solution and thence into the ammonium-magnesium phosphate.

To sum up, the citrate method only gives good results by compensation of its errors and under exactly defined conditions which must be empirically determined. A procedure good for calcium phosphates is quite inapplicable to ferric and aluminum phosphates.

Again, the molybdic method, when carried out rapidly at temperatures higher than 50°, or as high as 65° C. in presence of trivalent iron, aluminum, or manganese, gives results too high, and in presence of great excess of nitric acid may give results too low, unless the filtrates from the yellow precipitate are mixed with additional molybdic solution and further digested until no more precipitate can be thrown down.

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## DOUBLE BROMIDES OF PALLADIUM.

BY EDGAR F. SMITH AND DANIEL L. WALLACE.

BONSDORFF (*Poggendorff's Annalen der Physik*, [1], N. F., 19, 347) was one of the first chemists to attempt the preparation of double halides of palladium with other metals. Beyond mere mention of the fact that he obtained palladium bromide by the action of a mixture of nitric and hydrobromic acids upon the metal, that the resulting compound apparently combined "mit den Bromiden elektro-positiver Metalle," and that he made double salts of it with the chlorides of potassium, barium, manganese, and zinc, we have not discovered any additional literature relating to the above subject. It does not appear that Bonsdorff analyzed any of the double halides obtained by him.

Desirous of finding a salt or salts of palladium suitable for, but as yet not used in atomic mass determinations of palladium, we took occasion to prepare several double bromides of that metal, hoping to find among them one or more which might be available for the purpose.

Very pure metallic palladium was dissolved in nitro-hydrobromic acid. The residue was moistened with hydrobromic acid and repeatedly evaporated to dryness upon a water-bath. The palladium bromide, reddish-brown in color, was only soluble in water containing hydrobromic acid. Weighed quantities of this

dry bromide, with equivalent amounts of the metallic bromides, were dissolved in water containing hydrobromic acid. Upon evaporation, crystalline residues were obtained. These were always dissolved in water and again allowed to separate.

### POTASSIUM PALLADIUM BROMIDE.
$$K_2PdBr_4.$$

This salt separated from its aqueous solution in shining reddish-brown needles. It is anhydrous. It is very stable and suffers no change on exposure to the air. In analyzing it we determined the palladium by the method suggested by Frenkel, *Ztschr. anorg. Chem.*, **1**, *229*. By following this recommendation the bromine can be precipitated by silver nitrate without contamination with palladium.

*Analysis.*—0.4930 gram dried material gave 0.1045 gram metallic palladium, equal to 21.19 per cent. Pd, and 0.7428 gram silver bromide, equal to 63.79 per cent. Br, while the theoretical requirements of $K_2PdBr_4$ are 21.12 per cent. Pd and 63.50 per cent. Br. A second portion of substance, weighing 0.2613 gram, was gently heated in a current of hydrogen and, after cooling. the residue was extracted with hot water. Upon evaporating this aqueous solution to dryness. 0.1251 gram of potassium bromide was obtained. This is equal in percentage to 15.58 per cent., while the theoretical potassium bromide in this double salt is 15.45 per cent.

Hoping that by adding bromine to the aqueous solution of the above salt, and digesting the same with this reagent, at a temperature not exceeding 70°, we might possibly get a salt of the formula $K_2PdBr_6$, we carried out several such experiments. The result was not what was anticipated; the product being really a salt of the simpler type, $K_2PdBr_4$, with two molecules of water of crystallization, $K_2PdBr_4 + 2H_2O$. It separated in long, dark-brown and shining needles. which on exposure rapidly lose their luster, become dull, and acquire a reddish-brown color. Owing to the rapid loss of water by the crystals, the analytical results do not approach the theoretical requirements as closely as might be expected.

*Analysis.*—0.3235 gram substance gave 0.0660 gram, or 20.37 per cent. of metallic palladium; 0.4565 gram of silver bromide,

equal to 60.00 per cent. of bromine and 0.0201 gram of water, equivalent to 6.21 per cent. The formula $K_2PdBr_4 + 2H_2O$ requires 19.71 per cent. Pd, 59.2 per cent. Br, and 6.65 per cent. $H_2O$.

### AMMONIUM PALLADIUM BROMIDE.
$$(NH_4)_2PdBr_4$$
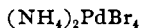
This salt crystallizes in beautiful and quite large olive-brown colored forms which apparently possess an orthorhombic habitus. They are anhydrous and are perfectly stable in ordinary air. They possess about the same solubility as the corresponding potassium salt.

*Analysis.*—0.2528 gram dry material gave 0.0585 gram metallic palladium, equal to 23.14 per cent., and 0.4090 gram silver bromide, equivalent to 68.82 per cent. of bromine, while the theoretical percentages are $Pd = 22.91$, and $Br = 69.17$.

As this salt and the corresponding potassium salt are anhydrous and can be obtained pure without great difficulty, it is our intention to use them in a redetermination of the atomic mass of palladium.

### SODIUM PALLADIUM BROMIDE.

We experienced much trouble in getting this salt, and it was only after the solution, containing equivalent amounts of sodium and palladium bromides, was allowed to remain in a vacuum desiccator over concentrated sulphuric acid for some time that it separated out in large deep red colored plates which proved to be very deliquescent. It was therefore necessary to conduct the analysis with imperfectly dried material. Through an accident we are not able to give a result upon the bromine content, and are limited to a presentation of the palladium and water percentages. These are, 19.68 per cent. Pd, and 14.67 per cent. $H_2O$. A salt of the composition $Na_2PdBr_4 + 4\frac{1}{2}H_2O$ would require 19.25 per cent. Pd, and 14.63 per cent. $H_2O$.

This salt is very deliquescent and even to a much greater degree than the corresponding double chloride of sodium and palladium.

### STRONTIUM PALLADIUM BROMIDE.

The solution of this salt also stood for many days before crystals made their appearance. It consists of short, black prisms, which are stable on exposure to the air.

*Analysis.*—0.2256 gram air-dried substance gave 0.0366 gram Pd, or 16.22 per cent.; 0.2643 gram silver bromide. or 49.82 per cent. Br, and 0.0679 gram strontium sulphate, equal to 14.09 per cent. strontium.

A second analysis gave 0.0518 gram Pd, or 16.79 per cent.; 0.3595 gram silver bromide, or 49.57 per cent. Br; 0.0861 gram strontium sulphate, equal to 13.29 per cent. Sr, and 0.0544 gram water, corresponding to 17.63 per cent.

A salt of the composition $SrBr_2.PdBr_2 + 6H_2O$ would require

$$17.11 \text{ per cent. Pd}$$
$$13.99 \text{ " " Sr}$$
$$51.47 \text{ " " Br}$$
$$17.37 \text{ " " } H_2O$$

Our deficiency in bromine, we believe, is due to a slight loss of that constituent occurring during the drying process.

### MANGANESE PALLADIUM BROMIDE.

This salt is very soluble in water. Like the two preceding salts it only separated from its aqueous solution after long standing. Its crystalline form is apparently like that of the ammonium salt. The crystals are dull-black in color.

*Analysis.*—0.1829 gram air-dried substance was carefully heated to constant weight in an air-bath. The loss, representing water, equaled 20.39 per cent. The anhydrous residue was then exposed at a moderate temperature to the action of hydrogen gas. On cooling, the mass was extracted with dilute hydrochloric acid. The spongy palladium weighed 0.0331 gram, equal to 18.09 per cent. Pd. The filtrate from the palladium gave 9.29 per cent. of manganese.

These results indicate a salt with the formula $MnPdBr_4 + 7H_2O$, which would require

$$17.52 \text{ per cent. Pd}$$
$$9.05 \text{ " " Mn}$$
$$20.73 \text{ " " } H_2O$$

An effort was made to prepare the double halides of zinc and of cadmium with palladium, but the products crystallized so poorly that the analysis of the same was abandoned.

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April 25, 1894.