distils off, and tested it for boric acid both qualitatively and quantitatively. In a few cases we have been able to get a very faint test with turmeric paper, but in no case have we found an amount equivalent to 1 drop of 0.1 *N* NaOH. We even collected the distillate from three determinations and tested it all in one portion, but this, too, showed less than the equivalent of 1 drop of 0.1 *N* NaOH.

6. The changes of color that take place during the titration are worthy of mention. When the glycerol or mannite is added to the solution the yellow color due to the para-nitrophenol at once disappears. This is due to the fact that the combination of these reagents with the boric acid forms an acid of sufficient strength to affect the indicator, although boric acid alone does not. As the titration proceeds the color reappears, and grows stronger and stronger, becoming very intense just before the phenolphthalein end appears. The latter will be noticed first as a faint brownish tinge; and then another drop of the 0.1 N alkali changes it to an intense brownish red. The brownish tinge marks the real end point, of course.

7. Compared with the time required for other gravimetric determinations the time necessary to carry out this method is not excessive. After apparatus and reagents are ready, a series of determinations at the rate of four a day may be easily run, counting eight hours as a working day.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ATOMIC WEIGHT OF PALLADIUM.[1]

BY GEORGE I. KEMMERER.

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The atomic weight of palladium has been the subject of no less than twelve separate investigations. The results vary so much that it seemed desirable to give this problem further consideration. Accordingly, thirty-two grams of sheet palladium were purified by the method pursued by Keller and Smith.[2] From it, salt *A* was prepared. A second sample of metal was purified in the same way as the first but the mercuric cyanide was replaced by ammonium cyanide and ammonium compounds were applied wherever sodium and potassium salts had been used in the first process. All reagents, *e. g.*, water, hydrochloric acid, sodium carbonate, mercuric cyanide, ammonium formate, sulphur dioxide, ammonium thiocyanate, etc., were made pure by well established and generally accepted processes.

The salts studied were:

[1] From the author's Ph.D. thesis.

[2] *Am. Chem. J.*, 14, 423 (1892).

Salt *A*—palladammonium chloride (purified by method of Keller and Smith).

Salt *B*—the same palladamine obtained without the use of mercuric cyanide or salts of sodium or potassium.

Salt *C*—palladammonium cyanide—$Pd(NH_3CN)_2$—made from metal purified in the same manner as that which furnished Salt *B*. This salt was carefully dried at 43° to 46° for a period of two weeks. Its weight was constant.

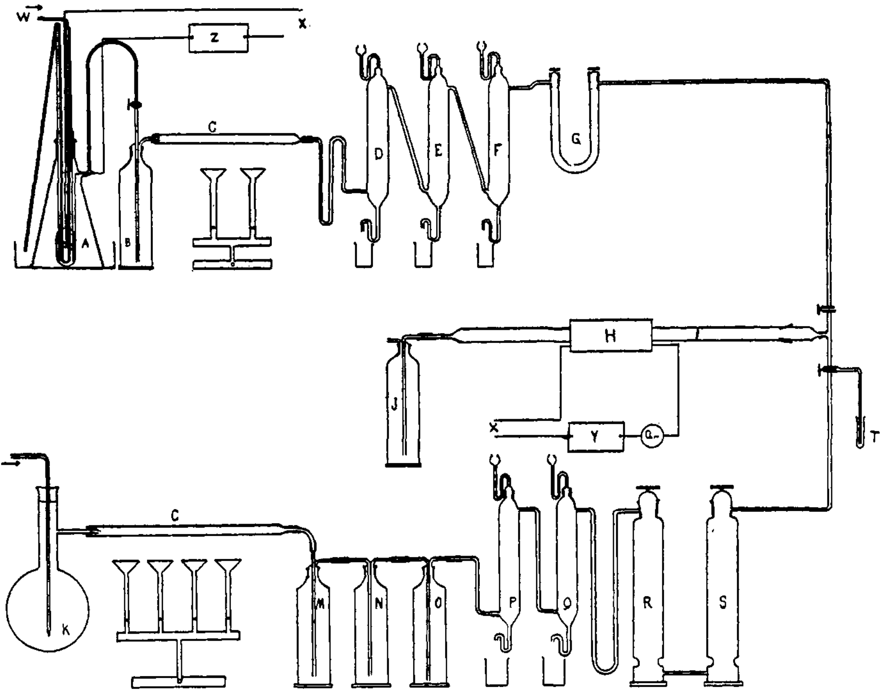
The weighings were made on a Troemner balance used exclusively for atomic weight work. It was sensitive to 0.02 of a milligram. The brass and platinum weights were carefully calibrated. The several salts were reduced in hydrogen in boats of porcelain contained in weighing bottles. These were counterbalanced by bottles and boats of equal weight. All weights were reduced to the vacuum standard, using the following specific gravities:

Palladium metal	11.45
Palladammonium chloride	2.55
Palladammonium cyanide	2.50

During the course of the experiments, the glaze on the boat gradually darkened, probably due to minute traces of palladium. Platinum boats were tried, but it was not possible to heat them sufficiently high without danger of alloying. To eliminate any possible error from the absorption of palladium, after each experiment, the porcelain boat was boiled in aqua regia and soaked in hot water. It was then dried and heated to bright redness in hydrogen for an hour. After cooling in nitrogen it was removed to the desiccator and allowed to stand in the balance room for two hours before weighing. While using this method the weight of the boats did not vary more than 0.03 of a milligram between any two consecutive experiments.

The reduction of the salts to metal by hydrogen was carried out in an apparatus easily understood by the accompanying sketch.

Electrolytic hydrogen was prepared by passing a current of six amperes through a solution of sodium hydroxide. The platinum electrodes were so arranged that no oxygen could diffuse into the hydrogen compartment and the electrolyte was cooled by passing water through a coil of glass tubing immersed in the anode compartment. The hydrogen thus generated passed through a wash bottle containing concentrated sulphuric acid, then over red hot copper to remove any oxygen or hydrogen peroxide which might be present. The gas next passed through an apparatus made entirely of glass composed of towers filled with glass balls. In the first tower the balls were moistened with a solution of silver nitrate. The second and third towers contained concentrated sulphuric acid. The drying was completed in a U tube containing phosphorus pentoxide, from which the hydrogen passed directly to the combustion tube.



A, Hydrogen generator. B, Sulphuric acid wash bottle. C, Combination tubes containing copper gauze. D, Silver nitrate tower. E and F, Sulphuric acid towers. G, U tube containing phosphorus pentoxide. H, Electric heating coil. I, Combination tube. J, Sulphuric acid trap. K, Ammonia flask. L, Air supply. M, N, O, Wash bottles containing dilute sulphuric acid. P, Silver nitrate tower. Q, Tower containing concentrated sulphuric acid. R, Fused potassium hydroxide tower. S, Tower containing phosphorus pentoxide. T, Trap for escape of nitrogen. W, Water for cooling coil. X, 100-volt direct current. Y, Lamp bank resistance. Z, Resistance box. Am., Amperemeter.

The nitrogen was prepared by passing ammonia gas and air over red-hot copper. The excess of ammonia was absorbed by passing the gas through three wash bottles containing dilute sulphuric acid, and the nitrogen was further purified by conveying it through a series of towers constructed entirely of glass containing the following reagents in the order mentioned: a solution of silver nitrate, concentrated sulphuric acid, fused potassium hydroxide, and phosphorus pentoxide. From the last tower the glass passed to the two-way stopcock by means of which it was admitted to the combustion tube or allowed to escape into the air through a sulphuric acid trap. This trap was necessary in order to entirely free the apparatus of air while the hydrogen was passing through the combustion tube.

The Jena tube in which the reduction took place was connected with the apparatus by a carefully ground joint which was not lubricated, but held in close contact by a rubber band. The farther end of the tube was supplied with a sulphuric acid trap to prevent the entrance of air.

This tube was heated with an electric heater made by covering a sheet-iron tube with asbestos then winding it with 6 feet of No. 32 platinum wire. The whole was covered with several thicknesses of asbestos to prevent loss of heat. The current supplied the heater was controlled by a lamp bank resistance and varied from 0.25 to 1.6 amperes. By this means the temperature could be raised very gradually until the salt was reduced and the ammonium compound volatilized.

Reduction of the Palladammonium Compounds.

The counterbalanced boat was filled with salt and, after standing in the balance room for two hours, was weighed. The boat and its contents were then transferred to the combustion tube where the boat rested on a piece of platinum foil. The apparatus was then closed, the hydrogen generator started and 0.25 ampere allowed to flow through the heating coil for two hours. The current was then raised to 0.5 ampere which completed the reduction in another hour. The current was gradually increased to 1.6 amperes which heated the boat and contents to 955°.[1] With the palladammonium chloride the metal usually came to constant weight after heating for five hours. The hydrogen and heating currents were then broken and nitrogen passed through the tube while it cooled, which required about one hour. The boat was then placed in its bottle and weighed, after it had attained the temperature of the balance room. This weight was checked by heating in hydrogen for two hours and cooling in nitrogen as before. No weight was accepted which did not check 0.05 milligram or less.

The reduction of the double cyanide was similar, only it required 8 to 10 hours heating in hydrogen to obtain constant weight.

The reduction and volatilization of the ammonium salts by this method took place very slowly so that there was very little chance of any palladium being carried out of the boat by the volatile compounds; but to be sure of this, the combustion tube was washed out with aqua regia and water after each experiment, and the solution carefully tested for palladium, but always with negative results.

The following results were obtained by the reduction of the salts in hydrogen, using the following values: chlorine, 35.473; hydrogen, 1.008; nitrogen, 14.01.

[1] This temperature was determined by melting finely divided silver in a boat placed within the tube.

Palladammonium Chloride, $Pd(NH_3Cl)_2$.—Salt A.

	Weight of salt.	Weight of metal.	Atomic weights, O = 16.
1	0.89187	0.44885	106.40
2	0.77931	0.39218	106.38
3	0.66980	0.33711	106.41
4	1.08373	0.54541	106.40
5	0.96048	0.48338	106.40
		Mean,	106.399

Palladammonium Chloride, $Pd(NH_3Cl)_2$.—Salt B.

	Weight of salt.	Weight of metal.	Atomic weights, O = 16.
1	0.95615	0.48129	106.43
2	0.94037	0.47356	106.42
3	0.90106	0.45353	106.42
4	1.16994	0.58908	106.50
		Mean,	106.442

Palladammonium Cyanide, $Pd(NH_3CN)_2$.—Salt C.

	Weight of salt.	Weight of metal.	Atomic weights, O = 16.
1	0.85860	0.47463	106.41
2	1.19378	0.66002	106.45
3	1.41818	0.78408	106.45
4	1.05254	0.58206	106.51
5	1.39510	0.77153	106.51
6	1.66196	0.91881	106.42
		Mean,	106.458

The mean of the 15 determinations, 106.434

When this study was begun, it was hoped to determine the electrochemical equivalent of palladium as compared with silver. Numerous experiments were tried, using the Richards type of coulometer, but the results were never concordant. About this time, L. Wöhler and F. Martin[1] stated that palladium used as the anode in nitric acid solution was oxidized to Pd_2O_3 and PdO_2. This explained the variable results and seems to prove the method useless for atomic weight purposes.

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[Contribution from the John Harrison Laboratory of Chemistry.]

THE SEPARATION OF THE ALKALI METALS IN THE ELECTROLYTIC WAY.

By Jacob S. Goldbaum and Edgar F. Smith.

Received August 21, 1908.

By reference to earlier work,[2] done in this laboratory, it will be noticed how readily and completely halide salts of a number of metals, particu-

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[1] *Chem.-Ztg*, 1908.

[2] This Journal, **29**, 447; *Ibid.*, **29**, 1445; *Ibid.*, **29**, 1455.