

The values for the molecular weights given in Table V and VI show that the two varieties of sulfur trioxide used, behave essentially alike in phosphorus oxychloride, and that the molecules of both are represented by the formula SO_3 . While the first three pairs of molecular weights of the β -variety recorded in Table VII are not in good agreement with 80, they certainly do not lead to 160 as the molecular weight. The values obtained with the β -trioxide which had been exposed to moist air are higher than any others found during this work. It may fairly be questioned whether this is due to some association, to the somewhat complicated experimental process, or to partial combination with water.

These points and others regarding the physical changes which sulfur trioxide undergoes, as well as the relation between the α - and β -forms, are now under investigation.

Summary.

1. In addition to values for the melting and boiling points of α -sulfur trioxide, which seem to be more trustworthy than those heretofore obtained, new values for the density and the coefficient of expansion were obtained.

2. Nowhere between 11.8° and 45° was there observed a slow attainment of constancy of volume at fixed temperature, such as Schenck observed at 35.3° in α -trioxide.

3. It has been shown that there exists a solid sulfur trioxide, apparently identical with the ordinary solid form, and designated the β -form, whose molecular weight in phosphorus oxychloride is 80, the same as that of the persistently liquid α -variety.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ATOMIC WEIGHT OF PALLADIUM.

BY OWEN LOUIS SHINN.

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Berzelius in 1828 first determined the atomic weight of palladium by decomposing potassium palladiochloride in an atmosphere of hydrogen. Since that time twelve investigators have worked on this problem, nine of whom have used this method of analysis, the other three reducing by electrolysis. Two have determined chlorine also, but the vast majority of the work has been the reduction of a salt in hydrogen at an elevated temperature.

It was thought desirable to try to throw out the metal from a solution of some salt, collect the precipitate upon a filter and weigh, thus getting a ratio without using a high temperature and thereby avoiding danger of volatilizing palladium. The idea of a Munroe crucible also eliminated

any error due to mechanical losses such as occur with an asbestos mat in a Gooch crucible.

The salt selected was the one used by most of the investigators, palladioammonium chloride, $\text{Pd}(\text{NH}_4\text{Cl})_2$. The well known reducing action of carbon monoxide was expected to completely precipitate the metal, but this was not the case for, even after passing the gas through for 35 hours, some palladium still remained in solution.

When the work was started it was thought that various ratios could be obtained from the same sample by determining the chlorine and ammonia in the filtrate from the metal, but the long treatment showed very plainly that no reliable results could be obtained in that manner.

Reduction by ammonium formate was then tried and the results were more satisfactory. The difficulty of removing the excess of reducing agent from the filtrate made the determination of the chlorine or ammonia impossible.

Preparation of Material.—Metallic palladium that had been used by Kemmerer¹ in his determination, was dissolved in *aqua regia*, evaporated almost to dryness, hydrochloric acid added and evaporated again. This evaporation with hydrochloric acid was repeated three times, the last evaporation being carried to complete dryness on a steam bath. The residue was dissolved in water and ammonia gas distilled in to slight excess. A slight insoluble residue was filtered out, the excess of ammonia expelled by boiling and the yellow salt precipitated by hydrochloric acid. This salt was filtered, washed repeatedly with cold water, then suspended in water and ammonia gas distilled in until solution was complete. This solution was then treated with carbon monoxide (made by the action of sulfuric acid upon oxalic acid, the carbon dioxide not being removed), and metallic palladium thus obtained. The precipitated palladium was washed by repeatedly boiling first with water containing ammonia, then with pure water, and was then dissolved in *aqua regia*. The nitric acid was removed by numerous evaporations with hydrochloric acid, the last evaporation being carried almost to dryness. The palladium chloride was dissolved in water and ammonia gas distilled into it until the hydroxide, which first formed, had almost dissolved. The solution was then filtered and the palladioammonium chloride precipitated with hydrochloric acid. This salt was filtered, washed thoroughly with cold water, again almost dissolved in ammonia, filtered and reprecipitated with hydrochloric acid. This treatment was repeated three times. The salt was then filtered, washed repeatedly with cold water after which it was allowed to stand over soda lime for three weeks. The drying was completed by heating in an electric oven to 98–102° for 6 hours, air being

¹ THIS JOURNAL, 30, 1701.

drawn through the oven during the heating. All tests for foreign material failed to show any impurities in this salt.

All of the water used in this work was twice distilled, using a block tin condenser. It was collected in Jena glass flasks and used at once.

Hydrochloric acid was made by dropping C. P. sulfuric into C. P. hydrochloric acid and absorbing the gas in redistilled water. The apparatus was made entirely of glass.

Nitric acid was redistilled C. P. acid, the middle fraction only being used.

Ammonia was only used in gaseous form. The gas was distilled as used from pure commercial ammonia water.

Formic acid was the best obtainable and was distilled into the solution as needed.

All weighings were made upon a balance having a constant sensibility of 2.4 divisions per milligram, using weights which were carefully calibrated. All weighings were made by substitution and the weights given were reduced to vacuum standard, using 11.45 as the specific gravity of metallic palladium and 2.55 as that of the salt. The weighing bottle, crucible, tares and weights were permitted to remain upon the balance pan for at least 1 hour before the final weighings were made.

Manipulation.—A quantity of palladioammonium chloride was shaken from a tared weighing bottle into a Jena glass beaker of about 400 cc. capacity, 200 cc. of water poured over this and, while gently warming, ammonia gas was conducted over the surface. When the salt had completely dissolved, formic acid vapors were passed over the surface until an excess of ammonium formate was formed and the metal began to deposit. The solution was then boiled for an hour, the palladium usually was deposited in the form of a mirror which peeled off as the boiling continued. The precipitated palladium was filtered through a Munroe crucible and washed with hot water. A few small particles of metal always adhered to the side of the beaker; this was not scraped off but was converted into chloride by placing a few drops of nitric and hydrochloric acid in the beaker, covering with a watch glass and warming. This chloride was rinsed into a smaller beaker and treated as the original solution with ammonia and formic acid. In three cases a second reprecipitation was necessary in order to collect all of the metal. By filling the beaker with chlorine gas the strong color of palladium chloride made it very easy to detect minute specks of the metal. The filtrate and wash water was always evaporated and treated with ammonium formate but no deposit was ever detected. The residue from evaporating the filtrate was ignited in three cases, but no trace of metal could be detected.

The crucible containing the palladium, after thorough washing with

hot water, was placed in a porcelain electric oven and heated to 120° for 2 hours, cooled in a desiccator and weighed as previously mentioned, the results being given in the following table:

Ratio calculated:

$$(\text{wt. of salt} - \text{wt. of Pd}) : \text{wt. of Pd} :: 2\text{NH}_4\text{Cl} : x.$$

Atomic weights used in the calculation were, nitrogen 14.01, hydrogen 1.008 and chlorine 35.46.

Weight of salt taken.	Weight of palladium.	Atomic weight.
1.03021	0.51923	106.685
1.45506	0.73323	106.675
1.10384	0.55645	106.705
0.88141	0.44448	106.804
1.53091	0.77160	106.688
1.98887	1.00212	106.625
1.45102	0.73174	106.808
1.57909	0.79563	106.620
1.61705	0.81583	106.779

Mean 106.709 \pm 0.016

These determinations were made from two lots of material, made and treated in exactly the same way but kept separate at all times, the first four being one set, the last five the other.

The variation in these results, 0.188, is greater than that which is usually accepted as satisfactory for such work. The care taken in the preparation of the material, the simplicity of the method and the care taken in carrying out the determinations suggest that the cause is some other than that of faulty manipulation. A careful review of the work of others, who have used this salt in their investigations, shows similar discrepancies, which would suggest a question as to the absolute uniformity of the salt $\text{Pd}(\text{NH}_4\text{Cl})_2$. From the way in which it is made, may not some of the palladium be present in some other than the bivalent form or may not some of the double salt $\text{PdCl}_2 \cdot 2\text{NH}_4\text{Cl}$ still remain undecomposed? The problem will be attacked in an entirely different way with the idea of eliminating this complex and, therefore, doubtful compound.

Attempts were made to get ratios between palladium and some metal by replacement, but all efforts in that direction were fruitless. Magnesium and zinc hydrolyze so readily that the palladium precipitated was only about 70%. Silver did precipitate palladium from an ammoniacal solution of its chloride, but never completely, and some silver always remained undissolved. When metallic palladium was placed into a solution of gold, it went into solution but the gold was only reduced to the aurous condition and no metal was thrown out.