tion was not always complete. The final results showed very satisfactory agreement among themselves.

In this way it was found that the heats of combustion of the following substances possess relative magnitudes, indicated by the numbers following the respective names: sugar, 1.0000; benzene, 2.5382; orthoxylene, 2.605; metaxylene, 2.605; paraxylene, 2.596; normal octane, 2.885; diisobutyl, 2.882; 2-methyl heptane, 2.888; 3,4-dimethyl hexane, 2.883; 3-ethyl hexane, 2.880. If the heat of combustion of sugar is taken with Fischer and Wrede as 16.545 kilojoules per gram and O = 16.000 is taken as the standard of molecular weight, the molal heats of combustion of the nine liquid hydrocarbons (in kilojoules, determined in constant volume at 20°) are as follows, respectively: benzene, 3,278; orthoxylene, 4570; metaxylene, 4570; paraxylene, 4554; normal octane, 5256; diisobutyl, 5250; 2-methyl heptane, 5261; 3,4-dimethyl hexane, 5252; 2-ethyl hexane, 5247 kilojoules. The deviations from one another, shown by the simple isomers, are comparatively small. The addition of CH_2 in aromatic compounds is seen to cause an increase in this heat of combustion of 644 kilojoules, or 154 Calories.

The differences between the isomers are so small that an attempt at definite explanation of their causes would be premature. Much more work of the most precise nature is necessary to afford firm basis for theory. It is hoped that this investigation will be continued, and that in the near future further data of this kind will be obtained in the laboratory of Harvard College, where these researches were made.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF PHOSPHORUS.

FIRST PAPER.—THE ANALYSIS OF SILVER PHOSPHATE.

BY GREGORY PAUL BAXTER AND GRINNELL JONES.

Received January 14, 1910.

Although phosphorus is one of the best known and most important elements, present knowledge concerning its atomic weight is somewhat inadequate. The early determinations of this constant by Dulong,[1] Pelouze,[2] Berzelius,[3] and Jacquelain[4] are widely discrepant and have no particular significance. Those by Schrötter, Dumas, van der Platts, and Berthelot, on the other hand, all give values not far from 31.0, and this value has been selected by the International Committee on Atomic Weights. Although these investigations have already been critically

[1] *Ann. chim. phys.*, 2, 149 (1816).

[2] *Compt. rend.*, **20**, 1053 (1845).

[3] Lehrbuch, 5th Ed., **3**, 1188 (1845).

[4] *Compt. rend.*, **33**, 693 (1851).

discussed by Clarke,[1] Brauner,[2] and others, a few of the more important sources of error are briefly pointed out here.

Schrötter,[3] the discoverer of red phosphorus, converted weighed quantities of this substance into phosphorus pentoxide by combustion in a stream of oxygen. As the mean of ten determinations which varied from 30.94–31.06, he obtained 31.03 for the atomic weight of phosphorus. The oxygen used was slightly moist, as Brauner has pointed out, since, although it was dried by phosphorus pentoxide, it was finally passed through a tube containing calcium chloride! The phosphorus pentoxide formed during the combustion must have retained this small amount of water, which would make the atomic weight of phosphorus appear too low. Schrötter admits that the combustion was incomplete, and since this error would tend to raise the atomic weight of phosphorus, he concludes that the true value is 31.00.

Dumas[4] titrated the trichloride of phosphorus against silver after decomposing the trichloride with water. Since the sample used did not boil at a constant temperature but distilled between 76° and 78°, it must have been impure. If it contained oxychloride, as Clarke has suggested, the atomic weight of phosphorus would be found too high. Dumas overlooked the solubility of silver chloride and therefore used the wrong end-point in these titrations. Furthermore, no precautions are mentioned either for preventing access of water to the material before weighing or for preventing the reduction of the silver salt by the phosphorous acid formed in the decomposition of the trichloride with water. Recalculated on the basis of the atomic weight of silver as 107.88, his five analyses give results which vary between 30.99 and 31.08. The average is 31.03.

Van der Platts[5] made two determinations by each of three different methods. He obtained the values 30.90 and 30.97 by the precipitation of silver from silver sulphate solution with phosphorus. His results from the analysis of silver phosphate were 31.08 and 30.95. He gives no details of the method of preparing and analyzing this substance, merely making the statement: "It is difficult to be sure of the purity of this salt." Finally, by the combustion of yellow phosphorus in oxygen he obtained the results 30.99 and 30.96. The very meager descriptions of these experiments preclude criticism.

Using Leduc's data for the densities and compressibilities of phosphine and oxygen, Daniel Berthelot[6] has calculated, by the method of

---

[1] "A Recalculation of the Atomic Weights," Smith. Misc. Coll., 1897.

[2] Abegg, "Handb. der anorg. Chem.," 1907, Vol. III, Part 3, p. 366.

[3] *Ann. chim. phys.*, [3] **38**, 131 (1853).

[4] *Ann. Chem. Pharm.*, **113**, 28 (1860).

[5] *Compt. rend.*, **100**, 52 (1885).

[6] *Ibid.*, **126**, 1415 (1898).

limiting densities, the molecular weight of phosphine to be 34.00 and the atomic weight of phosphorus to be 30.98.

Very recently Gazarian[1] has obtained a considerably lower value for the molecular weight of phosphine, 33.93. This value was calculated from the experimentally determined weight of the standard liter by the four methods of molecular volumes (Leduc), limiting densities (Berthelot), critical constants (Guye), and "indirect" limiting densities (Berthelot). The different methods give essentially identical results, except in the case of the direct method of limiting densities. By the latter method a value six-hundredths of a unit higher is obtained, but Gazarian rejects the result on the basis of inaccurate knowledge of the compressibility of phosphine. It is highly desirable to obtain more certain knowledge of the compressibility of phosphine, since the method of limiting densities is the most reliable of all the methods for applying the correction to the densities made necessary by deviations from the laws of a perfect gas.

The other methods are burdened with arbitrary assumptions and empirical constants, and furthermore Baumé[2] has shown that both the method of molecular volumes and the method of critical constants give correct results only with gases for which the ratio $\frac{T_c}{4P_c}$ is nearly 1, whereas for phosphine this ratio is 1.26.

If the molecular weight of phosphine be assumed to be 33.93, the atomic weight of phosphorus is 30.91. In the light of this low result it is unfortunate that Gazarian prepared phosphine by only one method, and that he did not determine the purity of the gas, *i. e.*, by absorption. Gazarian used the method of Matignon and Trannoy[3] which consists in heating calcium phosphate and aluminium together until they react, and then treating the product of this reaction without further purification with water in a gas generator. Matignon and Trannoy show that the gas prepared in this way by them contained about 3 per cent. of hydrogen, probably derived from calcium contained by the phosphide. In this case some calcium nitride would be formed, since the phosphide was made in air, and this would produce ammonia as an impurity in the phosphine. Although the gas was purified by fractional distillation, according to Gazarian's statements hydrogen is difficult to eliminate, and a proportion of only four-tenths of 1 per cent. would be sufficient to lower the atomic weight of phosphorus one-tenth of a unit. Ammonia would be even more difficult to remove, since its boiling point is only 50° higher than that of phosphine. The effect of a given percentage of impurity is, however, much less with ammonia than with hydrogen, although in the same direction.

[1] *J. chim. phys.*, 7, 337 (1909).

[2] Baumé, *J. chim. phys.*, 6, 76 and 86 (1908).

[3] *Compt. rend.*, 148, 167 (1909).

From the preceding brief summary it is evident that the uncertainty in the atomic weight of phosphorus is as great as one-tenth of a unit, and that, as Brauner remarks at the conclusion of his review of the subject, "a revision of the atomic weight of phosphorus with modern means is urgently necessary."

The analysis of silver phosphate was selected as one of the most promising methods of attacking the problem, since the per cent. of silver can be determined exactly by a method which has been carefully studied, especially in this laboratory. The accuracy of the result will therefore depend primarily upon the success attained in preparing silver phosphate in a perfectly definite and pure state. The greater part of the following research was devoted to the solution of this problem, which van der Platts found so difficult.

The analysis of the halogen compounds of phosphorus offers certain difficulties, owing to the ease with which these substances are decomposed by water, and to the necessity for oxidizing the phosphorous acid resulting from the decomposition of the halogen compounds with water before the addition of silver nitrate. An investigation upon the tribromide of phosphorus is now in progress in this laboratory. Phosphonium compounds were found utterly unsuited for exact analysis on account of their instability.

Purification of Materials.

Water.—All the water used in this research was made from the laboratory supply of distilled water by distillation, first from an alkaline permanganate solution, and then, after the addition of a trace of sulphuric acid, through a block-tin condenser.

Ammonia.—The best commercial ammonia was distilled into the purest water.

Nitric Acid.—The best commercial concentrated acid was twice fractionally distilled through a platinum condenser, with the rejection of the first third of the distillate. Every sample was shown to be free from chloride by careful nephelometric tests.

Hydrochloric Acid.—The best commerical C. P. acid, diluted with an equal volume of water, was distilled through a platinum condenser.

Hydrobromic Acid.—This substance was prepared in conjunction with Mr. F. B. Coffin, who was engaged in a parallel research upon the atomic weight of arsenic.[1] Commercial bromine was converted into potassium bromide by addition to recrystallized potassium oxalate. In a concentrated solution of this bromide, in a distilling flask cooled with ice, bromine was dissolved, and distilled from the solution into a flask cooled with ice. A portion of the purified bromine was then converted into potassium bromide with pure potassium oxalate as before, and the re-

---

[1] Baxter and Coffin, THIS JOURNAL, 31, 297 (1909).

mainder of the bromine was distilled from solution in this pure potassium bromide. The product obtained was thus twice distilled from a bromide, the bromide in the second distillation being essentially free from chlorine. This treatment has already been proved sufficient to free bromine from chlorine.[1]

Hydrobromic acid was synthesized from the pure bromine by bubbling hydrogen gas (made by the action of water on "hydrone") through the bromine warmed to 40–44° and passing the mixed gases over hot platinized asbestos in a glass tube. The apparatus was constructed wholly of glass. The hydrogen was cleansed by being passed through two wash-bottles containing dilute sulphuric acid, and through a tower filled with beads also moistened with dilute sulphuric acid. The hydrobromic acid gas was absorbed in pure water contained in a cooled flask. In order to remove iodine the solution of hydrobromic acid was diluted with water and twice boiled with a small quantity of free bromine. Then a small quantity of recrystallized potassium permanganate was added to the hydrobromic acid solution, and the bromine set free was expelled by boiling. Finally the acid was distilled with the use of a quartz condenser, the first third being rejected. It was preserved in a bottle of Nonsol glass provided with a ground-glass stopper.

The purity of the hydrobromic acid was tested by a quantitative synthesis of silver bromide. The silver used, which was kindly furnished by Mr. G. S. Tilley, had been prepared with all the necessary precautions for work on the atomic weights of silver and iodine.[2] The procedure used by Baxter[1] for the synthesis of silver bromide from a weighed amount of silver was followed in detail. In this experiment 6.02386 grams of silver yielded 10.48627 grams of silver bromide; hence, silver bromide contains 57.4452 per cent. of silver, while Baxter found as the mean of 18 determinations 57.4453 per cent. The hydrobromic acid was evidently pure.

Silver Nitrate.—Crude silver nitrate was reduced with ammonium formate, made by passing ammonia gas into redistilled formic acid. The reduced silver was washed with the purest water, until the wash-waters no longer gave a test for ammonia with Nessler's reagent, and was fused on sugar charcoal. The buttons were then scrubbed with sea-sand and thoroughly cleansed with ammonia and nitric acid. They were then dissolved in redistilled nitric acid, in a platinum dish. After the silver nitrate solution had been evaporated on a steam bath until saturated, an equal volume of redistilled nitric acid was added and the solution was cooled. The precipitated silver nitrate was very completely drained in a centrifugal machine, provided with platinum Gooch crucibles

---

[1] Baxter, THIS JOURNAL, 28, 1322 (1906).

[2] Baxter and Tilley, *Ibid.*, 31, 201 (1909).

to retain the salt.[1] A similar recrystallization followed. The final product was preserved in Jena glass vessels under a bell-jar.

Disodium Phosphate.—One kilogram of Merck's best disodium phosphate was dissolved in hot water in a porcelain dish and hydrogen sulphide passed into the solution for several hours. After standing for twenty-four hours, the solution was again heated, saturated with hydrogen sulphide and filtered. The filtrate was slightly green, owing to the presence of iron. The solution was boiled to expel the hydrogen sulphide and a small amount of green precipitate filtered out. The filtrate was still distinctly green. The sodium phosphate was then crystallized fifteen times, five times in porcelain with centrifugal drainage of the crystals in a large porcelain centrifugal machine, ten times in platinum vessels with centrifugal drainage of the crystals in platinum Gooch crucibles. The green color concentrated in the first mother liquor.

When tested by means of the Marsh test, this material was found to contain only a mere trace of arsenic, which was estimated to be 0.01 mg. in 10 grams of the salt. This small amount could have no effect on the analytical results, especially since the percentage of silver in silver arsenate is nearly the same as in silver phosphate. By means of the nephelometer it was proved that this material contained no chloride or other substances which could be precipitated by silver nitrate in the presence of dilute nitric acid.

Sodium Ammonium Hydrogen Phosphate.—The best commercial microcosmic salt was recrystallized four times in platinum vessels. It was tested for arsenic by Marsh's method with negative results and gave no opalescence visible in the nephelometer when tested with silver nitrate and dilute nitric acid.

Preparation of Trisilver Phosphate.

Silver phosphate was prepared by mixing dilute solutions of silver nitrate with solutions of sodium and ammonium phosphates. Since it is not feasible to purify silver phosphate by recrystallization, the conditions of precipitation must be so chosen that a pure product will be obtained at once.

In order to avoid inclusion and occlusion of silver nitrate, sodium nitrate, sodium phosphate, or mono- or disilver phosphate, all of the solutions for precipitation were made about 0.03 *N*. All samples after precipitation were thoroughly washed and allowed to stand in water for at least twenty-four hours, in order to convert occluded acid phosphates into trisilver phosphate. Qualitative tests for nitrate with diphenylamine and for sodium by the spectroscope showed that all of the first three substances named could be completely washed out.

---

[1] Baxter, This Journal, 30, 286 (1908).

Joly[1] states that disilver phosphate is stable in the presence of phosphoric acid containing 40 per cent. (11.8 *N*) of phosphoric anhydride, but is transformed into trisilver phosphate if the acid contains 38 per cent. (11.0 *N*) or less phosphoric anhydride. Since all the solutions used for the preparation of silver phosphate were nearly neutral, it is evident that the precipitation of disilver phosphate as a distinct phase in equilibrium with the solution is not to be feared.

It is, however, not such a simple matter to prove the absence of *occluded* disilver hydrogen phosphate or monosilver hydrogen phosphate. Much light is thrown on this point in a recent paper by Abbott and Bray[2] upon the dissociation constants of the three hydrogens of phosphoric acid, which were found to be 1.1×10^{-2}, 1.95×10^{-7} and 3.6×10^{-13} respectively. Since phosphate ion ($PO_4^{\equiv}$) is almost completely hydrolyzed to monohydrophosphate ion ($HPO_4^{=}$), even in slightly alkaline solutions, and since in slightly acid solutions dihydrophosphate ion ($H_2PO_4^{-}$) acquires an appreciable concentration, the possibility of occlusion must be examined with special care.

The concentrations in the following table are either taken directly from a table given by Abbott and Bray or calculated from these numbers with the help of the values of the dissociation constants of phosphoric acid. The values are expressed in formular weights per liter, the total concentration of the salt being in each case 0.05.

	$NaNH_4HPO_4$.	$Na_2NH_4PO_4$.
$H_2PO_4^{-}$............	0.001184[3]	0.000002[4]
$HPO_4^{=}$............	0.03265[3]	0.03219[3]
$PO_4^{\equiv}$.............	0.0000016[4]	0.001123[3]
OH^{-}..............	0.00000079[3]	0.000502[3]
H^{+}...............	0.0000000075[4]	0.000000000012[4]

It will be noted that the replacement of the remaining hydrogen in sodium ammonium hydrogen phosphate by sodium decreases the concentration of the hydrogen ion to 0.16 per cent. of its value in the microcosmic salt solution and decreases the concentration of dihydrophosphate ion to 0.2 per cent. of its former value. The concentration of monohydrophosphate ion remains essentially unchanged, while the concentration of phosphate ion is increased seven hundred times. Disodium phosphate doubtless takes a position intermediate between the other two solutions

---

[1] *Compt. rend.*, 103, 1071 (1886).

[2] THIS JOURNAL, 31, 755 (1909).

[3] These values are taken directly from the table of Abbott and Bray.

[4] These values are calculated from the others in the above table by the aid of the following equations:

$$(H^{+})(OH^{-}) = 0.59 \times 10^{-14}$$

$$\frac{(H^{+})(PO_4^{\equiv})}{(HPO_4^{=})} = 3.6 \times 10^{-13} \qquad \frac{(H^{+})(HPO_4^{=})}{(H_2PO_4^{-})} = 1.95 \times 10^{-7}$$

in this regard, since it is more alkaline than microcosmic salt and less so than disodium ammonium phosphate. The numbers given above refer to solutions which are five times as strong as those used in this research, but the conditions in the more dilute solutions must be very similar. Furthermore, the exact values have no great importance, as the concentrations of the various ions change continuously during precipitation. It is evident from the figures given above and from the value of the dissociation constant of the second hydrogen of phosphoric acid that if the concentration of hydrogen ion increases above its value in a microcosmic salt solution, the concentration of dihydrophosphate ion must increase greatly at the expense of monohydrophosphate ion. If there is any tendency for the occlusion of disilver hydrogen phosphate or monosilver hydrogen phosphate, the amounts of these salts occluded would be expected to depend on the concentration of the undissociated molecules of these salts in the solution, and therefore on the concentration of silver ion and on the concentration of monohydrophosphate or dihydrophosphate ion respectively.

The exact concentrations of the ions during the precipitation cannot be calculated, since the solubility of silver phosphate in slightly acid solutions and the solubility-product of silver phosphate are not known. It is, however, easy to understand from a study of the conditions under which the various samples of silver phosphate were precipitated, that these concentrations must have varied greatly in the preparation of the different samples and therefore constancy of composition gives a strong presumption that there is very little or no tendency for the occlusion of the undesired acid salts.

Samples N and O.—A 0.03 normal solution of silver nitrate was slowly poured into a 0.03 normal solution of disodium hydrogen phosphate with frequent shaking. This reaction may be roughly considered to take place in two stages represented by the equations:

$$3AgNO_3 + 2Na_2HPO_4 = Ag_3PO_4 + NaH_2PO_4 + 3NaNO_3$$
$$3AgNO_3 + NaH_2PO_4 = Ag_3PO_4 + NaNO_3 + HNO_3$$

At the beginning of the precipitation the solution is very slightly alkaline and remains very nearly neutral during the addition of the first half of the silver nitrate. The concentration of the silver ion is kept very low by the excess of phosphate and, therefore, little occlusion of the acid salts is to be expected in spite of the fact that the solution contains appreciable concentrations of the monohydrophosphate and dihydrophosphate ions. The precipitate during this stage is very finely divided and does not settle well and, therefore, no attempt was made to collect it separately.

During the addition of the second half of the silver nitrate the solution becomes slightly acid and the solubility of the silver phosphate increases rapidly. The precipitate settles readily. During the second stage the conditions are more favorable for the occlusion of the acid phosphate, but only a small amount of silver phosphate is precipitated during this stage.

After standing a short time the mother liquor was decanted from the precipitate, and exactly the calculated amount of redistilled ammonia, diluted to one liter, was added to neutralize the excess of acid and complete the precipitation. Since this sample was evidently produced from a solution which was slightly acid at the beginning of the precipitation, although very nearly neutral at the end, and since it contained a considerable amount of silver, the conditions were favorable for the formation of acid salts.

Both precipitates were transferred to a large platinum dish and washed many times by decantation with the purest water. This washing was prolonged over more than twenty-four hours in order to give time for all soluble matter to be leached out. When the precipitates were tested for nitrate with diphenylamine, negative results were obtained. Sodium was found to be absent by spectroscopic tests. The precipitates were drained as far as possible in a platinum centrifugal machine, and the drying was completed by heating in platinum crucibles in an electric air bath for several hours, first at 90° and finally at about 130°. The dried lumps of silver phosphate were then gently ground in an agate mortar. The samples were preserved in platinum crucibles over sulphuric acid in the dark. All of the operations were performed in a dark room.

The sample prepared by pouring silver nitrate into disodium phosphate is designated Sample N, and the sample prepared by adding ammonia to the mother liquors is designated Sample O.

Sample P.—A 0.03 normal solution of disodium ammonium phosphate was prepared by dissolving a weighed amount of disodium hydrogen phosphate and then adding the calculated amount of redistilled ammonia. The solution was then slowly poured into a 0.03 normal solution of silver nitrate. By this method of precipitation the solution is maintained as nearly neutral as is possible, because the excess of silver prevents the concentration of phosphate in solution from exceeding a very small value, so that neither can the solution become alkaline by hydrolysis nor can the concentration of hydrophosphate attain an appreciable value. The absence of the hydrophosphate ions would be expected to prevent the formation and occlusion of acid silver phosphate in this sample, whereas in Sample N the same result is probably brought about by the absence of the silver ion. Unfortunately both of these favorable conditions cannot be combined in one precipitation, as will be shown later. This precipitate settled readily. The washing, testing, and drying were carried out as already described for Samples N and O. This sample is designated Sample P.

Sample R.—A 0.03 normal solution of sodium ammonium hydrogen phosphate was slowly poured into a similar solution of an equivalent amount of silver nitrate. Under these conditions the solution contains an excess of silver, which tends to produce occlusion of acid phosphates, since the solution becomes more and more acid as the precipitation proceeds, and as the precipitation is therefore far from complete, the concentrations of the two hydrophosphate ions gradually approach a very considerable value. At no stage could the solution become alkaline by hydrolysis. It should be noticed that the procedure differs from that used in preparing Sample N in that the precipitate is formed in the presence of an excess of silver nitrate instead of an excess of phosphate, and that this difference in the method of mixing greatly changes the conditions of precipitation.

The precipitate, which was designated Sample R, coagulated and settled quite readily. The washing and drying were completed as usual.

It will be shown that samples of silver phosphate prepared under these various conditions have nearly, if not exactly, the same composition. Further proof of the absence of acid phosphate in these samples is given by experiments to be described later which show that no water is given off when this material is fused.

An attempt to prepare a sample by pouring silver nitrate into disodium ammonium phosphate yielded unsatisfactory results. Since the disodium ammonium phosphate solution was alkaline, owing to hydrolysis, it contained free ammonia, which prevented the precipitation of silver phosphate at first. Nearly one-quarter of the silver nitrate was added before a permanent precipitate was produced. At the end of the precipitation the solution was of course essentially neutral. Even after standing for four days the precipitate had not appreciably settled. Since the coagulation of the precipitate seems to occur much more readily in the presence of excess of silver, a considerable amount of silver nitrate in solution was added. The precipitate coagulated and settled immediately. It was washed and dried as usual. This sample was somewhat darker in color than the other samples and gave a large amount of insoluble residue when treated with dilute nitric acid. The analysis showed that it contained about two hundredths per cent. too much silver. This method of preparation is evidently unsatisfactory.

Three unsuccessful attempts were made to prepare silver phosphate from trisodium phosphate. The samples obtained in this way did not appear homogeneous after being dried and contained considerable sodium in spite of protracted washing. Two of these samples were found by analysis to contain, respectively, 4.4 and 4.1 per cent. less silver than pure trisilver phosphate. The third of these samples was so unsatisfactory in appearance and in its behavior during its preparation that it was not analyzed. This method of preparing silver phosphate is evidently not suitable for our purpose. Time was lacking to investigate further this anomalous behavior.

Method of Analysis.

Unfortunately, owing to the high melting point of silver phosphate, it was not feasible to fuse the silver phosphate before its analysis in order completely to eliminate all water. Instead it was heated in a platinum boat, in a current of pure dry air, at a temperature of about 400° for seven hours, and then by means of bottling apparatus[1] it was enclosed in its weighing-bottle without coming in contact with the moist air of the laboratory. During this heating the access of light to the sample was prevented. The continuous current of air which passed over the silver phosphate during the heating was driven by a water pump successively through an Emmerling tower containing beads moistened with silver nitrate solution, through a tower containing small pieces of fused caustic potash, then through three towers containing beads drenched with concentrated sulphuric acid, and finally through a long tube containing phosphorus pentoxide which had been resublimed in a current of air. The hard glass tube containing the platinum boat was surrounded by blocks of aluminium[2] which were jacketed with asbestos on the top and sides and heated directly from below by a large burner. The platinum boat was not attacked in the least, as was shown by the fact that its weight remained constant.

It was feared that in spite of this prolonged heating the silver phosphate still retained a trace of water, but by making the conditions in the different experiments as nearly uniform as possible it was hoped that the amount of water retained would be constant. Proof will be given later that the drying was highly efficient.

The salt thus prepared for analysis was allowed to stand over night in a desiccator covered with a black cloth in the balance room, and was then weighed in its glass-stoppered bottle by substitution, with the use of another weighing-bottle of very similar surface and volume as a counterpoise.

The balance was a nearly new No. 10 Troemner balance. It was easily sensitive to 0.02 mg. The weights had already been used in an investigation of the atomic weight of sulphur,[3] and were restandardized with a very gratifying result. None of the corrections found differed by as much as 0.02 mg. from those found a year before, and only a few by

---

[1] Richards and Parker, *Proc. Amer. Acad.*, 32, 59 (1896).

[2] Baxter and Coffin, *Loc. cit.*

[3] Richards and Jones, THIS JOURNAL, 29, 826 (1907).

0.01 mg. The balance was provided with a few milligrams of radium bromide of radioactivity 10,000 to dispel electrical charges generated during the handling of the weighing-bottles with cork-tipped pincers.

The platinum boat containing the silver phosphate was transferred to an Erlenmeyer flask of "non-sol." glass of one liter capacity and treated with about 30 cc. of 5 normal nitric acid. Solution took place rapidly. The solution was not perfectly clear, however, owing to a very slight insoluble residue which sometimes settled out on standing. The solution was then heated on a steam bath until the residue dissolved completely. Upon the addition of about one liter of cold water a very slight opalescence was produced, which was visible only when the solution was carefully examined in a very favorable light. The solution was again warmed until it became perfectly clear. The water and nitric acid used in these processes did not give an opalescence visible in the nephelometer when treated with silver nitrate. The nature of this residue will be discussed more in detail after describing the remainder of the analytical process.

About 800 cc. of water were placed in a large glass-stoppered precipitating flask and a very slight excess of hydrobromic acid was added from a burette. The silver phosphate solution was then very carefully poured into the hydrobromic acid solution. This method of precipitation gives less opportunity for the occlusion of silver phosphate or nitrate than the reverse method. The occlusion of hydrobromic acid can do no harm. The flask was shaken for twenty minutes and was allowed to stand for several days until the precipitate had completely settled. Then the precipitate was collected upon a weighed Gooch crucible after many rinsings with pure water. In order to protect the mat of the Gooch crucible from disintegration, it was covered by a circular disk of thin platinum foil, perforated with many small holes. The precipitate was dried in an electrically heated air bath for several hours at 90°, then for some time at 130°, and finally for at least eight hours at 180°. After the crucible containing the precipitate had been weighed, the silver bromide was transferred to a porcelain crucible and the loss on fusion determined. The presence of the platinum disk covering the mat makes it possible to transfer very nearly all the silver bromide to the porcelain crucible without contamination with asbestos and therefore it is unnecessary to correct the loss on fusion for the small amount of silver bromide which is not fused. The loss on fusion, which represents water remaining in the silver bromide, was subtracted from the weight of the silver bromide. The asbestos shreds carried away by the wash-waters and any silver bromide which may have escaped the Gooch crucible were collected by passing the filtrate through a very small filter paper. The paper was then burned and the residue, after treatment with a drop of nitric and hydrobromic acids to convert any reduced silver into silver bromide, was again gently heated and finally weighed. The weight of the asbestos, corrected for the ash of the paper, was added to the weight of the silver bromide. In order to determine the soluble silver bromide, the filtrate was evaporated until most of the excess of nitric acid was driven off. The precipitating flask and all the flasks which had held the filtrate were rinsed with strong ammonia and the rinsings added to the evaporated wash-water. Enough ammonia was added to make the solution alkaline and it was then diluted to 100 cc. in a graduated flask. The amount of silver bromide present was determined by comparison in the nephelometer with a very similar solution containing a known amount of silver bromide. Both precipitates were dissolved in ammonia and reprecipitated at the same time and under precisely similar conditions[1] in the nephelometer tubes by a slight excess of nitric acid. The amount found in this way was added to the weight of the silver bromide.

In order to determine whether silver phosphate is occluded by silver chloride, about 6 grams of silver phosphate were dissolved in nitric acid and the solution was diluted and poured into an excess of hydrochloric acid. After standing until the supernatant liquid was clear, the precipitate was washed very thoroughly with water and then dissolved in redistilled ammonia. The solution was diluted to one liter and the silver chloride was reprecipitated with nitric acid. The precipitate was filtered out and the filtrate evaporated in a platinum dish until concentrated. A little sodium carbonate was added and the dish was heated to expel all volatile ammonium salts. The residue was dissolved in about 3 cc. of water and treated with an excess of ammonium molybdate reagent with gentle warming. After standing for three days, not the slightest precipitate or yellow color had appeared, showing that no phosphate had been occluded by the silver chloride. Although not tested experimentally, it is reasonable to suppose that silver bromide also does not possess the property of occluding appreciable quantities of silver phosphate or phosphoric acid.

Insoluble Residue.

The presence of a slight residue or opalescence, after dissolving the dried silver phosphate in dilute nitric acid, proved the most perplexing difficulty which was encountered. The effort to discover the nature of this insoluble matter and eliminate it consumed a large part of the time devoted to this research. In an effort to make sure that it was not due to some unknown impurity, nineteen different samples of silver phosphate were prepared, the source of material, method of purification, and precipitation being varied. Disodium phosphate, trisodium phos-

---

[1] See Richards and Staehler, THIS JOURNAL, 29, 635 (1907).

phate, and sodium ammonium phosphate were carefully purified and converted into silver phosphate under varying conditions without appreciable effect upon the amount of the residue. Phosphorus oxychloride was twice fractionally distilled, converted into phosphoric acid, and then into disodium phosphate by means of sodium hydroxide made from sodium amalgam. The product was crystallized three times. Silver phosphate made from this material gave a slight residue, very similar to that obtained from the best samples made in other ways. Unfortunately, it was necessary to reject the analytical results obtained with this specimen because it was found to contain a small amount of metaphosphate. We did not succeed in preparing a sample of silver phosphate entirely free from the residue.

In the meantime attention had been devoted to the residue itself. The small amount of material available rendered this part of the investigation difficult. The silver phosphate, after its precipitation and washing, but undried, dissolves in dilute nitric acid, giving a solution which is perfectly clear to the naked eye, although some samples gave a barely visible opalescence in the nephelometer. The opalescence was much too small to have any effect on the analytical results. The dried samples invariably gave an opalescence.

Dry silver phosphate is very slowly darkened in color by the action of light. This effect is even more pronounced when silver phosphate is exposed to the light in the presence of water. These darkened samples gave a much greater residue than the undarkened material. The residue was insoluble in ammonia, slowly soluble in dilute nitric acid, especially when heated, and readily soluble in strong nitric acid. The addition of hydrochloric acid to these nitric acid solutions gave a precipitate of silver chloride, while ammonium molybdate indicated the presence of phosphate.

In order to determine whether or not a loss of weight occurs during the darkening by light, a sample of silver phosphate was dried and weighed as usual and found to weigh 3.01901 grams. It was then exposed to the direct action of bright sunlight for a day, while contained in a weighing bottle which was placed in a desiccator over sulphuric acid. It was found to have darkened slightly in color and to weigh 3.01903. The gain of 0.02 mg. is within the limit of error in the weighing. This sample, when treated with dilute nitric acid, gave a much larger residue than usual, which weighed 1.8 mg. This is much more residue than was usually found in samples containing 4–8 grams of silver phosphate. It is estimated that the samples which had been protected from the action of light as much as possible, except when unavoidably exposed to diffused daylight while being weighed or transferred to the furnace and solution flask, contained about one one-hundredth of a per cent. of this residue.

Two analyses were made of the residue obtained by exposing silver phosphate *under water* to the action of light for several days, then dissolving the excess of silver phosphate in dilute nitric acid and thoroughly washing and drying the residue. 0.02674 gram of this residue yielded 0.03551 gram of silver chloride, which indicates that the residue contained 99.9 per cent. of silver. In the case of another sample of the residue prepared and analyzed in the same way, 0.04320 gram of residue yielded 0.05747 gram of silver chloride, which indicates that the residue contained 100.1 per cent. of silver. The mean of the two analyses is 100.0 per cent. of silver. These analyses prove conclusively that when silver phosphate is acted on by light in the presence of water, it is so altered (perhaps by the formation of a subphosphate similar to subchloride) that when treated with very dilute nitric acid metallic silver remains.

It does not follow, however, that it would be a correct procedure to determine the per cent. of this residue obtained from the samples used for analysis and apply a correction on the assumption that the material consisted of pure silver phosphate and a small amount of pure silver. This procedure would assume that the other product of decomposition is eliminated and not weighed. There are two facts which show that this assumption would be incorrect. In nearly every analysis, when the solution was diluted, after bringing the residue into solution by heating on the steam bath, a slight opalescence was produced. Careful tests of the water used showed that this opalescence was not due to impurity in the water. It seems probable that the substance which caused this opalescence was derived in part from the phosphate radical during the decomposition which produced the residue. The other fact is that dry silver phosphate does not lose weight when darkened by exposure to sunlight, although this treatment increases the amount of residue. The conclusion in regard to this residue may be summarized as follows: The washed moist silver phosphate was free from residue and contained silver and phosphoric acid combined in atomic proportions. During the drying and weighing a slight decomposition took place, undoubtedly owing in part at least to the action of light. It seems probable that during this decomposition no loss in weight took place, and therefore the sample contained the proper percentage of silver. When this slightly darkened silver phosphate is treated with cold, dilute nitric acid, the unchanged silver phosphate and perhaps also a portion of the altered material dissolve, leaving a slight opalescence, which in some cases is deposited as a very slight residue on standing. This residue is estimated to be about 0.01 per cent. of the weight of the silver phosphate. When the solution is warmed until perfectly clear, and then diluted, a very slight opalescence is usually produced which could be again cleared up by warming the solution. This opalescence is probably caused by the presence of the altered phosphate anion. If this explanation is correct, the presence of the residue cannot influence the result, and no correction need be applied. Until the exact nature of the decomposition products can be determined, there must remain some uncertainty in regard to whether or not any correction is necessary.

The uncertainty from this cause is, however, not very great. Even if all the phosphorus and oxygen corresponding to the residue of silver are removed before the weighing, the correction would be only 23 per cent. of the weight of the residue. If the residue amounts to 0.01 per cent., as has been estimated, the maximum correction would be 0.002 per cent. If part of the oxygen is lost, but the phosphorus remains, the correction would of course be smaller. If there is no loss in weight by the action of light on the dry silver phosphate, no correction need be applied. From the evidence so far obtained the latter assumption seems rather more probable than any of the others, and therefore no correction has been applied.

The Determination of Water in the Dried Silver Phosphate.

In order to find out how efficient the drying of the silver phosphate had been, experiments were made to determine the amount of water retained by silver phosphate which had been dried for analysis as described above (see page 308). The water was determined by fusing the dried phosphate in a current of dry air and collecting the moisture set free in a weighed phosphorus pentoxide tube. Since the melting point of pure silver phosphate is considerably above the softening point of hard glass, it was found advantageous to lower the melting point of the phosphate by the use of silver chloride as a flux.

About 15 grams of silver phosphate were placed in one end of a large silver boat and in the other end about 12 grams of previously fused silver chloride. The boat was then inserted in a hard glass tube and dried under the same conditions as prevailed in preparing the samples for the determination of the silver content. After the silver phosphate had been heated for seven hours in a current of purified air dried by phosphorus pentoxide, the air passing over the boat in the furnace was conducted through a weighed U-tube containing resublimed phosphorus pentoxide for one-half hour. This was done to make sure that all the water which had been liberated from the silver phosphate without fusion had been swept out of the apparatus. In no case was there a gain in weight during this process of more than 0.05 mg., which is about the limit of error in weighing the phosphorus pentoxide tubes. The backward diffusion of moisture was prevented by a second tube containing pentoxide.

The carefully weighed phosphorus pentoxide tube was again attached to the tube containing the silver boat with its charge of silver phosphate and silver chloride. The latter tube was then heated hot enough to fuse the silver chloride, which flowed down to the silver phosphate and readily caused the entire charge to fuse completely. The liberated water was swept into the phosphorus pentoxide tube by a current of dry air for about thirty minutes. The tube was then reweighed to determine the water evolved by the fusion of silver phosphate. The pentoxide tube was weighed by substitution for a very similar counterpoise tube, one stopcock of each tube being open during the weighing. Before being weighed both tubes were wiped with a damp cloth and allowed to stand near the balance for at least thirty minutes.

The following table gives the results of these experiments:

Sample.	Weight of silver phosphate	Weight of water.	Per cent. of water.
P	13.50	0.00012	0.0009
P	15.64	0.00007	0.0004
O	15.66	0.00005	0.0003
O	16.62	0.00003	0.0002
		Average,	0.0005

The amount of water evolved is hardly greater than the probable error in weighing the phosphorus pentoxide tubes, and is less than the probable error in determining the amount of silver in the salt. We are therefore justified in concluding that the material which was used for the determination of silver was essentially free from water and that no correction need be applied to the results for inefficient drying.

This result also furnishes evidence that the samples are free from acid phosphates, which, owing to conversion into pyro- or metaphosphate, would evolve water when fused, although it is possible that occluded acid phosphates might have been converted into pyro- or metaphosphates during the drying. Sample O, which was prepared under conditions most favorable for the formation of the acid silver phosphate, does not appear to contain more water than Sample P, which was prepared under conditions which were unfavorable to the formation of acid phosphate. Since these two samples, which differed most widely in their method of preparation, showed no difference in the amount of water retained, it seemed unnecessary to test the other samples also. Unfortunately this method of detecting acid phosphate is not very sensitive, owing to the unfavorable relation of the atomic weights involved—one molecule of water corresponding to a deficiency of two atoms of silver.

The Specific Gravity of Silver Phosphates.

In order that the apparent weight of the silver phosphate might be corrected to the vacuum standard, the specific gravity of this salt was found by determining the weight of toluene displaced by a known quantity of salt. The specific gravity of the toluene at 25° referred to water at 4° was 0.8633. Great care was taken to remove air from the salt when covered with the toluene by warming the pycnometer, then placing it in a vacuum desiccator and boiling the toluene under reduced pressure. The salt and toluene were mechanically stirred to assist the escape of air bubbles. This process was repeated several times.

Weight of silver phosphate in vacuum. Grams.	Weight of displaced toluene in vacuum. Grams.	Volume of silver phosphate. cc.	Density of silver phosphate. 25°/4°.
22.955	3.113	3.606	6.366
16.942	2.295	2.658	6.374
		Mean,	6.37

Therefore the apparent weight of silver phosphate was corrected to the vacuum standard by adding 0.000044 gram per gram of salt. Similarly 0.000041 gram was added for every gram of silver bromide.

The Adsorption of Air by Silver Phosphate.

Since the silver phosphate was in a very finely divided condition and since many fine powders have the power of adsorbing appreciable quantities of air or other gases, the possibility of the adsorption of air by silver phosphate was investigated. The method of experimenting and the apparatus were very similar to that used by Baxter and Tilley for investigating the behavior of iodine pentoxide.

"Two weighing bottles were constructed with long, very well ground stoppers which terminated in stopcocks through which the tubes could be exhausted. These tubes were very closely of the same weight and very nearly the same internal capacity. The tubes were first exhausted and compared in weight by substitution. Next they were filled with dry air and again weighed, the weighing being carried out with stopcocks open. Both steps were then repeated with essentially the same results."[1]

In these two experiments, when air was admitted, the counterpoise gained 0.00028 and 0.00021 gram respectively (average 0.00025) more than the tube which was later to contain the silver phosphate. After 22.69 grams of pure dry silver phosphate had been placed in the tube the tube and its counterpoise were exhausted and the difference in weight determined. When dry air at 25° and 766 mm. was admitted to both the tube containing the silver phosphate and the counterpoise, the counterpoise gained 0.00443 gram more than the tube. Therefore the air displaced by the silver phosphate was 0.00443 — 0.00025 = 0.00418 gram. Since 22.69 grams of silver phosphate of density 6.37 have a volume of 3.56 cc., the volume of pure air displaced at 25° and 766 mm. should weigh 0.00425 gram.[2]

---

[1] Baxter and Tilley, THIS JOURNAL, 31, 214 (1909).

[2] Rayleigh's value for the density of air at 0° and 760 mm., 1.293 grams per liter, is used. *Proc. Roy. Soc.*, **53**, 147.

The experiment was then repeated. After the air had been exhausted from the tube and its counterpoise, the tube containing the silver phosphate was heated gently. No gas was evolved. The tube and its counterpoise were then weighed by substitution. When dry air at 24.5° and 767 mm. was admitted to both, the counterpoise gained 0.00445 gram more than the tube containing the silver phosphate. Therefore the air displaced by the silver phosphate was 0.00445 — 0.00025 = 0.00420 gram, whereas the weight of air displaced, calculated from the density of the salt, is 0.00426 gram.

The agreement between the experimental results and those calculated from the density of silver phosphate on the assumption that no adsorption takes place is close enough to show that no significant amount of adsorption occurs.

Discussion of the Results.

The following table contains all of the analyses not vitiated by a known impurity in the sample or by an accident during the analysis. One feature of this table requires further explanation. In Analysis 5 the silver was determined by precipitation as chloride instead of bromide. For every gram of silver phosphate there was obtained 1.02707 grams of silver chloride. Since Baxter found AgBr : AgCl = 1.31017 : 1.00000,[1] this analysis indicates that 1 gram of Sample N is equivalent to 1.02704 × 1.31017 = 1.34560 grams of silver bromide. This result is placed in the table for comparison with the other analyses and is used in the computation of the mean.

SERIES I.

$3AgBr : Ag_3PO_4$.

Number of Analysis.	Sample of Ag_3PO_4.	Weight of Ag_3PO_4 in vacuum. Grams.	Weight of AgBr in vacuum. Grams.	Weight of asbestos. Gram.	Dissolved AgBr. Gram.	Loss on fusion. Gram.	Corrected weight of AgBr. Grams.	Ratio $\frac{3AgBr}{Ag_3PO_4}$.
1	O	6.20166	8.34427	0.00036	0.00034	0.00007	8.34490	1.34558
2	O	6.35722	8.55386	0.00041	0.00003	0.00011	8.55419	1.34559
3	N	5.80244	7.80792	0.00029	0.00005	0.00007	7.80819	1.34567
4	N	5.05845	6.80658	0.00019	0.00020	0.00012	6.80685	1.34564
5	N	3.34498	(AgCl) 3.43514	0.00029	0.00009	0.00008	(AgCl) 3.43544	1.34560
6	P	7.15386	9.62648	0.00046	0.00013	0.00013	9.62694	1.34570
7	P	7.20085	9.68929	0.00023	0.00005	0.00010	9.68947	1.34560
8	R	6.20182	8.34466	0.00041	0.00027	0.00012	8.34522	1.34561
9	R	5.20683	7.00543	0.00029	0.00040	0.00007	7.00605	1.34555
							Average,	1.34562
						Per cent. of Ag in Ag_3PO_4,		77.300

A careful study of these results shows that the composition of silver

---

[1] THIS JOURNAL, 28, 1322 (1906).

phosphate is very nearly, if not quite, independent of the changes in the acidity of the solutions from which it is precipitated. Samples O and R were prepared under slightly more acid conditions than Samples N and P. The average amount of silver bromide obtained from 1 gram of Samples O and R is 1.34558 (77.297 per cent. of silver), whereas the average from Samples N and P is 1.34564 (77.301 per cent. of silver). This difference, if real and significant, is probably due to a very slight occlusion of disilver hydrogen phosphate by samples O and R. It does not seem probable that any basic salt was present in Samples N and P, because silver shows little tendency to form basic salts and the conditions of precipitation were not favorable for the formation of basic salts.

The difference between composition of the samples is so slight, both in absolute amount and by comparison with the differences between different analyses of the same sample, that in the present state of our knowledge it does not seem justifiable to reject the analyses of Samples R and O. This conclusion is supported by the fact that the water determinations failed to show a difference between these samples. The results, however, indicate that the average ratio 1.34562 (77.300 per cent. of silver) may be slightly too low, owing to the presence of disilver hydrogen phosphate. The ratio 1.34562, assuming the atomic weight of silver to be 107.88, and assuming that silver bromide contains 57.4453 per cent. of silver, leads to an atomic weight of 31.043 for phosphorus, whereas the ratio 1.34564 derived from Samples N and P gives the value 31.037. The rounded-off value, 31.04, may be considered to be essentially free from error from this source. With values for the atomic weight of silver of 107.87 and 107.86, the atomic weight of phosphorus becomes 31.03 and 31.02 respectively.

Owing to the high molecular weight of silver phosphate and to the small percentage of phosphorus, a given percentage error in determining the ratio of silver bromide to silver phosphate is multiplied over thirteen times in the atomic weight of phosphorus. Thus while the extreme values for the ratio differ by only a little over one one-hundredth of a per cent., the values for the atomic weight of phosphorus differ by fifteen hundredths of a per cent., or 0.047.

We are greatly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in pursuing this investigation; also to the Cyrus M. Warren Fund for Research in Harvard University for many pieces of platinum apparatus.

Summary.

1. A careful study has been made of the conditions necessary for the preparation of pure trisilver phosphate.

2. It is found that silver phosphate can be almost completely dried without fusion by heating in a current of dry air.

3. The density of silver phosphate is found to be 6.37.

4. It is found that silver phosphate does not adsorb a significant amount of air.

5. Nine analyses, made with four different samples, show that 1 gram of silver phosphate yields 1.34562 grams of silver bromide, whence the per cent. of silver in silver phosphate is 77.300.

Therefore,

If Ag = 107.88 P = 31.04
If Ag = 107.87 P = 31.03
If Ag = 107.86 P = 31.02

CAMBRIDGE, MASS., November 12, 1909.

THE SOLUBILITY OF GOLD IN NITRIC ACID.[1]

BY FREDERIC P. DEWEY.

Received December 29, 1909.

If there is any statement that is firmly established in general chemical literature it is that gold is not soluble in any single acid. In the literature of assaying, however, may be found various statements to the effect that, in parting gold from silver in assaying, gold may go into solution in the nitric acid used.

Makins[2] boiled a series of samples of parted gold in nitric acid of two different strengths and found an increasing loss of gold depending upon the amount of boiling, but he did not establish the purity of the acid used, nor the presence of gold in the acid after boiling. Neither did he determine the amount of silver remaining in his cornets.

In discussing the causes of loss of gold in making gold bullion assays, Rose[3] states that 8 per cent. of the loss is due to the gold going into solution in the nitric acid during parting. This statement is apparently based upon the author's own work, but no details are given to explain or sustain it.

Rickets and Miller[4] quote this statement from Rose without comment.

In his latest book Rose,[5] immediately after the general statement that gold is not perceptibly attacked by nitric acid, adds that finely divided gold is slightly soluble in boiling nitric acid, but gives no experimental data.

In speaking of the silver remaining in the gold after parting, Lodge[6] says, "If strong nitric acid (1.42 sp. gr.) is used this amount of silver may

---

[1] Presented by permission of the Director of the Mint.

[2] *Quarterly Journal Chemical Society,* 13, 99 (1861).

[3] "Metallurgy of Gold," p. 479.

[4] "Notes on Assaying," p. 129.

[5] "Precious Metals," p. 14.

[6] "Notes on Assaying," p. 144.