of silver and thallium are somewhat less dissociated. The degree of dissociation of uni-univalent salts is probably much smaller than commonly supposed. If we assume that potassium chloride is 74% dissociated at 0.1 *M*, 82% at 0.05 *M* and 89% at 0.02 *M*, then in all cases up to a few hundredths molal, and probably in most cases up to tenth molal, the activity of the ions is proportional to the concentrations thus calculated.

The familiar deviation of strong electrolytes from the mass law is, according to this view, as in the theory of Jahn, to be attributed largely to a general increase in mobility of ions with the total ion concentration. This view differs essentially from the theory advanced by Franklin and Kraus[1] and by Lewis and Wheeler.[2] According to that theory, the abnormalities of the conductivity curves for electrolytes were attributed to a change in the dissociating power of the solvent due to the addition of a stronger electrophile as solute. According to the one explanation, it is the speed of the ions which does not obey the laws announced by the founders of the ionic theory; according to the other, it is the degree of dissociation. It is probable that neither of these explanations alone suffices, but the evidence which has been here adduced in support of the view that the ions in aqueous solution have a variable mobility makes it extremely desirable that further investigations should be made of the mobility of ions in non-aqueous solvents. Especially it should be noted whether in such cases there is a change of transference number over a wide range of concentration.

In conclusion I wish to express my thanks to Dr. Merle Randall for valuable assistance in the collection of the data used in this paper.

BOSTON, June 14, 1912.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF PHOSPHORUS.[3]

[THIRD PAPER.]

THE ANALYSIS OF PHOSPHORUS TRICHLORIDE.

BY GREGORY PAUL BAXTER AND CHARLES JAMES MOORE.

Received October 17, 1912.

In two recent investigations in this laboratory, tri-silver phosphate[4] and phosphorus tribromide[5] have been analyzed with the following results for the atomic weight of phosphorus:

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[1] Franklin and Kraus, THIS JOURNAL, **27**, 216 (1905).

[2] Lewis and Wheeler, *Z. physik. Chem.*, **56**, 179 (1906).

[3] Reprinted from *Original Communications, Eighth International Congress of Applied Chemistry*, **2**, 21 (1912).

[4] Baxter and Jones, *Proc. Am. Acad.*, **45**, 137 (1910); THIS JOURNAL, **32**, 268; *Z. anorg. Chem.*, **66**, 97.

[5] Baxter, Moore and Boylston, *Proc. Am. Acad.*, **47**, 385 (1912); THIS JOURNAL, **34**, 259; *Z. anorg. Chem.*, **74**, 365.

	Ag = 107.880	107.870	107.860
Ag_3PO_4	P = 31.04	31.03	31.02
PBr_3	P = 31.027	31.024	31.021

While the agreement between the values yielded by the two researches is reasonably close, yet because of the low percentage of phosphorus in both compounds, 7.7 and 11.5 respectively, and the consequent magnification of the percentage experimental error in calculating the atomic weight of phosphorus, the subject has been further investigated by the analysis of phosphorus trichloride. This substance contains a higher percentage of phosphorus than either the phosphate or tribromide, 22.6, and might be expected therefore to yield results of fully as much value as those given by the other two compounds.

Silver phosphate and phosphorus tribromide are compounds of so different character, containing phosphorus in two states of valence, and the analytical processes were so different, that there is little probability that both methods were affected by constant errors to the same extent. Yet any uncertainty of this sort would be further removed if still a third method is found to be in accord with the first two.

The method of preparing and analyzing phosphorus trichloride was very similar to the one previously employed with the tribromide. Phosphorus trichloride was synthesized from pure dry phosphorus and a very slight excess of pure dry chlorine in a vacuum. The product was freed from the less volatil pentachloride by fractional distillation in a vacuum. A series of fractions was then collected and analyzed for chlorine in the usual way, after decomposition with water and oxidation of the phosphorous acid produced.

Purification of Materials.

Water.—All the water used in this research was prepared from the laboratory supply of distilled water by further distillation, first from an alkalin permanganate solution, and then a second time, after the addition of a trace of sulfuric acid, through a block tin condenser. No rubber or cork was used in the connection between the condenser tube and the Jena glass still.

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

Nitric Acid.—C. P. concentrated acid was distilled through a platinum condenser, with rejection of the first two-thirds of the distillate. It was always carefully tested in a nephelometer for traces of halogens.

Chlorine.—This substance was prepared by warming C. P. concentrated hydrochloric acid with granulated manganese dioxide. In order to remove hydrochloric acid, the gas was scrubbed with water in two large gas washing bottles and two towers filled with moist glass pearls. Drying took place in two towers filled with glass pearls drenched with concentrated sulfuric acid and a long tube filled with resublimed phosphorus pentoxide. Finally the gas was condensed to the liquid state in a bulb cooled to a temperature of about —78° by immersion in a bath of solid carbon dioxide and alcohol. The preparation and purification of the chlorine took place in an apparatus constructed wholly of glass, with ground stoppers and connections throughout.

On account of the ready action of moisture on the halides of phosphorus, it was particularly necessary to dry the chlorine as completely as possible. Hydrochloric acid also was undesirable, since its elimination from the trichloride by distillation would be somewhat uncertain. Air and carbon dioxide were of lesser importance. However, the air at any rate must have been largely removed during the liquefaction of the gas.

Phosphorus.—As in the previous research, phosphorus was purified by distillation with steam at atmospheric pressure in an apparatus constructed wholly of glass. The purified material was preserved under water until used. Similar phosphorus was found in the earlier work to be essentially free from arsenic.[1] The material used in the synthesis of the first series of fractions of phosphorus trichloride was once distilled, that used in the second, twice.

Silver.—The same preparation of silver was used here that was employed in the tribromide analyses. The method of purification consisted in double precipitation as chloride, precipitation as metal by ammonium formate, and electrolytic deposition. The electrolytic crystals were fused in a current of hydrogen on a boat of pure lime, and finally, after cleansing with nitric acid, the buttons were dried in a vacuum at about 400°.

Hydrogen Peroxide.—Merck's "Perhydrol," containing 30% hydrogen peroxide, was found to be free from sulfuric acid and halogens and to leave no residue upon evaporation. Hence it was employed without further treatment.

Nitrogen.—Atmospheric nitrogen free from oxygen was obtained by Wanklyn's well known method of passing air through a very concentrated ammonia solution, and then over hot copper gauze in a hard glass tube. The excess of ammonia was removed by scrubbing with a dilute solution of sulfuric acid in three large gas washing bottles. Since hydrogen is formed by the catalytic decomposition of a portion of the excess of ammonia, this impurity was oxidized in a hard glass tube filled with red hot copper oxide, and the gas was then dried in six towers filled with beads drenched with concentrated sulfuric acid and in a long tube filled with resublimed phosphorus pentoxide. Finally, the gas was passed through a third hard glass tube filled with hot copper to combine with

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[1] *Proc. Am. Acad.*, 47, 587 (1912); THIS JOURNAL, 34, 259; *Z. anorg. Chem.*, 74, 365.

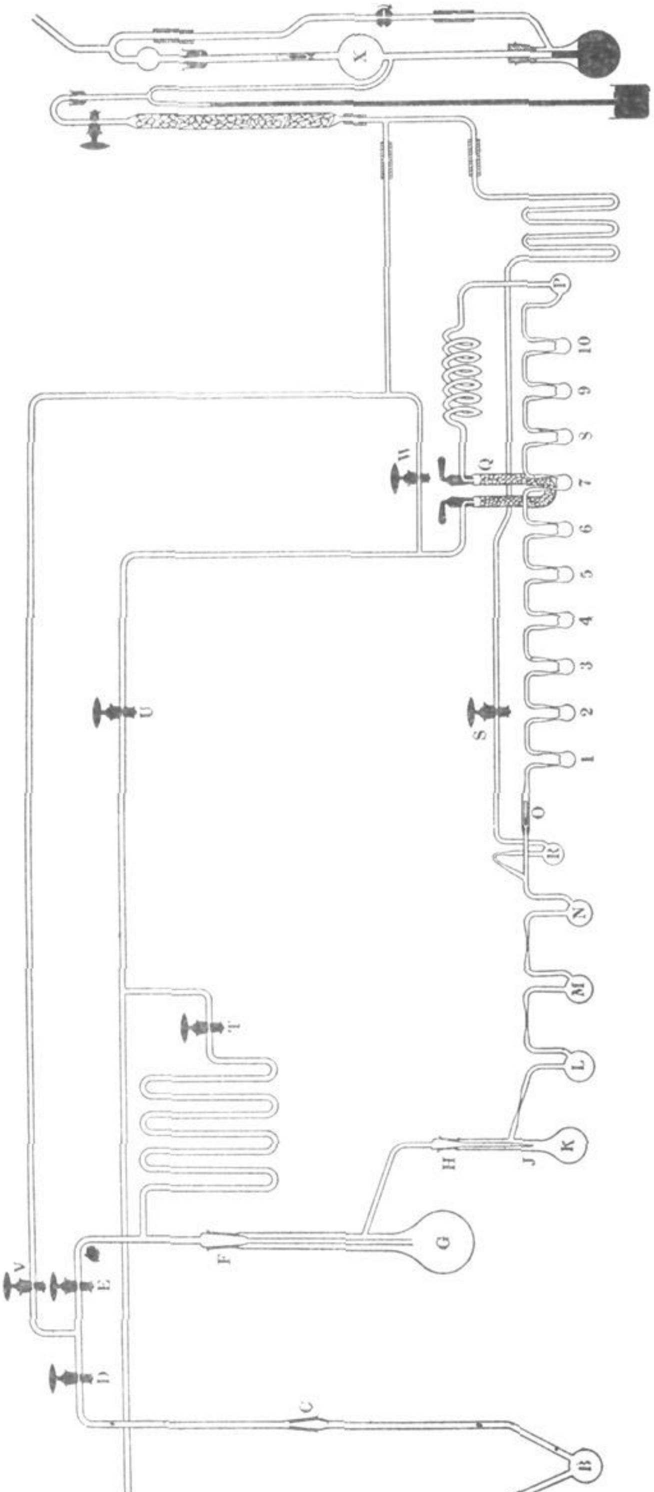
any last trace of oxygen. The apparatus in which these operations were carried out was constructed entirely of glass with ground glass connections throughout.

The Preparation of Phosphorus Trichloride.

Although the phosphorus trichloride was made in the same way as the tribromide, by allowing a slight excess of pure dry chlorine to react with pure dry phosphorus in a vacuum, the problem of freeing the trichloride from pentachloride differed somewhat from the preparation of the tribromide free from pentabromide. When the tribromide is distilled, even at so low a temperature as its boiling point in a partial vacuum, any pentabromide present is largely dissociated into tribromide and bromine so that the excess of bromine may be removed with the first fractions by distillation. With the pentachloride, however, the dissociation is very much less at the same temperature, and since the trichloride boils nearly 100° lower at atmospheric pressure than the tribromide, the conditions were far less favorable for the elimination of pentachloride by decomposition. On the other hand, the inappreciable dissociation of the pentachloride at room temperatures and the slight volatility of this substance facilitate the separation of the tri- and pentachloride by simple fractional distillation, for the pentachloride accompanies the relatively very volatil trichloride to only a barely perceptible extent.

The synthesis of the trichloride was effected in an apparatus constructed entirely of glass, shown in the figure on page 1648. About 25 grams of phosphorus were freed as completely as possible from water by cooling and pressing between the folds of hardened filter paper. Then it was weighed to a centigram and placed in the distilling flask G, which had previously been filled with nitrogen through the stopcock T. The flask was fitted to the well ground and polished joint F, but it was not connected to the remainder of the apparatus at H, and the constricted tube J opened into the air.

In order to dry the phosphorus completely, the flask was surrounded with boiling water, and for four hours a slow current of pure dry nitrogen was forced in at T and flowed out at the end of the constricted tube J. The melted phosphorus was agitated from time to time by shaking the flask in order to liberate any steam which might have been mechanically entangled and to bring new material to the surface of the phosphorus. During this operation a portion of the phosphorus distilled into the cool tube J, and a small amount was vaporized into the air. Probably, too, small amounts of acids of phosphorus were produced, since slight oxidation of the phosphorus necessarily took place while it was being introduced into the flask. As soon as the phosphorus had been dried in this way, the end of the constricted tube J was sealed, the stopcock T was closed and the flask, after being cooled, was exhausted as completely as possible through the stopcocks E and V by means of the Töpler pump X. All the ground glass joints were made gas tight by means of a minimum



quantity of syrupy phosphoric acid, and outside this, to prevent the absorption of moisture, soft paraffin was smeared.

In the meantime, the bulb B was being filled with liquid chlorine in the fashion already described. A considerable excess of this substance was collected at first. The bulb was then suspended on a balance and the excess of chlorine was allowed to evaporate. When the weight of the residual chlorine was 0.3–0.4 gram larger than the amount theoretically equivalent to the phosphorus, the bulb was again plunged into the alcohol-carbon dioxide bath to check the evaporation. Next, the bulb B was connected with the remainder of the apparatus by the joint C. The stopcock A was closed and the bulb B was still further cooled with liquid air. At this temperature the chlorine not only becomes solid but its vapor pressure becomes so low that when the bulb B was exhausted through the stopcocks D and V, while E remained closed, the mercury of the pump showed no signs of attack.

The stopcock V was now closed and E was opened so as to establish communication between the bulbs B and the flask G. Then the liquid air bath was removed from B and the chlorine was allowed to absorb heat slowly, but by occasional immersion in alcohol and carbon dioxide the temperature of the chlorine was prevented from exceeding —40°. At first the phosphorus was only slowly affected by the chlorine but once the reaction was started by warming the phosphorus gently, it progressed rapidly to completion; so rapidly in fact, that it was necessary to cool the flask G with water in order to prevent rapid volatilization of the trichloride formed. While the reaction was progressing, a large amount of the white solid pentachloride formed on the walls of the flask, but at the end of the synthesis this pentachloride was dissolved in the liquid trichloride by gently shaking and warming the flask nearly to the boiling point of the trichloride at atmospheric pressure. The unchanged phosphorus still remaining then was able to convert the greater part of this pentachloride to trichloride. The flask was filled with nitrogen and allowed to stand over night.

The next morning the flask and its contents were cooled with solid carbon dioxide and alcohol, and nitrogen was admitted through T until the internal pressure was greater than atmospheric. Then the end of the constricted tube J was cut off and the remainder of the apparatus, which had previously been filled with nitrogen, was attached by the joint H. Next, the bulbs G, K, L, M, N, and R were exhausted through S, while stopcocks D, E, T, V, and W were closed. In order to prevent access of chlorine or phosphorus trichloride to the pump, the bulb R was immersed in liquid air. The pump was further protected by a tube containing solid potassium hydroxide.

During the fractional distillation of the trichloride, the bulbs 1–10, in which the final fractions of trichloride were to be collected, were protected from contact with the first fractions. This was effected by maintaining nitrogen at atmospheric pressure beyond the valve O. This valve was very well ground and polished so as to be nearly gas tight without any lubricant. The very slight leakage which occurred produced a slow reverse current of nitrogen through the valve into the pump by way of the bulb R.

Under as low a pressure as could be maintained by the pump the trichloride was distilled from G to K by warming G to about 15° and cooling K to —78°. When about four-fifths of the trichloride had been distilled into K, this bulb was warmed to 15° while L was cooled to —78°. Again four-fifths of the trichloride in K was collected in L. At this point K was cooled and the capillary between K and L was sealed. In this way the residues of the first two distillations were cut off completely from the rest of the apparatus. It is certain that the trichloride originally contained pentachloride because a white incrustation appeared on the sides of G toward the end of the first distillation. The distillation was continued from L to M and from M to N, the residual fifth being rejected in each distillation by sealing off the containing flask. Thus the greater part of the less volatil pentachloride was eliminated. Next, in order to expel the more volatil impurities such as hydrochloric acid, if present at all, about one-quarter of the remainder was distilled into the bulb R and this bulb was then cut off by sealing the capillary.

The purification of the trichloride was now considered complete, so that the next step consisted in filling the numbered bulbs by distillation. The bulb N was cooled to —78°, the bulb P was immersed in liquid air to protect the pump and the train of bulbs was exhausted through the U-tube Q, containing resublimed phosphorus pentoxide, and the stopcock W. The valve O, inside which a piece of soft iron had originally been sealed, could now be pulled from its seat by means of a magnet. When the remaining system had been exhausted as completely as possible, the right hand capillary of the bulb 10 was sealed. The weighing bulbs were now filled in order beginning with 10, by warming the bulb N to 15° and cooling the bulbs in turn to —78°. Each of the numbered bulbs was about four-fifths filled with trichloride. As soon as four bulbs had been filled they were sealed off as a unit, and the next four to be filled were treated in the same way. Finally, while the trichloride was still cold, each individual bulb was sealed off at the capillaries. Great care was taken in sealing the capillaries to avoid decomposition of the trichloride by unnecessary heating. There never was any sign of decomposition of the trichloride during the process.

The trichloride was a colorless, highly refractive liquid which gave every outward evidence of purity, and showed no change in appearance on long standing. One of the rejected residues was left in the sunlight for several months without showing any sign of decomposition.

Two series of fractions of phosphorus trichloride were prepared. In the first series only eight bulbs were available for collecting the material, and as more than enough trichloride to fill all these bulbs was contained in N, the residue from the distillation could not be analyzed. Furthermore, in this first preparation, the bulbs K, L, M contained tiny crystals of electrolytic silver. This was introduced to assist in the elimination of the pentachloride by combining with the chlorine, but as it seemed in practice to serve no useful purpose, it was omitted in making the second preparation. In the second experiment, however, twelve bulbs were actually available and the material in N was sufficient only to fill ten. As soon as the bulbs numbered 4–12 inclusive had been filled, instead of distilling the residue into bulb 3, it was distilled into bulb 2. When all the trichloride had disappeared from N a slight white solid residue appeared, showing that, in spite of all precautions, a trace of pentachloride had accompanied the trichloride even in the fourth distillation. Since it seemed possible that the last fraction contained pentachloride, it was again distilled from bulb 2 into bulb 3, a small residue being rejected.

The Determination of the Weight of the Trichloride and its Analysis.

The analysis of the trichloride followed very closely the procedure employed with the tribromide. First, the trichloride was decomposed with water, then, on account of the reducing effect of phosphorous acid on silver salts, the phosphorous acid was oxidized with hydrogen peroxide and nitric acid. Finally, the chloride was precipitated with a weighed equivalent amount of pure silver and the silver chloride was weighed. Since the determination of the weight of trichloride and its analysis are very intimately connected, they are described together.

The weight of the trichloride was found in each analysis by weighing the bulb with its contents and then, after breaking the bulb, collecting and weighing the glass. The bulb was first carefully cleaned on the outside and dried, and left in a desiccator over sulfuric acid for at least 24 hours. Its weight in air was then found by substituting standardized weights for the bulb on the balance. The buoyant effect of the air was estimated by finding the volume of the bulb in the usual way from the loss in weight under water of known temperature. The conditions of the atmosphere were taken into account in calculating the buoyant effect of the air on the bulbs and weights. Since the bulb was exhausted when sealed, no correction is necessary for the space in the bulb not filled with liquid.

After the bulb had been weighed and its volume determined, it was placed in a 1000 cc. thick walled Erlenmeyer flask together with somewhat over 200 cc. of redistilled ammonia and 10 cc. of pure 30% hydrogen peroxide. The flask was warmed to about 60°, then, after a glass stopper which had been carefully ground into the neck of the flask had been inserted, and the flask cooled to 0°, it was shaken violently enough to break the bulb. The heavy trichloride reacted quietly at the bottom of the aqueous solution, until at the end of five minutes decomposition was complete. The flask was then allowed to stand 24 hours, with occasional shaking. This long standing was necessary to allow a small quantity of ammonium chloride fumes to be collected in the aqueous solution. The precaution of cooling to 0° was found advisable because the reaction was too violent at room temperature.

Next, the flask, cooled to produce inward pressure, was carefully opened and the solution was filtered into a three-liter, ground-stoppered precipitating flask, while the particles of glass were collected upon a small filter paper. This paper was very thoroughly rinsed with pure water until the filtrate and washings amounted to about 1200 cc.

In order to find the weight of the glass, the filter was burned at as low a temperature as possible in a weighed platinum crucible. When the weight of the glass, corrected to vacuum, was subtracted from the corrected weight of the bulb and the trichloride, the weight of the trichloride in vacuum was obtained.

In the investigation upon the tribromide it was shown by several blank experiments that this method of collecting the glass and finding the weight of the trichloride is a satisfactory one.

The filtrate containing ammonium chloride was next acidified by the addition of about 40 cc. of concentrated nitric acid which had been diluted to about 300 cc. In order to avoid possible loss of chlorine, the acid was poured into the solution through a thistle tube, the stem of which extended to the bottom of the flask. Thus, any chlorine locally set free by the nitric acid was reduced by the phosphorous acid still remaining. There was never any evidence that chlorine was set free even locally by the nitric acid.

The solution was allowed to stand for 48 hours before precipitation, in order to allow the oxidation of the phosphorous acid to become as nearly as possible complete, because in the tribromide work this delay was found advisable.

A quantity of silver equivalent to the trichloride within a very few tenths of a milligram was weighed out and dissolved in nitric acid in a flask fitted with a column of bulbs to prevent loss of material by spattering. After the silver solution had been freed from oxides of nitrogen by dilution and heating, about 40 cc. of concentrated nitric acid were added and the whole was diluted to a volume of about 1 liter. The silver solution was then quantitatively added to the chloride solution with constant agitation, and the stoppered precipitating flask was allowed to stand for several days with occasional shaking. Then the solution was cooled to 0° to lower the solubility of the silver chloride and again allowed to stand until the precipitate had coagulated and settled so completely that the supernatant liquid was apparently clear. Portions of the solution were then tested in a nephelometer[1] for excess of chloride or silver. As a matter of fact, chloride was always found in slight excess. The deficiency of silver, which was never more than a few tenths of a milligram, was made up as nearly as could be estimated by means of a hundredth normal solution of silver nitrate. After thorough shaking and standing until the solution was clear, tests for excess of chloride or silver were again made. If necessary, this process was repeated, until eventually the amounts of chloride and silver were equivalent.

The solution was now allowed to stand for a week with occasional shaking and then was tested again in the nephelometer. In a few cases a deficiency of one- or two-tenths of a milligram of silver was found, owing apparently to extraction of occluded soluble chloride from the silver chloride. This deficiency of silver was supplied and the solution was left for another week before being tested again, and the process was repeated until in the course of a week no further change in the solution took place. In a few analyses the solutions were tested over a period of eight weeks but in no case was any appreciable change in the end point found after it had remained constant for a week. In most cases the final end point was reached within two weeks.

In a number of analyses both the chloride and silver solutions were cooled to 0° before precipitation. This procedure had no perceptible effect on the result, nor did it seem to lengthen appreciably the period necessary for reaching a permanent end point.

Less difficulty was experienced from occlusion by the silver chloride in this research than by the silver bromide in the previous one. The amount of occluded substance seemed to be smaller and the time required for equilibrium to be reached was less. This is probably due to the greater solubility of the chloride.

As soon as a permanent end point had been reached in an analysis, the silver chloride was collected and determined. Owing to the fact that silver chloride is many times as soluble as silver bromide, more difficulty was experienced in finding a suitable method for its determination, and the first series of analyses were sacrificed in unsuccessful experiments.

It was an easy matter to collect the precipitate itself upon a Gooch-Munroe-Neubauer crucible, and to determin its weight after drying it at 190° for some hours. Residual moisture was found by fusing the main bulk of the precipitate and determining the loss in weight. The latter was never as much as 0.006% the weight of the salt.

The difficulty lay in finding the silver chloride dissolved in the filtrate and washings. In analyses 16 and 17, after filtration of the ice cold

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[1] **Richards and Wells**, *Am. Chem. J.*, **31**, 235 (1904); **35**, 510 (1906).

mother liquor, the precipitate was washed and transferred to the crucible with ice cold water. The filtrate and washings, amounting to about 4 liters, were evaporated to a very small bulk, until the excess of nitric acid had been expelled. After dilution and filtration, the silver was deposited electrolytically in a small platinum dish. When deposition was complete, the electrolyte was displaced by water while the current was still running. The film of silver was then dissolved in nitric acid and the silver precipitated as silver iodide. The precipitate was collected on a small Gooch-Munroe-Neubauer crucible and weighed.

The filter used for the filtration of the mother liquor before electrolysis was incinerated and after the ash had been treated with nitric acid, the solution was added to the solution of the electrolytic film. The mother liquor of the electrolysis was saturated with pure hydrogen sulfide gas and the precipitate, chiefly sulfur, was found, after incineration of the paper, to be free from silver.

Because this process was a long and tedious one, the experiment was tried of reducing the solubility of the silver chloride by means of an excess of silver nitrate and partially washing the precipitate with similar solution. This method is the usual one in treating silver halides for quantitative purposes, but it was not attempted here at first because, in the phosphorus tribromide work, even a slight excess of silver was found to be partially reduced by unoxidized phosphorous acid.

To our great satisfaction this method was successful. The silver chloride precipitate was perfectly white both before and after the addition of the silver nitrate and remained so during all the subsequent steps. Probably this difference in behavior was due to a somewhat higher concentration of nitric acid, and to more complete oxidation of the phosphorous acid.

When the end point had been reached, an excess of about 0.1 gram of silver nitrate in solution together with considerable nitric acid was added to the analysis. The flask was shaken and packed in ice, where it was left, with occasional shaking, for a day. The clear solution was then passed through the crucible and the precipitate was washed three times with a solution of silver nitrate containing 0.05 gram per liter, and once with pure water. The filtrate and these four washings were discarded and a correction of 0.00001 gram per liter was applied for dissolved silver chloride. Richards and Wells[1] found the solubility of silver chloride in dilute hydrochloric acid at room temperature to be 0.00003 gram per liter, but as Richards and Willard[2] found the solubility in water at 0° to be about one-sixth that at 25°, the above estimate seems to be a liberal one for the solubility at 0° in dilute silver nitrate. The precipitate was

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[1] *Pub. Car. Inst.*, Publication No. 28 (1905); THIS JOURNAL, 27, 459; *Z. anorg. Chem.*, 47, 56.

[2] *Pub. Car. Inst.*, Publication No. 125 (1910); THIS JOURNAL, 32, 4; *Z. anorg. Chem.*, 66, 229.

then further washed with pure water eight to ten times and transferred to the crucible.

The silver chloride dissolved in the wash waters was carefully determined by comparison with standard silver solutions in a nephelometer. The unknown and the standard solutions were both treated with an excess of ammonia and then an excess of nitric acid, after the addition of an excess of silver solution, and the two tubes were treated in as nearly as possible an identical fashion.

The precipitating flask was rinsed with ammonia, and, if the solution was found to contain silver, the quantity was determined in a similar fashion in the nephelometer and a correction applied.

The following tables contain the results of all the analyses which met with no accidents.

Weighings were made on a No. 10 Troemner balance sensitive to a very few hundredths of a milligram, while the gold-plated weights were carefully standardized to hundredths of a milligram by the method described by Richards.[1]

Vacuum corrections were applied as follows:

	Specific gravity.	Vacuum correction.
Weights	8.3	+0.000145
AgCl	5.56	+0.000071
Ag	10.49	—0.000030
Glass	2.5	+0.000335

In the calculations the atomic weight of silver is assumed to be 107.880 and that of chlorine 35.457.

SERIES I.

No. of analysis.	Fraction of PCl_3.	Weight of PCl_3 in vacuum. Grams.	Weight of Ag in vacuum. Grams.	Deficiency of Ag. Gram.	Corrected weight of Ag in vacuum. Grams.	Ratio: $PCl_3 : 3Ag$.	Atomic weight of phosphorus.
1	1	3.60897	8.50038	0.00110	8.50148	0.424511	31.018
2	8	3.49255	8.22664	0.00070	8.22734	0.424505	31.016
3	4	3.80549	8.96377	0.00050	8.96427	0.424517	31.020
4	5	4.64502	10.94182	0.00030	10.94212	0.424508	31.017
5	2	3.99011	9.39923	0.00020	9.39943	0.424505	31.016
6	7	3.38036	7.96291	0.00010	7.96301	0.424508	31.017
					Average,	0.424509	31.017

SERIES II.

No. of analysis.	Fraction of PCl_3.	Weight of PCl_3 in vacuum. Grams.	Weight of Ag in vacuum. Grams.	Deficiency of Ag. Gram.	Corrected weight of Ag in vacuum. Grams.	Ratio: $PCl_3 : 3Ag$.	Atomic weight of phosphorus.
7	3	4.59507	10.82411	0.00030	10.82441	0.424510	31.017
8	10	4.40117	10.36751	0.00020	10.36771	0.424508	31.016
9	4	5.71561	13.46368	0.00040	13.46408	0.424508	31.017
10	9	5.18668	12.21784	0.00030	12.21814	0.424506	31.016
11	5	5.15583	12.14525	0.00030	12.14555	0.424504	31.015
12	8	5.13108	12.08685	0.00040	12.08725	0.424504	31.015
13	1	4.85457	11.43585	0.00000	11.43585	0.424505	31.016
14	2	3.58844	8.45324	0.00000	8.45324	0.424505	31.016
15	6	5.91915	13.94317	0.00060	13.94377	0.424502	31.015
					Average,	0.424506	31.016

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[1] THIS JOURNAL, **22,** 144 (1900).

SERIES III.

No. of analysis.	Fraction of PCl_3.	Weight of PCl_3 in vacuum. Grams.	Weight of AgCl in vacuum. Grams.	Loss on fusion. Gram.	AgCl from filtrate and washings. Gram.	Corrected weight of AgCl in vacuum. Grams.	Ratio: $PCl_3 : 3AgCl$.	Atomic weight of phosphorus.
16	3	4.59507	14.37888	0.00061	0.00291	14.38118	0.319520	31.026
17	10	4.40117	13.77320	0.00046	0.00220	13.77494	0.319506	31.020
18	4	5.71561	17.88965	0.00096	0.00064	17.88933	0.319506	31.020
19	9	5.18668	16.23441	0.00085	0.00074	16.23430	0.319489	31.019
20	5	5.15583	16.13756	0.00095	0.00066	16.13727	0.319498	31.017
21	8	5.13108	16.05934	0.00054	0.00082	16.05962	0.319502	31.018
22	1	4.85457	15.19201	0.00054	0.00098	15.19245	0.319538	31.034
23	2	3.58844	11.23055	0.00054	0.00090	11.23091	0.319515	31.024
24	6	5.91915	18.52577	0.00077	0.00092	18.52592	0.319506	31.020
						Average,	0.319509	31.022

The chief point of interest to determin in the examination of the foregoing results is whether the material really represents pure phosphorus trichloride. Judging from the agreement of the results obtained with the different fractions in each series, the material was as uniform as could possibly be expected. While evidence was obtained that the pentachloride is to a very slight extent carried into the trichloride distillate either as such or in the form of its dissociation products, the amount thus accompanying the trichloride diminishes very rapidly with successive distillations. Of course it is possible that a constant boiling mixture of tri- and pentachloride exists, but such a possibility is somewhat remote. If the trichloride actually contained a trace of pentachloride it would account for the fact that the average result of this research, 31.018, is very slightly lower than that of the tribromide work. It is worth noting, however, that five out of thirty-one analyses of the tribromide yield a value as low as the average of the trichloride analyses, and that three of the six series of tribromide analyses yield averages of 31.022, a value only 0.004 higher than the trichloride average. A difference no larger than this is extremely difficult to detect even where the substances analyzed are ideal for the purpose.

The three compounds of phosphorus analyzed, then, yield the following results:

	Ag = 107.880	Ag = 107.870	Ag = 107.860
Ag_3PO_4	31.04	31.03	31.02
PBr_3	31.027	31.024	31.021
PCl_3	31.018	31.015	31.012
Averages,	31.028	31.023	31.018

On the whole the tribromide and trichloride may be expected to yield somewhat more certain results than silver phosphate, and the averages of these, given in the following results, are therefore to be preferred.

Ag = 107.880 Ag = 107.870 Ag = 107.860
P = 31.023 P = 31.020 P = 31.017

On any basis the rounded off value 31.02 is as exact as the experimental work warrants.

Summary of Results.

1. Methods are described for the preparation of pure phosphorus trichloride and its analysis.

2. The molecular weight of phosphorus trichloride referred to silver 107.880 is found to be 137.389 whence phosphorus has the atomic weight 31.018.

3. Using the same value for silver, the average result of the analyses of silver phosphate, phosphorus tribromide and phosphorus trichloride is 31.028, while the average of the more reliable tribromide and trichloride analyses is 31.023.

We are particularly indebted to the Carnegie Institution of Washington for generous pecuniary assistance in carrying out this investigation.

CAMBRIDGE, MASS., July 1, 1912.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF IRON.[1]

[FIFTH PAPER.]

THE ANALYSIS OF FERRIC OXIDE.

BY GREGORY PAUL BAXTER AND CHARLES RUGLAS HOOVER.

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The atomic weight of iron has already been subjected to three separate investigations in this laboratory. Richards and Baxter[2] first analyzed ferric oxide by reduction in hydrogen, and obtained the result 55.88, a value much lower than the one in general use at that time, 56.02. The problem was further investigated by Baxter[3] by the analysis of ferrous bromide, and the result yielded by material known to be slightly impure, 55.845 (Ag = 107.880), agrees very closely with that obtained by Baxter, Thorvaldson, and Cobb[4] in a very recent investigation with much purer material, 55.838. Furthermore, Baxter and Thorvaldson[5] found that meteoric material is identical, so far as could be told by the analysis of ferrous bromide, with material of terrestrial origin.

Thus, although the analysis of ferrous bromide supports the verdict of the oxide analysis in yielding a low value for the atomic weight of iron,

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[1] Reprinted from Original Communications, Eighth International Congress of Applied Chemistry, Vol. II, p. 37 (1912).

[2] *Proc. Am. Acad.*, **35**, 253 (1900); *Z. anorg. Chem.*, **23**, 245.

[3] *Ibid.*, **39**, 245 (1903); **38**, 232.

[4] THIS JOURNAL, **33**, 319 (1911); *Z. anorg. Chem.*, **70**, 325.

[5] *Ibid.*, **33**, 337 (1911); **70**, 348.