ferred to as active molecules, and it is due to these that "slow" reactions have a high temperature coefficient.

3. The theory predicts that chemical reactions will fall into comparatively few classes, each class having a characteristic temperature coefficient.

4. In this theory the assumption is made that the unhydrated hydrogen and hydroxyl ions are the catalytically active particles, and this leads to the conclusion that stoichiometrically neutral water is distinctly alkaline catalytically, and it is not until the hydrogen-ion concentration has a value about P_H 5 that the concentrations of the unhydrated ions become equal, and the catalytic activity is at a minimum.

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[Contribution from the Bureau of Standards, United States Department of Commerce]

INVESTIGATIONS ON THE PLATINUM METALS. IV.[1] THE DETERMINATION OF IRIDIUM IN PLATINUM ALLOYS BY THE METHOD OF FUSION WITH LEAD[2]

By Raleigh Gilchrist[3]

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Introduction

A critical study of the Deville and Stas[4] method for the determination of iridium in platinum alloys was undertaken at the Bureau of Standards as the first of a series of investigations into the analytical methods for the metals of the platinum group.

The Deville and Stas Method

Deville[5] found that when platinum alloyed with iridium, rhodium, palladium, iron and copper is dissolved in lead at a high temperature, the lead forms alloys with all of the platinum, rhodium, palladium and copper, and with a very small proportion of the iron. The iridium, ruthenium and iron form a separate alloy containing no lead. Boiling dil. nitric acid removes the bulk of the lead together with the palladium and copper and

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[1] (a) I. The Preparation of Pure Platinum, by Edward Wichers, This Journal, **43**, 1268 (1921). (b) II. Investigations on Platinum Metals at the Bureau of Standards, by Edward Wichers and Louis Jordan, *Trans. Am. Electrochem. Soc.*, **43**, 385 (1923). (c) III. The Preparation of Platinum and of Platinum-Rhodium Alloy for Thermocouples, by R. P. Neville, *Trans. Am. Electrochem. Soc.*, **43**, 371 (1923).

[2] Published by permission of the Director of the Bureau of Standards of the United States Department of Commerce.

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[4] Deville and Stas, "Procès-verbaux, Comité International des Poids et Mesures," **1877**, p. 185.

[5] Ref. 4, p. 162.

a small proportion of the platinum and rhodium. Digestion of the residue with warm, dil. aqua regia leaves insoluble only the alloy of iridium, ruthenium and iron.

The Deville and Stas procedure has been used at the Bureau of Standards for six years but with a few modifications in apparatus and technique.

Details of the Analysis Made the Subject of Investigation

In order to arrive at the optimum conditions for the determination of iridium in platinum alloys a study was made of the following details: magnitude of the error caused by the incomplete separation of iridium; variation of the concentration of nitric acid and of aqua regia used; variation of the proportion of lead to alloy and of the time and temperature of the lead fusion; effect of ruthenium, rhodium, palladium, gold and iron and the effect of ignition in air and of reduction in hydrogen on the weight of crystalline iridium.

Preparation of Alloys for Analysis

The alloys were specially prepared for this investigation from metals of the highest purity. The platinum had been prepared for use in thermocouples and its spectrum showed only a trace of calcium. The iridium had been fused with lead and its spectrum showed the presence of traces of platinum, rhodium, ruthenium, lead and iron that were so small, however, that they could have no appreciable effect on the composition of the alloys. The palladium was free from base metals, while the rhodium sponge may have contained a trace of lead, but both were free from the other platinum metals. The spectrum of the gold indicated a trace of silver and copper.

The alloys were melted in an Ajax-Northrup high frequency induction furnace[1c] using pure lime or purified thoria as the refractory. The platinum used was either in the form of an ingot or of wire compressed into a pellet in a steel mold. The finely crystalline iridium was wrapped in a small cylindrical shell of pure platinum in order to avoid loss. The molten alloys were stirred vigorously by the effect of the induced electric current. With the exception of the iron-iridium alloy which was cast in graphite the melts were allowed to freeze in the crucibles.

From experience gained in the melting of preliminary samples of pure platinum and of platinum-iridium alloys, the small loss in weight on melting was considered to be a loss of iridium. The percentage of iridium put into the mixture of metals represented, therefore, the maximum iridium percentage of the alloy, while the minimum average percentage was calculated by deducting the percentage loss in weight which occurred in melting.

Danger of Non-Uniform Sampling

Early analyses indicated the necessity of careful sampling because of the non-homogeneity of some of the alloys. The first alloy of the final series (containing 20% of iridium) was drawn to wire of 0.60mm. diameter and cut into fragments varying from 1 to 2 mm. in length. The variation in analytical results led to the belief that this method of sampling was inadequate. The subsequent alloys made were drawn to 0.36 mm. and cut into lengths of 1 mm. The cut wire in every case was cleaned from superficial iron by hot concd. hydrochloric acid, washed with distilled water and ignited to dull redness in a porcelain crucible. Samples for analysis were taken from different parts of the mass.

Results of Analyses

Incomplete Determination of Iridium.—Early in the experimental work iridium was detected qualitatively in the aqua regia solution. Although the amount in this case was small, it was evident that some iridium was being lost. In order to determine the magnitude of this error, iridium was recovered from the aqua regia solutions in the analysis of a number of the alloys. The total aqua regia solution was evaporated to dryness, the nitric acid eliminated by hydrochloric acid, ammonium chloride added, the mass of salt dried, reduced in hydrogen and the resulting metal fused with lead as in the regular procedure for an alloy. Calculated in percentage on the basis of the weight of the alloy samples taken, of the 33 recoveries made 20 were less than 0.05%, 7 were between 0.05 and 0.10%, 4 were between 0.10 and 0.15%, and 2 were between 0.15 and 0.30%.

There was no uniformity in the quantity of iridium which escaped the first determination, considering either individual experiments or the averages from different alloys, although these alloys differed considerably in iridium content. It seems unlikely that more than a very small quantity could have been involved in a mechanical loss, since the utmost precautions were taken to effect a quantitative transfer and a double filter was used, both layers of which were of paper of close texture. There was probably some solution of the iridium by the aqua regia in all cases, but the reason why the amount dissolved should vary between wide limits is not apparent. In reporting the analyses in which this second determination of iridium was made, the total iridium is the value considered in the discussion of the results. Such recoveries were made except in the analyses discussed under the headings "Variation of the Concentration of Nitric Acid," "Effect of Palladium and Gold" and the "Effect of Iron."

Experiments on the Variation of the Concentration of Nitric Acid Used to Disintegrate the Lead Button.—Eight analyses were made on 4g. samples of an alloy containing a maximum of 4.85% of iridium and a minimum of 4.82%. Each of the three analyses in which the nitric acid concentration was 1:8 gave the value 4.83%. Three determinations with 1 : 4 nitric acid gave 4.83, 4.85 and 4.83%. Two determinations with 1 : 2 nitric acid gave 4.79 and 4.80%.

Although the variation of the concentration of nitric acid had little effect on the iridium determination, it was found that the 1:2 nitric acid produced a residue which was finely divided and difficult to filter, thereby offsetting any advantage gained over the 1:4 nitric acid by a saving of time.

In this and subsequent experiments the temperature of the solutions was maintained at about 85° (steam-bath) and double filters were always used.

Experiments on the Variation of the Concentration of Aqua Regia Used to Separate the Iridium from the Lead-Platinum Alloy.—Seven analyses were made on 2g. samples of an alloy containing a maximum of 20.20% of iridium and a minimum of 20.11%. The average of three experiments, with 1:10 aqua regia was 19.99%; that of two experiments with 1:5 aqua regia, was 20.09%; and that of two experiments using 1:2.5 aqua regia was 20.06%. The seven individual results varied from 19.98 to 20.12%.

Such variations as appear in the results are probably to be ascribed to somewhat inadequate sampling rather than to the variation of the concentration of the aqua regia. Consistent results were obtained in the analysis of a 10% iridium alloy and of a 5% iridium alloy containing gold and palladium, in which analyses the concentration of aqua regia was 1:2.5.

Experiments on the Variation of the Duration of the Lead Fusion.—Nine analyses were made on 2g. samples of an alloy containing a maximum of 20.20% of iridium and a minimum of 20.11%. The average of three experiments with a 4-hour fusion period at 1000° was 19.99%, of two with a 2-hour period was 20.05%, of two with a 1-hour period was 20.11%, and of two with a $^1/_2$-hour period was 20.05%. The nine individual results varied from 19.98 to 20.12%.

The results show that the time of fusion with the temperature at 1000° may vary over a wide range without affecting the determination.

Experiments on the Variation of the Proportion of Lead to Alloy.—Seven analyses were made on 2g. samples of an alloy containing a maximum of 20.20% of iridium and a minimum of 20.11%. The average of two experiments, with 10 g. of lead to 1 g. of alloy, was 20.05%, of three, with 20 parts of lead, was 19.99% and of two, with 40 parts of lead, was 20.02%. The seven individual results varied from 19.97 to 20.09%. The proportion of lead can, therefore, be varied over a wide range without appreciably affecting the determination.

Experiments on the Variation of the Temperature of the Lead Fusion.—Analyses were made of an alloy containing a maximum of 10.26% of iridium and a minimum of 10.22%. Experiments in which 10 parts of lead to 1 part of alloy at 600° were used resulted unsatisfactorily. It was not possible to effect complete fusion. Two analyses on 1.3g. samples with a lead fusion at 800° for $^1/_2$ hour gave 10.26 and 10.34%. Two analyses on 1.3g. samples at 800° for 4 hours gave 10.18 and 10.13%. Three analyses on 4g. samples at 1000° for $^1/_2$ hour each gave 10.22%. Three analyses on 4g. samples at 1000° for 4 hours gave 10.18, 10.18, and 10.12%. The results show that the temperature of the lead fusion may vary between 800° and 1000° without seriously affecting the determination. However it appears that a short fusion at 800° is not sufficient.

Experiments to Determine the Effect of Ruthenium.—Three analyses were made of an alloy containing a maximum of 9.96% of iridium and 0.51% of ruthenium and a minimum of 10.35% of iridium plus ruthenium. One experiment on a 4g. sample gave 10.44% and two experiments on 3.5g. samples gave 10.39 and 10.41%. The results confirmed the observation of Deville and Stas[6] that ruthenium separates quantitatively with the iridium.

Experiments to Determine the Effect of Rhodium.—Five analyses were made of an alloy containing a maximum of 5.06% of iridium and a minimum of 5.01% and in addition 5.04% of rhodium. Three analyses on 4g. samples gave 5.14, 5.15, and 5.18%. Two analyses on 3.4g. samples gave 5.13 and 5.17%. The results of the two series of analyses, although concordant, are higher than the maximum percentage of iridium in the alloy. The iridium from two experiments was examined chemically for rhodium, but in both cases a quantity of rhodium not greater than 0.01% of the weight of the alloy sample taken for analysis was extracted. Iridium from a third experiment was examined by spectrographic analysis but the quantity of rhodium detected was very small. It was, therefore, concluded that the actual experimental values for iridium represented the true composition of the portion of the ingot which was prepared for analysis. Deville and Stas[5] state that rhodium does not interfere in the determination of iridium.

Experiments to Determine the Effect of Palladium and Gold.—Six analyses were made on 4g. samples of an alloy containing a maximum of 5.35% of iridium and a minimum of 5.31% and in addition 3.07% of palladium and 2.32% of gold. Three experiments, with 1:8 nitric acid, gave 5.25, 5.29, and 5.30%. Three experiments, with 1 : 4 nitric acid, gave 5.29, 5.28, and 5.31%. The results show that palladium and gold have no effect upon the determination of iridium.

Experiments to Determine the Effect of Iron.—Five analyses were made on 4g. samples of an alloy containing a maximum of 4.75% of iridium and in addition 0.31% of iron. The results ranged from 5.03 to 5.12% with an average of 5.07%. The iron in the combined nitric acid and aqua regia solutions from three of these analyses was determined colorimetrically and found to be 0.02, 0.01, and 0.005% of the sample. One of the remaining solutions showed a trace of iron and the other none. Colorimetric analysis of iron in a separate sample of the alloy gave 0.31% of iron.

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[6] Ref. 4, pp. 162, 191.

A procedure for the separation of iron from iridium, suggested by W. H. Swanger of this Laboratory, was tested. It consisted of a fusion of the iridium with zinc, removal of the excess of zinc with hydrochloric acid, and fusion of the zinc-iridium alloy with potassium pyrosulfate. The insoluble residue from the digestion of the pyrosulfate fusion with dil. sulfuric acid should contain all of the iridium free from iron but contaminated with silica. After the removal of silica in the usual manner four experiments gave 4.65, 4.65, 4.71 and 4.72%.

To determine whether this procedure could be conducted without loss of iridium, experiments were made with samples of iridium containing no iron. The samples weighed 0.1940 g., 0.1945 g. and 0.1938 g. and the recoveries were 0.1951 g., 0.1933 g. and 0.1937 g., respectively.

The results of the experiments confirm the observation of Deville and Stas[7] regarding the behavior of iron and show in this case that even a greater proportion of the iron separated with the iridium. In the analysis of some contact points containing approximately 5% of iridium and 0.16% of iron, it was also found that nearly all of the iron was weighed as iridium.

Analysis of an Alloy Containing a Small Amount of Iridium.—Three analyses were made of an alloy calculated to contain 0.084% of iridium. The samples weighed 5 g. and the results were 0.070, 0.068, and 0.066%, with an average of 0.068%. The values are seen to be slightly low. It was in the analysis of this alloy, among the first made in this investigation, that iridium was observed to be present in the aqua regia solution.

Miscellaneous Experiments.—A correction of 0.0005 g., the quantity of insoluble material introduced into the iridium during the analysis from the reagents and apparatus used, was applied to the weight of the iridium in all of the analyses reported in this paper.

It was found experimentally that in the time required for the ignition of the iridium in air in the regular analysis, namely, about one hour, there would be no significant loss in weight.

It was found experimentally that the practice of reducing and cooling the iridium in hydrogen introduced no error into the weight of the iridium.

Spectrographic examination of samples of iridium obtained from analysis showed that platinum and lead were either absent or their presence doubtful. No zinc was found in the iridium which had been fused with zinc and subsequently with potassium pyrosulfate.

Proposed Modified Procedure

The following modification of the Deville and Stas method is recommended.

1. **Lead Fusion.**—Fuse the carefully sampled platinum alloy with 10 times its weight of granular test lead for a period of one hour at a tem-

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[7] Ref. 4, p. 177.

perature of about 1000°. A covered crucible, whose outside dimensions are 4 cm. in diameter and 7 cm. in height, machined from Acheson graphite, is suitable for fusions made with 20 to 40 g. of lead. The inside of the crucible should possess a slight taper to facilitate the removal of the cooled ingot. Do not pour the fusion from the crucible, but allow it to solidify, since the iridium has largely settled to the bottom of the crucible. The crucible is best heated with an electric furnace.

2. **Disintegration with Nitric Acid.**—Brush the cooled lead ingot free from carbon with a camel's hair brush, and place it in a beaker. Add nitric acid of the concentration one volume of acid (d., 1.42) to 4 volumes of water, using 1 cc. of acid per g. of lead. Place the beaker on the steam-bath or on a hot-plate which maintains the temperature of the solution at about 85°. Disintegration of the lead ingot is usually complete in about two hours, and leaves a rather voluminous, grayish-black mass. Dilute the solution to twice its volume and decant the liquid through a double filter, consisting of a 9cm. paper of fine texture[8] on which is superimposed a 7cm. paper of looser texture. Wash the residue quite thoroughly with hot water and pass the washings through the filters. The residue is not transferred to the filters at this point. The lead nitrate solutions and washings are best caught in an Erlenmeyer flask to make easier the detection of the presence of any residue which has passed through the filters. This is done by whirling the liquid in the flask. Any particles of the residue collect at the center of the bottom of the flask. Return the filters to the beaker without ignition.

3. **Solution of the Lead-Platinum Alloy by Aqua Regia.**—Add in order 15 cc. of water, 5 cc. of hydrochloric acid (d., 1.18) and 0.8 cc. of nitric acid (d., 1.42) for each gram of the platinum-alloy sample taken. Heat the solution in the beaker on the steam-bath or on a hot-plate which maintains the temperature at about 85°. The lead-platinum alloy is usually completely dissolved within one and a half hours. Dilute the solution with twice its volume of water and filter through a double filter, similar to the one used for the lead nitrate solution. The iridium, insoluble in the aqua regia, is in the form of fine crystals, possessing a bright metallic luster and having a high density. Pass the clear solution through the filter first and then transfer the thoroughly macerated paper. It is very important to examine the beaker to see that no iridium remains. To do this the interior of the beaker is wiped with a piece of filter paper to collect any metal adhering to the sides. Then by whirling a small quantity of water in the beaker any iridium remaining gravitates toward one place whence it can be removed with a piece of paper. Wash the filters and iridium thoroughly, first with hot water, then with hot dil. hydrochloric

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[8] Such as S. and S. No. 589 blue ribbon and No. 589 black ribbon papers, respectively.

acid (1:100), and lastly with hot water. The chloroplatinic acid filtrate and washings should be examined for iridium, which may have passed through the filters, in the manner described under the nitric acid treatment. The last washings should be tested for the absence of lead.

4. **Ignition and Reduction of the Iridium.**—Place the washed filters and iridium in a porcelain crucible and dry, before igniting in air. After the destruction of the filter paper, ignite the iridium strongly with the full heat of a Tirrill burner. After all carbon is burned out, cover the crucible with a Rose lid, preferably of quartz. Introduce into the crucible a stream of hydrogen, burning from the tip of a Rose delivery tube (a quartz tube is preferred). After five minutes remove the burner and a few minutes later extinguish the hydrogen flame by momentarily breaking the current of hydrogen. This is best done by having a section of the rubber delivery tube replaced by a glass tube, one end of which can easily be disconnected. Allow the iridium to cool in an atmosphere of hydrogen and then weigh as metallic iridium.

In commercial analysis no effort is made to correct the weight of iridium for small amounts of ruthenium. Correction, if desired, can be made according to the original directions of Deville and Stas. The correction for iron can be made according to the procedure given with the discussion of the analysis of the iron-iridium-platinum alloy.

Acknowledgments are made to Edward Wichers, under whose supervision the chemical work on the platinum metals was conducted, to R. P. Neville, who melted the alloys and prepared them in the form of wire, and to Florence J. Stimson, who made the spectrographic analyses of the iridium samples.

Summary

A study has been made of the analytical details of the Deville and Stas method for the determination of iridium in platinum alloys containing from 0.1 to 20% of iridium. Specially prepared alloys, made from highly purified metals, were used in the investigation. It was found that the concentration of nitric acid, the concentration of aqua regia, the proportion of lead, and the time and the temperature of the lead fusion can be varied over a wide range without affecting the determination. The observations of Deville and Stas that palladium and rhodium have no effect upon the determination and that ruthenium separates quantitatively with the iridium were confirmed. In addition, gold was found not to interfere. Iron separates nearly quantitatively with the iridium as observed by Deville and Stas. A method for the separation of iron from the iridium was tested and found to give satisfactory results. The loss in weight of crystalline iridium during the ignition periods is insignificant and the weight of crystalline iridium is not affected by heating and cooling in an atmosphere of

hydrogen. Spectrographic examination of samples of iridium from analysis showed that neither platinum nor lead was present in sufficient quantities to affect the determination. The iridium results tend to be low by a variable but usually small amount. One factor in this error is a slight solution of iridium by aqua regia. A modified procedure for the method is offered which combines the optimum conditions for speed and accuracy in the various details of manipulation.

A full report of this investigation including the actual experimental data will be found in a forthcoming publication of the Bureau of Standards.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

SOLUBILITY. IX. METALLIC SOLUTIONS

BY J. H. HILDEBRAND, T. R. HOGNESS AND N. W. TAYLOR

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In a series of papers[1] appearing during the past seven years by the senior author and various collaborators considerable evidence has been presented to show that deviations from Raoult's law, and accompanying effects upon solubilities, can be predicted approximately for substances that are sufficiently non-polar, provided they do not tend to form compounds with each other. These deviations were correlated chiefly with differences in "internal pressure," as estimated by various criteria.

Metallic solutions offer a particularly inviting field for the application of a theory of solubility because a large amount of data is available and also because the metals differ among themselves in surface tension, compressibility, expansion, internal pressure and other characteristics far more than do the familiar non-metallic liquids, so that they offer a much more severe test of a theory than do most non-metallic solutions. For example, although but few non-metallic liquids, excluding water, are sufficiently unlike to yield two liquid phases, there are known no less than 47 metallic pairs which are incompletely miscible in the liquid state.

We do not have data upon the coefficients of compressibility and expansion for molten metals necessary for the calculation of their internal pressure by the expression[2] $T\alpha/\beta$, used in earlier papers, except for mercury, where the value is 13,200 megabars. This is several times as large as the values for the common non-metallic liquids, which explains, at least partly, their immiscibility with mercury. We may, perhaps, form a rough idea of the internal pressures of liquid metals from the values of α/β of their solid forms. Table I gives some figures of this sort taken

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[1] Compare particularly THIS JOURNAL, **38**, 1452 (1916); **39**, 2301 (1917); **41**, 1067 (1919); **42**, 2180 (1920); **42**, 2213 (1920); **43**, 500 (1921); **43**, 2172 (1921); **45**, 682 (1923). *Phys. Rev.*, 21, 46 (1923).

[2] α is coefficient of expansion; β of compressibility.