and ammonium, $NH_4Cl, IrCl_2$, I give a decided preference to the method which I have described, with oxalic acid. It is simple and less trouble, and there is the further advantage that the platinum is left in the condition of double chlorid, whereas when the usual method of treating with aqueous sulphuretted hydrogen is used, the platinum is apt to be converted partly into sulphid, together with any traces of rhodium and ruthenium which may be present. When

oxalic acid is used, the platinum remains behind as a reddish powder, containing some iridium, from which it may be freed in the ordinary manner, if it is present in quantity sufficient to be worth working.

For treating a mixture such as that which I have here designated as (C) containing no platinum and ruthenium only as $NH_4Cl, RuCl_2$, it is unnecessary to apply reducing agents, and the first method which I have described is the best. But if it be proposed to effect the separation by the reduction of the iridium compound, the method which I describe in this paper, is preferable to that based on the use of sulphuretted hydrogen, even in this case.

The action of oxalic acid on the platinum metals is interesting. Its reducing effect upon bichlorid of iridium at the boiling point is immediate. On bichlorid of ruthenium it seems to have no effect whatever, may be boiled with it for a length of time without sensible result. In a trial made with sesquichlorid of ruthenium and ammonium the oxalic acid was boiled with the metallic salt for a considerable time without any apparent effect becoming visible, but by long-continued boiling a gradual precipitation took place. When platinum-salammoniac, NH_4Cl, $PtCl_2$, was boiled with oxalic acid, no effect was produced for a considerable time, but gradually the platinum salt diminished in quantity and the liquid acquired a stronger yellow color, perhaps owing to formation of soluble platinic oxalate. I was at first in hopes that the treatment with oxalic acid would have furnished a most easy and convenient method of purifying commercial platinum from the iridium always found in it. But the reduction of very small quantities of double bichlorid of iridium and ammonium in the presence of a large proportion of the corresponding platinum salt is difficult and slow, and the platinum salt itself is evidently attacked. It is for this reason that at the beginning of this paper I recommended in purifying iridium-salammoniac to use a sufficient quantity of water to hold all the iridium salt in solution at the boiling point, and to stop the operation as soon as the cessation of effervescence indicated that the action upon the iridium was terminated. The difference between the time of action of the oxalic acid on the two bichlorids is so very wide as to make it perfectly easy with proper care to effectually reduce the one without acting upon the other, except where the platinum is present in very large excess.

(II.)

The reactions of the alkalies on the chlorids of iridium are altogether peculiar. Upon the bichlorid they exert a reducing effect, converting it into sesquichlorid. An excess of alkali does

not precipitate the sesquioxyd, but seems to hold it in solution. On the application of heat the sesquioxyd gradually oxydizes itself at the expense of the atmosphere, and is then precipitated as deutoxyd of iridium. If to the cold solution containing excess of alkali, an acid be added, in small quantity, an impure sesquioxyd is precipitated in consequence of the neutralization of the alkali which held it in solution. But the sesquioxyd thus precipitated always contains a considerable quantity of the alkali used. It is very unstable, and by the action of the air is rapidly converted into blue oxyd. This is nearly all that we know of the sesquioxyd of iridium.

Under these circumstances it appeared to me desirable to investigate the action of some of the alkaline earths upon iridium solutions which it seemed possible, might throw a clearer light upon the relations of the sesquioxyd.

When a solution of caustic baryta is poured over iridium-sal-ammoniac, the iridium salt rapidly dissolves with a slight effervescence, the solution presently becomes comparatively decolorized, and a dark olive-green precipitate falls. This reaction, it will be observed, is completely different from that caused by potash.

The filtrate from this precipitate, which precipitate is but small in quantity, still contains a large quantity of iridium. If it be exposed to heat, as soon as it is moderately warm, its dark olive color changes almost suddenly to an Isabella color, it becomes cloudy, and an abundant precipitate falls, which in different experiments varies from pale grayish-yellow to yellowish-brown.

It was intended to submit both of these precipitates to a rigorous analysis. But the first was obtained in too small quantity, a few centigrams only. The second substance was much more abundant in quantity. A portion of it was prepared with great care, and with thorough exclusion of air, to prevent any admixture of carbonate of baryta. But upon careful examination, it was not sufficiently homogeneous in its composition to enable one to draw positive conclusions from an analysis, and the intention was therefore abandoned. The following were the properties observed.

The olive green precipitate seemed to be permanent in the air, and contained no baryta, or, at most, only traces. It dissolved in acids, leaving however a trace of black powder behind, and gave an olive colored solution, indicating that the iridium was in the condition of sesquioxyd.

The Isabella colored precipitate contained a considerable quantity of baryta. It dissolved in acids, and gave, when freshly prepared, also olive colored solutions. When dried at 212°, it was completely converted into an indigo colored mass, which dissolved in acids to an intense blue solution. When allowed to

dry at ordinary temperatures, even by exposure to the air, it was only oxydized in small part.

To observe the action of potash on this compound, a portion of the Isabella colored precipitate was placed in a watch glass, and a little caustic potash solution was poured over it. In a few minutes a blue tint was observable along the borders of the solution, and by exposure for a few hours the whole precipitate became intensely blue. We thus see that while potash is capable of reducing the bi-salts of iridium to sesqui-salts, its presence causes the sesquioxyd to take up oxygen from the atmosphere, with production of bioxyd. And that, for this action to take place, it is not necessary that the sesquioxyd should be in that anomalous state of solution in alkali, in which it seems to exist in solutions of bichlorid decolorized with excess of alkali; but that the barytic compound here described, which is comparatively permanent by itself, commences immediately to oxydize rapidly when placed in contact with potash.

Other reactions of platinum metals with baryta are as follows:

Sesquichlorid of ruthenium and ammonium is immediately and completely precipitated by baryta in the cold.

Bichlorid of ruthenium and ammonium gives no precipitate to the cold. Heated, it turns yellowish brown and becomes troubled. This troubling is completely removed by the addition of a large excess of the precipitant. If the baryta have been added to large excess at first, no troubling is occasioned by the application of heat.

Protochlorid of palladium is precipitated immediately in the cold by Ba. The brownish yellow precipitate does not redissolve in excess of the precipitant. In this the reaction of baryta differs from that of potash.

Bichlorid of platinum is scarcely affected by baryta water in the cold. Heat immediately produces a dirty white precipitate, the supernatant liquid remaining of a yellow color.

Sesquichlorid of rhodium gives an immediate light colored precipitate with baryta, which completely redissolves in a very large excess of the precipitant, even in the cold.

It will be seen from the foregoing that the reactions of baryta with the platinum metals differ widely from those produced by potash, and are highly characteristic.

Two of these solutions which much resemble each other, those of bichlorid of ruthenium and sesquichlorid of rhodium, are very well distinguished from each other by baryta, the former remaining for some time clear, the latter being instantly precipitated. The production of a well marked precipitate is generally a better test than a mere change of color, as produced by potash, which has hitherto been considered the best reagent to distinguish between these two substances.

The relations to color of the double sesquichlorid of iridium and ammonium, $3NHCl, Ir_2Cl_3 + 3HO$, are curious, and have not been exactly described. It is generally said that its solution is olive-green by reflected, and reddish by transmitted light. The following is a more correct description.

A dilute solution of the salt is always olive-green, whether seen by reflected or transmitted light. If it appears red by transmitted, when very dilute, this can only arise from the presence of bichlorid of ruthenium, or sesquichlorid of rhodium.

As its concentration increases, it gradually acquires a red color, visible by both reflected and transmitted light, but more conspicuous by the latter. A very strong solution is almost opaque to transmitted rays; by dilution, passes to a deep wine red. This wine-red solution is by reflected light olive-green, but with a distinct tinge of red. Nor has it before been remarked, I believe, that the crystallized salt exhibits the same dichroism. The crystals are deep green by reflected light, almost black. When placed so that light can strike through a dihedral angle, its color is ruby red.

Strong and weak solutions of this salt differ so much in color (in tint, not merely in intensity,) that at first one has a difficulty in believing that they contain one and the same substance.

New Ruthenium Reaction.—A series of experiments on the reactions of the platinum metals are as yet unfinished, but I take the present opportunity to mention a new and very beautiful reaction of the sesquichlorid of ruthenium.

When a solution of hyposulphite of soda is mixed with ammonia, and a few drops of solution of Ru_2Cl_3 are added, and the whole boiled, a magnificent red-purple liquid is produced, which, unless the solutions are very dilute, is black by transmitted light. The coloration is permanent, and the liquid may be exposed to the air without alteration.

This reaction is obtained with great ease and certainty, and will, I believe, be found far superior to any known test for ruthenium.

In order to determine the limits of the sensibility of this reagent, experiments were made with ruthenium solutions of different strengths. A portion of perfectly pure Ru_2Cl_3 was weighed out in a delicate balance, and the following indications were obtained:

With $\frac{1}{5000}$ Ru_2Cl_3, bright rose purple.

With $\frac{1}{30000}$ and $\frac{1}{300000}$, fine rose-color.

With $\frac{1}{500000}$, paler, but still perfectly distinct.

With $\frac{1}{1000000}$, the color, though very pale, was still unmistakably present.

Where the solutions are so very dilute as these last, the boiling must be continued for some minutes.[2]

Although the sulphocyanid test is very delicate, it is not equal to this, as was determined by a comparative trial. It is also liable to the objection that when employed to examine mixtures, the presence of iron might be confusing. For although the reaction of ferric salts with sulphocyanid gives a different shade of red, yet it is to be observed that the two colors approach each other considerably when much diluted. Moreover, in using the sulphocyanid test, I find it best to acidulate the liquid strongly with chlorhydric acid, and to obtain chlorhydric acid absolutely free from iron, so that it does not give the slightest coloration with the sulphocyanid; it is generally necessary (in this country, at least,) to prepare it for oneself.

The delicacy of this test does not however constitute its greatest value and superiority. The reactions of ruthenium are remarkably affected by the presence of iridium; and in proportion as this last named metal is present in larger quantity, the indications afforded by all the tests hitherto known grow less and less decided, and some lose all efficacy. The test here proposed is the first known reagent that is capable of detecting ruthenium in the presence of any excess of iridium. No precautions are necessary, and the reaction is always obtained with the greatest facility. The iridium solution is to be rendered alkaline with ammonia, a crystal of hyposulphite of soda is dropped into it, and the whole is boiled for two or three minutes. If no indication of a red-purple tint appears, (or, in case of small quantities of ruthenium, a rose color,) the iridium solution may be pronounced free from ruthenium.[3]

It would appear that there must exist very beautiful purple and green compounds of ruthenium, with which we are at present unacquainted. The purple compound appears to be produced in several reactions, and notably in that just described and in the sulphocyanid. There can be little doubt that sulphur enters into its composition. The green compound is produced when a solution of Ru_2Cl_3 is boiled with ferrocyanid of potassium. Claus remarks, in reference to this coloration, that he is unable to explain its cause. It is, however, unquestionably due to a compound of ruthenium, and not to the production of any

[2] When the presence of ruthenium in very small quantity, or in very dilute solution, is suspected, it is often advisable to boil the solution with a little chlorhydric acid, previous to the application of the hyposulphite, sulphocyanid, or other test. The explanation of this will be given in the second part of this paper. With the hyposulphite test the acidulated solution must be rendered alkaline by addition of ammonia before heating with hyposulphite.

[3] The second part of this paper will contain an examination of the reaction of hyposulphite of soda, and other reagents, upon the various metals of the platinum group.

prussian blue or green compound; for I find that the green reaction can be obtained in presence of a large excess of free ammonia, together with which, it is hardly necessary to remark, the last mentioned compounds could not exist. I propose to return to the subject of the ruthenium reactions at a future occasion.

Philadelphia, March, 1864.

(To be continued.)