of both inorganic and organic compounds, upon dilute chloride solutions of the six platinum metals has been studied.

2.   These tests were carried out under various conditions of concentration, temperature and degree of acidity, and the results have been tabulated.

3.   The degree of completeness of the precipitation was determined in many cases and so noted in the tables given.

4.   Several new color reactions have been found which are useful in qualitatively detecting several of the metals when free from large amounts of the others of the group.

5.   Theoretical considerations relative to the formation of coördinated salts are discussed.

CHAPEL HILL, NORTH CAROLINA

A QUALITATIVE SEPARATION OF THE PLATINUM METALS

BY S. C. OGBURN, JR.[1]

The analytical separation of the platinum metals presents difficulties that are seldom encountered with the other metals.   Their resistance to chemical solution, the volatility, from solution, of the tetroxides of osmium and ruthenium, the interferences they present in a mixture, their catalytic effect in causing the oxidation or reduction of analytical reagents, and the general similarity of their actions towards chemical compounds are but a few of the obstacles that might be mentioned.   The actual success of methods of analysis now in general use, composed of both assay determinations and tedious distillation and fractional precipitation procedures, is contingent upon many factors—more than those apparent from a glance— in the steps of the process.

It was with a view of obtaining a short, successive gravimetric separation of the metals, that would be as nearly quantitative as possible, that this investigation was begun.

During a study of their reactions[2] with a large number of organic and inorganic compounds, certain precipitates were obtained that effected the removal of the metals from individual chloride solutions.   These were carefully reviewed and tables made showing the nature of the precipitation, that is, whether qualitative or quantitative, and whether the tests were valid in a mixture of the metals of the group.   Using the reagents from

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these tables, nearly a dozen possible schemes of analysis were outlined and experimentally carried out. The final scheme contained the best parts of the previous attempts and, on careful examination, proved to give an excellent qualitative separation, which was within 2.5% of quantitative for each of the six metals.

Procedure

To the mixture of the pure chloride (or double chloride) solutions of the six metals was added hydrochloric acid in sufficient amount to make the acid content equivalent to 7 or 8 cc. of concd. hydrochloric acid per 100 cc. of solution used. The quantity of each metal used was approximately 0.003 g. per cc. of final solution.

To Remove Palladium.—A 1% alcoholic solution of dimethylglyoxime was added in the cold (A). (The letters in parentheses refer to the corresponding notes, below.) After stirring, the mixture was warmed to 35° or 40° on an electric hot-plate. Alcohol was added (B) to aid in the coagulation of the precipitate and the whole allowed to stand for one hour. The bright yellow precipitate, $Pd(C_4H_7O_2N_2)_2$, was filtered under slight suction onto double filter paper and washed with a small quantity of cold water containing a few cubic centimeters of alcohol, until the washings were colorless (C). It was then dried in an electric oven to 105°, ignited carefully in air, then heated for 20 minutes at red heat in a stream of hydrogen, cooled and the metallic palladium thus obtained weighed.

To Remove Platinum.—The filtrate (containing platinum, rhodium, ruthenium, osmium, iridium) was treated with a 2% alcoholic solution of α-furil-dioxime (D) and a quantity of alcohol equivalent to 10% of the total volume, and boiled for 30 minutes. The mixture was filtered, while hot, under slight suction. After complete precipitation of the platinum was attained (E), the red-brown (F) precipitate, $Pt(C_{10}H_7O_4N_2)_2$, was washed with small portions of cold water containing a few cubic centimeters of alcohol, until the washings were colorless. It was then dried, carefully ignited, first in air, then in hydrogen, cooled and the metallic platinum thus formed weighed.

To Remove Rhodium.—The filtrate (containing rhodium, ruthenium, osmium, iridium) was evaporated to one-third its volume (G), cooled and treated with 5 cc. of concd. hydrochloric acid per 100 cc. of solution and 5 g. of sodium chlorate, and cautiously warmed until the greenish fumes of chlorine ceased to be evolved. The whole was diluted with an equal volume of water, then an equal volume of alcohol was added and the solution boiled. During boiling, a small quantity of a saturated solution of potassium nitrite was stirred in. This salt was added until the solution was alkaline to litmus, and the boiling continued until a permanent, white cloudy precipitate began to form and a marked lightening in color of the

solution was noted (H).   After boiling for 15 to 20 minutes, the mixture was allowed to stand overnight.   The yellow-white crystalline precipitate, $K_3Rh(NO_2)_6$, was filtered off (I), washed with 50% alcoholic solution until the washings were colorless, then dissolved in boiling aqua regia (3:1 water).   The solution obtained was evaporated with concd. hydrochloric acid to remove nitrogen oxides, then diluted.   The rhodium chloride was reduced with magnesium turnings (or zinc dust), and the black, finely divided metallic rhodium filtered off, washed with very dilute hydrochloric acid, then with water, dried, ignited in air, heated in hydrogen, cooled and weighed.

To **Remove Ruthenium.**—The filtrate (containing ruthenium, osmium, iridium) was boiled (J) until no further fumes of nitrogen dioxide appeared and until the alcohol had been removed, then slowly treated with 10 cc. of concd. hydrochloric acid per 100 cc. of solution.   The whole was evaporated until it assumed a dark red color and crystallization began (K).   It was then diluted with three or four times its volume of water and made alkaline with sodium hydroxide.   A further quantity of the latter reagent was added in sufficient amount to precipitate all ruthenium present and to maintain an excess (L).   Alcohol, to the extent of one-half the volume, was added and the whole slowly boiled for 15 to 20 minutes on an electric hot-plate. After the mixture had been allowed to stand for several hours and until the precipitate settled and the supernatant liquid was clear, the black hydrated oxide of ruthenium, $Ru_2O_3.3H_2O$, was filtered and washed well with dil. alcohol and water.   This was dissolved in boiling, dil. hydrochloric acid (M) and the metal precipitated by the addition of metallic magnesium (or zinc).   This was washed with water, dried, ignited first in air (not above 550°), then in hydrogen, cooled and weighed.

To **Remove Iridium.**—The filtrate (containing osmium, iridium) was evaporated to remove excess of alcohol, cooled, made acid with dil. hydrochloric acid and treated with zinc dust, until the solution was rendered colorless (N).   The black, finely divided metals were then filtered off under slight suction and washed well with cold water slightly acidulated with hydrochloric acid.   The ashless filter paper containing the residue was placed in a small beaker, treated with fresh sodium hypochlorite solution and stirred occasionally for one hour; then the mixture was filtered.   The black residue of metallic iridium was washed, dried, ignited in air, then in hydrogen, cooled and weighed.

To **Remove Osmium.**—The orange filtrate (containing now only osmium) was acidified with hydrochloric acid and treated with zinc dust until complete precipitation of the metallic osmium was effected as evidenced by the clear, colorless supernatant liquid (N).   The solid was then filtered off, washed well with water, dried, heated in an electric oven to 190°, then in hydrogen, cooled and the metallic osmium weighed.

Notes

(A). The dimethylglyoxime solution should be added in slight excess of the palladium present, if its approximate content is known. A large excess is to be avoided as it interferes in the removal of rhodium.

(B). The quantity of alcohol added should be about 15% of the volume of the solution. It also reduces the iridium to the iridous condition.

(C). Several cubic centimeters of the filtrate was tested with dimethylglyoxime solution to insure complete precipitation. The first precipitation, in every case tried, was complete. None of the other metals was affected by this reagent in the cold.

(D). This reagent was prepared as directed by Soule.[3] A slight excess of the reagent, with respect to the platinum content, is needed but a large excess is to be avoided. The solution should not be allowed to stand overnight; after boiling and prolonged standing, some rhodium tends to precipitate with the platinum.

(E). Several cubic centimeters of the filtrate was tested with α-furil-dioxime. When any of the red-brown precipitate formed on boiling, the whole was treated again with the reagent. This was continued until the test showed negative results. Usually two precipitations were sufficient. The positiveness of the test can be verified by treating several cubic centimeters of the filtrate with a solution of potassium iodide. When no red coloration results, the platinum has been completely removed.

(F). When dimethylglyoxime is present in large excess of the furil-dioxime, some green precipitate is formed. This, however, does not interfere with the platinum separation as this green precipitate, on ignition, yields its metallic platinum.

(G). When the platinum has not been completely removed, it is precipitated during this evaporation.

(H). An excess of potassium nitrite is to be avoided for the following reasons. (a) The double nitrite of ruthenium is formed, instead of the nitrosochloride. This latter salt affords the subsequent removal of the ruthenium by precipitation with alcoholic sodium hydroxide, while the former does not. (However, if any of the double nitrite is formed, it will be converted into the nitrosochloride by evaporation with concd. hydrochloric acid, which is done at a later point in the separation.) (b) The double nitrite of iridium will be partially precipitated in a strong potassium chloride solution on cooling. It is soluble in a hot aqueous solution. (c) The osmium salt is converted into its osmyl derivative by the addition of potassium nitrite in an acid solution. The action of an excess of acid (hydrochloric acid), however, converts this derivative into the chloro-osmate, which retains the osmium in solution. When an excess of nitrite is used, some osmium tends to be converted into osmium tetroxide by the nitrous acid. It is improbable, however, that any appreciable amount of osmium is lost from the solution, even under such conditions.

(I). Several cubic centimeters of the filtrate was tested for rhodium with potassium nitrite and alcohol. This can be confirmed by testing also with an aqueous solution of morphine sulfate or dimethylamine. Absence of a precipitate indicates complete removal of the rhodium.

(J). If any white precipitate of rhodium appears, it is filtered off and added to the previous rhodium precipitate.

(K). This color is evidence of the conversion of any double nitrites of the metals (ruthenium, osmium, iridium) into chlorides (osmium, iridium) or nitrosochlorides (ruthenium). The evaporation is carried out nearly to dryness. Any crystallized products are dissolved in the dilution process; it is necessary that complete solution should take place and the solution possess a clear, rose-red color.

(L). The excess of sodium hydroxide is *necessary* to dissolve any hydrated iridium

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[3] Soule, THIS JOURNAL, **47**, 981 (1925).

sesquioxide (Ir$_2$O$_3$.5H$_2$O) formed. (If this is not done, it will be found with the ruthenium precipitate.)

(M). If any of the precipitate fails to dissolve, it is filtered off, washed with dil. hydrochloric acid; the washings are added to the filtrate and the residue is dried and added to the remainder of the ruthenium precipitate. If the insoluble portion is excessive, it is probably iridium; see Note L.

(N). Excess of zinc (or magnesium), in each case, is dissolved by further treatment with cold, dil. hydrochloric acid before the mixture is filtered. The time required for complete reduction depends upon the concentration and condition of the metals in solution, varying from a few minutes to several hours. The filtrate, in every case, is tested a second time with zinc (or magnesium) and hydrochloric acid until no black residue is obtained that is insoluble in excess of dil. hydrochloric acid.

Results of Quantitative Analysis.—Several analyses were made with weighed quantities of the six metals in various proportions in order to determine the accuracy of the procedure for quantitative work, but checks were not obtained; the best of these are shown in Table I.

TABLE I

ANALYSIS OF A CHLORIDE SOLUTION CONTAINING THE SIX METALS

Metal	Present, g.	Found, g.	Error, %
Ruthenium	0.3630	0.3710	1.96
Rhodium	.3538	.3597	1.67
Palladium	.4062	.3960	2.47
Osmium	.0571	.0540	1.91
Iridium	.4049	.3938	2.73
Platinum	.3408	.3374	1.06

The author wishes to acknowledge the helpful criticism of the paper given by Dr. James M. Bell of the University of North Carolina.

Summary

A new gravimetric scheme of analysis of the platinum metals is given. It is short and comparatively easy for those unfamiliar with the detailed chemistry of the metals to carry out. It is well adapted for qualitative or semi-quantitative determinations, having an accuracy within 2.5% for each of the six metals. It is based upon well-known principles; the only new analytical reagent used is α-furil-dioxime for the removal of platinum. The order of separation is as follows. Starting with a mixture of the metals in solution as chlorides (or double chlorides) containing a hydrochloric acid content equivalent to 7 or 8 cc. of concd. hydrochloric acid per 100 cc. of solution, the *palladium* is removed by a 1% alcoholic solution of dimethylglyoxime in the cold. From the filtrate, the *platinum* is removed by precipitation with a 2% alcoholic solution of α-furil-dioxime on boiling. After concentrating the filtrate by evaporation and adding hydrochloric acid and sodium chlorate to remove excess of the oximes, the *rhodium* is precipitated with alcoholic potassium nitrite solution on boiling and standing overnight. The residue is dissolved in boiling aqua regia, evaporated with concd. hydrochloric acid, diluted and the metallic rhodium

precipitated with magnesium turnings. The filtrate is made acid with concd. hydrochloric acid, evaporated nearly to dryness, diluted and the *ruthenium* precipitated with alcoholic sodium hydroxide on boiling. The residue is dissolved in hydrochloric acid and the metallic ruthenium precipitated with zinc dust. The filtrate is then made distinctly acid with hydrochloric acid, after evaporating to remove alcohol, and the metals iridium and osmium are precipitated in the finely divided state with metallic zinc. The two metals are then treated with a fresh solution of sodium hypochlorite; this dissolves the osmium and leaves the *iridium* unattacked. The latter is filtered off. The osmium filtrate is made acid with hydrochloric acid and the metallic *osmium* is precipitated with zinc dust. Each of the metallic precipitates is subsequently dried, ignited in air (osmium to 190° only), heated in hydrogen, cooled and the metal weighed.

CHAPEL HILL, NORTH CAROLINA

THE FREEZING-POINT LOWERING AT INFINITE DILUTION

BY MERLE RANDALL

In calculating the activity coefficients of strong electrolytes in dilute solution it is convenient to use a method that will give a criterion of the accuracy of the experimental points in the most dilute solutions. Moreover, it is most important that the method used should be, so far as is possible, empirical.

If we plot the j-function of Lewis and Randall[1] divided by the square root of the molality against the square root of the molality, then we obtain a series of points such as is shown in Fig. 1 of the following article. Because of the experimental errors and the sensitiveness of such a plot to small errors in the dilute end, the points are scattered, but with more exact data the scattering is diminished. From a study of the freezing-point data of all strong salts we may conclude that the best average curve that can be drawn in each case is the one that will extrapolate to the limit at $m = 0$ which is given below.

In the following paper it will be shown that the activity coefficient of a salt is given by the equation

$$\log \gamma = -\frac{j}{2.303} - \frac{2}{2.303} \int_0^m \frac{j}{m^{1/2}} \, dm^{1/2} \tag{1}$$

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[1] Lewis and Randall, (a) THIS JOURNAL, **43**, 1112 (1921); (b) "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, pp. 285–290, 341–352. $j = 1 - (\theta/1.858\,\nu m)$, where θ is the freezing-point lowering, ν the number of ions formed per molecule, and m the molality. A quantity Φ identical in value with $1 - j$ was called the osmotic coefficient by Bjerrum [*Z. Elektrochem.*, **24**, 321 (1918)]. While the molality of the solute is involved in the definition of j, it is an empirical quantity directly related to the properties of the solvent alone.