RESEARCHES

UPON

THE ATOMIC WEIGHTS

OF

CADMIUM, MANGANESE, BROMINE, LEAD, ARSENIC, IODINE, SILVER CHROMIUM, AND PHOSPHORUS

BY

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IN COLLABORATION WITH

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PREFACE.

This collection of papers upon the atomic weights of certain common elements embodies the results of researches of which the experimental work has been carried on in the Chemical Laboratory of Harvard College during the past six years. All of the papers have already been published separately both in American and in German periodicals, and references to the places of publication are given at the beginning of each article.

In reprinting the papers in the present form the only changes of importance which have been made are due to more exact knowledge of the fundamental atomic weights upon which the calculations depend. Many recent investigations, especially that upon the analysis of lithium chloride and perchlorate by Richards and Willard,[1] have shown that the atomic weight of silver, referred to oxygen 16.000, is certainly as low as 107.880, and possibly as low as 107.870. Since the International Committee upon Atomic Weights at the date of writing have chosen the higher of these values, the calculations have been based upon the value 107.880 for silver, the atomic weights of chlorine and bromine being assumed to be 35.457[2] and 79.916[3] respectively. The effect of a change from 107.880 to 107.870 in the atomic weight of silver is, however, plainly indicated in each instance.

In the case of cadmium the subject-matter of two papers has been rearranged in a manner differing considerably from that of the original publication. In the case of iodine the subject-matter of two papers has been combined in one. In all other cases the presentation is essentially that of the original publication.

Generous grants from the Carnegie Institution of Washington have been of the greatest assistance in the progress of this work, while grants from the Cyrus M. Warren Fund for Research in Harvard University have materially aided all the investigations.

G. P. BAXTER.

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[1] *Publications of the Carnegie Institution*, No. **125** (1910); *Jour. Amer. Chem. Soc.*, **32**, 4.

[2] *Publications of the Carnegie Institution*, No. **28** (1905); *Jour. Amer. Chem. Soc.*, **27**, 459; *Zeit. anorg. Chem.*, **47**, 56.

[3] *Proc. Amer. Acad.*, **42**, 201 (1906); *Jour. Amer. Chem. Soc.*, **28**, 1322; *Zeit. anorg. Chem. Soc.*, 389. (See page 49.)

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I.

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

THE. ANALYSIS OF CADMIUM CHLORIDE.

By Gregory Paul Baxter and Murray Arnold Hines.

Journal of the American Chemical Society, **27**, 222 (1905); **28**, 770 (1906).
Zeitschrift für anorganische Chemie, **44**, 158 (1905); **49**, 415 (1906).

Contributions from the Chemical Laboratory of Harvard College.

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

THE ANALYSIS OF CADMIUM CHLORIDE.

INTRODUCTION.

From the following list of investigations upon the atomic weight of cadmium it can be seen that this subject has attracted considerable attention, especially in recent years.[1]

Date.	Investigator.	Reference.	Ratio determined.	Result.
1818	Stromeyer	Schweigger's Jour., **22**, 366	$Cd:CdO$	111.5
			$Cd:CdS$	113.8
			$Cd:Cl_2$	112.8
			$Cd:I_2$	111.7
1857	von Hauer	J. pr. Chem., **72**, 350	$CdSO_4:CdS$	111.9
1860	Lenssen	J. pr. Chem., 281	$CdC_2O_4:CdO$	112.0
1860	Dumas	Ann. Chem. Pharm., **113**, 27	$CdCl_2:2Ag$	112.14
1881	Huntington . . .	Proc. Amer. Acad., **17**, 28	$CdBr_2:2Ag$	112.18
			$CdBr_2:2AgBr$	112.17
1890	Partridge	Amer. Jour. Sci., (3) **40**, 377	$CdC_2O_4:CdO$	111.80
			$CdSO_4:CdS$	111.73
			$CdC_2O_4:CdS$	111.67
1891	Morse and Jones .	Amer. Chem. Jour., **14**, 261	$Cd:CdO$	112.07
			$CdC_2O_4:CdO$	112.02
1892	Lorimer and Smith	Zeit. anorg. Chem., **1**, 364	$CdO:Cd$	112.04
1895	Bucher	Doctoral Dissertation, Baltimore, Md.	$CdC_2O_4:CdO$	111.88
			$CdC_2O_4:CdS$	112.12
			$CdCl_2:2AgCl$	112.31
			$CdBr_2:2AgBr$	112.33
			$Cd:CdSO_4$	112.35
			$Cd:CdO$ (porcelain)	112.08
			$Cd:CdO$ (platinum)	111.89
1896	Hardin	Jour. Amer. Chem. Soc., 18, 1016	$CdCl_2:Cd$	112.03
			$CdBr_2:Cd$	112.02
			$Cd:Ag$	111.94
1898	Morse and Arbuckle	Amer. Chem. Jour., **20**, 536	$Cd:CdO$	112.38

The relative value of many of these determinations has already been several times discussed,[2] and since it is invariably a difficult matter intelligently to

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[1] The greater portion of this list is to be found in Clarke's "Recalculation of the Atomic Weights," Smithsonian Misc. Coll., 1910.

The results have been calculated with the use of the following atomic weights: $O=16.00$; $C=12.00$; $S=32.07$; $Cl=35.46$; $Br=79.92$; $Ag=107.88$; $I=126.92$.

[2] Clarke, Partridge, Morse and Jones: *Loc. cit.;* Richards: *Amer. Chem. Jour.*, **20**, 547 (1898).

criticize experimental work without an actual repetition of the experiments, for frequently some constant source of error is so securely hidden that it may be detected only by the most careful investigation, no attempt at criticism is made here.

Nevertheless, it is worth while calling especial attention to the careful researches of Morse and Jones and Morse and Arbuckle upon the ratio Cd : CdO, which yielded the value 112.38, and that of Bucher upon the ratios $CdCl_2 : 2AgCl$ and $CdBr_2 : 2AgBr$ which yielded the values 112.31 and 112.33. Our experiments indicate that the real value for the constant in question is slightly higher than any of these results.

In a recent determination of the specific gravity of cadmium chloride,[1] anhydrous cadmium chloride was prepared by ignition of a double chloride of cadmium and ammonium in a current of hydrochloric-acid gas, in a state of so great purity that it was considered worth while to make use of the salt for a determination of the atomic weight of cadmium.

PURIFICATION OF MATERIALS.

CADMIUM CHLORIDE.

The general method of purification of the cadmium material was that of fractionally precipitating cadmium sulphide. One kilogram of metallic cadmium was dissolved in aqua regia, and the solution, after being boiled to expel chlorine and oxides of nitrogen, was filtered, and diluted to about 4 liters. The solution contained traces of lead, copper, thallium, nickel, iron, and zinc. When a current of hydrogen sulphide was passed through the solution, the first small fraction of cadmium sulphide which was precipitated was dark-colored, nearly black, owing to the presence of lead, copper, and thallium. This fraction was removed by filtration and rejected. A second larger fraction of the sulphide, although it contained no appreciable amount of the latter metals, also was discarded. The third fraction consisted of all that could be precipitated by saturating the solution with hydrogen sulphide. However, this did not contain more than one-quarter of the original material, for the solution was very strongly acid, owing to the large excess of acid used in dissolving the metal and the accumulation of the acid formed during the precipitation. The solution was separated from the precipitate by decantation, and was then diluted to 16 liters. Upon saturating this solution with hydrogen sulphide a fourth fraction of cadmium sulphide was obtained, and a second dilution of the solution made possible the precipitation of nearly all the remainder of the cadmium in still a fifth fraction.

The third, fourth, and fifth fractions of the sulphide were separately washed until free from chlorides. As the electrolytes were eliminated, the cadmium sulphide showed a tendency to pass into colloidal condition, which necessitated

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[1] Baxter and Hines: *Amer. Chem. Jour.*, 31, 220 (1904).

long standing for the precipitate to settle after each washing, although the flasks which contained the precipitates were kept warm by being placed upon a steam radiator. During the washing the original fine yellow precipitate was gradually converted into an orange-red crystalline modification. When, as was usually the case, both forms were present in the same flask, the red form quickly settled to the bottom with a sharp line of division from the yellow form. Nearly all the yellow form was changed into the red modification upon standing about three weeks.

In order to free the sulphide from included and occluded impurities each fraction was dissolved and reprecipitated. The red form of the sulphide was apparently nearly insoluble in dilute sulphuric acid, for in one case the washed sulphide was boiled with the acid for 12 hours without any appreciable amount of solution. Finally, hydrochloric acid was used to dissolve the cadmium sulphide. The solution of each fraction was diluted to 8 liters and was saturated with hydrogen sulphide. Since only a portion of the cadmium was precipitated in this way, owing to the large excess of acid, the acid was partially neutralized with ammonia. This resulted in the precipitation of more cadmium sulphide, although the solution still contained considerable cadmium, for cadmium sulphide is soluble to a marked extent in an acid solution of ammonium chloride.

The sulphide obtained from each of the original three fractions, both before and after the addition of ammonia, was combined and washed until free from chlorides. Each fraction was dissolved in redistilled nitric acid, then enough redistilled sulphuric acid to convert the nitrate into sulphate was added, and the solutions were evaporated and the residues heated until all volatile acids were expelled. Finally the sulphate was recrystallized three times from aqueous solution.

The cadmium sulphate was converted into cadmium chloride by first obtaining metallic cadmium electrolytically. A saturated solution of cadmium sulphate was electrolyzed with about one ampere current per square decimeter in a platinum dish, which served as the cathode, until deposition ceased. After the deposit of metal had been thoroughly washed with hot water until free from sulphate, it was dissolved in hydrochloric acid which had been distilled with the use of a platinum condenser.

In order to prepare the double chloride of cadmium and ammonium of the formula $CdCl_2NH_4Cl$, the calculated amount of ammonium chloride was added to the cadmium chloride and the solution evaporated to crystallization. This ammonium chloride was synthesized from hydrochloric acid and ammonia. The hydrochloric acid had been distilled in platinum, and the ammonia had been freed from amines and purified as follows: Ammonium chloride was boiled with concentrated nitric acid for about 20 hours, and then after crystallization was converted into ammonia by distillation with sodium hydroxide. The solution of pure ammonia was distilled into the pure hydrochloric acid in a platinum dish, and the solution of ammonium chloride was evaporated to crystallization.

The cadmium ammonium chloride was crystallized in a platinum dish, eight times in the case of the first fraction, four times in the case of the second fraction. The third fraction of the sulphide was not converted into the double chloride, but was investigated in a later research upon cadmium bromide (see page 21). The first fraction is designated as Sample I, the second as Sample II.

A third specimen used in the analyses was a portion of that employed in the determination of the specific gravity of cadmium chloride.[1] This is designated as Sample A. The method of purification of Sample A was almost exactly identical with that described above, except that the original material was precipitated but not fractionated with hydrogen sulphide.

SILVER.

In the preparation of pure silver essentially the same method was employed as in other atomic weight investigations in this laboratory.[2] In this case the various treatments consisted in thrice precipitating the silver from a dilute solution of silver nitrate in nitric acid by a large excess of hydrochloric acid, with intermediate reduction of the silver chloride in each case by means of invert sugar and sodium hydroxide. The sodium hydroxide for the third reduction was freed from heavy metals by electrolysis. Both the silver chloride and the metallic silver were of course very thoroughly washed by decantation with pure water. The final product was fused on charcoal in the flame of a clean blowpipe. Next the buttons were converted into electrolytic crystals by slow deposition upon a pure silver cathode from a concentrated, nearly neutral solution of silver nitrate, the anode being composed of the pure silver buttons. After thorough washing and drying the crystals were fused in a current of pure electrolytic hydrogen in a boat of pure lime.[3] The lime boat was made by lining an unglazed porcelain boat with a mixture of freshly ignited lime and calcium nitrate, both having previously been carefully freed from iron and other heavy metals. The boat was thoroughly ignited before use.[4] During the fusion it was contained in a large Royal Berlin porcelain tube, the ends of which were closed with hollow brass stoppers made to fit tightly by means of narrow rings of rubber, the stoppers being cooled by a current of cold water.[5] Richards and Wells, in a recent investigation of the purity of silver purified by different

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[1] *Loc. cit.*

[2] See especially Richards and Wells: *Pub. Car. Inst.*, No. 28, 16 (1905); *Jour. Amer. Chem. Soc.*, 27, 472; *Zeit. anorg. Chem.*, 47, 70.

[3] Baxter: *Proc. Amer. Acad.*, 39, 249 (1903); *Zeit. anorg. Chem.*, 38, 237 (1904).

[4] Richards: *Proc. Amer. Acad.*, 30, 379 (1894); *Zeit. anorg. Chem.*, 8, 262 (1895); Richards and Parker: *Proc. Amer. Acad.*, 32, 63 (1896); *Zeit. anorg. Chem.*, 13, 89 (1897).

[5] Richards and Parker: *Loc. cit.*

methods, have found that silver prepared in the above fashion is at least as pure as any.[1] Since the buttons of silver obtained from the fusion in hydrogen were of very considerable size, they were cut into fragments of from 1 to 5 gm. by means of a clean steel chisel and anvil. A slight surface contamination with iron was removed by etching the fragments several times with dilute nitric acid, until the acid remained free from iron, and drying them at 200°.

Two different samples, purified in the same way, were employed. One was prepared especially for this investigation and was used in analyses 4, 5, 6, and 14. The other was a portion of the material employed in an investigation upon the atomic weight of iodine by one of us[2] (analyses 7, 8, and 9). Still a third specimen of silver, used in analyses 13 and 15, was twice deposited electrolytically before the final fusion in hydrogen.

Water was purified by double distillation through tin condensers, first from alkaline permanganate solution, finally with a trace of sulphuric acid. Connection between the flasks and the condensers was made by constricting the necks of the flasks to fit the ends of the condenser tubes, avoiding thus the use of rubber and cork.[3]

Nitric acid was twice distilled with a platinum condenser, the first third being rejected in both distillations. The product of the first distillation contained only the merest trace of chlorine.

PREPARATION OF THE CADMIUM CHLORIDE FOR THE PRELIMINARY ANALYSES.

The method of analysis differed little from that used in the analysis of other halogen salts in atomic weight investigations in this laboratory. The cadmium chloride was freed from ammonium chloride by fusion. Then, after solution in water, the chlorine content was found either gravimetrically as silver chloride or by titration against weighed amounts of silver.

The apparatus used for the expulsion of the ammonium chloride from the double salt was similar to that employed for a like purpose by Richards and Parker[4] in their analysis of magnesium chloride. Since this apparatus was used in two other researches described in this collection, a detailed description is given here. Hydrochloric-acid gas was generated by the action of concentrated sulphuric acid upon concentrated hydrochloric acid in the flask A (fig. 1), and, after bubbling through concentrated hydrochloric-acid solution in the wash bottle B, it was dried by passing through four towers about 30 cm. long and 4 cm. in diameter filled with glass beads saturated with concentrated sulphuric acid, C, D, E, F. In the first series of experiments the hydrochloric-acid

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[1] *Loc. cit.*

[2] Baxter: *Proc. Amer. Acad.*, **40**, 419 (1904); *Jour. Amer. Chem. Soc.*, **26**, 1577; *Zeit. anorg. Chem.*, **43**, 14 (1905). (See page 92.)

[3] Richards: *Proc. Amer. Acad.*, **30**, 380 (1894); *Zeit. anorg. Chem.*, **8**, 261 (1895).

[4] *Proc. Amer. Acad.*, **32**, 59 (1896): *Zeit. anorg. Chem.*, **13**, 85 (1897).

gas was further dried by passing through a tube containing resublimed phosphorus pentoxide. This tube is not shown in the diagram since it was eliminated in the final series of experiments.

Nitrogen was prepared by Wanklyn's method of passing air through concentrated ammonia solution in the bottle M and then over hot copper gauze in the hard glass tube N. The excess of ammonia was removed by dilute sulphuric acid in the bottles O and P, and the nitrogen was purified and dried by means of beads saturated with silver-nitrate solution in the tower Q, solid potassium hydroxide in the tower R, concentrated sulphuric acid in the towers S, T, and U, and resublimed phosphorus pentoxide in the tube L.

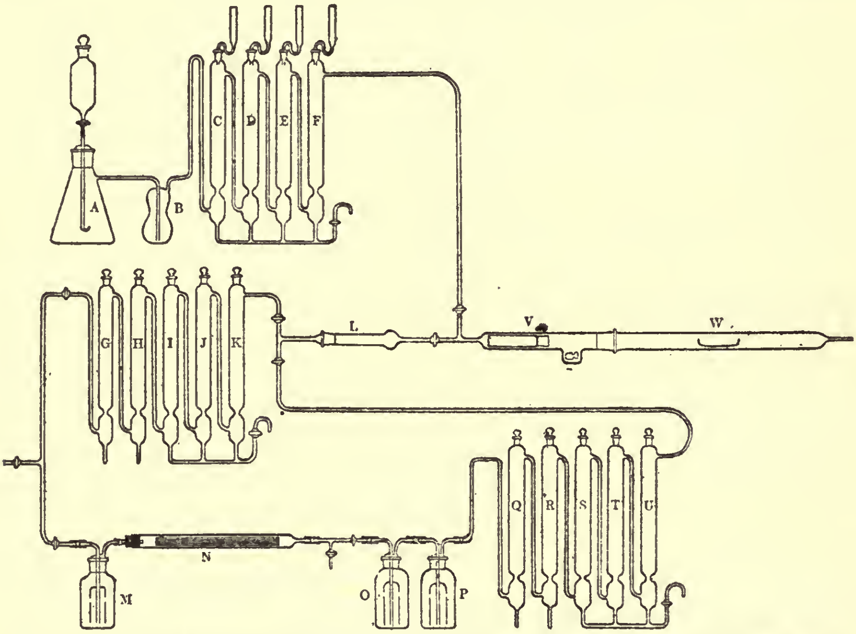

FIG. 1. — Apparatus for the fusion of chlorides in a current of hydrochloric-acid gas.

Air was purified and dried by reagents similar to those used in the purification of the nitrogen, in the towers G, H, I, J, K.

The hydrochloric-acid apparatus was constructed wholly of glass with either ground or fused joints, while the nitrogen and air purifying trains had short rubber connections only at the beginning. Glass gridirons at suitable points gave sufficient flexibility to the apparatus. Ground joints were made tight by means of either concentrated sulphuric acid or with syrupy phosphoric acid.

A portion of the cadmium ammonium chloride, contained in a weighed platinum boat in the hard-glass tube W, was heated gradually to fusion in a current of hydrochloric-acid gas and was kept fused until all the ammonium chloride had been expelled. After the salt had cooled, the hydrochloric acid was displaced by pure dry nitrogen and this in turn by dry air. Next, by means of a glass rod, the boat was pushed into the weighing-bottle contained in the soft-glass tube V, and the stopper was inserted without opening the apparatus or interrupting the current of dry air by rotating the tube V slightly so as to cause the stopper to roll from its position in the pocket of the tube into the main tube. By means of the rod the stopper was readily pushed into place. This bottling apparatus in its improved form was first used by Richards and Parker in their work upon magnesium chloride.[1] The bottle was transferred to a desiccator and, after standing near the balance case for some time, it was weighed by substitution for a counterpoise similar in weight and volume as well as shape.

Sublimation of the cadmium chloride always took place to some extent during the fusion, and the sublimed salt occasioned some difficulty since it flowed down the inside of the glass tube and, upon solidification, firmly cemented the boat to the tube. Furthermore, the salt which adhered to the outside of the boat had thus been fused in contact with glass, and hence may have been impure. Both these difficulties were avoided by supporting the boat upon a carriage of heavy platinum wire. While the salt was still warm and the current of hydrochloric-acid gas was still passing, the boat was pushed out of the carriage by means of a long glass rod. Neglect to observe the latter precaution usually resulted in the cementing of the boat to the carriage by the salt which had condensed upon the outside of the boat.

It has already been shown that barium and calcium chlorides when they have been fused and allowed to solidify in an atmosphere of hydrochloric-acid gas, occlude none of the gas,[2] for they give neutral solutions; hence it is reasonable to conclude that this is the case with cadmium chloride also. However, in order to test this point, in analysis 9 the hydrochloric acid was displaced by nitrogen while the salt was still warm, and in analysis 8 the salt was allowed to solidify only when the hydrochloric acid had been almost completely displaced by nitrogen. In one experiment where the hydrochloric acid had been *completely* displaced by nitrogen, the boat became covered with a gray coating which turned brown, and finally volatilized when the boat was ignited. This coating undoubtedly consisted of metallic cadmium, formed either by the dissociation of cadmium chloride vapor or by the action of the small amount of hydrogen contained in nitrogen produced by Wanklyn's method, owing to catalytic decomposition of the excess of ammonia by the hot copper. The close agreement of the results of analyses 8 and 9 with those obtained in the other analyses where the salt solidified and cooled in hydrochloric acid, shows conclusively that no appreciable amount of hydrochloric acid was occluded by the salt.

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[1] *Loc. cit.*

[2] Richards: *Proc. Amer. Acad.*, **29**, 59 (1893); *Zeit. anorg. Chem.*, **6**, 93 (1894); *Jour. Amer. Chem. Soc.*, **27**, 376 (1902); *Zeit. anorg. Chem.*, **31**, 273.

It was shown in our determination of the specific gravity of cadmium chloride, that the salt when prepared in this way contains no ammonium chloride. It is probable that the cadmium chloride contained no basic compound, since no insoluble salt was produced when the chloride was dissolved in water. The aqueous solution of the salt invariably contained a few tenths of a milligram of black insoluble matter which consisted chiefly of platinum. The presence of this platinum was undoubtedly due partially to slight attacking of the boat, owing perhaps to contamination of the hydrochloric acid with traces of air. The slight loss in weight of the boat which resulted in most of the analyses was not sufficient to account for all the insoluble residue, which, therefore, must have had its source, in part, in the original material. Whether the platinum was dissolved from the platinum condenser during the distillation of the hydrochloric acid, or from the platinum dish during the solution of the cadmium is uncertain. At all events, the temperature to which the salt was heated must have been sufficient to decompose all the platinic or platinous chlorides present, and since the insoluble residue was filtered out and weighed, and corrections applied to the weight of the salt both for the loss in weight of the boat and for the insoluble matter, no appreciable error could have been introduced by the platinum.

THE METHOD OF ANALYSIS.

After the salt had been weighed, the boat was transferred to a flask and the salt was dissolved in about 200 c.c. of the purest water. The weighing-bottle was rinsed and the rinsings were added to the solution. Next the solution was filtered into the precipitating flask through a tiny filter to collect the insoluble matter. Filter-paper and residue were then ignited in a weighed porcelain crucible.

In the preliminary analyses the ratio of cadmium chloride to silver chloride was determined by adding to the solution of cadmium chloride, which had been diluted in the (Erlenmeyer) precipitating flask until not stronger than 1 per cent, a solution of a slight excess of silver nitrate of very nearly the same concentration. The flask, which was provided with a ground-glass stopper, was shaken for some time, and was allowed to stand until the solution was clear. Then the precipitate of silver chloride was transferred to a Gooch crucible, after it had been washed by decantation six or eight times with about 150 c.c. of a 0.001 normal silver nitrate solution, and finally several times with pure water. Needless to say, the operations of precipitation and filtration were performed in a room lighted only with ruby light. The crucible with the precipitate was placed in an air-bath and heated for several hours at 130° to 140° C., and after it had cooled in a desiccator it was weighed. In order to determine how much moisture was retained by the precipitate in each case, it was transferred to a clean porcelain crucible and weighed, then the salt was fused by heating the small crucible, contained in a larger covered crucible, and again weighed. Two different specimens of silver chloride from analyses were separately dissolved in ammonia and reprecipitated with hydrochloric acid, and the filtrates, after evaporation, were tested for cadmium. Negative results were obtained in both cases, showing both that silver chloride does not occlude cadmium salts to an appreciable extent and that the washing of the silver chloride had been thorough.

The determination of the silver chloride dissolved in the wash-waters was the most difficult step in the analysis. At first the last few washings, those which had been carried out with pure water and which were the only ones which could have contained dissolved silver chloride, were evaporated to small bulk and an excess of silver nitrate was added. The precipitate of silver chloride, together with any asbestos which had been displaced from the Gooch crucible, was collected upon a small filter which was ignited and weighed. Owing to the combined effect of organic matter and light upon these solutions the precipitate was always too heavy. Hence this method was finally discarded. Four preliminary results obtained in this way varied between 112.34 and 112.40 for the atomic weight of cadmium.

In order to avoid this error, in the next series the silver chloride dissolved in the wash-waters was determined by precipitating the chloride in 25 c.c. portions of the solution with an excess of silver nitrate, and comparing in a nephelometer the precipitate produced with that from solutions prepared from standard hydrochloric-acid solutions. At least two comparisons were made in each analysis.

The nephelometer employed for the estimation of slight opalescences has already been described in detail by Richards and Wells.[1] All the precautions necessary for the accurate use of this instrument were carefully observed. The two tubes to be compared were always of the same size. The source of light in the nephelometer was so adjusted that tubes containing exactly equal amounts of precipitate gave identical readings. It was found advantageous to insert a plate of ground glass between the source of light and the test-tubes. In making up the test solutions, great pains were taken that the concentration of electrolytes in the two solutions and the conditions of precipitation should be as nearly as possible the same. Final readings were taken only after the ratio between the two tubes had become constant.

The weight of pure silver required exactly to combine with the chlorine in cadmium chloride also was determined. From the weight of cadmium chloride very nearly the necessary quantity of pure silver was calculated. This silver was weighed out and dissolved, in a flask provided with a column of bulbs to prevent loss of silver by spattering (see fig. 2) in distilled nitric acid diluted with an equal volume of water. Ordinarily the silver was caused to dissolve so slowly that practically no gas was evolved. Careful experiments have shown, how-

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[1] *Amer. Chem. Jour.*, **31**, 235 (1904); **35**, 510 (1906).

ever, that the column of bulbs is ample protection against loss by spattering, even when considerable effervescence takes place during the solution.

After the silver was dissolved, the solution was diluted somewhat and heated until free from nitrous fumes. Then it was further diluted until not more concentrated than 1 per cent, and was slowly added to the 1 per cent solution of cadmium chloride in the precipitating flask. After several minutes' shaking it was allowed to stand several days, with occasional shaking, until the solution was perfectly clear. Two 30 c.c. portions of the clear liquid were then pipetted into test tubes of similar size. To one portion was added 1 mg. of silver nitrate in the form of hundredth normal solution, to the other an equivalent amount of hydrochloric-acid solution, and the tubes were examined at frequent intervals in the nephelometer until the ratio of the opalescence shown by the two tubes became constant. Richards and Wells have shown that when equivalent amounts of silver and chloride have been used in the original precipitation, the nephelometer tubes show equal opalescence. If this was not the case in the first examination, the contents of the tubes were returned to the precipitating flask and either standard silver nitrate solution or standard hydrochloric-acid solution was added and the shaking and testing repeated until the amounts of chloride and silver in the solution were equivalent.

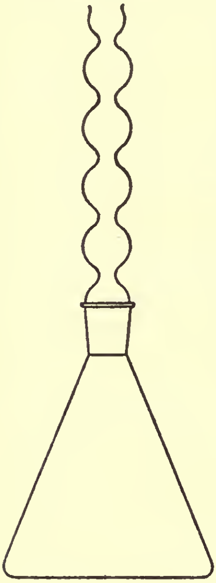
FIG. 2. — Flask for dissolving silver.

Finally a considerable excess of silver nitrate was added to the analysis to precipitate dissolved silver chloride, and the silver chloride was determined gravimetrically as previously described. Correction was of course made for chloride introduced in the course of the nephelometric tests.

A vacuum correction of +0.000152 gm. was applied for every apparent gram of cadmium chloride, of +0.000071 gm. for every apparent gram of silver chloride, and of −0.000031 gm. for every apparent gram of silver.[1]

All weighings were made by substitution, with tare vessels as nearly as possible like those weighed. The gold-plated brass weights were twice carefully standardized to hundredths of a milligram.

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[1] The specific gravity of cadmium chloride has been found to be 4.047. Baxter and Hines: *Amer. Chem. Jour.*, **31**, 220 (1904). Richards and Stull have determined the specific gravity of silver chloride to be 5.56, and Richards and Wells that of silver to be 10.49. *Pub. Car. Inst.*, No **28**, 11 (1905); *Jour. Amer. Chem. Soc.*, **27**, 466; *Zeit. anorg. Chem.*, **47**, 64.

The specific gravity of the weights is assumed to be 8.3. (See page 40.) The use of this low value for the specific gravity of the weights has led to slight changes in the vacuum corrections of cadmium and silver chlorides from the values used in the original publication of this paper.

Preliminary Series of Results. The Atomic Weight of Cadmium.

Ag = 107.880. Cl = 35.457.

Series I. $CdCl_2 : 2AgCl$.

No. of Analysis.	Sample of $CdCl_2$.	Weight of $CdCl_2$ in vacuum.	Weight of Residue.	Loss in weight of boat.	Weight of AgCl in Vacuum.	Loss on fusion.	Weight of AgCl from wash-water.	Weight of asbestos from filtrate.	Corrected weight of $CdCl_2$.	Corrected weight of AgCl.	Atomic weight of cadmium.
		gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	
1	A	5.53494	0.00082	0.00007	8.65042	0.00132	0.00304	0.00139	5.53419	8.65353	112.423
2	I	7.77843	0.00096	0.00008	12.16016	0.00180	0.00254	0.00071	7.77755	12.16161	112.419
3	II	8.87947	0.00034	0.00000	13.88229	0.00030	0.00130	0.00009	8.87913	13.88338	112.429
										Average,	112.424

Series II. $CdCl_2 : 2Ag$.

No. of Analysis.	Sample of $CdCl_2$.	Weight of $CdCl_2$ in vacuum.	Weight of residue.	Loss in weight of boat.	Weight of Ag in vacuum.	Weight of Ag added or subtracted.	Corrected weight of $CdCl_2$	Corrected weight of Ag.	Atomic weight of cadmium.
		gm.	gm.	gm.	gm.	gm.	gm.	gm.	
4	II	4.92896	0.00040	0.00003	5.80263	−0.00200	4.92859	5.80063	112.410
5	II	3.86523	0.00057	0.00019	4.54911	−0.00020	3.86485	4.54891	112.401
6	II	5.08569	0.00042	0.00022	5.98549	+0.00020	5.08549	5.98569	112.398
7	I	5.84373	0.00047	0.00007	6.87704	0.00000	5.84333	6.87704	112.415
8	I	5.99961	0.00011	0.00000	7.06084	0.00000	5.99950	7.06084	112.415
9	A	3.73112	0.00021	0.00000	4.39095	0.00000	3.73091	4.39095	112.414
								Average,	112.409
								Average of Series I and II,	112.417

The close agreement of the results in each series leaves little doubt of the identity of the different samples, although they represent material from different sources as well as different fractions of the same material. The slight discrepancy between the results by the two methods is undoubtedly due, in part, to the difficulty in determining silver chloride with accuracy, owing, in the first place, to loss of chlorine by the silver chloride in the processes of manipulation and drying, and in the second place to the slight solubility of silver chloride even in dilute silver nitrate solutions. In the light of these possibilities, it is probable that the results of Series I are slightly too high. On the other hand, it is probable that the average of Series II is slightly too low, for the average of experiments 7, 8 and 9, in which the experience gained in the previous analyses was a very considerable aid, is 112.415, 0.006 of a unit higher than the average of the whole series.

ACTION OF HYDROCHLORIC-ACID GAS UPON PHOSPHORUS PENTOXIDE.

Some time after the completion of the foregoing series of experiments it was found that in fusing manganous chloride, in a current of hydrochloric-acid gas which had been dried by concentrated sulphuric acid and finally by means of phosphorus pentoxide, an insoluble residue of manganous phosphate was invariably obtained when the salt was dissolved in water. The quantity of this residue varied with the amount of moisture contained by the salt when brought in contact with the hydrochloric-acid gas, being extremely slight if the salt was very nearly dry, but amounting to several milligrams if the salt still contained much of its crystal water. Although it seemed certain that the phosphorus had its origin in the phosphorus pentoxide, and was volatilized in the form of either phosphorus pentachloride or oxychloride through the action of the hydrochloric acid upon the pentoxide, in order to obtain still more positive evidence that this was really the case, the experiment was tried of passing hydrochloric-acid gas which had been dried thoroughly by means of sulphuric acid, first over phosphorus pentoxide which had been freshly sublimed in a current of dry air, and then into water. The aqueous solution, upon evaporation and testing with ammonium molybdate, gave a considerable amount of the characteristic ammonium phosphomolybdate. This result confirms that of Bailey and Fowler,[1] who have found that both hydrochloric and hydrobromic acids react with phosphorus pentoxide at ordinary temperatures to form the oxychloride and bromide of phosphorus respectively. The manganous phosphate, then, must have been produced by the action of the volatilized chloride of phosphorus upon the moisture contained by the manganous chloride to form phosphoric acid, with subsequent displacement of hydrochloric acid from the salt by the phosphoric acid.

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[1] *Chem. News*, **58**, 22 (1888).

Although in our work with cadmium chloride, the double cadmium ammonium chloride was fused in a current of hydrochloric-acid gas which had been finally dried with phosphorus pentoxide, the salt, which contains no crystal water, was essentially free from moisture before coming in contact with the hydrochloric acid. Nevertheless it seemed desirable to repeat the experiments with cadmium chloride in such a way that the danger mentioned above could be completely avoided. This result was easily attained by drying the hydrochloric-acid gas with concentrated sulphuric acid only.

In order to ascertain whether concentrated sulphuric acid is appreciably attacked by hydrochloric-acid gas, a large quantity of this gas was conducted through the columns and then into water. The aqueous solution was then evaporated and tested for sulphate with barium chloride. Although a slight precipitate of baric sulphate was produced, the quantity was estimated, by comparison in a nephelometer with a standard solution of a sulphate, to be less than 0.05 mg. Evidently nothing is to be feared from this source.

PREPARATION AND DRYING OF CADMIUM CHLORIDE FOR THE FINAL ANALYSES.

The material for these experiments was prepared from a portion of fraction II of cadmium sulphide, by first depositing the metal electrolytically from the sulphate. At first electrolysis was carried on in a solution of the sulphate in pure water, between two electrodes of platinum foil. A sponge of extremely small crystals was thus produced. These crystals contained occluded sulphate in considerable quantities, and no amount of washing with water was sufficient completely to leach out this occluded material. More satisfactory results were obtained by depositing the metal upon a platinum dish which had been covered with a very thin film of soft paraffine, so that the deposit could be readily separated from the dish.[1] The cadmium was first washed with water, then with ether, next with alcohol, and finally with water again. This treatment effectually cleansed the metal from paraffine.

The metal was next dissolved in pure hydrochloric acid in a platinum dish. The chloride does not lend itself readily to crystallization from aqueous solution on account of its great solubility even at low temperatures, but by conducting hydrochloric-acid gas into the solution the much less soluble double salt with hydrochloric acid, $CdCl_22HCl7H_2O$, was formed. The salt was thus crystallized 3 times with centrifugal drainage, to free it from the trace of sulphates occluded by the metal during electrolysis. Finally, it was dried and freed from hydrochloric acid as far as possible in a vacuum desiccator containing solid potassium hydroxide.

Before fusion the salt was largely freed from water and hydrochloric acid by gentle heating.

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[1] Richards: *Proc. Amer. Acad.*, **25**, 200 (1890).

FINAL SERIES OF RESULTS. THE ATOMIC WEIGHT OF CADMIUM.

Series III. $CdCl_2 : 2AgCl$.

No. of analysis.	Sample of $CdCl_2$.	Weight of $CdCl_2$ in vacuum.	Weight of residue.	Loss in weight of boat.	Weight of AgCl in vacuum.	Loss on fusion.	Weight of asbestos from filtrate.	Weight of AgCl from washwaters.	Corrected weight of $CdCl_2$.	Corrected weight of AgCl.	Atomic weight of cadmium.
		gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	
10	II	6.11755	0.00004	+0.00003	9.56428	0.00013	0.00024	0.00147	6.11748	9.56586	112.418
11	II	6.81037	0.00026	0.00017	10.64727	0.00010	0.00061	0.00136	6.81028	10.64914	112.419
12	II	5.50095	0.00017	0.00009	8.59937	0.00008	0.00052	0.00190	5.50087	8.60171	112.417
										Average,	112.418

Series IV. $CdCl_2 : 2Ag$.

No. of analysis.	Sample of $CdCl_2$.	Weight of $CdCl_2$ in vacuum.	Weight of residue.	Loss in weight of boat.	Weight of Ag in vacuum.	Weight of Ag added or subtracted.	Corrected weight of $CdCl_2$.	Corrected weight of Ag.	Atomic weight of cadmium.
		gm.	gm.	gm.	gm.	gm.	gm.	gm.	
13	II	5.62509	0.00015	0.00004	6.61993	0.00000	5.62498	6.61193	112.419
14	II	6.81037	0.00026	0.00017	8.01516	0.00020	6.81028	8.01496	112.417
15	II	5.50095	0.00017	0.00009	6.47393	0.00000	5.50087	6.47393	112.417
								Average,	112.418
								Average of Series III and IV	112.418

The average of these results is almost identical with that obtained in the first two series of analyses, 112.417, hence it is evident that no serious error was introduced in our earlier work by the use of phosphorus pentoxide for drying hydrochloric-acid gas.

The results of this investigation may be summarized as follows:

1. In the analysis of cadmium chloride, both gravimetrically by determination of the chlorine as silver chloride and volumetrically by comparison with silver, the atomic weight of cadmium is found to be 112.418 referred to silver 107.880, or 112.408 if silver has the atomic weight 107.870.
2. Phosphorus pentoxide is found to be attacked by pure hydrochloric-acid gas, and hence is unsuited for drying this gas, thus confirming the results of Bailey and Fowler.
3. It is shown that no appreciable error is introduced from this source, if a *dry* salt is fused in a current of hydrochloric acid which has been dried by phosphorus pentoxide.

II.

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

THE ANALYSIS OF CADMIUM BROMIDE.

By Gregory Paul Baxter, Murray Arnold Hines, and Harry Louis Frevert.

Journal of the American Chemical Society, **28**, 770 (1906).
Zeitschrift für anorganische Chemie, **49**, 415 (1906).
Chemical News, **94**, 224, 236, 248 (1906).

Contributions from the Chemical Laboratory of Harvard College.

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

THE ANALYSIS OF CADMIUM BROMIDE.

Since the research described in the preceding paper indicates that the atomic weight of cadmium is nearly one tenth of a unit higher than the results of recent prior determinations by other investigators, in order to confirm or disprove the higher value the analysis of cadmium bromide was undertaken.

PURIFICATION OF MATERIALS.

CADMIUM BROMIDE.

The cadmium material employed for the work consisted of fractions II and III of sulphide, which were obtained in the earlier investigation (page 4). Here also the sulphide was first converted into sulphate, and after crystallization of the sulphate the cadmium was deposited electrolytically upon a platinum dish which had been coated with a thin film of paraffine. The deposit was separated from the dish mechanically and after washing with water was freed from paraffine with redistilled ether and alcohol. By the method finally adopted for converting the cadmium into bromide, it was covered in a quartz dish with water slightly acidified with hydrobromic acid to prevent the formation of basic cadmium salts, and the purest bromine was added in small quantities until the metal was almost wholly dissolved. The solution was heated with the residual metallic cadmium upon a steam-bath until every trace of bromine had disappeared. Then it was filtered with a platinum funnel into a platinum dish, and was recrystallized three times, with centrifugal drainage in the platinum funnel after each crystallization.[1] The original solution contained only traces of sulphate, and, when tested with barium hydroxide, the mother-liquors of the third crystallization gave absolutely no test for sulphate, hence the crystals themselves must have been pure (Samples II and III). The crystals were dried over potassium hydroxide in a vacuum desiccator.

BROMINE.

Commercial bromine was freed from chlorine by two distillations from a concentrated solution of a bromide, the bromide in the second distillation being almost free from chloride. The bromine was covered with water, and hydrogen sulphide, which had been thoroughly washed with water, was passed into the

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[1] Richards: *Jour. Amer. Chem. Soc.*, 27, 110 (1905).

solution until reduction of the bromine was complete. The solution was boiled, after mechanical separation of the greater part of the free sulphur and bromide of sulphur, and was filtered. Iodine was eliminated by boiling the hydrobromic acid with several small portions of potassium permanganate and rejecting the bromine set free. By heating the remainder of the hydrobromic acid with an excess of permanganate, over half of the bromine was obtained in the free state. The process of reduction with hydrogen sulphide and oxidation with permanganate was then repeated with the resulting bromine, and the final product was redistilled shortly before use.

SILVER.

One sample of silver was purified especially for this research. The processes to which it was subjected consisted first of precipitation as chloride from nitric-acid solution and reduction with invert sugar and sodium hydroxide. After fusion with a blowpipe on a crucible of the purest lime the metallic buttons were freed from surface impurities by scrubbing with moist sand and etching with nitric acid. Next the buttons were dissolved in nitric acid and the solution was reduced with ammonium formate.[1] The precipitated silver was thoroughly washed and again fused on a lime crucible. The final process of purification consisted in electrolyzing the silver as described on page 6. The electrolytic crystals were fused in a current of hydrogen on a lime boat, and the buttons, after cleansing with nitric acid and drying at 200°, were cut into fragments of convenient size with a clean chisel and anvil. Then they were again treated with fresh portions of dilute nitric acid until free from iron, washed, dried, and finally heated to about 400° in a vacuum. This silver was employed in analyses 4 to 8.

In the first three analyses a mixture of two specimens of silver was employed, both of which had already been used in an investigation upon the atomic weight of iodine by one of us.[2] One was prepared from silver nitrate which had been seven times recrystallized from nitric acid, five times recrystallized from water, and finally precipitated with ammonium formate. The other was precipitated once as silver chloride, electrolyzed once, and finally reduced with ammonium formate.

DRYING OF CADMIUM BROMIDE FOR ANALYSIS.

The method of analysis was essentially that usually employed in this laboratory for the analysis of metallic halides. Weighed portions of the bromide, after fusion in nitrogen and hydrobromic-acid gases, were first titrated against weighed portions of silver. Then the precipitated silver bromide was collected and weighed.

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[1] Richards: *Pub. Car. Inst.* No. **28**, p. 19 (1905); *Jour. Amer. Chem. Soc.*, **27**, 475; *Zeit. anorg. Chem.*, **47**, 72.

[2] Baxter: *Proc. Amer. Acad.*, **41**, 79 (1905); *Jour. Amer. Chem. Soc.*, **27**, 881; *Zeit. anorg. Chem.*, **46**, 42. (See page 108.)

The apparatus used for the fusion of the salt in nitrogen and hydrobromic-acid gases was employed in the preparation of ferrous bromide by one of us,[1] and is a modification of apparatus used for a similar purpose in the determination of the atomic weight of cobalt,[2] in this laboratory. Nitrogen was prepared by passing air through concentrated ammonia solution in the bottle F (fig. 3) and then over hot copper gauze in the hard-glass tube G. The excess of ammonia was removed by dilute sulphuric acid in the bottles H and I. The gas was then conducted into an apparatus constructed wholly of glass, with ground joints, which consisted of a tower, J, filled with beads moistened with silver nitrate solution to remove sulphur compounds, two similar towers, K and L, containing dilute sulphuric acid to eliminate last traces of ammonia, and two towers, M and N, filled with sticks of fused potassium hydroxide to absorb moisture and carbon dioxide. The partially dried gas, after bubbling through bromine in a small flask, P, passed into a second flask, Q, containing concentrated hydrobromic-acid solution in which washed red phosphorus was suspended, to convert the bromine into hydrobromic acid. A U-tube, R, also containing red phosphorus and hydrobromic acid, removed traces of bromine which escaped reduction in the flask. Two additional U-tubes, S and T, containing beads moistened with concentrated hydrobromic acid only, served to eliminate phosphorus compounds which were found, in the investigation upon ferrous bromide,[3] to accompany the hydrobromic acid if the phosphorous acid in the reduction flask was allowed to become very concentrated. Finally, the mixture of

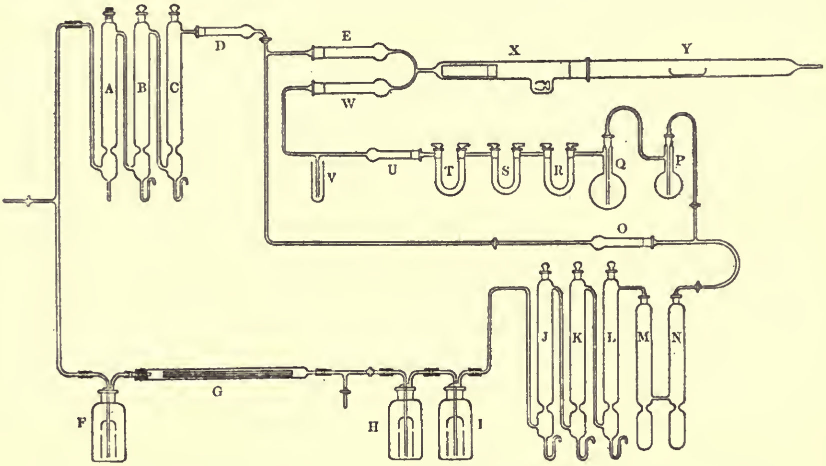

FIG. 3. — Apparatus for the fusion of bromides in a current of dry nitrogen and hydrobromic-acid gases.

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[1] Baxter: *Proc. Amer. Acad.*, **39**, 246 (1903); *Zeit. anorg. Chem.*, **38**, 233 (1904).

[2] Richards and Baxter: *Proc. Amer. Acad.*, **33**, 117 (1897); *Zeit. anorg. Chem.*, **16**, 372 (1898).

[3] *Loc. cit.*

nitrogen and hydrobromic-acid gases was thoroughly dried, first by pure fused calcium bromide, in the tube U, and then by resublimed phosphorus pentoxide in the tube W.

If desired the nitrogen could be passed directly through the phosphorus pentoxide tube O into the bottling apparatus XY, in which the fusion took place.

Air was purified and dried by passing over fused potassium hydroxide in the tower A, concentrated sulphuric acid in the towers B and C, and phosphorus pentoxide in the tubes D and E.

The cadmium bromide, contained in a weighed platinum boat, was heated gently in a current of nitrogen until a small quantity of residual crystal water was expelled, then strongly in a current of nitrogen and hydrobromic acid until fused. After the salt had cooled, the hydrobromic acid was displaced by nitrogen and this in turn by dry air. During the displacement of the hydrobromic acid by nitrogen and air a slight backward current of gas was maintained through the tube W and the trap V. The boat was then transferred to the weighing-bottle in which it was originally weighed, and the stopper was inserted without an instant's exposure of the salt to moisture, by means of the bottling apparatus which has been referred to on page 9. The weighing-bottle was then allowed to stand in a desiccator near the balance case for some time before it was weighed.

METHOD OF ANALYSIS.

Next the boat was transfered to a flask and the salt was dissolved in about 300 c.c. of the purest water. The weighing-bottle was rinsed and the rinsings were added to the solution. Then the solution was filtered into the glass-stoppered precipitating flask through a tiny filter to collect a trace of insoluble matter, and the filter-paper and residue were ignited at a low temperature in a weighed porcelain crucible. This residue, which usually amounted to less than 0.1 mg. and was never as much as 0.2 mg., did not contain detectable quantities of cadmium, and probably consisted of silica and a trace of platinum removed from the boat during the fusion, for the boat, when reweighed, in most cases was found to have lost a few hundredths of a milligram. No change in weight could be found when the boat was first dried and weighed, then ignited and reweighed. The difference between the weight of the residue and the loss in weight of the boat was subtracted from the weight of the cadmium bromide.

From the corrected weight of the cadmium bromide very nearly the requisite quantity of pure silver was calculated. This silver was weighed out and dissolved, in nitric acid diluted with an equal volume of water, in the flask described on page 12. After the silver was dissolved, the solution was diluted to twice its volume and was heated until free from nitrous fumes. Then it was still further diluted until not stronger than 1 per cent, and was slowly added, with constant stirring, to the 1 per cent solution of cadmium bromide in the precipitating flask. In three analyses (4, 5 and 8), this procedure was varied by adding the bromide to the silver nitrate. After being shaken for some time, the solution was allowed to stand several days, with occasional shaking, until the supernatant liquid was clear. 30 c.c. portions of the solution were then tested with hundredth normal solutions of silver nitrate and sodium bromide in the nephelometer[1] for excess of bromide or silver, and, if necessary, either standard silver nitrate or sodium bromide solution was added, and the process of shaking and testing repeated, until the amounts of bromide and silver in the solution were equivalent. If the solution was perfectly clear when tested, and contained no considerable excess of bromide or silver, the test solutions were discarded, since they contained only negligible amounts of dissolved silver bromide; otherwise they were returned to the flask and a correction was applied for the silver bromide thus introduced.

As soon as the exact end-point of the titration had been found, about 4 cg. of silver nitrate in excess were added, to precipitate dissolved silver bromide, and the flask was again shaken and allowed to stand until clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible, after it had been washed by decantation about eight times with pure water. Then it was heated in an electric air-bath, first for several hours at 140°, finally for an hour at 200°, and, after it had cooled in a desiccator, it was weighed. In order to determine how much moisture was retained by the precipitate, in each case it was transferred as completely as possible to a clean porcelain crucible and weighed; then the salt was fused by heating the small covered crucible, contained in a large crucible, and again weighed. After fusion the silver bromide was light yellow, with only a trace of darkening, showing that no appreciable reduction had taken place. The asbestos mechanically detached from the Gooch crucible, together with a minute quantity of silver bromide which occasionally escaped the crucible, was collected from the filtrate and wash-waters upon a small filter, the ash of which was treated with nitric and hydrobromic acids before weighing. Although the filtrates and first wash-waters were essentially free from dissolved silver bromide, the subsequent wash-waters usually contained a trace of this substance. The amount of dissolved salt was determined with the nephelometer by comparison with standard bromide solutions. Finally, the weight of silver bromide was corrected for the sodium bromide introduced.

Although in our analyses of cadmium chloride no evidence could be obtained of appreciable occlusion of either cadmium or silver salts by silver chloride, especial precautions were taken to avoid any possibility of such a difficulty in this research. In the first place both the cadmium bromide and the silver nitrate solutions were very dilute during precipitation, each one having a volume of about 1 liter. In the second place the method of precipitation was

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[1] See page 11.

varied by sometimes adding the silver nitrate to the cadmium bromide (analyses 1, 2, 3, 6, and 7), and sometimes adding the bromide to the silver nitrate (analyses 4, 5, and 8). And in the third place the solutions were allowed to stand varying periods before the titration was completed, so that occluded substances might have opportunity to be dissolved. Analysis 1, in which the largest quantity of bromide was employed, over 11 gm., which is to be expected to give the most marked evidences of occlusion, was not tested for 5 days after precipitation, and the titration was completed 8 days later. In the other analyses the period between precipitation and the completion of the titration varied from 7 days in analysis 4 to 3 days in analysis 8. Furthermore, in some cases, after the end-point had been reached, the solutions were allowed to stand some days longer with occasional testing. No change in end-point with standing was observed. In spite of these differences in the method of procedure, the variations in the final results do not exceed the experimental error to be expected, except in the case of analyses 4 and 12. Evidently, occlusion of any sort must have been very slight if it existed at all. Analyses 4 and 12, performed with the same portion of bromide, differ so markedly from the others that, although no reason for the difference is known, they are rejected in computing the final average.

The gold-plated brass weights were carefully standardized to hundredths of a milligram. Vacuum corrections of +0.000086 for cadmium bromide,[1] of +0.000041 for silver bromide and of −0.000031 for silver were applied. All weighings were made by substitution with counterpoises as nearly like the objects to be weighed as possible.

The analytical work was performed wholly by Dr. Hines. (See table on opposite page.)

RESULTS AND DISCUSSION.

The ratios of silver used to silver bromide obtained in the same analysis afford sufficient proof of the purity of the bromine and silver, as well as confirmatory evidence of the absence of appreciable occlusion by the silver bromide.

			Ag : AgBr.
Analyses 1	and	9	57.4446
2	"	10	57.4466
3	"	11	57.4438
4	"	12	57.4438
5	"	13	57.4423
6	"	14	57.4440
7	"	15	57.4430
8	"	16	57.4431
		Average,	57.4439

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[1] The specific gravities of cadmium and silver bromides have recently been found to be 5.192 and 6.473 respectively. Baxter and Hines: *Amer. Chem. Jour.*, **31**, 220 (1904).

As in the case of cadmium chloride, slight changes in the vacuum corrections of cadmium and silver bromides have been made from the values employed in the original publication of this paper, owing to more exact knowledge of the density of the weights.

The Atomic Weight of Cadmium.

Ag = 107.880 Br = 79.916

Series I. $CdBr_2 : 2Ag$.

No. of analysis.	Sample of $CdBr_2$.	Weight of $CdBr_2$ in vacuum.	Weight of residue.	Loss in weight of boat.	Weight of Ag in vacuum.	Weight of Ag added or subtracted.	Corrected weight of $CdBr_2$.	Corrected weight of Ag.	Atomic weight of cadmium.
		gm.	gm.	gm.	gm.	gm.	gm.	gm.	
1	II	11.46215	0.00008	0.00004	9.08409	−0.00030	11.46211	9.08379	112.419
2	II	6.82291	0.00018	0.00006	5.40734	−0.00010	6.82279	5.40724	112.412
3	II	6.75432	0.00011	+0.00004	5.35297	−0.00020	6.75417	5.35277	112.416
4	III	7.08587	0.00006	0.00004	5.61567	+0.00030	7.08585	5.61597	112.400
5	III	5.13865	0.00008	0.00000	4.07236	−0.00010	5.13857	4.07226	112.424
6	III	5.84326	0.00008	0.00004	4.63092	−0.00020	5.84322	4.63072	112.422
7	III	5.99710	0.00008	0.00000	4.75269	−0.00010	5.99702	4.75259	112.423
8	II	5.90809	0.00017	0.00002	4.68200	0.00000	5.90794	4.68200	112.423

Average, rejecting analysis 4, 112.421

Series II. $CdBr_2: 2AgBr$.

No. of analysis.	Sample of $CdBr_2$.	Weight of $CdBr_2$ in vacuum.	Weight of residue.	Loss in weight of boat.	Weight of AgBr in vacuum.	Loss on fusion.	Weight of asbestos from filtrate.	Weight of AgBr from wash-waters.	Corrected weight of $CdBr_2$.	Corrected weight of AgBr.	Atomic weight of cadmium.
		gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	
9	II	11.46215	0.00008	0.00004	15.81279	0.00024	0.00024	0.00033	11.46211	15.81311	112.415
10	II	6.82291	0.00018	0.00006	9.41246	0.00028	0.00044	0.00000	6.82279	9.41262	112.418
11	II	6.75432	0.00011	+0.00004	9.31810	0.00028	0.00043	0.00000	6.75417	9.31825	112.409
12	III	7.08587	0.00006	0.00004	9.77552	0.00013	0.00053	0.00052	7.08585	9.77644	112.393
13	III	5.13865	0.00008	0.00000	7.08893	0.00007	0.00043	0.00000	5.13857	7.08929	112.410
14	III	5.84326	0.00008	0.00004	8.06072	0.00005	0.00033	0.00026	5.84322	8.06126	112.416
15	III	5.99710	0.00008	0.00000	8.27317	0.00012	0.00020	0.00031	5.99702	8.27356	112.412
16	II	5.90809	0.00017	0.00002	8.15018	0.00015	0.00037	0.00026	5.90794	8.15066	112.412

Average rejecting analysis 12, 112.413

Average of Series I and II, 112.417

The most probable value for this ratio has been shown by Baxter to be 57.4453.[1]

In the preceding paper Bailey and Fowler's[2] statement that hydrochloric-acid gas is contaminated with volatile compounds of phosphorus, if it is dried with phosphorus pentoxide, is confirmed. Although Bailey and Fowler attribute to hydrobromic acid an effect similar to that of hydrochloric acid, for several reasons it is certain that in the experiments upon cadmium bromide no appreciable amount of phosphorus was introduced into the salt by the action of the hydrobromic acid upon the phosphorus pentoxide. In the first place, the experiment of passing into water hydrobromic-acid gas, formed as in our work by passing nitrogen through bromine and then through an emulsion of red phosphorus in concentrated hydrobromic-acid solution, and dried first by fused calcium bromide and then by phosphorus pentoxide, was performed in this laboratory some years ago in connection with the analysis of cobalt and nickel bromides. In this experiment no phosphorus could be discovered in the aqueous solution. In the second place, in two analyses of bromides which had been heated in hydrobromic-acid gas, the filtrates from the silver-bromide precipitates were evaporated to small bulk and tested for phosphoric acid, with negative results, while the slight residues obtained by filtering the aqueous solutions of the original bromides also showed in one case the complete absence of phosphorus, and in the other the presence of only a minute trace of this substance, although in the latter case the salt had been sublimed in a current of hydrobromic acid and therefore contained maximum amounts of phosphorus.[3] This result was to be expected from a consideration of the fact that the hydrobromic-acid gas used in these experiments was diluted with at least twice its volume of nitrogen. In the light of this evidence it seems safe to assume that in the numerous analyses of bromides which have been carried out in this laboratory in recent years, no error was introduced by the use of phosphorus pentoxide as drying agent for the hydrobromic-acid gas. Nevertheless, with more concentrated hydrobromic acid, doubtless it would be unwise to use this drying agent.

It is interesting to compare the results of the analyses of the different fractions of material in this research and in the preceding one. (See table on opposite page.)

The close agreement of the results from fraction II by different methods and of the results from all three fractions leaves no doubt of the identity of the different specimens of material.

No matter how the results are averaged, the same conclusion is reached as in the previous paper, *i. e.*, that the atomic weight of cadmium lies very near the

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[1] *Proc. Amer. Acad.*, **42**, 210 (1906); *Jour. Amer. Chem. Soc.*, **28**, 1332; *Zeit. anorg. Chem.*, **50**, 398. (See page 51.)

[2] *Chem. News*, **58**, 22 (1888).

[3] Baxter: *Proc. Amer. Acad.*, **39**, 248 (1903); *Zeit. anorg. Chem.*, **38**, 236.

value 112.417 (Ag = 107.880). If the atomic weight of silver is 107.870, then the atomic weight of cadmium is 112.407.

Fraction.	Ratio.	Atomic weight.	Average.
I	$CdCl_2$: 2Ag	112.415	112.417
I	$CdCl_2$: 2AgCl	112.419	
II, Series 1	$CdCl_2$: 2Ag	112.403	112.416
II, Series 1	$CdCl_2$: 2AgCl	112.429	
II, Series 2	$CdCl_2$: 2Ag	112.418	112.418
II, Series 2	$CdCl_2$: 2AgCl	112.418	
II	$CdBr_2$: 2Ag	112.418	112.416
II	$CdBr_2$: 2AgBr	112.414	
III	$CdBr_2$: 2Ag	112.423	112.418
III	$CdBr_2$: 2AgBr	112.413	
	Average . .	112.417	112.417

Attention should be called to the agreement with ours of the results of Morse and Arbuckle's synthesis of cadmium oxide, which yielded the value 112.38, and of Bucher's painstaking work upon the halogen compounds of cadmium. Bucher's values from cadmium chloride vary between 112.21 and 112.41, with an average of 112.32, but if the first 7 of his 21 experiments are rejected, his average becomes 112.35, and 6 of his results are as high as 112.38. His analyses of the bromide vary between 112.25 and 112.41, with an average of 112.34.

The results of this investigation are then as follows:

(1) The value for the atomic weight of cadmium previously found by analysis of cadmium chloride, 112.42 (Ag = 107.880), is supported by the analysis of cadmium bromide. If silver is 107.870, cadmium becomes 112.41.

(2) It is pointed out that phosphorus pentoxide is not perceptibly attacked by hydrobromic-acid gas which is diluted with twice its volume of nitrogen.

III.

A REVISION OF THE ATOMIC WEIGHT OF MANGANESE.

THE ANALYSES OF MANGANOUS BROMIDE AND CHLORIDE.

By Gregory Paul Baxter and Murray Arnold Hines.

Journal of the American Chemical Society, 28, 1560 (1906).
Zeitschrift für anorganische Chemie, 51, 202 (1906).
Chemical News, 95, 102, 111, 123 (1907).

Contributions from the Chemical Laboratory of Harvard College.

A REVISION OF THE ATOMIC WEIGHT OF MANGANESE.

THE ANALYSES OF MANGANOUS BROMIDE AND CHLORIDE.

INTRODUCTION.

The following table, adapted from Clarke's "A Recalculation of the Atomic Weights"[1] gives a brief résumé of previous work upon the atomic weight of manganese which has other than historical interest.

Date.	Investigator.	Reference.	Ratio determined.	Result.
1830	Berzelius . . .	Ann. Physik. Chem., **18**, 74	$MnCl_2 : 2AgCl$	55.10
1831	Turner	Trans. Roy. Soc., Edinb. **11**, 143	$MnCl_2 : 2AgCl$	54.90
1857	von Hauer . .	J. pr. Chem., **72**, 360	$MnSO_4 : MnS$	54.91
1859	Schneider . . .	Ann. Physik. Chem., **107**, 605	$Mn : 2CO_2$	54.03
	Rawack	Ibid.	$Mn_3O_4 : H_2O$	54.08
1860	Dumas	Ann. Chem. Pharm., **113**, 25	$MnCl_2 : 2Ag$	54.96
1883	Dewar and Scott	Proc. Roy. Soc., **35**, 44	$AgMnO_4 : AgMnO$	55.01
			$AgMnO_4 : KBr$	55.04
1883	Marignac . . .	Arch. sci. phys. nat., [3] **10**, 21	$MnO : MnSO_4$	55.01
1890	Weeren	Dissertation, Halle	$MnO : MnSO_4$	55.00
			$MnS : MnSO_4$	55.00

The close agreement of the greater part of these determinations is striking, the experiments of Schnieder and Rawack being the only ones which indicate a value for manganese very different from 55.0. The variations of their results from the others is not surprising, however, since manganoso-manganic oxide and manganous oxalate, with which they worked, are undoubtedly difficult to obtain in a pure condition. The remaining determinations all fall within limits two tenths of a unit apart, and all but two agree within thirteen hundredths of a unit.

For this investigation the substances chosen for examination were manganous bromide and chloride, since the analysis of halogen compounds may be effected with great accuracy. Furthermore, these compounds have not been investigated by any of the more recent experimenters except Dewar and Scott,[2] who performed one analysis each of the chloride and bromide and obtained the values 54.89 and 54.95 respectively.

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[1] *Smith. Misc. Coll.*, The Constants of Nature, Part V., 1910. The results have been calculated with the use of the following atomic weights: O = 16.00; C = 12.00; S = 32.07; Cl. = 35.46; K = 39.10: Ag = 107.88.

[2] *Loc. cit.*

THE ANALYSIS OF MANGANOUS BROMIDE.

PURIFICATION OF MATERIALS.

All of the water used in either the purification or the analyses was twice distilled, once from a dilute alkaline solution of potassium permanganate and then from a very dilute sulphuric-acid solution. Block-tin condensers were used in both distillations and the apparatus contained no rubber or cork connections. The water was collected as a rule in Jena glass flasks, although for special purposes either platinum or quartz receivers were substituted.

Acids and ammonia also were distilled shortly before use, either platinum or quartz condensers and receivers being employed when necessary. Solid reagents were recrystallized, usually with centrifugal drainage.

Special pains were taken in all the work to prevent the introduction of alkalies or silica into the purest materials, by avoiding as far as possible the use of glass vessels.

MANGANOUS BROMIDE.

Four different specimens of manganous bromide were employed, which were obtained from different sources and were purified in different ways. In the case of Samples A and B, purification of the manganese from other heavy metals was accomplished by recrystallization of Merck's "chemically pure" potassium permanganate. Sample A was crystallized three times only, while Sample B was thus treated ten times, the last two crops of crystals being thoroughly freed from the mother-liquors by centrifugal drainage.

In order to free the manganese from potassium and convert it into the bromide, the following processes were employed with Sample A: First the permanganate was dissolved in water and was reduced by passing sulphur dioxide into the solution. This sulphur dioxide was made by heating copper turnings with concentrated sulphuric acid and was purified from copper compounds mechanically carried along by passing through three gas washing-bottles, each containing a solution of sulphurous acid, and one column of beads moistened with a similar solution. From the solution of potassium and manganous sulphates the manganese was precipitated by the addition of an alkaline solution of ammonium carbonate. The manganous carbonate was washed with water until the washings were free from sulphates, then it was dissolved in nitric acid, which had been redistilled until free from chlorine, and the manganous nitrate was recrystallized six times from a solution strongly acid with nitric acid, four times in a glass vessel, twice in platinum.

Usually it was necessary to start crystallization by inoculation, and cooling with ice was found advisable for the sake of economy in material. From a dilute solution of the purified nitrate in a platinum vessel, the manganese was again precipitated as carbonate, by means of ammonium carbonate which had been freshly made by passing pure carbon dioxide into distilled ammonia in a platinum flask. The resulting manganous carbonate, after thorough washing with water containing a small amount of ammonia to prevent colloidal solution of the carbonate, was readily converted into bromide by solution in hydrobromic acid. Since it was probable that the carbonate contained occluded nitrate, and since a portion of the material had been oxidized to the manganic state during the washing, it was obvious that bromine would be set free during the solution in hydrobromic acid. The use of a platinum vessel for this purpose was therefore precluded. In order to avoid the introduction of silica, fused quartz dishes were employed, instead of glass vessels. The former have been shown to be practically insoluble in acid solutions.[1]

The free bromine was expelled from the solution of manganous bromide by prolonged heating on a steam-bath in a quartz dish. Finally it was crystallized six times, thrice in quartz, and, after filtration with a platinum funnel, thrice in platinum with centrifugal drainage after each crystallization. The crystals were dried as far as possible over stick potash in a vacuum desiccator. From the mother-liquors, by means of six similar crystallizations, Sample A_2 was obtained.

In the conversion of Sample B from permanganate to bromide minor changes were introduced. The ammonium carbonate was prepared in a pure state by distilling a solution of commercial ammonium carbonate in a platinum still. Instead of expelling free bromine from the solution of manganous bromide by prolonged heating upon the steam-bath, the solution was evaporated as far as possible upon the steam-bath and the residue was heated to 200° in an electric oven. The bromide was dissolved in water, and after filtration of the solution, was crystallized three times in a platinum dish. The third crop of crystals is designated as Sample B.

Sample C was prepared from a commercial specimen of pyrolusite. This was first dissolved in hydrochloric acid and the solution was boiled to expel chlorine. Hydrogen sulphide was passed into the diluted solution of manganous chloride to saturation, and the precipitate of sulphur and sulphides was removed by filtration. After the excess of hydrogen sulphide had been expelled by boiling, the solution was fractionally precipitated with sodium hydroxide until the precipitate was free from iron. Finally, the manganese was precipitated with ammonium carbonate and the precipitate was washed and dissolved in nitric acid. The nitrate was recrystallized and converted into bromide exactly as in the case of Sample A.

The source of Sample D was Merck's "chemically pure" manganous sulphate. A solution of 500 gm. of this salt was first saturated with hydrogen sulphide, and the precipitate, which consisted chiefly of manganous sulphide, was removed by filtration. After the addition of a small amount of ammonia, hydrogen sulphide was again passed into the solution to saturation, and the pre-

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[1] Mylius and Meusser: *Zeit. anorg. Chem.*, **44**, 221 (1905). (See also page 36 of this paper.)

cipitate discarded. In a similar way third and fourth fractions of sulphide were removed. Next the solution was thrice fractionated with small portions of potassium hydroxide, the precipitate being rejected in each case. Then the manganese was twice precipitated as carbonate by means of ammonium carbonate and the manganous carbonate was converted into bromide exactly as in the case of Sample B. The first crop of thrice recrystallized bromide is designated Sample D_1, a second similar crop obtained from the mother-liquors is Sample D_2.

HYDROBROMIC ACID.

Commercial bromine was freed from chlorine by twice converting the bromine into hydrobromic acid by means of thoroughly washed hydrogen sulphide and water, and heating the hydrobromic acid, after distillation, with recrystallized potassium permanganate. The bromine was thus twice distilled from a bromide, the bromide in the second distillation being almost free from chloride. Iodine was eliminated by boiling the hydrobromic acid in each case with a small quantity of permanganate and rejecting the bromine set free. A portion of the final product, when converted into ammonium bromide by means of ammonia, and added to a solution of 3.46875 gm. (in vacuum) of pure silver, yielded 6.03855 gm. (in vacuum) of fused silver bromide, whence the ratio of silver to silver bromide is 57.443, while 57.445 is the value to be expected.[1]

By treating this bromine, covered with water, with washed hydrogen sulphide, hydrobromic acid was again produced. The solution was boiled, after mechanical separation of the greater part of the free sulphur and bromide of sulphur, and was then filtered. In order to remove the sulphuric acid produced during the action of the bromine upon the hydrogen sulphide, the hydrobromic acid was first distilled. Then it was diluted, and a small quantity of recrystallized barium hydroxide was added to precipitate last traces of sulphuric acid. The slight precipitate of barium sulphate was collected upon a filter, and the acid was three times distilled with rejection of the first and last portions, with a glass retort and condenser. Finally the acid was once distilled with the use of a quartz condenser. The product of the final distillation was collected in quartz vessels and was used immediately for dissolving the manganous carbonate. That this acid was free from solid impurities, such as alkalies and silica, was shown by evaporating 30 c.c. in a weighed platinum crucible. No weighable residue remained after the crucible had been heated to very dull redness.

NITRIC ACID.

This acid was twice distilled, all but the last third of the distillate being rejected in each distillation. This acid gave no test for chloride in a nephelometer.

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[1] Baxter: *Proc. Amer. Acad.*, **42**, 210 (1906); *Jour. Amer. Chem. Soc.*, **28**, 1332; *Zeit. anorg. Chem.*, **50**, 398. (See page 59.)

SILVER.

Five different specimens of silver were employed, a portion of each one of which had already been used in an atomic weight research, and had been shown to be of the highest grade of purity. Two of these specimens, Samples H and J, were used in an investigation upon the atomic weight of iodine by one of us.[1] Sample H was prepared from silver nitrate which had been seven times recrystallized from nitric acid, five times recrystallized from water, and finally precipitated with ammonium formate. Sample J was precipitated once as silver chloride, electrolyzed once, and finally precipitated with ammonium formate. Sample K was used in our first investigation upon the atomic weight of cadmium.[2] This sample was thrice precipitated as silver chloride and once electrolyzed. Sample L was precipitated once as chloride, once as metal by ammonium formate and was once electrolyzed. This sample has been used in the analysis of cadmium bromide.[3] Sample M was prepared for an investigation upon the atomic weight of bromine, and had been twice electrolyzed after a preliminary purification.[4] Samples H, J, and L also were used in the latter research, and were found to give values identical with those obtained with Sample M. All five samples were finally fused in a current of pure hydrogen in a lime boat. The fused lumps were cleaned with dilute nitric acid, cut into fragments either with a clean steel chisel and anvil, or with a jeweler's saw, treated with dilute nitric acid until free from iron, washed, dried, and finally heated to about 300° in a vacuum.

DRYING OF MANGANOUS BROMIDE.

The method of analysis was essentially that usually employed in this laboratory for the analysis of metallic halides, and has been described in the preceding papers on the cadmium halides. Weighed portions of the bromide, after fusion in hydrobromic acid, were first titrated against weighed portions of pure silver. Then the precipitated silver salt was collected and weighed.

The apparatus used for the fusion of the manganous bromide in a current of nitrogen and hydrobromic-acid gases has already been described in detail on page 23.

The manganous bromide, contained in a weighed platinum boat, was heated gently in a current of nitrogen, until the greater part of the crystal water was expelled, then strongly in a current of nitrogen and hydrobromic acid until fused. After the salt had cooled, the hydrobromic acid was displaced by nitrogen and this in turn by pure dry air, the purifying apparatus being constructed in such a way that by means of stop-cocks any one gas or mixture of gases could be employed, to the exclusion of the others. The boat was then transferred to

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[1] See page 108.

[2] See page 6.

[3] See page 22.

[4] See page 56.

the weighing-bottle in which it was originally weighed, and the stopper was inserted without an instant's exposure of the salt to moisture, by means of the bottling apparatus described on page 9. The weighing-bottle was then allowed to stand in a desiccator near the balance case for some time before it was weighed.

METHOD OF ANALYSIS.

Next the boat was transferred to a flask and the salt was dissolved in about 300 c.c. of the purest water. The weighing-bottle was rinsed and the rinsings were added to the solution. Then the solution was filtered into the glass stoppered precipitating flask through a tiny filter to collect a trace of insoluble matter, and the filter-paper and residue were ignited in a weighed porcelain crucible.

From the weight of manganous bromide very nearly the requisite quantity of pure silver could be calculated. This silver was weighed out and after solution in nitric acid as described on page 12, and dilution until not stronger than 1 per cent, the solution was slowly added with constant stirring to the 1 per cent solution of manganous bromide in the precipitating flask. After having been shaken for some time, the solution was allowed to stand several days, one week in the case of analyses 14 and 15, with occasional shaking, until the supernatant liquid was clear. 30 c.c. portions of the solution were then tested with hundredth-normal solutions of silver nitrate and sodium bromide in the nephelometer for excess of bromide or silver, and, if necessary, either standard silver nitrate or sodium bromide solution was added, and the process of shaking and testing repeated, until the amounts of bromide and silver in the solution were equivalent. If the solution was perfectly clear when tested, and contained no considerable excess of bromide or silver, the test solutions were discarded, since they contained only negligible amounts of silver bromide, otherwise they were returned to the flask and a correction was applied for the silver bromide thus introduced.

As soon as the exact end-point of the titration had been found, about 4 cg. of silver nitrate in excess were added to precipitate dissolved silver bromide and the solution was again shaken and allowed to stand until clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible after it had been washed with water by decantation about ten times. Next it was heated for several hours at 140°, then for 2 hours at about 230° in an electric air-bath, and, after it had cooled in a desiccator, it was weighed. In order to determine how much moisture was retained by the precipitate, in each case it was transferred as completely as possible to a clean porcelain crucible and weighed; then the salt was fused by heating the small crucible, contained in a large covered crucible, and again weighed. The fused salt was light yellow as a rule, showing that no appreciable reduction had taken place. The asbestos mechanically detached from the Gooch crucible together with a minute quantity of silver bromide which occasionally escaped the crucible, was collected from the filtrate and wash-waters upon a small filter, the ash of which was treated with nitric and hydrobromic acids before weighing. Although the filtrates and first wash-waters were essentially free from dissolved silver bromide, the subsequent wash-waters usually contained a trace of silver bromide. The amount of dissolved salt was determined with the nephelometer by comparison with standard bromide solutions.

Several difficulties were met in carrying out the analyses. In the first place it proved difficult to wash the platinum boat absolutely clean. When rinsed with cold water only, and dried at 100°, the weight was in many cases a few hundredths of a milligram greater than before fusion of the bromide. Ignition to redness of the boat thus treated then produced a slight loss in weight. Rinsing with hot water reduced the gain in weight of the boat after drying but did not wholly prevent a slight loss on ignition. The cause of the variation was not discovered, hence it seems safer in the calculations to use the weight of the boat after drying. The total variation is so slight, however, that it scarcely affects the final result.

Two other difficulties arose from the fact that when a solution of a manganous salt, even as dilute as the filtrates from analyses, is filtered through filter-paper, in spite of long-continued washing a small amount of manganese is tenaciously retained by the paper. This was discovered from the fact that the asbestos residues always contained manganese. In analyses 29 to 31 it was found possible to eliminate the manganese completely by washing the filter finally with 5 per cent hydrobromic acid. In two cases the residues were analyzed for manganese and were found to contain 0.00023 and 0.00057 gm. of Mn_3O_4 respectively.

The average of these two quantities is, however, larger than the total residue in some cases, hence this value can not be used to correct the previous analyses. In order to determine accurately the proper correction for this error, a solution containing manganous nitrate in the porportion in which it was usually contained in the filtrate of an analysis was passed through filter-papers and the filters were then washed as thoroughly as possible with water. The ash of these papers invariably contained manganese, the weights of manganic oxide in several experiments being found to be 0.00018, 0.00011, 0.00006, 0.00018 and 0.00005 gm. with an average of 0.00012 gm. This quantity was subtracted from the weight of asbestos shreds in all cases except analyses 29 to 31, where the paper was washed with hydrobromic acid.

The residue obtained by the filtration of the manganous bromide proved to contain manganese and to be free from detectable amounts of platinum and silica. Probably this insoluble residue consisted chiefly of oxides of manganese, although prolonged fusion in hydrobromic acid failed to reduce materially the proportion of insoluble matter. The discovery of adsorption in the case of manganous nitrate led to the suspicion that at least a portion of this residue was due to adsorption of manganese compounds by the filter-paper. In order to test this point a solution of manganous bromide, containing about 5 gm. in 200 c.c., after one filtration was again filtered through a second filter about 3 cm. in diameter. Filters of this size were used in filtering the manganous bromide solution in the analyses. This filter was then washed with water as thoroughly as in an analysis, and was ignited. The weight of manganic oxide obtained was 0.00008 gm. Two repetitions of the experiment yielded 0.00008 and 0.00010 gm. respectively. If, as is probable, the manganese is adsorbed, not as bromide, but as some basic compound, possibly as manganic hydroxide, the bromine would have remained partially, if not wholly, in the solution. In that case a suitable correction could be applied by subtracting from the weight of the residue the average of the quantities of manganese adsorbed in the above experiments. An attempt to prevent the difficulty by adding dilute sulphuric acid to the solution of manganous bromide did not diminish the extent of the adsorption. Hence a negative correction of 0.00009 gm. is applied to the residue in all cases.

It has already been shown that chlorides and bromides which have been fused and allowed to solidify in an acid atmosphere occlude none of the gas, for they give neutral solutions.[1]

THE DENSITY OF MANGANOUS BROMIDE.

In order to find accurately the vacuum correction for manganous bromide, it was necessary to determine the density of this salt. The experiments were carried out exactly as described in our determinations of the specific gravities of cadmium halides,[2] with the following results:

DENSITY OF $MnBr_2$.
Density of Toluol 25° / 4° = 0.86156.

Weight of $MnBr_2$ in vacuum.	Weight of toluol displaced in vacuum.	Density of $MnBr_2$. 25°/4°
gm.	*gm.*	
3.0098	0.5914	4.385
3.0342	0.5963	4.384
		Aver. 4.385

The average density of several of the brass weights was found by displacement of water to be 8.3.

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[1] Richards: *Proc. Amer. Acad.*, **29**, 59 (1893); *Zeit. anorg. Chem.*, **6**, 93 (1894); *Jour. Amer. Chem. Soc.*, **24**, 376 (1902); *Zeit. anorg. Chem.*, **31**, 273; Richards and Baxter: *Proc. Amer. Acad.*, **34**, 367 (1899); *Zeit. anorg. Chem.*, **21**, 269; Baxter and Hines: *Jour. Amer. Chem. Soc.*, **27**, 227 (1905); *Zeit. anorg. Chem.*, **44**, 163.

[2] *Amer. Chem. Jour.*, **31**, 220 (1904).

All weights were reduced to the vacuum standard by applying the following corrections for each apparent gram of substance.

	Specific gravity.	Vacuum correction.
Weights	8.3	
$MnBr_2$	4.385	+0.000129
AgBr	6.473	+0.000041
Ag	10.50	−0.000031
Toluol	0.862	+0.00126

The balance was a new Troemner, No. 10, and was easily sensitive to 0.02 mg. with a load of less than 50 gm. The weights, which were of brass, gold-plated, were occasionally carefully standardized to hundredths of a milligram. The corrections did not vary with time, however. All weighings were made by substitution, with tare vessels as nearly like those being weighed as possible. (See tables on pp. 42 and 43.)

The close agreement of the averages of the two series is conclusive evidence that no serious error, such as occlusion by the silver bromide, affected the method of analysis. This is strikingly shown by the ratio between the silver used and the silver bromide obtained in the same analysis.

	Ag : AgBr
Analyses 1 and 18	57.4438
2 " 19	57.4459
3 " 20	57.4426
4 " 21	57.4425
5 " 23	57.4439
8 " 24	57.4439
9 " 25	57.4457
10 " 26	57.4432
11 " 27	57.4423
12 " 28	57.4421
13 " 29	57.4454
14 " 30	57.4387
15 " 31	57.4456
Average,	57.4435
Average, rejecting analyses 14 and 30	57.4439

The most probable value for this ratio has recently been shown to be 57.4453.[1]

Although the foregoing figures furnish strong evidence that the atomic weight of manganese lies very close to 54.93, it seemed advisable to attempt to confirm this result by the analysis of other manganese compounds. The success which accompanied this investigation of the bromide led to the selection of manganous chloride for the next series of experiments. A comparison of the different specimens of material and a discussion of all the results is to be found at the end of this paper.

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[1] Baxter: *Proc. Amer. Acad.*, **42**, 210 (1906); *Jour. Amer. Chem. Soc.*, **28**, 1332; *Zeit. anorg. Chem.* **50**, 398. (See page 59.)

RESULTS.

THE ATOMIC WEIGHT OF MANGANESE.

Series I. $MnBr_2 : 2Ag$.

Ag = 107.880. Br = 79.916.

No. of analysis.	Sample of $MnBr_2$.	Sample of Ag.	Weight of $MnBr_2$ in vacuum.	Corrected weight of residue.	Change in weight of boat.	Weight of Ag in vacuum.	Weight of Ag added or subtracted.	Corrected weight of $MnBr_2$.	Corrected weight of Ag.	Atomic weight of manganese.
			gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	
1	A_2	K	6.53738	0.00000	−0.00004	6.56772	−0.00017	6.53738	6.56755	54.937
2	A_1	K	4.81026	0.00019	+0.00002	4.83243	−0.00005	4.81005	4.83238	54.932
3	C	K	4.88124	0.00027	0.00000	4.90354	0.00000	4.88097	4.90354	54.935
4	C	H	5.63234	0.00022	−0.00007	5.65833	−0.00020	5.63219	5.65813	54.939
5	A_1	H	5.79927	0.00008	−0.00005	5.82610	−0.00010	5.79924	5.82600	54.938
6	C	J	6.59033	0.00046	+0.00004	6.62051	−0.00010	6.58983	6.62041	54.932
7	B	H	4.19917	0.00016	−0.00010	4.21809	+0.00030	4.19911	4.21839	54.942
8	A_1	J	3.59834	0.00015	+0.00010	3.61478	0.00000	3.59809	3.61478	54.932
9	B	J	5.16345	0.00019	−0.00008	5.18711	0.00000	5.16334	5.18711	54.940
10	B	K	3.92230	0.00014	−0.00010	3.94021	+0.00021	3.92226	3.94042	54.934
11	B	K	4.49181	0.00032	−0.00009	4.51220	+0.00030	4.49158	4.51250	54.928
12	C	H	3.60099	0.00016	+0.00012	3.61746	−0.00010	3.60071	3.61736	54.935
13	D_1	H	4.77414	0.00022	0.00000	4.79602	+0.00018	4.77392	4.79620	54.926
14	D_1	J	3.57674	0.00015	−0.00001	3.59323	−0.00004	3.57660	3.59319	54.932
15	D_2	H + J	5.69991	0.00026	−0.00007	5.72586	+0.00055	5.69972	5.72641	54.923
									verage,	54.934

The Atomic Weight of Manganese.

Series II. $MnBr_2 : 2AgBr$.

Ag = 107.880 Br = 79.916.

No. of analysis.	Sample of $MnBr_2$.	Weight of $MnBr_2$ in vacuum.	Corrected weight of residue.	Change in weight of boat.	Weight of AgBr in vacuum.	Loss on fusion.	Corrected weight of asbestos.	Weight of AgBr from wash-waters.	Corrected weight of $MnBr_2$.	Corrected weight of AgBr.	Atomic weight of manganese.
		gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	
16	A_2	5.58461	0.00037	+0.00008	9.76524	0.00032	0.00069		5.58416	9.76561	54.939
17	A_2	5.63458	0.00022	+0.00004	9.85295	0.00030	0.00073	0.00007	5.63432	9.85345	54.936
18	A_2	6.53738	0.00000	−0.00004	11.43246	0.00029	0.00078	0.00005	6.53738	11.43300	54.932
19	A_1	4.81026	0.00019	+0.00002	8.41199	0.00024	0.00031		4.81005	8.41206	54.934
20	C	4.88124	0.00027	0.00000	8.53619	0.00022	0.00039	0.00006	4.88097	8.53642	54.925
21	C	5.63234	0.00022	−0.00007	9.84971	0.00009	0.00046		5.63219	9.85008	54.929
22	C	6.52653	0.00017	+0.00010	11.41232	0.00018	0.00061	0.00018	6.52626	11.41293	54.943
23	A_1	5.79927	0.00008	−0.00005	10.14153	0.00013	0.00061	0.00005	5.79924	10.14206	54.932
24	A_1	3.59834	0.00015	+0.00010	6.29262	0.00014	0.00023		3.59809	6.29271	54.927
25	B	5.16345	0.00019	−0.00008	9.02941	0.00005	0.00023	0.00004	5.16334	9.02959	54.931
26	B	3.92230	0.00014	−0.00010	6.85939	0.00012	0.00012	0.00041	3.92226	6.85968	54.926
27	B	4.49181	0.00032	−0.00009	7.85527	0.00015	0.00059		4.49158	7.85571	54.917
28	C	3.60099	0.00016	+0.00012	6.29731	0.00014	0.00023		3.60071	6.29740	54.924
29	D_1	4.77414	0.00022	0.00000	8.34878	0.00020	0.00057		4.77392	8.34915	54.926
30	D_1	3.57674	0.00015	−0.00001	6.25541	0.00018	0.00046		3.57660	6.25569	54.908
31	D_2	5.69991	0.00026	−0.00007	9.96830	0.00020	0.00030		5.69972	9.96840	54.922

Average, rejecting analysis 30, 54.930

Average of Series I and II, 54.932

ANALYSIS OF MANGANOUS CHLORIDE.

PURIFICATION OF MATERIALS.

MANGANOUS CHLORIDE.

Portions of the pure material employed in the experiments upon manganous bromide served also for the preparation of manganous chloride. Two specimens of chloride were made. Sample B corresponds in its purity to Sample B of manganous bromide, since both were made by dissolving the same specimen of manganous carbonate (page 35). This carbonate had been made from potassium permanganate which had been crystallized ten times. The solution of the carbonate in hydrochloric acid was evaporated to dryness in a quartz dish and was heated to 200° in an electric oven. Then the filtered aqueous solution was evaporated to crystallization in a platinum dish and the first crop of crystals was twice recrystallized (Sample B).

The mother-liquors of the manganous nitrate used in preparing Samples B and D of bromide (page 35) were combined and crystallized six times, three times in glass vessels, three times in platinum vessels, and from this pure nitrate Sample E was prepared by precipitation of the carbonate with distilled ammonium carbonate, solution in hydrochloric acid and crystallization as with Sample B.

HYDROCHLORIC ACID.

The hydrochloric acid was purified by boiling the "chemically pure" acid for some time, after the addition of a small quantity of potassium permanganate. Then it was distilled in glass, the middle portion only being collected, and finally once with a quartz condenser shortly before use.

SILVER.

The same samples of pure silver were employed as in the work with manganous bromide (page 37).

DRYING OF MANGANOUS CHLORIDE.

The salt was prepared for analysis by fusion in a current of hydrochloric-acid gas and then the chlorine content was determined gravimetrically as silver chloride and by titration against a weighed amount of silver in solution.

The apparatus employed for the fusion was identical with that described in the paper on cadmium chloride (see page 8), the hydrochloric-acid gas in which the fusion took place being dried by passing through four towers containing concentrated sulphuric acid. In a few preliminary experiments the hydrochloric-acid gas was passed over freshly sublimed phosphorus pentoxide, but this drying agent was subsequently eliminated since it was found to introduce volatile phosphorus compounds into the hydrochloric-acid gas, and thus into the manganous chloride, if the latter was moist. This difficulty has been discussed elsewhere (page 14), and in the same place it has been shown that hydrochloric-acid gas attacks concentrated sulphuric acid to so slight an extent that the latter may safely be used to dry the former.

THE METHOD OF ANALYSIS.

The principal point of difference between the analyses of manganous bromide and manganous chloride was occasioned by the greater solubility of silver chloride. This introduced no difficulty in the case of the titrations, although the opalescence in both nephelometer tubes was of course more marked at the end-point. In order to make the precipitation of the silver chloride more complete, however, a much larger excess of silver nitrate was necessary than in the case of silver bromide, about 0.15 gm. being added in each analysis. Furthermore, the precipitate was washed at first with a solution of silver nitrate containing 0.04 gm. in a liter, although the final six washings were performed with water. The silver chloride dissolved in both filtrate and washings was determined by comparison with standard solutions in a nephelometer as previously described. Here even the filtrate showed a trace of dissolved silver chloride.

In the case of manganous chloride also the extent of the adsorption of manganese compounds by the filter-paper was investigated by filtering a solution of the salt through a filter-paper, and, after thoroughly washing the paper, determining the residue after ignition. The correction for adsorption thus found, 0.00006 gm., is in some cases larger than the weight of the residue minus the loss in weight of the boat, owing possibly to the fact that not all the platinum lost by the boat is collected upon the filter-paper. At any rate the uncertainty introduced by applying the correction wherever possible is very small.

The filter upon which the asbestos shreds were collected was washed with warm dilute hydrochloric acid to eliminate adsorbed manganese compounds, so that no correction for adsorption is here necessary. This acid was then tested for silver chloride with the nephelometer, and if any was found it was added to the main weight of this substance.

In analyses 1, 2, 3, 4, and 7 the silver nitrate was added to the manganous chloride, while in analyses 5 and 6 precipitation was performed in the reverse fashion.

The possibility of the existence of manganic compounds in the salt was considered. In order to determine whether or not this was the case, one specimen of manganous chloride, after fusion in hydrochloric acid, was tested for manganic compounds by adding a solution of starch paste and potassium iodide. No coloration resulted even after adding hydrochloric acid, although a mere trace of permanganate produced immediate coloration in the same solution.

The fused bromide and chloride were both pink, hence Forchhammer's statement that the pink color of manganous salt is due to the presence of manganic compounds is incorrect.[1]

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[1] *Ann. Phil.*, N. S., 1, 50 (1821).

DENSITY OF MANGANOUS CHLORIDE.

In order to find the vacuum correction for manganous chloride the density of the salt was determined by displacement of toluol. This was done with the special pycnometer which was devised for the determination of the densities of hygroscopic salts.[1]

Density of $MnCl_2$.
Density of toluol 25°/4° = 0.86166.

Weight of $MnCl_2$ in vacuum.	Weight of toluol displaced in vacuum.	Density of $MnCl_2$. 25°/4°.
gm.	*gm.*	
1.9436	0.5617	2.982
2.8532	0.8266	2.974
3.1202	0.9035	2.976
	Average,	2.977[2]

Weighings were made with the precautions usual in exact work. All weights were reduced to the vacuum standard by applying the following corrections for each apparent gram of substance:

	Specific gravity.	Vacuum correction.
Weights	8.3	
$MnCl_2$	2.977	+0.000259
AgCl	5.56	+0.000071
Ag	10.49	−0.000031
Toluol	0.862	+0.00126

RESULTS AND DISCUSSION.

Richards and Wells have proved beyond question that the ratio of silver to silver chloride is as low as 75.2634,[3] a value which is essentially identical with that obtained from the weights of silver used and the weights of silver chloride obtained.

	Ag : AgCl.
Analyses 1 and 8	75.2615
2 " 9	75.2662
3 " 10	75.2628
4 " 11	75.2607
5 " 12	75.2595
6 " 13	75.2662
7 " 14	75.2656
Average,	75.2632

Not only are the values obtained in the two series of analyses identical, but they differ only by an exceedingly small amount from those resulting from the analysis of manganous bromide (pages 42 and 43).

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[1] Baxter and Hines: *Amer. Chem. Jour.*, **31**, 220 (1904).

[2] Schröder obtained the value 2.478. Dichtigkeitsmessungen. Heidelberg, 1873.

[3] *Pub. Car. Inst.*, No. **28**, 65 (1905); *Jour. Amer. Chem. Soc.*, **27**, 520; *Zeit. anorg. Chem.*, **47**, 125.

The final averages of the four series are given in the following table:

Series		
I.	$MnBr_2 : 2Ag$	54.934
II.	$MnBr_2 : 2AgBr$	54.930
III.	$MnCl_2 : 2Ag$	54.933
IV.	$MnCl_2 : 2AgCl$	54.933
	Average,	54.933

It is interesting to tabulate the analyses according to the specimens of material employed.

	Averages
Samples A of $MnBr_2$	54.934
B of $MnBr_2$	54.933
C of $MnBr_2$	54.933
D of $MnBr_2$	54.926[1]
B of $MnCl_2$	54.935
E of $MnCl_2$	54.931
General average,	54.932

	Averages
Sample H of Ag	54.933
J of Ag	54.936
K of Ag	54.934
L of Ag	54.934
M of Ag	54.933
General average,	54.934

The purification of Sample B was exceptionally thorough. In the first place potassium permanganate is isomorphous with a comparatively limited number of substances, so that the initial purification by a large number of crystallizations of this substance may be expected to have eliminated every trace of impurity of heavy metals. In the second place the final product had been many times recrystallized in the form of two other compounds of manganese. It is almost inconceivable that any impurity could have eluded this large number of crystallizations in three different forms. That such a prolonged purification was unnecessary is shown by the agreement of the results from the other samples with that from Sample B. Even in the case of Samples A, C, D, and E the final product had been recrystallized in at least two forms. The slightly lower results in the case of Sample D differ from the others by an amount no greater than the possible experimental error, and can not be considered to indicate that the composition of this sample is different from that of the others. The various samples of silver also yielded essentially the same result, which confirms the statement as to the identity of the different samples made on page 37.

There can be little doubt that the final average of all four series, 54.933, represents with accuracy the relation of the atomic weight of manganese to that of silver 107.880. This value is in close agreement with the value derived from previous investigations.

The main results of this research may be briefly summarized as follows:

(1) The atomic weight of manganese, referred to silver 107.880, is found to be 54.933, by analysis of both manganous bromide and manganous chloride. With silver at 107.870, manganese becomes 54.927.

(2) The specific gravity of manganous bromide at 25°, referred to water at 4°, is found to be 4.385, and that of manganous chloride under the same conditions is found to be 2.977.

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[1] Analysis 30 is rejected.

The Atomic Weight of Manganese.

Series III. $MnCl_2 : 2Ag$.

Ag = 107.880. Cl = 35.457.

No. of analysis.	Sample of $MnCl_2$.	Sample of Ag.	Weight of $MnCl_2$ in vacuum.	Corrected weight of residue.	Change in weight of boat.	Weight of Ag in vacuum.	Weight of Ag added or subtracted.	Corrected weight of $MnCl_2$.	Corrected weight of Ag.	Atomic weight of manganese.
			gm.	gm.	gm.	gm.	gm.	gm.	gm.	
1	B	L	4.62985	0.00017	−0.00002	7.93730	+0.00010	4.62970	7.93740	54.935
2	B	L	3.52899	......	−0.00001	6.05071	−0.00030	3.52899	6.05041	54.933
3	B	L	3.30881	0.00000	−0.00010	5.67299	−0.00020	3.30881	5.67279	54.935
4	E	L	3.56859	0.00014	+0.00002	6.11818	0.00000	3.56843	6.11818	54.930
5	E	K	3.45114	0.00023	+0.00008	5.91647	−0.00010	3.45083	5.91637	54.933
6	B	L	4.47948	0.00008	−0.00015	7.68015	−0.00020	4.47948	7.67995	54.934
7	E	M	3.92089	0.00002	−0.00005	6.72232	−0.00005	3.92089	6.72227	54.933
									Average,	54.933

Series IV. $MnCl_2 : 2AgCl$.

No. of analysis.	Sample of $MnCl_2$.	Weight of $MnCl_2$ in vacuum.	Corrected weight of residue.	Change in weight of boat.	Weight of AgCl in vacuum.	Loss on Fusion.	Weight of asbestos.	Weight of AgCl from wash-waters.	Corrected weight of $MnCl_2$.	Corrected weight of AgCl.	Atomic weight of manganese.
		gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	
8	B	4.62985	0.00017	−0.00002	10.54532	0.00006	0.00017	0.00098	4.62970	10.54641	54.932
9	B	3.52899	......	−0.00001	8.03616	0.00013	0.00046	0.00219	3.52899	8.03868	54.937
10	B	3.30881	0.00000	−0.00010	7.53598	0.00014	0.00040	0.00107	3.30881	7.53731	54.934
11	E	3.56859	0.00014	+0.00002	8.12767	0.00005	0.00042	0.00128	3.56843	8.12932	54.925
12	E	3.45114	0.00023	+0.00008	7.85947	0.00012	0.00053	0.00141	3.45083	7.86129	54.927
13	B	4.47948	0.00008	−0.00015	10.20110	0.00007	0.00078	0.00191	4.47948	10.20372	54.938
14	E	3.92089	0.00002	−0.00005	8.92964	0.00004	0.00038	0.00142	3.92089	8.93140	54.937
										Average,	54.933
										Average of Series III and IV,	54.933

IV.

A REVISION OF THE ATOMIC WEIGHT OF BROMINE.

THE SYNTHESIS OF SILVER BROMIDE AND THE RATIO OF SILVER BROMIDE TO SILVER CHLORIDE.

BY GREGORY PAUL BAXTER.

Proceedings of the American Academy of Arts and Sciences, **42**, 201 (1906).
Journal of the American Chemical Society, **28**, 1322 (1906).
Zeitschrift für anorganische Chemie, **50**, 389 (1906).
Chemical News, **94**, 260, 261 (1906).
Experimentelle Untersuchungen über Atomgewichte, page 768. T. W. Richards. 1909.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

A REVISION OF THE ATOMIC WEIGHT OF BROMINE.

THE SYNTHESIS OF SILVER BROMIDE AND THE RATIO OF SILVER BROMIDE TO SILVER CHLORIDE.

INTRODUCTION.

In numerous investigations in this laboratory upon the atomic weights of certain metals, in which metallic bromides were first titrated against the purest silver, and then the precipitated silver bromide was collected and weighed, the relation between the silver used in the titrations and the silver bromide obtained has yielded data from which the atomic weight of bromine may be calculated. Furthermore, in all these investigations, as a check upon the purity of the silver and bromine employed, silver bromide was synthesized directly from weighed quantities of silver and an excess of ammonium bromide or hydrobromic acid. Many of these results have already been collected and discussed by Richards,[1] nevertheless they are cited in the following table together with a few more recent determinations. (See table on page 52.)

From the first of these ratios the atomic weight of bromine, referred to silver 107.880, is found to be 79.919, and from the second 79.918.

Very recently, in experiments in which silver iodide was heated first in a current of air and bromine until the iodine was completely displaced, and then in a current of chlorine to displace the bromine, the ratio of silver bromide to silver chloride was determined in six cases. From the results of these experiments the atomic weight of bromine was calculated to be 79.916,[2] if the atomic weight of chlorine is assumed to be 35.457.

These values for bromine are in close agreement with those of Stas.[3] In his experiments weighed quantities of pure silver and bromine were first titrated against each other, and then the precipitate of silver bromide was collected and weighed. Of the four results by the first method, one should be rejected according to his own statements, since the bromine was not thoroughly dried. The remaining three, 79.922, 79.924, and 79.923, give as an average 79.923. From the weight of silver bromide four values were obtained, 79.913, 79.915, 79.918, and 79.920, with an average of 79.917.

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[1] *Proc. Amer. Phil. Soc.*, 43, 119 (1904).

[2] Baxter: *Proc. Amer. Acad.*, 41, 82 (1905); *Jour. Amer. Chem. Soc.*, 27, 884; *Zeit. anorg. Chem.*, 46, 45. (See page 111.)

[3] *Œuvres Complètes*, 1, 603.

Marignac[1] also determined the ratio of silver to silver bromide, with somewhat lower results, — 79.922, 79.904, and 79.915; average, 79.913.

Scott,[2] in his analyses of ammonium bromide, obtained six values for the same ratio, varying between 79.899 and 79.911, with an average of 79.906. One of his results is here rejected, since the silver used in this experiment was known to be impure.

INDIRECT DETERMINATIONS.

No.	Bromide analyzed.	No. of experiments.	Analyst.	Reference.	Ratio $\frac{Ag}{AgBr}$.
1	$BaBr_2$	Last seven	Richards	Proc. Amer. Acad., **28**, 28	57.444
2	$SrBr_2$	Seven	Richards	Ibid., **30**, 389	57.444
3	$ZnBr_2$	One	Richards	Ibid., **31**, 178	57.445
4	$NiBr_2$	Seven	Cushman	Ibid., **33**, 111	57.444
5	$CoBr_2$	Last five	Baxter	Ibid., **33**, 127	57.446
6	UBr_4	Three	Merigold	Ibid., **37**, 393	57.447
7	CsBr	Three	Archibald	Ibid., **38**, 466	57.444
8	$FeBr_2$	Two	Baxter	Ibid., **39**, 252	57.443
9	$CdBr_2$	Eight	Hines	Jour. Amer. Chem. Soc., **28**, 783	57.444
10	$MnBr_2$	Thirteen	Hines	Ibid., **28**, 1578	57.444
	Average, weighted according to the number of determinations				57.4443

DIRECT DETERMINATIONS.

No.	Bromide analyzed.	No. of experiments.	Analyst.	Reference.	Ratio $\frac{Ag}{AgBr}$.
11	HBr	Two	Richards	Proc. Amer. Acad., **28**, 17, 18	57.445
12	NH_4Br	One	Richards	Ibid., **30**, 380	57.446
13	HBr	Two	Richards	Ibid., **31**, 165	57.444
14	NH_4Br	One	Cushman	Ibid., **33**, 106	57.445
15	NH_4Br	One	Baxter	Ibid., **33**, 122	57.444
16	NH_4Br	Two	Baxter	Ibid., **34**, 353	57.447
17	NH_4Br	Three	Baxter	Ibid., **39**, 250	57.444
18	NH_4Br	One	Hines	Jour. Amer. Chem. Soc., **28**, 1565	57.443
	Average, weighted according to the number of determinations				57.4447

Dumas[3] by heating silver bromide in chlorine found the values 80.02, 79.87, and 79.94.

In computing the atomic weight of bromine from these data, great weight is always given to Stas's determinations, the value 79.918 being usually assumed as the most probable one for the constant in question. Certainly, as pointed out by Richards,[4] the true value must lie between 79.91 and 79.92. Clarke calculates the value 79.912 as the weighted average of the different investigations previous to Scott's.[5]

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[1] *Œuvres Complètes*, **1**, 81.

[2] *Jour. Chem. Soc. Trans.*, **79**, 147 (1901).

[3] *Ann. Chem. Pharm.*, **113**, 20 (1860).

[4] *Proc. Amer. Phil. Soc.*, **43**, 119 (1904).

[5] A Recalculation of Atomic Weights, *Smith. Misc. Coll.*, 1897.

Considerable uncertainty exists as to the purity of the materials employed in much of the foregoing work. Richards and Wells[1] have already exhaustively investigated the various methods of preparing pure silver, and have found that while it is a comparatively simple matter to free this substance from metallic impurities, the absence of gaseous impurities is by no means so easy to secure. Oxygen may be eliminated best by fusion in an atmosphere of pure hydrogen gas,[2] or by prolonged fusion in a vacuum, while a lime boat was found to be the most suitable support for the silver during fusion.

In most of the experiments cited on page 52, one of the final steps in the purification of the silver was fusion of electrolytic crystals on lime, in many cases in a vacuum, but without especial care to prolong the fusion. Silver prepared in this way was found by Richards and Wells to contain traces of oxygen, derived from silver nitrate occluded by the electrolytic crystals. In cases 8, 9, 10, 17, and 18, however, the silver was fused in hydrogen. Richards and Wells showed also that Stas's silver contained at least 0.01 per cent of impurity, since it yielded 0.01 per cent less silver chloride than their purest silver.[3] Scott's silver in three cases was merely heated, not fused, in hydrogen, and in two of the others was fused before a blowpipe on calcic phosphate. In one experiment only the metal was fused on lime. No details are given as to the purification of the silver used by Marignac.

Bromine also may be freed from impurities only with some difficulty. Experience in this laboratory has shown that chlorine may be eliminated most conveniently by distilling or precipitating the bromine from solution in a bromide. One such distillation is sufficient to remove chlorine completely only when the substance is initially comparatively pure. If, however, the process is repeated by converting a portion of the partially purified product into a bromide, and dissolving the remainder of the bromine in this comparatively pure bromide, the chlorine is eliminated so completely that further repetition of this process has no apparent effect.[4] The removal of iodine may be easily effected by converting the bromine into hydrobromic acid or a soluble bromide, and boiling the solution with a small quantity of free bromine. Here again it is well to repeat the process several times, since the reaction between free bromine and the iodine ion, like that between free chlorine and the bromine ion, is undoubtedly incomplete.

The greater part of the results given on page 52 were obtained with bromine which had been purified with due observance of these precautions. Of the other investigators, Stas seems to have been the only one to use sufficient

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[1] *Pub. Car. Inst.* No. **28**, 16; *Jour. Amer. Chem. Soc.*, **27**, 472; *Zeit. anorg. Chem.*, **47**, 70.

[2] Baxter: *Proc. Amer. Acad.*, **39**, 249 (1903); *Zeit. anorg. Chem.*, **38**, 232 (1904).

[3] *Loc. cit.*, page 62.

[4] Attention has already been called to these points by Richards and Wells: *Proc. Amer. Acad.*, **41**, 440 (1906); *Zeit. physikal. Chem.*, **56**, 354.

pains to secure purity of the bromine. Stas removed iodine by shaking potassium bromide several times with free bromine and carbon disulphide, and in the course of the prolonged purification distilled the bromine twice from solution in a bromide. Marignac's purification consisted solely in crystallization of barium bromate and Scott's in distillation of hydrobromic acid.

Of the methods employed in these early determinations, that involving the analysis of metallic halides is least suited for the purpose, on account of the danger of occlusion of metallic salts by the precipitated silver bromide. That such an error actually exists to a slight extent is shown by the fact that the average of the "indirect" determinations is slightly larger than the average of the "direct" determinations. Obviously, if silver bromide is precipitated by means of either ammonium bromide or hydrobromic acid, occluded ammonium salts or free acids can be easily expelled by fusion of the bromide. This precaution was observed in most of the determinations recorded on page 52, and is absolutely essential for the complete elimination of water from the salt. Stas and Marignac both fused the silver bromide in their syntheses, but this operation was omitted by Scott, who dried the bromide at 180°. Scott's statement that the loss on fusion of silver bromide which had been dried at 180° was due to the presence of asbestos is contradicted by the experiments recorded later in this paper, in which the loss on fusion amounted to about 0.01 per cent in the case of silver bromide which had been dried in a similar fashion and which was almost entirely free from asbestos.

From this brief discussion of the more important errors which may have influenced previous determinations of the atomic weight of bromine, it is evident that some uncertainty still exists as to the true value of this constant. In the hope of throwing new light upon the subject, experiments were carried out by two of the methods outlined above, with especial precautions to insure purity of materials and to eliminate known possible errors in the experimental methods.

Both the methods chosen — synthesis of silver bromide from a weighed amount of silver, and conversion of silver bromide into silver chloride — have already been recently tested in this laboratory,[1] and have been found to be at least as satisfactory as any.

PURIFICATION OF MATERIALS.

BROMINE.

In purifying bromine for this research, the principles set forth on page 53 of this paper were applied; but in some cases the purifying processes were repeated after the product was apparently pure, in order to make certain that further treatment had no effect.

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[1] Baxter: *Proc. Amer. Acad.*, **40**, 419; **41**, 73; *Jour. Amer. Chem. Soc.*, **26**, 1577; **27**, 876; *Zeit. anorg. Chem.*, **43**, 14; **46**, 36; Richards and Wells: *Pub. Car. Inst.*, No. 28; *Jour. Amer. Chem. Soc.*, **27**, 459; *Zeit. anorg. Chem.*, **47**, 56.

Sample I was first completely dissolved in calcic bromide which had been made from about one-third of the original material by means of lime and ammonia, and was then distilled from the solution. The product was covered with several times its volume of water, and was converted into hydrobromic acid by means of pure hydrogen sulphide which had been generated from ferrous sulphide with dilute sulphuric acid, and which had been thoroughly washed with water. After filtration from the precipitated sulphur and bromide of sulphur, the acid was boiled for some time, with occasional addition of small quantities of recrystallized potassium permanganate to eliminate the iodine. Finally the residual hydrobromic acid was heated with an equivalent amount of recrystallized permanganate, and the bromine was condensed in a flask cooled with ice.

Sample II was first converted into hydrobromic acid by means of red phosphorus and water, and the hydrobromic acid was then distilled, after having been boiled with an excess of bromine. An equivalent amount of permanganate was added, and the bromine liberated was separated from the solution by distillation. About one-fourth of the product was next transformed into calcic bromide by means of ammonia and lime which was free from chloride, and the remaining three-fourths of the bromide were dissolved in the calcic bromide and distilled. Still a third distillation from a bromide was carried out by reducing the product of the second distillation with hydrogen sulphide and subsequently oxidizing the hydrobromic acid with the purest recrystallized potassium permanganate, after boiling the acid with several small portions of permanganate to eliminate last traces of iodine.

Sample III was obtained by preparing calcic bromide from a portion of Sample II and distilling the remainder of Sample II from solution in this bromide.

In the case of Sample IV the processes of reduction to hydrobromic acid with hydrogen sulphide and oxidation of the hydrobromic acid with pure permanganate were four times repeated. After each reduction the hydrobromic acid was boiled with free bromine to remove iodine.

Sample V was three times reduced with hydrogen sulphide and oxidized with permanganate. One-fourth the product was converted into calcic bromide and the remainder was dissolved in this calcic bromide and distilled.

Thus Sample I was twice distilled from a bromide; Sample II was treated three times in the same way; and Samples III, IV, and V four times.

Shortly before use each sample was distilled and converted into ammonium bromide by slow addition to an excess of redistilled ammonium hydroxide. The solution was then boiled to expel the excess of ammonia.

SILVER.

Several different samples of silver were employed, many of which have already been used in atomic weight researches in this laboratory, and have shown evidence of great purity. For details concerning the purification the papers referred to should be consulted.

Sample A was employed in a determination of the atomic weight of iodine.[1] This specimen had been twice precipitated as chloride and once electrolyzed.

Sample B was used in experiments upon the atomic weight of iodine[2] and of manganese.[3] It was precipitated once as chloride, electrolyzed once, and finally precipitated as metal with ammonium formate.

Sample C also was employed in a determination of the atomic weight of manganese, and was purified by recrystallizing silver nitrate, 7 times from nitric acid and 5 times from aqueous solution. Finally the silver nitrate was reduced by means of ammonium formate.

Sample D was prepared for the determination of the atomic weights of cadmium[4] and manganese, by precipitation as chloride, precipitation with ammonium formate, and electrolysis.

Sample E was first purified in part by precipitation as chloride, in part by precipitation with ammonium formate. The combined material was then subjected to two electrolyses.

In all cases the electrolytic crystals were fused in a boat of the purest lime, contained in a porcelain tube, in a current of electrolytic hydrogen. After the buttons had been cleansed with dilute nitric acid and dried at 200°, they were cut into fragments of from 4 to 8 gm. either by means of a clean chisel and anvil or with a fine jeweller's saw. The latter method was employed in the case of samples D and E, because it proved easier completely to free the silver from surface contamination with iron by etching the fragments with nitric acid, than when a chisel was used. The cleansing process with nitric acid was repeated until the solution thus obtained, after precipitation with hydrochloric acid and evaporation, proved free from iron. That every trace of iron could be removed by this treatment was proved by testing for iron the evaporated filtrates from several of the analyses subsequently recorded in this paper. Negative results were obtained in all cases.

After thorough washing with water and drying at 100°, the pieces of metal were heated to about 400° in a vacuum, and were preserved over solid potassium hydroxide in a desiccator.

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[1] Baxter: *Proc. Amer. Acad.*, **40**, 420 (1904); *Jour. Amer. Chem. Soc.*, **26**, 1578; *Zeit. anorg. Chem.*, **43**, 15. (See page 92.)

[2] Baxter: Ibid., **41**, 79 (1905); *Jour. Amer. Chem. Soc.*, **27**, 881; *Zeit. anorg. Chem.*, **46**, 42. (See page 108.)

[3] Baxter and Hines: *Jour. Amer. Chem. Soc.*, **28**, 1560 (1906); *Zeit. anorg. Chem.*, **51**, 207. (See page 37.)

[4] Baxter and Hines: *Jour. Amer. Chem. Soc.*, **28**, 772 (1906); *Zeit. anorg. Chem.* **49**, 417. (See page 6.)

SYNTHESIS OF SILVER BROMIDE.

The ratio of silver to silver bromide was determined as follows: Weighed quantities of silver were dissolved in the purest redistilled nitric acid diluted with an equal volume of water, in the dissolving flask described on page 12. Next, the acid solution of the silver was diluted with an equal volume of water, and was heated until free from nitrous acid and oxides of nitrogen. After still further dilution, the solution was added slowly with constant agitation to a dilute solution of an excess of ammonium bromide in a glass-stoppered precipitating flask, and the whole was violently shaken for some time to promote coagulation. By adding the silver solution to the bromide, occlusion of silver nitrate was almost wholly precluded. In some experiments the solutions were as dilute as twentieth normal, in others as concentrated as fourth normal. The final results seem to be independent of the concentration of the solutions. At the end of about 24 hours the flask with its contents was again shaken, and then it was allowed to stand until the supernatant liquid was perfectly clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible, after thorough washing by decantation with water, and was dried in an electric oven, first for several hours at 130°, finally for about 14 hours at 180°. Then it was cooled and weighed.

The operations of precipitation and filtration were performed in a large cupboard lighted with red light, and if the flask was taken out of this cupboard it was enveloped in several thicknesses of black cloth.

Even after the prolonged drying, traces of moisture were retained by the salt, and could be expelled only by fusion. This was done by transferring the bulk of the silver bromide, freed as completely as possible from asbestos, to a small porcelain crucible which was weighed with its cover. The silver bromide was then fused by heating the small crucible, contained in a large crucible to prevent direct contact with the flame of the burner. A temperature much above the fusing point of silver bromide was avoided so that volatilization of the salt could not take place. This treatment must have eliminated occluded ammonium salts as well as water. Finally, in order to convert any occluded silver nitrate, metallic silver, or silver sub-bromide into silver bromide, the salt was again fused in a current of dry air containing bromine vapor. This treatment seldom produced any measurable effect either upon the weight or the appearance of the salt, which was perfectly transparent and of a light yellow color, even after the first fusion in air.

A few shreds of asbestos displaced from the crucible, together with an occasional trace of silver bromide which escaped the crucible, were collected upon a tiny filter paper, which was then ignited in a porcelain crucible. Before weighing, the ash was either treated with a drop of nitric and hydrobromic acids and again heated, or else was heated for some minutes in a current of air and bromine.

The filtrate and washings were evaporated to small bulk. The precipitating flask and all other glass vessels used in the analysis were rinsed with ammonia

RESULTS. (The Atomic Weight of Bromine. Series I.)

Ag: AgBr   Ag = 107.880.

No. of analysis.	Sample of silver.	Sample of bromine.	Weight of silver in vacuum.	Weight of silver bromide in vacuum.	Loss on fusion in bromine.	Weight of asbestos.	Dissolved silver bromide.	Corrected wt. of silver bromide.	Ratio $\frac{Ag}{AgBr}$.	Atomic weight of bromine.
			gm.	gm.	gm.	gm.	gm.	gm.		
1	A	II	4.71853	8.21362	0.00027	0.00007	0.00021	8.21363	57.4476	79.909
2	B	II	5.01725	8.73387	0.00020	0.00019	0.00007	8.73393	57.4455	79.915
3	A	II	5.96818	10.38799	0.00023	0.00034	0.00122	10.38932	57.4453	79.916
4	C	II	5.62992	9.80000	0.00017	0.00039	0.00017	9.80039	57.4459	79.914
								Aver.	57.4461	79.913
5	A	IV	8.13612	14.16265	0.00002	0.00047	0.00024	14.16334	57.4449	79.917
6	C	IV	5.07238	8.82932	0.00013	0.00043	0.00035	8.82997	57.4451	79.917
7	B	IV	4.80711	8.36838	0.00015[1]	0.00000	0.00004	8.36827	57.4445	79.919
								Aver.	57.4448	79.918
8	C	V	4.27279	7.43771	0.00010[1]	0.00009	0.00007	7.43776	57.4473	79.910
9	A	V	5.86115	10.20299	0.00007[1]	0.00004	0.00003	10.20299	57.4454	79.916
10	B	V	7.91425	13.77735	0.00010	0.00010	0.00001	13.77736	57.4439	79.921
11	D	V	6.40765	11.15461	0.00000	0.00006	0.00001	11.15468	57.4436	79.922
12	D	V	6.38180	11.10942	0.00025	0.00012	0.00001	11.10930	57.4456	79.915
13	D	V	6.23696	10.85722	0.00005	0.00004	0.00001	10.85722	57.4453	79.916
								Aver.	57.4452	79.916
14	E	I	9.18778	15.99383	0.00014	0.00019	0.00004	15.99392	57.4455	79.916
15	E	I	8.01261	13.94828	0.00018	0.00009	0.00007	13.94826	57.4452	79.916
16		I	10.48638	18.25467	0.00025[1]	0.00007	0.00001	18.25452	57.4454	79.916
								Aver.	57.4454	79.916
17	E	III	8.59260	14.95790	0.00014	0.00016	0.00005	14.95797	57.4450	79.917
18	E	III	8.97307	15.62013	0.00004	0.00007	0.00006	15.62022	57.4452	79.916
								Aver.	57.4451	79.917
		Total.	121.67653	....	....	....	....	211.81305	57.4452	79.916

Average of all 18 determinations,	57.4453	79.916
Average of last 7 determinations,	57.4453	79.916

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[1] Fusion in bromine lost, after the salt had been fused in air.

and the rinsings were added to the evaporated filtrate and wash-waters. The whole was then tested in a nephelometer for silver and the quantity found was estimated by comparison with standard silver solutions. In most cases the correction thus obtained was less than 0.1 mg.

The asbestos which formed the felt in the Gooch crucible, after having been shredded, was digested for some hours with aqua regia and was then thoroughly washed with water. Before the empty crucible was weighed, the felt was ignited with a Bunsen burner. Crucibles thus treated and then, after being moistened with water, again heated to 180°, did not change in weight.

In the table on page 58 are cited all the analyses which were completed without accident. Vacuum corrections of -0.000031 for every apparent gram of silver and of $+0.000041$ for every apparent gram of silver bromide are applied.[1]

The platinum-plated brass weights were standardized from time to time and were found to retain their original values within a very few hundredths of a milligram in all cases.

CONVERSION OF SILVER BROMIDE INTO SILVER CHLORIDE.

The ratio of silver bromide to silver chloride was determined much as described in previous papers upon the atomic weight of iodine.[2] Pure silver bromide was prepared by precipitation of silver nitrate with an excess of ammonium bromide. The silver employed was purified either by precipitation as chloride and reduction with invert sugar, or by electrolysis, or by precipitation with ammonium formate. The metal was then fused before a blowpipe upon a crucible of the purest lime, and the buttons were thoroughly cleansed with nitric acid. No further purification was considered necessary since the weight of the metal was of no consequence.

After the silver bromide had been washed by decantation with water, in some cases it was collected in a Gooch crucible in which a disk of filter paper was employed instead of asbestos, and after drying at 100° it was carefully separated from the filter paper. In other cases the precipitate was transferred to a platinum dish, and was drained with a platinum reverse filter[3] with a disk of filter paper. In still others a platinum Gooch crucible with small holes was found to be sufficiently effective as a filtering medium without the use of either asbestos or filter paper.

Before being weighed the silver bromide was fused in a current of air saturated with bromine in a weighed quartz crucible. The air was purified by passing successively over beads moistened with silver nitrate solution, over sodium carbonate, and finally over concentrated sulphuric acid which had been heated to its boiling-point with a small quantity of recrystallized potassium dichromate to eliminate volatile and oxidizable impurities. The air was then passed

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[1] See page 41.

[2] Baxter: *Proc. Amer. Acad.*, **40**, 432 (1904); **41**, 75 (1905); *Jour. Amer. Chem. Soc.*, **26**, 1590; **27**, 876; *Zeit. anorg. Chem.*, **43**, 27; **46**, 36. (See page 102.)

[3] Cooke: *Proc. Amer. Acad.*, **12**, 121 (1876).

through dry bromine in a small bulb. This apparatus was constructed entirely of glass with ground joints. The tube which conducted the gases into the crucible passed through a Rose crucible-cover of glazed porcelain in all experiments except analyses 28 to 31, in which a quartz cover was employed. The quartz crucibles were always contained in large porcelain crucibles while being heated. They remained almost absolutely constant in weight during the experiments. The bromine was in each case a portion of the sample from which the silver bromide had been made.

Next the bromide was heated barely to fusion in a slow current of chlorine, generated by the action of hydrochloric acid upon manganese dioxide, and dried by means of concentrated sulphuric acid. The apparatus for this purpose also was constructed wholly of glass. When the bromine was apparently completely displaced, the silver chloride was heated in the air for a few minutes to expel dissolved chlorine, and then was cooled and weighed. A repetition of the heating in chlorine seldom affected the weight of the salt more than a few hundredths of a milligram, although occasionally a third heating was necessary to effect this result.

That no loss of silver chloride by volatilization took place is certain for two reasons. In the first place the cover of the crucible and the delivery-tube for the bromine, when rinsed with ammonia and the solution treated with a slight excess of hydrochloric acid, gave no visible opalescence in the nephelometer. In the second place the weight of the chloride became constant without difficulty. It has already been shown that silver chloride which has been fused in chlorine, if subsequently heated in air, retains no excess of chlorine.[1]

The following vacuum corrections were applied: silver bromide, + 0.000041; silver chloride + 0.000071.[2] (See table on page 61.)

RESULTS AND DISCUSSION.

Aside from the close agreement of all the results of Series I, the fact is to be emphasized that of the last seven analyses, which were consecutive, only two differ from the average of the series, 79.916, by as much as 0.001 unit. Furthermore, there is no evidence of any dissimilarity in the different preparations of bromine. Material which has received only two distillations from a bromide gives values no lower than bromine which has been thus treated four times. The various specimens of silver also show no difference in purity.

In the case of Series II, the extreme variation of the results is only 0.004 unit, and only one of the 13 experiments yielded a value which differs from the average by more than 0.001 unit.

Finally, the difference between the averages of Series I and II is only 0.0007 unit. It is extremely unlikely that constant errors could have affected both

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[1] Baxter: *Proc. Amer. Acad.*, 40, 432 (1904); *Jour. Amer. Chem. Soc.*, **26**, 1591; *Zeit. anorg. Chem.*, **43**, 29. (See page 103.)

[2] See page 41.

series equally, so that this striking agreement is strong proof that both series are free from such errors.

THE ATOMIC WEIGHT OF BROMINE. SERIES II. AgBr: AgCl.
Ag = 107.880 Cl = 35.457.

No. of analysis.	Sample of bromine.	Weight of silver bromide in vacuum.	Weight of silver chloride in vacuum.	Ratio $\frac{AgBr}{AgCl}$	Atomic weight of bromine.
		gm.	*gm.*		
19	II	8.03979	6.13642	131.0176	79.916
20	II	8.57738	6.54677	131.0170	79.915
21	II	13.15698	10.04221	131.0168	79.915
			Average	131.0171	79.915
22	IV	12.71403	9.70413	131.0167	79.915
23	IV	13.96784	10.66116	131.0162	79.914
			Average	131.0164	79.915
24	V	13.08168	9.98469	131.0174	79.916
25	V	12.52604	9.56059	131.0175	79.916
26	V	11.11984	8.48733	131.0170	79.915
27	V	8.82272	6.73402	131.0172	79.916
			Average	131.0173	79.916
28	I	11.93192	9.10721	131.0162	79.914
29	I	12.53547	9.56767	131.0190	79.918
			Average	131.0176	79.916
30	III	17.15021	13.09009	131.0167	79.915
31	III	10.31852	7.87572	131.0168	79.915
			Average	131.0168	79.915
	Total	153.94242	117.49801	131.0170	79.915
Average of all 13 experiments				131.0171	79.915
Average of Series I and II					79.916

It has already been pointed out that the average of Stas's syntheses, 79.917, probably represents with considerable accuracy the atomic weight of bromine, and that certainly his determinations are more accurate than those of later experimenters. His syntheses are few in number, however, and differ among themselves by several thousandths of a unit, so that they do not define within this amount the constant in question. Their average, however, confirms the value obtained in this paper. From all the experiments here described the number 79.916 seems to be the most probable value for the atomic weight of bromine, if silver has the atomic weight 107.880. If silver is taken at 107.870, bromine becomes 79.909.

In conclusion, attention may be called to the fact that a diminution in the atomic weight of bromine referred to silver raises slightly all atomic weights resulting from the analysis of metallic bromides by precipitation with silver.

I am deeply indebted to the Cyrus M. Warren Fund for Research in Harvard University for assistance in pursuing this investigation.

V.

A REVISION OF THE ATOMIC WEIGHT OF LEAD.

THE ANALYSIS OF LEAD CHLORIDE.

By Gregory Paul Baxter and John Hunt Wilson.

Proceedings of the American Academy of Arts and Sciences, **43**, 365 (1907).
Journal of the American Chemical Society, **30**, 187 (1908).
Zeitschrift für anorganische Chemie, **57**, 174 (1908).
Chemical News, **98**, 64, 78 (1908).

Contributions from the Chemical Laboratory of Harvard College.

A REVISION OF THE ATOMIC WEIGHT OF LEAD.

THE ANALYSIS OF LEAD CHLORIDE.

INTRODUCTION.

Although lead is one of the most common elements, its atomic weight has received comparatively little attention, the value at present accepted being based almost wholly upon the work of Stas.[1] Of the earlier determinations of this constant those of Döbereiner[2] and Longchamps[3] can hardly be considered as possessing other than historic interest. The first results which can lay claim to accuracy are those of Berzelius,[4] who obtained values ranging from 206.7 to 207.3 by reduction of litharge in a current of hydrogen. Berzelius also synthesized the sulphate from metallic lead with the result 207.0.[5] Shortly after, Turner[6] criticized the first method employed by Berzelius and attributed the irregularity of his results to the action of lead oxide on the silicious matter of the tube at the temperature employed in the reduction. By the conversion of both the metal and the oxide into sulphate Turner in a painstaking research deduced the values 207.0 and 207.6 respectively, and by converting the nitrate into sulphate, 204.2. Marignac[7] converted metallic lead into the chloride by heating in a stream of chlorine and obtained the result 207.42. Both Marignac[8] and Dumas[9] analyzed lead chloride. Marignac, who dried the salt at 200°, by titration against silver found the atomic weight of lead to be 206.81, and from the ratio of lead chloride to silver chloride, 206.85. Dumas subsequently showed that lead chloride, even when dried at 250°, retains moisture and is somewhat basic, and in one analysis, in which corrections are applied for these errors, found a somewhat higher value, 207.07, as was to be expected. Chloride analyses by early investigators are, however, to be universally distrusted, owing to neglect of the very considerable solubility of silver chloride, thus producing too low results.

Stas's work upon the syntheses of lead nitrate and sulphate from the metal is undoubtedly the most accurate contribution upon the subject,[10] although a

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[1] Earlier work on the atomic weight of lead has been carefully summarized by Clarke. *Smithsonian Miscellaneous Collections*, Constants of Nature, "A Recalculation of the Atomic Weights," 1910. The earlier results have been recalculated on the basis of the following atomic weights: O = 16.00; N = 14.01; S = 32.07; Cl = 35.46; Ag = 107.88.

[2] *Schweig. Jour.*, **17**, 241 (1816).

[3] *Ann. Chim. Phys.*, **34**, 105 (1827).

[4] *Pogg. Ann.*, **19**, 314 (1830).

[5] Lehrbuch, 5th ed., **3**, 1187 (1845).

[6] *Phil. Trans.*, 527 (1833).

[7] *Lieb. Ann.*, **59**, 289 (1846).

[8] *Jour. Prakt. Chem.*, **74**, 218 (1858).

[9] *Lieb. Ann.*, **113**, 35 (1860).

[10] *Œuvres Complètes*, **1**, 383.

careful consideration of his work discloses minor defects, many of which he recognizes himself. The metallic lead used in the syntheses was finally fused under potassium cyanide. Whether or not this treatment introduced impurities into the metal is uncertain. Stas himself suspected the presence of alkali metals. Since the nitrate could not be dried above 150° without decomposition, it undoubtedly contained moisture, and Stas calls attention to this point. The sulphate was made by treatment of lead nitrate, resulting from the nitrate syntheses, with sulphuric acid. The sulphate was dried finally at dull redness, and was probably free, or nearly free, from moisture, although it may have contained traces of lead oxide resulting from occluded nitrate, as well as sulphuric acid. Most of these probable errors tend to lower the observed atomic weight, so that Stas's value from the series of nitrate syntheses, 206.81, and that from the sulphate series, 206.92, are to be regarded as minimum values. The reader of Stas's own account of his work upon lead can not fail to be impressed with the fact that he was somewhat dissatisfied with the outcome of his research. Mention should also be made of the work of Anderson and Svanberg [1] on the conversion of lead nitrate into oxide, although the method was primarily employed in an endeavor to fix the atomic weight of nitrogen. Their results yield the value 207.37.

The discrepancies between the results of these various experiments only serve to emphasize the need of a redetermination of the value in question, and it was with this object in view that the work embodied in this paper was undertaken.

The search for a suitable method for determining the atomic weight of lead failed to reveal any more promising line of attack than those already employed for the purpose. With an element of so high an atomic weight as lead, in any method involving the change of one of its compounds into another, errors which may be insignificant with elements of small atomic weight are magnified in the calculations to undesirable proportions. Furthermore, during the following investigation, reduction of the chloride and oxide in hydrogen was investigated far enough to show that complete reduction of either compound was extremely difficult, if not impossible, without loss of material from the containing vessel by sublimation, aside from the fact that all available material for containing vessels is acted upon by either the fused salt or the reduced metal. The elimination of moisture from lead nitrate or lead sulphate without decomposition of the salts seemed likely to prove a stumbling-block in the use of these substances. Finally, in spite of the slight solubility of lead chloride, the determination of the chlorine in this salt by precipitation with silver nitrate was chosen as presenting fewest difficulties. In the first place, the determination of a halogen can be effected with great accuracy. In the second place, the elimination of moisture from lead chloride is an easy matter, since the salt may be fused in a platinum vessel in a current of hydrochloric-acid gas without attacking the platinum

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[1] *Ann. Chim. Phys.* (3), **9**, 254 (1843).

in the least and without the production of basic salts. In the third place, silver chloride, which has been precipitated from a dilute solution of lead chloride by means of silver nitrate, was shown experimentally not to contain an amount of occluded lead salt large enough to be detected.

PURIFICATION OF MATERIALS.

Water, hydrochloric acid, and nitric acid were carefully purified by distillation as described in the preceding papers. In the preparation of pure silver also the usual methods were employed, one precipitation as chloride, one as metal by ammonium formate, and one by electrolysis being followed by the final fusion in hydrogen on a boat of pure lime.

LEAD CHLORIDE.

Three samples of lead chloride from two entirely different sources were employed. Sample A was prepared from metallic lead. Commercial lead was dissolved in dilute nitric acid, and the solution, after filtration, was precipitated with a slight excess of sulphuric acid. The lead sulphate was thoroughly washed, suspended in water, and hydrogen sulphide was passed in until the sulphate was almost completely converted into sulphide. Next the sulphide was washed with water, dissolved in hot dilute nitric acid, and the solution was freed from sulphur and unchanged sulphate by filtration. The lead nitrate thus obtained was crystallized twice, dissolved in water, and precipitated in glass vessels with a slight excess of hydrochloric acid. The chloride was washed several times with cold water and then crystallized from hot water eight times, the last five crystallizations being carried out wholly in platinum, with centrifugal drainage after each crystallization. In crystallizing the lead chloride the whole sample was not dissolved at one time, but the same mother-liquor was used for dissolving several portions of the original salt. Needless to say, the chloride was not exposed to contact with the products of combustion of illuminating gas, lest lead sulphate be formed.

Sample B was prepared from commercial lead nitrate. This salt was dissolved and crystallized from dilute nitric acid once in glass and six times in platinum vessels, with centrifugal drainage. Hydrochloric acid was then distilled into a large quartz dish, and the solution of the nitrate was slowly added with constant stirring with a quartz rod. The chloride was freed from aqua regia as far as possible by washing with cold water, and was once crystallized from aqueous solution in quartz dishes to remove last traces of aqua regia. Finally the salt was crystallized three times in platinum.

It could reasonably be expected that both of these samples were of a high degree of purity; nevertheless, upon heating the salt in an atmosphere of hydrochloric acid, the salt itself turned somewhat dark, and upon solution of the fused salt in water a slight dark residue remained. Although in a few preliminary experiments attempts were made to determine this residue by filtration and ignition, it was subsequently found that even a small filter paper adsorbs appreciable amounts of lead compounds from a solution of the chloride, which can not be removed by washing with water. From 0.03 mg. to 0.13 mg. of residue were obtained in several blank experiments, by ignition of filters through which 0.5 per cent solutions of lead chloride had been passed, with subsequent very thorough washing. In order to avoid the uncertainty of this correction, further attempts were made to obtain a sample of the salt which would give a perfectly clear solution in water after fusion, and thus render filtration unnecessary. With this end in view a considerable quantity of Sample A was fused in a large platinum boat in a current of hydrochloric acid. The fused salt was powdered in an agate mortar, dissolved in water in a platinum vessel, and the solution was freed from the residue by filtration through a tiny filter in a platinum funnel into a platinum dish, where it was allowed to crystallize. This sample was then twice recrystallized with centrifugal drainage. Notwithstanding the drastic treatment to which it had been subjected, when a portion of this material was fused in hydrochloric acid, the same darkening as before was observed, and the same residue was obtained. The suspicion that the difficulty was due to dissolving of the filter paper by the solution of the salt[1] led to a second more successful attempt by crystallization from hydrochloric acid solution in platinum vessels. In this way it was found possible to prepare salt which showed no tendency to darken upon heating, and which, after fusion, left absolutely no residue upon solution in water. Portions of Samples A and B were thus recrystallized three times more. Since these two specimens of material gave identical results, for two final experiments, portions from each of these samples were mixed and then subjected to three additional crystallizations. This last sample was designated Sample C.

DRYING OF LEAD CHLORIDE AND METHOD OF ANALYSIS.

The method of analysis did not differ materially from that used in the analysis of cadmium and manganese chlorides (pages 7 and 45). The lead chloride, contained in a weighed platinum boat, was first fused in a current of hydrochloric-acid gas, and the boat was transferred to its weighing-bottle and weighed. On account of the small solubility of lead chloride it was a somewhat troublesome matter to dissolve the fused material. This was done in most of the analyses by prolonged contact with water nearly at the boiling point in a Jena glass flask. In the last two analyses, in order to show that no error was introduced through the solubility of the glass, the solution was prepared in a large platinum retort and was transferred to the precipitating flask only when cold.

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[1] Mr. P. B. Goode in this laboratory has recently found a similar difficulty with the chlorides of the alkaline earths.

When the lead chloride was dissolved, a dilute solution of a very nearly equivalent amount of pure silver was added, and, after standing, the amounts of chloride and silver were carefully adjusted until exactly equivalent by means of the nephelometer. When the exact end-point had been found, about 0.2 gm. of silver nitrate in excess was added to precipitate dissolved silver chloride, and the precipitate was collected and determined upon a Gooch crucible. Dissolved silver chloride in the filtrate and wash-waters was estimated by comparison with standard solutions in the nephelometer. Asbestos displaced from the Gooch crucible was collected, and the moisture retained by the dried precipitate was found by loss of weight during fusion.

In order to find out whether lead or silver nitrates were appreciably adsorbed by the filter paper, a solution containing lead nitrate, silver nitrate, and nitric acid of the concentration of these filtrates, was passed through several small filter papers, which were then very carefully washed. In four cases, after incineration of the papers, there was found, − 0.00001, + 0.00002, + 0.00003, + 0.00001 gm. of residue, exclusive of ash. This correction is so small that it is neglected in the calculations. In all the analyses the platinum boat behaved admirably, the loss in weight never amounting to more than a few hundredths of a milligram.

The balance used was a short-arm Troemner, easily sensitive to 0.02 mg. The gold-plated brass weights were carefully standardized to hundredths of a milligram. All the weighings were made by substitution with tare vessels as nearly like those to be weighed as possible.

Vacuum corrections. The values of the density of lead chloride as given by various observers range from 5.78 to 5.805,[1] the mean of the more accurate determinations being 5.80. This gives rise to a vacuum correction of + 0.000062 for each apparent gram of lead chloride, the density of the weights being assumed to be 8.3. The other vacuum corrections applied were for silver chloride, + 0.000071, and for silver, −0.000031.

All analyses which were carried to a successful completion are recorded in the tables on page 70.

RESULTS AND DISCUSSION.

The close agreement of the averages of the two series is strong evidence that no constant error, such as occlusion, affects the results. In all, 19.55663 gm. of silver produced 25.98401 gm. of silver chloride, whence the ratio of silver chloride to silver is 132.865, a value in close agreement with the result 132.867 obtained by Richards and Wells. Furthermore, the different samples, A, B, and C, all give essentially identical results.

It appears, then, that if the atomic weight of silver is taken as 107.880, the atomic weight of lead is 207.09, nearly 0.2 unit higher than the value now in

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[1] Landolt-Börnstein-Meyerhoffer, Tabellen.

use. If the atomic weight of silver is 107.87, lead becomes 207.08, a number still much higher than that depending upon Stas's syntheses, as is to be expected.

The Atomic Weight of Lead.

Series I. $PbCl_2 : 2Ag$.

$Ag = 107.880$ $Cl = 35.457$

No. of analysis.	Sample of $PbCl_2$.	Weight of $PbCl_2$ in vacuum.	Weight of Ag in vacuum.	Weight of Ag added or subtracted.	Corrected weight of Ag.	Atomic weight of Pb.
		gm.	gm.	gm.	gm.	
1	A	4.67691	3.63061	−0.00074	3.62987	207.083
2	A	3.67705	2.85375	0.00000	2.85375	207.093
3	A	4.14110	3.21388	+0.00020	3.21408	207.077
4	A	4.56988	3.54672	0.00000	3.54672	207.089
5	B	5.12287	3.97596	−0.00028	3.97568	207.105
6	B	3.85844	2.99456	0.00000	2.99456	207.090
7	B	4.67244	3.62628	0.00000	3.62628	207.093
8	C	3.10317	2.40837	0.00000	2.40837	207.092
9	C	4.29613	3.33427	−0.00020	3.33407	207.106
Average						207.092

Series II. $PbCl_2 : 2AgCl$.

No. of analysis.	Sample of $PbCl_2$.	Weight of $PbCl_2$ in vacuum.	Weight of AgCl in vacuum.	Loss on fusion.	Weight of asbestos.	Wt. AgCl from wash-waters.	Corrected weight of AgCl.	Atomic weight of Pb.
		gm.	gm.	gm.	gm.	gm.	gm.	
10	A	4.67691	4.82148	0.00100	0.00021	0.00204	4.82273	207.092
11	A	4.14110	4.26848	0.00020	0.00008	0.00180	4.27016	207.096
12	B	5.12287	5.28116	0.00054	0.00013	0.00197	5.28272	207.085
13	B	3.85844	3.97759	0.00035	0.00033	0.00192	3.97949	207.040
14	C	3.10317	3.19751	0.00045	0.00014	0.00189	3.19909	207.165
15	C	4.29613	4.42730	0.00020	0.00004	0.00268	4.42982	207.108
Average								207.097
Average, rejecting the least satisfactory analyses, 13 and 14								207.095
Average of Series I and II								207.094

VI.

A REVISION OF THE ATOMIC WEIGHT OF ARSENIC.

THE ANALYSIS OF SILVER ARSENATE.

By Gregory Paul Baxter and Fletcher Barker Coffin.

Proceedings of the American Academy of Arts and Sciences, **44**, 179 (1909).
Journal of the American Chemical Society, **31**, 297 (1909).
Zeitschrift für anorganische Chemie, **62**, 50 (1909).

Contributions from the Chemical Laboratory of Harvard College.

A REVISION OF THE ATOMIC WEIGHT OF ARSENIC.

THE ANALYSIS OF SILVER ARSENATE.

INTRODUCTION.

Below is a summary of the previous work upon the atomic weight of arsenic,[1] the results obtained by the several investigators having been recalculated with the use of the most recent [2] atomic weights:

Date.	Investigator.	Reference.	Ratio determined.	Result.
1816	Thomson	Schweigger's Jour., 17, 421	$2As : As_2O_5$	76.35
1818	Berzelius	Pogg. Ann., 8, 1	$2As_2O_3 : 3SO_2$	75.03
1845	Pelouze	Compt. Rend., 20, 1047	$AsCl_3 : 3Ag$	74.93
1855	Kessler	Pogg. Ann., 95, 204	$3As_2O_3 : 2K_2Cr_2O_7$	74.95
			$3As_2O_3 : 2KClO_3$	75.23
1859	Dumas	Ann. Chim. Phys. (3), 55, 174	$AsCl_3 : 3Ag$	74.87
1859	Wallace	Phil. Mag. (4), 18, 279	$AsBr_3 : 3Ag$	74.20
1861	Kessler	Pogg. Ann., 113, 140	$3As_2O_3 : 2K_2Cr_2O_7$	75.01
1896	Hibbs	Doctoral Thesis, Univ. of Penn.	$Na_4As_2O_7 : 4NaCl$	74.88
1902	Ebaugh	Jour. Amer. Chem. Soc., 24, 489	$Ag_3AsO_4 : 3AgCl$	75.02
			$Ag_3AsO_4 : 3Ag$	74.92
			$Pb_3(AsO_4)_2 : 3PbCl_2$	75.06
			$Pb_3(AsO_4)_2 : 3PbBr_2$	74.88

A glance at this rather discordant series of results shows the necessity for a redetermination of the atomic weight of arsenic. Even in the more recent investigations of Hibbs and Ebaugh there exists an extreme variation of nearly 0.2 unit in the averages of the five series.

In this research silver arsenate was chosen for analysis, first, because the compound is unchanged by moderate heating, and hence may be dried at a temperature high enough to expel all but a very small amount of moisture. In the second place, silver compounds may be analyzed with great ease as well as accuracy by precipitation of the silver as silver halogen compounds. Furthermore, preliminary experiments confirmed the statement by Ebaugh that

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[1] Clarke: A recalculation of the atomic weights, *Smith. Misc. Coll.*, Constants of Nature, Part V (1910). For an excellent critical discussion by Brauner of previous work, see Abegg's *Handbuch der anorganischen Chemie*, 3, (2), 491 (1907).

[2] O = 16.00; Na = 22.98; S = 32.07; Cl = 35.46; K = 39.10; Cr = 52.01; Br = 79.92; Ag = 107.88; Pb = 207.09.

it is possible completely to convert the arsenate into chloride by heating in a current of hydrochloric-acid gas. Such a process has the advantage that no transfer of material is involved.

THE PREPARATION OF TRISILVER ARSENATE.

All the samples of silver arsenate were prepared by adding to a fifteenth normal solution of silver nitrate a solution of similar concentration of an equivalent amount of an arsenate of sodium or ammonium, the differences between the different samples consisting chiefly in the nature of the soluble arsenate employed. Precipitation was carried out in a room lighted only with ruby light. After the silver arsenate had been washed by decantation many times with pure water, it was dried in a preliminary way by centrifugal settling in platinum crucibles, and then by being heated in an electric oven at about 130° C. The salt was powdered in an agate mortar before the final heating in a quartz tube or platinum boat, as explained later. It was shown by tests with diphenylamine that the arsenate could be washed free from nitrates.

Although one of the hydrogens of arsenic acid resembles the hydrogen of strong acids in its dissociating tendency, the other two hydrogens are those of weak acids.[1] Hence perceptible hydrolysis takes place in solutions of salts of this acid, even when the base is strong, that of the tertiary salts being of course greatest in extent. It is not an easy matter to predict the effect of this hydrolysis upon the composition of a precipitate of silver arsenate; for while the Phase Rule allows the existence of only one solid in equilibrium with the arsenate solution except at certain fixed concentrations, the possibility of the occlusion of either basic or acid arsenates by the silver arsenate still exists. Experiments only are able to throw light on this point. Accordingly arsenate solutions of different conditions of acidity and alkalinity were used in the precipitations, and the compositions of the different precipitates were compared.

Sample A. Commercial C. P. disodium arsenate was recrystallized four times, all but the first crystallization being conducted in platinum vessels. The mother-liquor from the fourth crystallization, after the removal of the arsenic by hydrogen sulphide, gave no test for phosphate. The calculated amount of redistilled ammonia to make disodium ammonium arsenate was added to a solution of the purified salt before the precipitation of the silver arsenate. During this precipitation the mother-liquor remains essentially neutral.

Sample B. This sample was made from disodium arsenate which had been recrystallized five times in platinum vessels. Silver arsenate was precipitated

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[1] Washburn calculates from Walden's conductivity measurements the constant for the first hydrogen of arsenic acid to be 4.8×10^{-3}. *Jour. Amer. Chem. Soc.*, **30**, 35 (1908). The constants for the second and third hydrogens are probably lower than those of phosphoric acid, 2.0×10^{-7} and 3.6×10^{-13}. Abbott and Bray: *Ibid.*, **31**, 755 (1909).

with a solution of this salt without the addition of ammonia. Here the mother-liquor becomes more and more acid as precipitation proceeds.

Sample C. Commercial C. P. arsenic trioxide was recrystallized three times from dilute hydrochloric-acid solution, and, after being rinsed with water and centrifugally drained, it was converted into arsenic acid by means of nitric and hydrochloric acids in a porcelain dish. The hydrochloric and nitric acids were expelled by evaporation nearly to dryness, and the residue was twice evaporated to dryness with nitric acid in a platinum dish. After the residue had been dissolved in water, the solution was allowed to stand for some time in order to allow pyro- and meta-arsenic acids to be converted as completely as possible into ortho-arsenic acid. Then sodium carbonate, which had been twice crystallized in platinum, was added to the solution in amount sufficient to form disodium arsenate, and the product was crystallized four times in platinum vessels. The precipitation of silver arsenate by adding a solution of this salt to a solution of silver nitrate resembles the preparation of Sample B.

Sample D. A portion of the arsenic acid made for the preparation of Sample C was converted into ammonium dihydrogen arsenate by adding the calculated amount of redistilled ammonia, and the salt was recrystallized five times in platinum. A sufficient quantity of ammonia to form tri-ammonium arsenate was added to a solution of this salt before the precipitation of the silver arsenate. One specimen of silver arsenate made in this way was discarded, since its composition was very irregular.

Sample E. To a portion of the arsenic acid used for Sample C recrystallized sodium carbonate was added in amount sufficient to form disodium arsenate. After the solution had been evaporated to dryness, the salt was recrystallized four times in platinum. Enough ammonia to form disodium ammonium arsenate was added to a solution of this salt before the precipitation of the silver arsenate. This material resembles Sample A.

Sample F. A portion of the disodium arsenate prepared for Sample B was converted into trisodium arsenate by means of recrystallized sodium carbonate, and the trisodium arsenate was recrystallized six times in platinum vessels.

Sample G. Arsenic trioxide was twice resublimed in a current of pure dry air and then once crystallized from dilute hydrochloric-acid solution. Next the arsenious acid was oxidized to arsenic acid exactly as described under Sample C. Finally the arsenic acid was converted into trisodium arsenate by means of pure sodium carbonate, and the salt was crystallized four times in platinum. Samples F and G are evidently very similar.

In all the foregoing crystallizations the crystals were thoroughly drained in a centrifugal machine employing large platinum Gooch crucibles as baskets,[1] and each crop of crystals was once rinsed with a small quantity of pure water and subsequently drained in the centrifugal machine.

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[1] Baxter: *Jour. Amer. Chem. Soc.*, **30**, 286 (1908).

PURIFICATION OF OTHER MATERIALS.

SILVER NITRATE.

The silver nitrate used in the preparation of the different samples of silver arsenate was recrystallized several times in platinum vessels, with centrifugal drainage, until the mother-liquor gave no opalescence upon dilution when tested in the nephelometer.

HYDROBROMIC ACID.

One quarter pound of commercial bromine was converted into potassium bromide by addition to recrystallized potassium oxalate. In the concentrated solution of this bromide, in a distilling flask cooled with ice, 3 pounds of bromine were dissolved in several separate portions, each portion being distilled from the solution into a flask cooled with ice before the addition of the next succeeding portion. A portion of the purified bromine was then converted into potassium bromide with pure potassium oxalate as before, and the remainder of the bromine was distilled in small portions 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 purification of the hydrobromic acid was carried on in conjunction with Dr. Grinnell Jones, who was engaged in a parallel research upon the atomic weight of phosphorus. Using this acid, he found that 10.48627 gm. of silver bromide were obtained from 6.02386 gm. of the purest silver. This ratio of silver bromide to silver, 100.0000 to 57.4452, is in close agreement with the most probable value, 100.0000 to 57.4453.[2]

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[1] Baxter: *Proc. Amer. Acad.*, **42**, 201 (1906); *Jour. Amer. Chem. Soc.*, **28**, 1322; *Zeit. anorg. Chem.*, **50**, 389. (See page 59.)

[2] Baxter: *Loc. cit.*

A solution of hydrochloric acid was purified by distillation after dilution.

Hydrochloric-acid gas was generated by dropping C. P. concentrated sulphuric acid into C. P. concentrated hydrochloric acid. The acids were shown to be essentially free from arsenic.

All the water used in the research was purified by distilling the ordinary distilled water of the laboratory, once with alkaline permanganate and then once alone, in both cases with the use of block-tin condensers which required no cork or rubber connections to the distilling flasks.

Quartz or platinum vessels were always employed in place of glass, whenever glass was unsuitable.

METHODS OF ANALYSIS.

The first method of analysis employed was that of converting the silver arsenate into silver chloride by heating in a current of hydrochloric-acid gas. Since this process does not involve transfer of material it should be capable of giving results of great accuracy. Glass and porcelain are unsuitable for containing the arsenate during this process on account of the certainty of their being attacked. The first attempts at using quartz for the purpose resulted in slight etching of the surface of the tube where it came in contact with the salt. Experience showed, however, that with careful manipulation the attacking of the quartz could be wholly prevented. The vessel used to contain the arsenate was a quartz tube nearly 2 cm. in diameter but joined to small tubes at each end. These tubes were exactly like those employed by Richards and Jones in the conversion of silver sulphate into silver chloride.[1] After the tube had been weighed by substitution for a counterpoise similar in shape and size, a suitable quantity of silver arsenate was introduced, and the tube and contents were heated in a current of pure dry air for between 7 and 8 hours at 250° C. Although this treatment is not sufficient to expel last traces of moisture, it was hoped that by uniform treatment of the arsenate in all the analyses the proportion of water retained by the salt could be reduced to a constant percentage, which could be determined in separate experiments.

The complete drying of the salt by fusion was not permissible because of decomposition of the arsenate at temperatures in the neighborhood of its fusing point. During the drying of the arsenate the quartz tube was surrounded with a cylinder of thin platinum foil and was contained in a hard-glass tube connected with an apparatus for furnishing a current of pure dry air. The hard-glass tube was heated by means of two aluminum blocks 15 cm. by 13 cm. by 5 cm., one placed above the other, the upper surface of the lower block and the lower surface of the upper being suitably grooved to contain the tube. The blocks were bored to contain a thermometer, the bulb of which was located near the middle of the tube. This oven (fig. 4) could be readily maintained at constant temper-

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[1] *Pub. Car. Inst.*, No. 69, 69 (1907); *Jour. Amer. Chem. Soc.*, 29, 833; *Zeit. anorg. Chem.*, 55, 80.

ature within a very few degrees by means of a Bunsen flame. We are indebted to Dr. Arthur Stähler of the University of Berlin for the suggestion of this method of heating.

In order to purify and dry the air it was passed through a tower filled with beads moistened with dilute silver-nitrate solution, through a tower filled with small lumps of solid potassium hydroxide, then through 3 towers filled with beads moistened with concentrated sulphuric acid, and finally through a tube filled with resublimed phosphorus pentoxide.

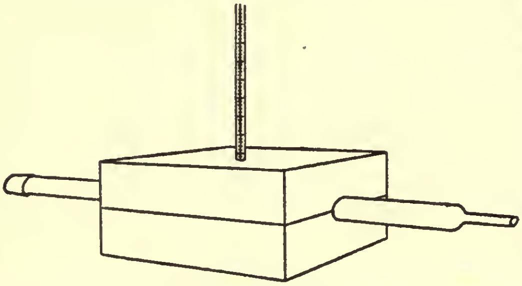
Fig. 4. — Solid aluminum drying oven.

The apparatus was constructed wholly of glass, with ground joints, and was similar to that shown in fig. 1, page 8.

After being heated, the quartz tube was transferred to a desiccator and was allowed to come to the temperature of the balance case before being weighed. The quartz tube was then placed upon hard-glass supports, in a horizontal position, one end being slipped into a larger tube, through which could be passed a current of either dry hydrochloric-acid gas or dry air. The other end of the quartz tube slipped into one of the arms of a large U-tube filled with glass pearls, which served to condense any silver-chloride vapor, which might escape from the quartz tube. The other arm of the U-tube was connected with the flue of a hood, the suction thus caused being sufficient to prevent the escape of gaseous arsenic compounds from the apparatus. The quartz tube was protected from dust by a covering of sheet mica.

The usual method of procedure was as follows: The quartz tube containing the silver arsenate being in place, a current of hydrochloric-acid gas was passed through the tube, and the tube was slowly revolved with pincers tipped with platinum wire in order that the salt might be thoroughly exposed to the action of the acid. Neglect to do this at the commencement of the reaction always resulted in the caking of the salt in the tube, thereby rendering the action of the acid less rapid. The hydrochloric acid was dried by passing through three towers containing beads moistened with concentrated sulphuric acid. The apparatus for generating and purifying the acid was constructed wholly of glass, and was similar to that shown in fig. 1, page 8.

In the earlier experiments the salt was gently heated from the commencement of the reaction. To all outward appearance it was entirely converted into silver chloride in a few hours. Upon fusion, however, it presented a very cloudy appearance, owing to the presence of arsenic compounds, which could not be completely removed even by keeping the silver chloride fused in the current of hydrochloric acid for as long as 8 hours. This is the cause of the larger quantities of arsenic found in the chloride obtained in the earlier analyses. Furthermore, the longer period of heating at a temperature above the fusing point of silver chloride accounts for the larger amounts of volatilized silver chloride found in these experiments.

As experience was gained, it was found best to expose the salt first in the cold for about 8 hours to the action of the hydrochloric-acid gas, next to heat the salt gently below its fusing point for from 10 to 15 hours, and finally to keep it barely fused for from 5 to 10 hours longer. When the reaction was apparently at an end, the current of hydrochloric-acid gas was stopped, and dry air was passed through the tube for about 15 minutes in order to eliminate hydrochloric acid. The silver chloride was then allowed to solidify in a uniform thin layer around the inside of the quartz tube by slowly revolving the tube during solidification. The platinum wire used in weighing the tube was slipped on, the tube was transferred to its desiccator, and after standing several hours beside the balance it was weighed.

In order to make sure that the reaction was complete the silver chloride was again fused, and exposed to the action of hydrochloric acid for several hours longer. As a rule, no change in weight was observed. In all cases constant weight was obtained upon heating in the same way for a third time.

After making certain that only a small quantity of arsenic, if any, remained in the silver chloride, the contents of the quartz tube were dissolved in ammonia, and the silver chloride was reprecipitated by boiling the solution to expel the ammonia and adding a small quantity of sulphuric acid. The solution, after evaporation, was added to a Berzelius-Marsh apparatus containing arsenic-free zinc and sulphuric acid, and a mirror of arsenic was deposited in a hard-glass capillary tube in the usual way. The hydrogen was dried by calcium chloride before passing into the hard-glass tube, and the generating flask was cooled with water to prevent the evolution of hydrogen sulphide.

The arsenic mirror formed was compared with a photograph of standard arsenic mirrors,[1] the original mirrors showing that comparison with the photograph was equally satisfactory. The correction was applied by assuming that the arsenic was present in the silver chloride as arsenic trichloride, although if present as silver arsenate the correction would be much smaller. In any case the correction for residual arsenic is so small as to be almost without effect upon the final result.

Ebaugh used essentially the same method of heating the arsenate in hydrochloric acid, although the periods were shorter, so that it is probable that the small quantities of arsenate used (scarcely over one gram in any analysis) did not retain weighable amounts of arsenic.

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[1] Sanger: *Proc. Amer. Acad.*, **26**, 24 (1891).

The U-tube used for collecting volatilized silver chloride was washed out thoroughly with dilute ammonia, and the solution was made up to definite volume after nearly all the ammonia had been expelled by boiling. The silver content of the solution was then compared in the nephelometer with that of standard solutions of silver, care being taken that the tubes were treated in as nearly as possible the same way.

The second method of analysis consisted in heating the silver arsenate in a platinum boat and, after weighing, dissolving the arsenate in nitric acid and precipitating the silver as chloride or bromide. The platinum boat was heated in a hard-glass tube forming part of a bottling apparatus,[1] and was thus transferred without exposure to moist air to the weighing-bottle in which it was always weighed. The boat and bottle were weighed by substitution by comparison with a counterpoise similar both in shape and volume.

After the silver arsenate had been weighed, the boat with its contents was transferred to a flask, and the salt was dissolved in warm 5N nitric acid. The weighing-bottle was rinsed with acid, and the rinsings were added to the main solution; then the solution was carefully transferred to a large glass-stoppered precipitating flask and diluted to a volume of about 1 liter.

From the weight of silver arsenate the amount of either hydrochloric or hydrobromic acid necessary to precipitate the silver was calculated. A slight excess of one acid or the other was then diluted to about 600 c.c., and the solution was slowly poured into the solution of silver arsenate in the precipitating flask. After a few moments' shaking the precipitate was allowed to stand for several days, with occasional agitation.

The precipitated silver chloride or silver bromide was next collected upon a weighed Gooch crucible, after it had been washed by decantation about ten times with dilute hydrochloric acid in the case of silver chloride, with water in the case of silver bromide. After several hours' heating in an electric air bath at 150° C., and about 2 hours' heating at 200° C., the precipitate was cooled in a desiccator and weighed.

In order to determine the moisture retained by the precipitate it was transferred as completely as possible to a small porcelain crucible and weighed. Then the salt was fused by heating the small covered crucible contained in a large crucible and was again weighed.

The asbestos mechanically detached from the Gooch crucible, together with a small quantity of silver chloride or silver bromide which escaped the crucible, was collected upon a small filter through which the filtrate and wash-waters were passed, and the filter paper was ignited in a small weighed porcelain crucible. Before being weighed the ash was treated with a drop of nitric and a drop of either hydrochloric or hydrobromic acid and again heated.

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[1] See page 9.

The filtrate and wash-waters were evaporated to small bulk. The precipitating flask was rinsed with ammonia, and the rinsing was added to the evaporated filtrate and wash-water. Then the solution was diluted to definite volume, and the silver content was determined by comparison with standard silver solutions in the nephelometer.

The operations of precipitating and collecting the silver halides were all carried out in a room lighted only with ruby light.

INSOLUBLE RESIDUE.

All the specimens of silver arsenate, after being heated at 250° C., when dissolved in dilute nitric acid, were found to contain a small amount of insoluble residue, which would dissolve only in rather concentrated nitric acid. Although the proportion of this residue was apparently increased by exposure to light, specimens of the arsenate which had been prepared wholly in the dark room were not free from it. No process of purification to which the soluble arsenate used in the preparation of the silver arsenate was subjected seemed to have the slightest effect upon the proportion of insoluble matter. A similar phenomenon was met by Dr. Grinnell Jones in the preparation of silver phosphate (page 178).

Although the amount of this residue in one gram of silver arsenate which had been treated as in the analyses for silver was not over 0.00005 gm., it was important to determine its silver content. This was done in three cases in which the proportion of residue had been purposely increased as much as possible by exposure to light. The arsenate was dissolved in dilute nitric acid, and the residue was collected upon a weighed platinum Gooch crucible, the detached asbestos shreds being carefully determined by filtration upon a filter paper. The weight of residue was found by reweighing the crucible. After the residue had been dissolved in concentrated nitric acid and the solution had been diluted to definite volume, the silver content of the solution was ascertained by comparison with standard silver solutions in a nephelometer.

Weight of silver arsenate.	Weight of insoluble residue.	Weight of silver.	Per cent of silver.
gm.	*gm.*	*gm.*	
4.26	0.00198	0.00143	72.3
10.00	0.00228	0.00162	71.1
9.28	0.00657	0.00500	76.1
Average			73.2
Theoretical per cent of silver in silver arsenate . . .			70.0

The first of the above determinations was made with a sample of silver arsenate which had been exposed to bright light inside a desiccator for a month.

During this time the quartz tube containing the salt showed no perceptible change in weight. The third determination also was made with a sample of salt which had been exposed to bright light for 3 weeks in a dry state. In the second determination the salt was exposed to light under water for one week.

Two facts show that the presence of the small proportion of the residue in the arsenate could have had no important effect upon the results. In the first place, the formation of the insoluble matter under the influence of light is not attended by change in weight. In the second place, the silver content of the residue is very near that of silver arsenate. Nevertheless, care was taken to protect the arsenate as far as possible from exposure to light.

DETERMINATION OF MOISTURE IN DRIED SILVER ARSENATE.

T. W. Richards[1] and others have already drawn attention to the fact that it is not possible, without fusion, to dry completely a substance formed in aqueous solution, owing to the mechanical retention of liquid in pockets within the solid. In the case of silver arsenate, although it is possible to fuse the salt, the temperature necessary is so high that decomposition of the salt takes place to some extent. Hence the loss in weight on fusion can not be used as a true measure of the water content of the salt. Since decomposition of the salt could produce only easily condensible substances and oxygen, the difficulty was overcome in the present instance by fusing weighed quantities of the salt in a current of pure dry air and collecting the water vapor in a weighed phosphorus pentoxide tube. Of course great pains were taken to treat the salt used in the water determinations in exactly the same way as that used in the analyses for silver.

The procedure was as follows: A sample of salt very nearly as pure as that used in the silver analyses was weighed out in a copper boat which had been previously cleaned and ignited in the blast lamp to remove organic matter. The boat was placed in a hard-glass tube and was heated for between 7 and 8 hours at 250° C., in a current of dry air. In these experiments, before passing through the drying towers the air had first been passed over hot copper oxide in order to oxidize any organic matter it might contain. Furthermore, the concentrated sulphuric acid in the drying towers had been heated with a small quantity of potassium dichromate. One end of the hard-glass tube was connected to the apparatus for supplying pure air, by means of a well-fitting ground joint upon which no lubricant was used. The other end was sealed to a small hard-glass tube which was surrounded with a damp cloth during the fusion of the salt in order to facilitate condensation of any silver or arsenic compounds vaporized from the salt. As a matter of fact, very little sublimation actually took place.

In order to fuse silver arsenate within the hard-glass tube it was necessary to use the hottest flame of the blast lamp, the tube being covered with a semi-

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[1] *Zeit. physik. Chem.*, 46, 194 (1903).

cylinder of sheet iron. Furthermore, since at this temperature even the hard glass became very soft, it was found necessary to wrap the tube with asbestos and closely wound iron wire for several inches at the piont where fusion took place. This also served to distribute the heat more evenly and to prevent the tube from cracking during the experiment.

Just before the salt was fused a carefully weighed U-tube containing resublimed phosphorus pentoxide was attached to the end of the tube, and beyond this was joined another similar tube which served as a protection against any moisture which might diffuse back into the weighed tube from the outside air. These phosphorus pentoxide tubes were provided with one way ground glass stopcocks lubricated with Ramsay desiccator grease.

The salt was heated for 25 minutes with the hottest flame of the blast lamp, being then completely fused, and was further heated for 35 minutes at a considerably lower temperature in order to make certain that all moisture was carried into the absorption tube by the current of air. Finally the phosphorus pentoxide tube was reweighed.

The pentoxide tube was weighed by substitution with the use of a counterpoise of the same size and weight filled with glass beads. Before being weighed both tubes were carefully wiped with a damp cloth and were allowed to stand near the balance case for one hour. One stopcock in each tube was opened immediately before the tube was hung upon the balance, in order to insure equilibrium between the internal and external air pressure. The stopcock of the counterpoise was left open during the weighing. Owing to the considerable length of time required for the tubes to come to equilibrium on the balance, it was considered unsafe to leave the stopcock of the pentoxide tube open during the weighing. As a check on the first weight of the pentoxide tube one stopcock was opened and closed and its weight determined a second time. Ordinarily no change in weight was observed.

Weight of silver arsenate.	Weight of water.	Weight of water per gram of salt.
gm.	*gm.*	*gm.*
11.09	0.00083	0.000075
13.59	0.00073	0.000054
17.23	0.00085	0.000049
12.57	0.00057	0.000045
Average		0.000056

Since it seemed possible that the hard-glass tube itself, when heated nearly to fusion, might give off traces of water vapor, two blank determinations were made by heating the empty hard-glass tube in exactly the same way as in the water determinations. These determinations showed a gain in weight of the pentoxide tube of 0.00022 and 0.00037 gm. respectively, the average being

0.00030 gm. This correction was confirmed in another experiment in which the hard-glass tube was kept at the highest temperature obtainable with the blast lamp for an hour. The observed gain in weight of the absorption tube was 0.00048 gm. A negative correction of 0.00030 gm. was applied in each water determination.

In order to allow for moisture the weight of the arsenate was therefore always corrected by subtracting 0.000056 gm. per gram of salt. Ebaugh took no notice of the water contained in silver arsenate which had been dried at only 170°.

SPECIFIC GRAVITY OF SILVER ARSENATE.

In order that the apparent weight of the silver arsenate might be corrected to a vacuum standard, the specific gravity of the arsenate was found by determining the weight of toluol displaced by a known quantity of salt. The toluol was first dried by means of stick soda and was then distilled, with rejection of the first portion of the distillate. Its specific gravity at 25° referred to water at 4° was found to be 0.8620. Pains were taken to remove air from the arsenate when covered with toluol by placing the pycnometer in an exhausted desiccator.

Weight of silver arsenate in vacuum.	Weight of displaced toluol in vacuum.	Specific gravity of silver arsenate 25°/4°.
gm.	*gm.*	*gm.*
5.1690	0.6688	6.662
5.6729	0.7350	6.652
Average		6.657

The following vacuum corrections were applied:

	Specific gravity.	Vacuum correction.
Weights	8.3	
Toluol	0.862	+0.00126
Silver arsenate	6.657	+0.000036
Silver chloride	5.56	+0.000071
Silver bromide	6.473	+0.000041

All weighings were made upon a nearly new short-armed Troemner balance, easily sensitive to 0.02 mg. with a load of 50 gm.

The gold-plated Sartorius weights were several times carefully standardized to hundredths of a milligram by the method described by Richards,[1] and were used for no other work.

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[1] *Jour. Amer. Chem., Soc.*, **22**, 144 (1900).

RESULTS AND DISCUSSION.

Series I. $3AgCl: Ag_3AsO_4$.

No. of analysis.	Sample of Ag_3AsO_4.	Corrected weight of Ag_3AsO_4 in vacuum.	Weight of AgCl in vacuum.	Residual $AsCl_3$.	Volatilized AgCl.	Corrected weight of AgCl in vacuum.	Ratio $3AgCl: Ag_3AsO_4$.
		gm.	gm.	gm.	gm.	gm.	
1	A	3.17276	2.94912	0.00004	0.00014	2.94922	0.929544
2	A	2.65042	2.46364	0.00004	0.00007	2.46367	0.929539
3	A	3.51128	3.26395	0.00001	0.00002	3.26396	0.929564
4	B	5.83614	5.42499	0.00001	0.00005	5.42503	0.929558
5	C	5.72252	5.31947	0.00001	0.00001	5.31947	0.929568
Average							0.929555

Series II. $3AgCl: Ag_3AsO_4$.

No. of analysis.	Sample of Ag_3AsO_4	Corrected weight of Ag_3AsO_4 in vacuum.	Weight of AgCl in vacuum.	Weight of asbestos.	Dissolved AgCl from filtrate.	Loss on fusion.	Corrected weight of AgCl in vacuum.	Ratio $3AgCl: Ag_3AsO_4$.
		gm.	gm.	gm.	gm.	gm.	gm.	
6	C	4.59149	4.26815	0.00008	0.00012	0.00039	4.26796	0.929537
7	D	3.38270	3.14401	0.00037	0.00013	0.00015	3.14436	0.929542
Average								0.929540
Average of all analyses in Series I and II								0.929550
Per cent of Ag in Ag_3AsO_4								69.9609[1]

Series III. $3AgBr: Ag_3AsO_4$.

No. of analysis.	Sample of Ag_3AsO_4	Corrected weight of Ag_3AsO_4 in vacuum.	Weight of AgBr in vacuum.	Weight of asbestos.	Dissolved AgBr from filtrate.	Loss on fusion.	Corrected weight. of AgBr in vacuum.	Ratio $3AgBr: Ag_3AsO_4$.
		gm.	gm.	gm.	gm.	gm.	gm.	
8	C	8.75751	10.66581	0.00008	0.00004	0.00040	10.66553	1.21787
9	D	6.76988	8.24529	0.00024	0.00007	0.00015	8.24545	1.21796
10	D	5.19424	6.32569	0.00017	0.00009	0.00005	6.32590	1.21787
11	D	5.33914	6.50251	0.00009	0.00006	0.00008	6.50258	1.21791
12	E	8.24054	10.03497	0.00053	0.00014	0.00012	10.03552	1.21782
13	E	7.57962	9.23134	0.00021	0.00005	0.00013	9.23147	1.21793
14	E	6.05230	7.37066	0.00038	0.00005	0.00003	7.37106	1.21789
Average								1.21789
Per cent of Ag in Ag_3AsO_4								69.9622[2]
Average per cent of Ag in Ag_3AsO_4								69.9616

[1] Ag: AgCl = 0.752632: 1.000000. Richards and Wells: *Loc. cit.*

[2] Ag: AgBr = 0.574453: 1.000000. Baxter: *Loc. cit.*

Series IV. $3AgCl : Ag_3AsO_4$.

No. of analysis.	Sample of Ag_3AsO_4.	Corrected weight of Ag_3AsO_4 in vacuum.	Weight of AgCl in vacuum.	Residual $AsCl_3$.	Volatized AgCl.	Corrected weight of AgCl in vacuum.	Ratio $3AgCl : Ag_3AsO_4$.
		gm.	gm.	gm.	gm.	gm.	
15	F	4.67268	4.34393	0.00006	0.00002	4.34389	0.929636
16	F	7.71882	7.17602	0.00007	0.00002	7.17597	0.929672
17	G	5.28049	4.90908	0.00001	0.00001	4.90908	0.929664
18	G	4.25346	3.95422	0.00000	0.00002	3.95424	0.929652
19	G	3.47340	3.22892	0.00000	0.00001	3.22893	0.929616
20	G	5.17269	4.80877	0.00000	0.00002	4.80879	0.929650
21	G	4.10766	3.81856	0.00000	0.00002	3.81858	0.929624

Average 0.929645

Series V. $3AgCl : Ag_3AsO_4$.

No. of analysis.	Sample of Ag_3AsO_4.	Corrected weight of Ag_3AsO_4 in vacuum.	Weight of AgCl in vacuum.	Weight of asbestos.	Dissolved AgCl from filtrate.	Loss on fusion.	Corrected weight of AgCl in vacuum.	Ratio $3AgCl : Ag_3AsO_4$.
		gm.	gm.	gm.	gm.	gm.	gm.	
22	G	5.47133	5.08686	0.00009	0.00014	0.00066	5.08643	0.929652

Average of all analyses in Series IV and V 0.929646
Per cent of Ag in Ag_3AsO_4 . . . . 69.9681

Series VI. $3AgBr : Ag_3AsO_4$.

No. of analysis.	Sample of Ag_3AsO_4.	Corrected weight of Ag_3AsO_4 in vacuum.	Weight of AgBr in vacuum.	Weight of asbestos.	Dissolved AgBr from filtrate.	Loss on fusion.	Corrected weight of AgBr in vacuum.	Ratio $3AgBr : Ag_3AsO_4$.
		gm.	gm.	gm.	gm.	gm.	gm.	
23	G	4.96261	6.04438	0.00004	0.00010	0.00012	6.04440	1.217988
24	G	5.31743	6.47645	0.00015	0.00009	0.00011	6.47658	1.217991
25	G	4.46882	5.44273	0.00026	0.00011	0.00010	5.44300	1.217995
26	G	4.16702	5.07533	0.00010	0.00004	0.00008	5.07539	1.217990

Average 1.217991
Per cent of Ag in Ag_3AsO_4 . . . . 69.9678
Average per cent of Ag in Ag_3AsO_4 . . . . 69.9680

The first point to be noted in the foregoing tables is that the results can be divided into two distinct groups according to the samples of arsenate employed, Series I, II, and III, with Samples A to E, giving values for the per cent of silver in the arsenate lower than Series IV, V, and VI, with Samples F and G.

In the second place, both methods for determining the ratio of the arsenate to the chloride give essentially identical results. This is shown by the agreement of Series I and II, and that of Series IV and V.

Finally, the per cent of silver in silver arsenate found in Series I and II agrees within less than 0.002 per cent with that found in Series III. This agreement, together with that of the individual analyses of each series, indicates both uniformity in the material employed and purity of the hydrochloric and hydrobromic acids, as well as accuracy in the analytical work. The agreement of Series IV and V with Series VI is closer still.

In the following table are given the sources of the various samples of silver arsenate:

Sample A . .	$Na_2NH_4AsO_4$	Sample E . .	$Na_2NH_4AsO_4$
Sample B . .	Na_2HAsO_4	Sample F . .	Na_3AsO_4
Sample C . .	Na_2HAsO_4	Sample G . .	Na_3AsO_4
Sample D . .	$(NH_4)_3AsO_4$		

Since in the precipitation of the silver arsenate the arsenate solution was always added to the silver-nitrate solution, the mother-liquor was in every case either neutral or acid, but in no case permanently alkaline. Still, local accumulations of arsenate undoubtedly exist for short periods, and precipitates formed at these points may be affected by the conditions existing in the arsenate solution. In the case of Samples F and G the arsenate solution is decidedly alkaline, owing to hydrolysis, but less so with Samples A, D, and E, and least with Samples B and C. In the case of Samples B and C, acid accumulates in the solution during the precipitation of the silver arsenate. In comparing the results from the different samples of silver arsenate it must be noted that occluded basic salt would increase the apparent percentage of silver in the arsenate. In the case of Samples F and G the conditions are most favorable for the occlusion of basic salts, and *these two samples actually yield a higher percentage of silver than the other samples.* On the other hand accumulation of acid in the solution in which the precipitation of the silver arsenate is taking place is found to have no tendency to promote occlusion of acid salts, since Samples B and C give results agreeing closely with those of Samples A, D, and E. These two facts lead to the conclusion that Samples A to E represent normal trisilver arsenate, and that Samples F and G contain basic impurities.

In order to calculate the atomic weight of arsenic from the per cent of silver in silver arsenate a knowledge of the ratio of the atomic weights of silver and oxygen is necessary. A slight uncertainty exists as to this ratio, hence calculations have been made upon the basis of two extreme values for silver, 107.880 and 107.870 . This has been done only with the results of Series I, II, and III, since, as has been pointed out, they are probably nearer the truth than those of Series IV, V, and VI. The difference between the two sets of results amounts only to 0.06 per cent in the atomic weight of arsenic.

	Series I and II.	Series III.
If Ag = 107.880, As =	74.961	74.953
If Ag = 107.870, As =	74.948	74.940

When the results of Series I and II are averaged with those of Series III, it is found that

If Ag = 107.880 As = 74.957
If Ag = 107.870 As = 74.944

The atomic weight of arsenic is being subjected to further investigation in this laboratory, by determination of the ratio of arsenic trioxide to iodine.

The most important results of this research may be briefly summed up as follows:

1. Methods for the preparation of normal trisilver arsenate were devised.

2. It is shown that trisilver arsenate precipitated by means of trisodium arsenate probably contains occluded basic impurity.

3. It is shown that silver arsenate can not be completely dried without fusion.

4. The specific gravity of unfused trisilver arsenate is found to be 6.66 at 25° C., referred to water at 4° C.

5. The per cent of silver in silver arsenate is found to be 69.9616 by three closely agreeing methods.

6. With two assumed values for the atomic weight of silver referred to oxygen 16.000, the atomic weight of arsenic is found to have the following values:

If Ag = 107.88 As = 74.96
If Ag = 107.87 As = 74.94

VII.

A REVISION OF THE ATOMIC WEIGHT OF IODINE.

THE SYNTHESIS OF SILVER IODIDE AND THE RATIO OF SILVER IODIDE TO SILVER BROMIDE AND SILVER CHLORIDE.

By Gregory Paul Baxter.

Proceedings of the American Academy of Arts and Sciences, **40**, 419 (1904); **41**, 73 (1905).
Journal of the American Chemical Society, **26**, 1577 (1904); **27**, 876 (1905).
Zeitschrift für anorganische Chemie, **43**, 14 (1905); **46**, 36 (1905).

Contributions from the Chemical Laboratory of Harvard College.

A REVISION OF THE ATOMIC WEIGHT OF IODINE.

THE SYNTHESIS OF SILVER IODIDE AND THE RATIO OF SILVER IODIDE TO SILVER BROMIDE AND SILVER CHLORIDE.

INTRODUCTION.

The atomic weight of iodine was for some time considered one of the best determined of chemical constants, owing to the extremely concordant results of Stas and Marignac, who both deduced the value 126.79 (O = 16.000 and Ag = 107.880) from syntheses of silver iodide. Recently, however, two series of determinations, one by Ladenburg and one by Scott, have yielded results over 0.1 higher than the above. Ladenburg's method consisted in heating silver iodide in a current of chlorine until all the iodine had been displaced, and gave the result 126.90, while Scott, like Stas and Marignac, synthesized silver iodide and obtained in two analyses the values 126.90 and 126.92.[1] The anomaly in the atomic weights of iodine and tellurium has always been of the greatest interest, and has led to a large number of investigations upon the atomic weight of tellurium during the last few years, which have shown conclusively that the value of this constant lies in the neighborhood of 127.6. The doubt thrown upon the atomic weight of iodine by the work of Ladenburg and Scott made it imperative to subject iodine to further careful investigation.

In choosing a compound for an atomic weight determination, two of the most important points to be considered are the stability of the substance under various conditions, and the certainty with which the atomic weights are known of those elements, besides the one under examination, which compose it. One of the few compounds of iodine which satisfy both the above conditions is silver iodide. Accordingly synthesis of silver iodide from a weighed amount of silver was selected for the first method of investigation.

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[1] The higher values of Scott and Ladenburg were confirmed, shortly before the publication of the first portion of this paper, by Köthner and Aeuer, in a preliminary notice of experiments involving syntheses of silver iodide as well as a repetition of Ladenburg's work, from which they conclude that the atomic weight of iodine can not be lower than 126.90. Details of their work are not given. See *Ber. d. d. chem. Gesell.*, **37**, 2536 (1904). A critical discussion of all the earlier work upon the atomic weight of iodine is to be found at the end of this paper.

RATIO OF SILVER TO SILVER IODIDE.

PURIFICATION OF MATERIALS.

SILVER.

This substance was purified, by methods which have been described previously in detail,[1] by twice precipitating silver chloride from strongly acid solution, with subsequent reduction by means of invert sugar and sodium hydroxide in each case, especially purified reagents being employed in the second precipitation and reduction. The product, after fusion before a blowpipe upon a crucible lined with the purest lime, was converted into electrolytic crystals and these were fused in a current of hydrogen upon a boat of pure lime. The resulting buttons of metal, after being freed from adhering lime by treatment with dilute acid, were cut into fragments of from 3 to 5 gm. by means of a clean chisel and anvil, and the iron adhering to the surface was removed by warming the pieces repeatedly with fresh portions of dilute nitric acid, until iron could no longer be detected in the acid. The fragments were washed thoroughly with the purest water, then with ammonia, and again with water as before. They were allowed to dry in the air, and finally the last traces of moisture were eliminated by heating in a vacuum, since silver which is heated to a high temperature in the air has been shown by Stas to absorb considerable oxygen.[2] Silver prepared in a similar fashion by investigators in this laboratory has always been found to be pure, and since two different samples were used in the following work with identical results, there can be no doubt of the purity of that employed here. Furthermore, one synthesis of silver chloride, carried out with a portion of this silver by Wells in the investigation of Richards and Wells upon the atomic weight of chlorine, yielded a value which is identical with the average of other similar determinations made with his own silver.[3]

IODINE.

The chief impurities in commercial iodine are halogens of lower atomic weight and iodide of cyanogen. These were removed by dissolving iodine in a strong solution of half its weight of potassic iodide, and distilling the greater portion of the iodine from a retort into a flask cooled with cold water. The iodine thus obtained was next converted into hydriodic acid by covering it with considerable water and passing through the solution a stream of hydrogen sulphide. This gas was generated by the action of dilute sulphuric acid upon ferrous sulphide, and was purified by bubbling through three gas-washing bottles containing water and through two towers filled with beads moistened with water. The reaction between the hydrogen sulphide and the iodine results

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[1] See pages 6 and 22.

[2] *Œuvres Complètes*, 3, 125.

[3] *Pub. Car. Inst.*, No. **28**, p. 65 (1905); *Jour. Amer. Chem. Soc.*, **27**, 524; *Zeit. anorg. Chem.*, **47**, 130.

chiefly in the formation of hydriodic acid and the precipitation of sulphur, although a small quantity of sulphuric acid is always produced. Iodide of cyanogen with hydrogen sulphide yields hydrocyanic acid, hydriodic acid, and sulphur.[1] The solution was first boiled for a short time until the sulphur had clotted together, and the sulphur was removed by filtration. The clear solution was then boiled for several hours in order to eliminate the hydrocyanic acid.[2] Finally the hydriodic acid was partially converted into iodine by distilling the solution with a slight excess of potassium permanganate. This permanganate must also have had the effect of oxidizing any organic impurities. Since in the reaction three-eighths of the iodine remain in the form of iodides, the resulting iodine was thus subjected to a second distillation from an iodide. The product was again converted into hydriodic acid by means of hydrogen sulphide, and this again into iodine by recrystallized potassium permanganate which was free from even a trace of chlorine. Since in the case of bromine it has already been shown that two distillations from a pure bromide are sufficient to free this element from chlorine,[3] three distillations of iodine from a solution of an iodide should insure complete elimination of chlorine and bromine even if the original substance were very impure. The purified iodine was again converted into hydriodic acid by hydrogen sulphide, and this into ammonium iodide by an excess of freshly distilled ammonia. This material was used in the analyses made with Sample I.

It was suggested to me by Prof. T. W. Richards that an undiscovered element resembling the halogens, but of a higher atomic weight, might exist, and an attempt to detect the existence of such an element was carried out as follows: One pound of iodine was purified as described above, but the process of converting the iodine into hydriodic acid by hydrogen sulphide, and the hydriodic acid into iodine by potassic permanganate, was repeated four times. The iodine obtained in the last distillation with permanganate, amounting in all to about 50 gm., was set free in 4 fractions by introducing the permanganate in portions of about 2 gm. each. An element belonging to the halogen family, and of higher atomic weight than iodine, should be more easily set free than iodine, hence the first of the 4 fractions should have contained nearly all of such an element which occurred in the pound of iodine. Each one of the fractions was once distilled with pure water, and was then converted into ammonium iodide, as in the case of Sample I. The first fraction was fraction 1 of Sample II, the fourth was fraction 4 of Sample II. No difference in appearance between these samples and Sample I or even the original crude iodine could be detected.

All reagents used in the course of the purification or in the analyses were carefully purified. Acids and ammonia were redistilled, usually with the use of

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[1] Dammer, *Handb. d. anorg. Chem.*, II, 1, 432.

[2] Richards and Singer, *Amer. Chem. Jour.*, 27, 205 (1902).

[3] See page 60.

a platinum condenser. The water was distilled twice, once from alkaline permanganate, once from a solution containing a trace of sulphuric acid. In both distillations block tin condensers were used.

METHOD OF SYNTHESIS.

In order to convert a known weight of silver into silver iodide essentially the same method was used as that employed in the research upon the synthesis of silver bromide (page 57). The silver was dissolved slowly in redistilled nitric acid which had been diluted with an equal volume of water in the flask described on page 12. The solution was diluted and was heated until all nitrous acid was destroyed and all oxides of nitrogen were expelled. It was then transferred to a glass-stoppered precipitating-flask and after dilution until not more than 1 gm. of silver was contained in 100 c.c., an excess of ammonia was added and then a slight excess of the solution of pure ammonium iodide, which also had been diluted until not more concentrated than 1 per cent. The flask was stoppered and shaken for some time, and was allowed to stand for about a day. Next a very slight excess of nitric acid was introduced, the flask was again shaken for some time, and was allowed to stand for one or two days until the solution above the precipitate seemed perfectly clear. The precipitate was washed by decantation with 1 per cent nitric acid at least eight times, and was transferred with water to a weighed Gooch crucible through which the washings had been poured. Finally the crucible was heated in an electric air-bath for several hours, first at 100° to 110°, then at 200° C.

Although silver iodide is very slightly sensitive to diffused daylight, the operations of precipitation and filtration were performed in a large cupboard lighted with orange light. When taken out of the dark room, the flask was enveloped in several thicknesses of black cloth.

The tendency of precipitated silver iodide to pass into a colloidal condition when washed with pure water is very marked. It has been found by Stas and others that if the water is previously heated to about 60° C., and plenty of time is allowed for the precipitate to settle at that temperature, this tendency can be overcome. When washed with warm water, however, silver iodide adheres to the flask to such an extent that it is impossible entirely to remove the precipitate even by vigorous rubbing.

The conditions most favorable for preserving the precipitate in such a state that it could be easily and rapidly manipulated were as follows. In the first place precipitation was carried out in ammoniacal solution, because the silver iodide clotted together much more rapidly than in acid solution, owing probably to the greater solubility of silver iodide in the ammoniacal solution. A large excess of nitric acid also coagulated the precipitate, but since the acid caused the separation of a large amount of iodine, it could not be employed in the present case. Dilute nitric acid, on the other hand, proved to be a satisfactory medium for washing the silver iodide, for it was found that the precipitate could be washed indefinitely with even 1 per cent nitric acid without passing into the colloidal state. The washings obtained in this way, when treated with an iodide, gave no trace of opalescence even on long standing, showing that silver iodide is essentially insoluble in the dilute acid. When silver iodide which has been washed with nitric acid only is dried at a high temperature, a loss of iodine takes place, owing to action on the silver iodide by the nitric acid. This was evident from the dark color of the iodide. In order to avoid this difficulty, the precipitate was finally transferred to the Gooch crucible with pure water, sometimes after one rinsing with water. The nitric acid was so completely displaced by this means that the precipitate did not darken even on fusion. Unfortunately, even this slight washing with water in most cases caused some of the precipitate to pass through the crucible in a colloidal condition, consequently these last washings were collected separately.

In the earlier analyses the silver iodide in this colloidal solution was determined by first boiling the solution with a small quantity of ammonium iodide until the silver iodide was coagulated, and then collecting the precipitate upon a small filter paper, together with the asbestos shreds and any silver iodide which were contained in the remainder of the filtrate and washings. As a rule this operation was performed only after the wash-waters had stood for 2 or 3 days, in order that insoluble matter might have time to settle. The bottom of each flask was rubbed gently with a rubber-tipped stirring-rod to detach adhering particles. Finally the filter paper was burned in a weighed porcelain crucible at as low a temperature as possible, for if a high temperature is employed, a loss of silver iodide by volatilization occurs. The ash was treated with a drop of nitric acid, and, after warming, a drop of ammonium iodide solution was added. The excess of acid and ammonium salt was driven off and the crucible was weighed.

In these earlier analyses it was found necessary to detach small particles of adhering silver iodide from the neck of the precipitating flask by rubbing with a rubber-tipped rod. Later a better method was devised for collecting this small amount of precipitate together with that contained in the colloidal washings. First the flask was rinsed with a small quantity of a solution of potassium cyanide, and this solution was poured into the colloidal washings. Then the solution was evaporated to small bulk and was electrolyzed in a weighed platinum crucible, which was heated to 130° in an electric oven and was finally reweighed. The film was dissolved in dilute nitric acid and the solution was precipitated with an excess of ammonium iodide. This precipitate of silver iodide, if over 0.0005 gm. in weight, was collected on a small weighed Gooch crucible, and the filtrate, together with the original filtrate and wash-waters, was passed through a small filter repeatedly until clear. If the precipitate weighed less than the above quantity, it was collected wholly upon a filter. These filters were, of course, ignited and treated as before. The weight of the silver iodide and asbestos was used in computing the results, the weight of electrolyzed silver serving merely as a check upon the weight of silver iodide.

In order to drive off the last traces of moisture from the silver iodide it was fused in a porcelain crucible. The bulk of the precipitate, freed as completely as possible from asbestos, was transferred to a clean crucible, which was then weighed with its cover. The crucible and cover were placed inside a large porcelain crucible, and were heated until fusion took place. A temperature much above the melting point of silver iodide was avoided, since this substance is distinctly volatile at higher temperatures. The loss in weight was then determined. The fused salt when cold was light yellow in color, with no trace of darkening, showing that no appreciable loss of iodine had taken place.

SPECIFIC GRAVITY OF SILVER IODIDE.

The specific gravity of pure silver iodide was found by displacement of water. Three determinations were made with material which had been fused in a porcelain crucible and cooled by pouring the fused mass upon a cold tile. The solidified salt was broken into small fragments and was introduced into a weighed pycnometer for solids, which was then reweighed. Water sufficient to cover the salt was introduced into the pycnometer and the system was placed in a vacuum desiccator which was kept exhausted until it seemed probable that all air had been extracted from the solid. Then the pycnometer was immersed in a bath at 25° C. and exactly filled with water. Finally the system was weighed. Two more determinations were carried out with material which had been cast into sticks by pouring the fused salt into a porcelain boat. These

Weight of silver iodide in vacuum.	Weight of water displaced in vacuum.	Density of silver iodide 25°/4°.
gm.	*gm.*	
15.5871	2.7590	5.650
14.5141	2.5652	5.658
16.3685	2.8853	5.673
	Average . . .	5.660
21.5876	3.8017	5.678
16.7274	2.9505	5.669
	Average . . .	5.674[1]

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[1] The values for the density of silver iodide found by other experimenters are as follows:

Boullay, *Ann. de Chim. et de Phys.*, (2) **43**, 266 (1830)	5.614
Karsten, *Jour. für Chem. und Phys.*, **65**, 417 (1832)	5.026
Filhol, *Ann. de Chim. et de Phys.*, (3) **21**, 417 (1847)	5.500
Schiff, *Ann. der Chem. und Pharm.*, **108**, 21 (1858)	5.35
H. St. Clair Deville, *Comptes Rendus*, **64**, 325 (1867)	5.687 at 0°
Schroeder, *Ann. der Chem. und Pharm.*, **192**, 295 (1878)	5.650 to 5.718

sticks were used in an elongated form of pycnometer for solids.[1] The average of the last two experiments is undoubtedly more accurate than that of the first three, since it was extremely difficult to pump out the air from the more porous material used in the first experiments.

The vacuum correction for silver iodide, when weighed with brass weights, calculated from this value for its specific gravity, is +0.000067 gm. for every apparent gram of salt.[2] A vacuum correction of −0.000031 gm. was applied to every apparent gram of silver.

THE ATOMIC WEIGHT OF IODINE.

No. of analysis.	Sample of iodine.	Weight of silver in vacuum.	Weight of silver iodide in vacuum.	Loss on fusion.	Weight of silver from filtrate.	Weight of silver iodide and asbestos fr. filtrate.	Corrected weight of silver iodide in vacuum.	Ratio Ag:AgI	Atomic weight of iodine. Ag = 107.880.
Series I. Ag: AgI.									
		gm.	gm.	gm.	gm.	gm.	gm.		
1	I	5.23123	11.38074	0.00030	. . .	0.00482	11.38526	0.459474	126.910
2	I	3.57039	7.77023	not fused	. . .	0.00007	7.77030	0.459492	126.901
3	I	4.60798	10.02747	0.00047	. . .	0.00100	10.02800	0.459511	126.891
4	I	4.52467	9.84834	0.00036	. . .	0.00020	9.84818	0.459448	126.925
5	I	4.66256	10.14601	0.00062	. . .	0.00048	10.14587	0.459552	126.870
Average								0.459495	126.899
Series II. Ag: AgI.									
6	I	4.77244	10.38664	0.00020	0.00033	0.00050	10.38694	0.459464	126.915
7	I	4.82882	10.50872	0.00035	0.00053	0.00140	10.50977	0.459460	126.917
8	II,1	4.04262	8.79714	0.00058	. . .	0.00095	8.79751	0.459519	126.887
9	II,1	1.64711	3.58502	0.00020	0.00015	0.00032	3.58514	0.459427	126.934
10	II,2	4.86054	10.57436	0.00122	0.0025	lost.	10.57314	0.459470	126.912
11	II,2	4.83482	10.52209	0.00044	0.00032	0.00072	10.52237	0.459480	126.907
12	II,3	4.97120	10.81692	0.00025	0.00052	0.00129	10.81796	0.459532	126.881
13	II,3	3.53858	7.70136	0.00038	0.00017	0.00035	7.70133	0.459476	126.909
14	II,3	3.89693	8.48178	0.00026	0.00012	0.00032	8.48184	0.459444	126.926
15	II,4	5.33031	11.59780	0.00034	0.00185	0.00360	11.60106	0.459467	126.914
16	II,4	5.08748	11.07227	0.00035	0.00017	0.00063	11.07255	0.459468	126.913
Average								0.459473	126.910
Average, rejecting Analysis 12								0.459468	126.913
Average of analyses with Sample I								0.459462	126.916
Average of analyses with Sample II, Fraction 1 . . .								0.459473	126.911
“ “ “ “ 2 . . .								0.459475	126.911
“ “ “ “ 3 . . .								0.459460	126.918
“ “ “ “ 4 . . .								0.459468	126.914

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[1] Baxter and Hines: *Amer. Chem. Jour.*, 31, 222 (1904).

[2] In the original publication of this paper a slightly higher vacuum correction was employed owing to an incorrect assumption as to the specific gravity of the weights, which are here taken at 8.3.

The platinum-plated brass weights were twice carefully standardized to hundredths of a milligram, and the two sets of corrections agreed to within two hundredths of a milligram in every case. Two short-armed Troemner balances, sensitive to 0.02 mg. with a load of 50 gm. were used in the work. All weighings were made by substitution. In the case of the Gooch crucible a platinum tare, and in the case of the porcelain crucibles, porcelain tares were used.

In the preceding table are given the results of all the syntheses which were completed without accident.

The results tabulated in Series I were undoubtedly less accurate than those of Series II, since it was in the earlier analyses that experience in handling silver iodide was gained. Hence these analyses are collected by themselves. In Series II the rejection of analysis 12 seems justifiable, since two other analyses made with the same material yielded results in close agreement and considerably higher than that of analysis 12.

From an examination of this table two important deductions may be drawn. First, there can be little doubt of the identity of the different samples of iodine; for the extreme averages of the results from the various samples differ by only seven thousandths of a unit. The variation in the values from the analysis of Sample II, fraction 1, is undoubtedly due in the case of analysis 8 to lack of experience in manipulating silver iodide, for this analysis was the first one to be completed in the second series, and in the case of analysis 9 to the small quantity of available material. One may conclude without hesitation that, in the material examined in this investigation at least, no important quantity of a new halogen existed.

The second important deduction is that the atomic weight of iodine is evidently very slightly greater than 126.913; for most of the experimental errors, such as loss of silver iodide, or loss of iodine by the silver iodide, would have caused the result to be too low.

RATIO OF SILVER TO IODINE.

The ratio of silver to iodine was next investigated. The problem of obtaining iodine in a *dry* state presented most difficulties in this portion of the research, and was finally solved as follows: Iodine, which had been prepared in the same way as Sample I, was first freed from the greater part of the water which it contained by exposure to concentrated sulphuric acid, which had been boiled to remove every trace of hydrochloric acid. It was then sublimed from a crystallizing dish to the bottom of a glass dish half filled with water, which covered the crystallizing dish. In this way the greater part of the "included" moisture must have been eliminated. The sublimed crystals were finally again sublimed in a current of pure dry air from a porcelain boat contained in a hard-glass tube into the weighing tube. This weighing tube was about 10 cm. long and 15 mm. diameter, and was drawn down to less than half this diameter at both ends. Glass stoppers were ground into both ends of the tube. The air was purified and dried by passing over beads moistened with a solution of silver nitrate, then over sodic carbonate, and finally over 3 feet of beads moistened with concentrated sulphuric acid, all in an apparatus made entirely of glass and connected with the sublimation tube by means of a ground glass joint. During the final sublimation of the iodine, the end of the hard-glass tube, which had been drawn down to small diameter, was inserted into one end of the weighing tube. After the weighing tube had been filled, the glass stoppers were inserted, the tube was carefully wiped with a slightly damp "chemically clean" cloth, and was allowed to stand in a desiccator for some time. It was then weighed. Needless to say, the weighing tube had been originally treated as above before being weighed empty. Both weighings were made with a counterpoise exactly similar to the weighing tube.

In all but one of the experiments the weighing tube was broken during the solution of the iodine, so that it was impossible to weigh the tube after the experiment, and determine how much the glass was attacked by the warm iodine. In one experiment, however, a loss in weight of 0.00032 gm. was found. Whether or not this change was accompanied by the evolution of a gas, the loss in weight must have been at least partially due to combination of the iodine with the alkaline metals of the glass, with the formation of soluble iodides which were dissolved by the solution of sulphurous acid. Hence the error must have been considerably less than 0.3 mg., if, as was necessarily the case owing to breakage of the tubes, the first weight of the tube was used in determining the weight of the iodine.

Immediately after being weighed, in order to avoid loss by volatilization, the iodine was converted into hydriodic acid by means of pure sulphurous acid. This acid was made by heating sulphuric acid with metallic copper and collecting the sulphurous oxide in water, and then distilling the sulphurous oxide from the solution into the purest water. During this distillation any trace of halogen acid which might have had its source in either copper or sulphuric acid must have been completely eliminated, for it must have been almost wholly in the ionized condition.

A considerable quantity of this sulphurous acid was poured into one of the precipitating flasks, and the weighing tube, containing the iodine, was introduced, after the lower stopper had been allowed to drop out of the tube into the flask. The sulphurous acid immediately sealed the open end of the tube so that no iodine vapor could escape. The other stopper was then removed by means of a platinum wire, the wire was rinsed into the flask, and the flask was quickly closed by means of its glass stopper. Solution of the iodine in the sulphurous acid was hastened by gently agitating the flask. Any iodine vapor which escaped from the tube must have been instantly converted into hydriodic acid. After sufficient time had been allowed for every trace of this hydriodic acid to be absorbed by the solution, the flask was opened and the solution was transferred to another precipitating flask, and a slight excess of the purest ammonia was added. When iodine is dissolved in a large excess of sulphurous acid the solution becomes colored yellow, owing to the formation of an iodide of sulphur,[1] and upon standing, this solution may deposit sulphur. But since the solution was made alkaline with ammonia as soon as the iodine was dissolved, with the complete disappearance of the color and without the formation of the slightest trace of a precipitate, no danger was to be feared from this source.

From the weight of the iodine, the weight of silver necessary exactly to combine with it was calculated. This silver was weighed out and dissolved in nitric acid as described previously. The solution was diluted until not stronger than 1 per cent and was added slowly to the already dilute solution of ammonic iodide in the precipitating flask. The flask was shaken for some time, and was then made acid with a considerable excess of nitric acid. Long-continued shaking, followed by several days' standing, yielded a clear supernatant solution. 25 c.c. portions of this solution were pipetted into nephelometer tubes and were tested with cubic centimeter portions of hundredth normal silver nitrate and hydriodic acid solutions in a nephelometer. If an excess of either iodine or silver was present, the deficiency of the other was made up in the remaining solution by addition of standard silver nitrate or hydriodic acid until the exact end-point was reached. It was never necessary to add more than 0.1 mg. of either iodine or silver, so that the liquid removed from the flask for the tests could be neglected. This end-point is very sharp in the case of silver and pure iodine; for so little silver iodide is dissolved that the two nephelometer tubes remain almost absolutely clear. An excess of 0.1 mg. of silver in a liter of solution is easily detected. This almost complete lack of opalescence in the nephelometer tubes is strong evidence of the absence of even a trace of either chlorine or

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[1] Dammer: *Handb. d. anorg. Chem.*, 1, 557.

bromine in the iodine, for silver chloride or bromide, on account of their greater solubility, would have produced much more marked precipitates.

The specific gravity of solid iodine is assumed to be 4.933,[1] hence a vacuum correction of +0.000099 is applied to every apparent gram of iodine, as well as one of −0.000031 to every apparent gram of silver.

RESULTS.

THE ATOMIC WEIGHT OF IODINE. Series III. Ag: I.

No. of analysis.	Weight of silver in vacuum.	Weight of iodine in vacuum.	Ratio. Ag : I.	Atomic weight of iodine. Ag = 107.880.
	gm.	gm.		
17	5.54444	6.52286	0.850001	126.917
18	6.27838	7.38645	0.849986	126.920
19	4.57992	5.38812	0.850004	126.917
	Average		0.849997	126.918

As is to be expected, the average of this series is slightly higher than that of the previous one, and undoubtedly represents more closely the true value of the atomic weight of iodine. Nevertheless, the investigation was not allowed to rest at this point.

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[1] Ladenburg: *Ber. d. d. Chem. Gesell.*, 35, 1256 (1902). In the original publication of this paper a slightly higher vacuum correction was employed, owing to an incorrect assumption as to the specific gravity of the weights, which are here taken at 8.3.

RATIO OF SILVER IODIDE TO SILVER CHLORIDE.

In any atomic weight investigation it is extremely desirable to obtain the value sought by reference to as many different well-known atomic weights as possible. The method of heating silver iodide in a current of chlorine, which has already been used by Berzelius and Dumas as well as by Ladenburg, furnishes the ratio between silver iodide and silver chloride, and seemed capable of yielding trustworthy results; for since the silver halides fuse at a comparatively low temperature, there is no possibility of inclusion of silver iodide by the silver chlorides formed in the reaction, and hence there is certainty that the reaction will be complete.

First, silver iodide was prepared by precipitating an ammoniacal solution of the purest ammonium iodide (Sample I) with a solution of recrystallized silver nitrate. In this operation a slight excess of ammonium iodide was used. The precipitate was well washed with 1 per cent nitric acid, rinsed with water, and was collected on a Gooch crucible with the use of a disk of filter paper instead of an asbestos mat. In this way contamination of the precipitate with asbestos shreds was avoided. The silver iodide was finally dried in an air-bath at about 100° C. for at least 8 hours. After removal of the filter paper, those portions of the precipitate which had come in contact with the filter paper were cut away with a clean knife. Next the substance was fused in a weighed crucible protected from the flame by a very large crucible. While the silver iodide was fused, a small quantity of the purest iodine was placed upon the lower side of a second crucible cover, and this cover was substituted for the one which had been weighed with the crucible. The iodine immediately vaporized and the silver iodide was thus fused in an atmosphere containing iodine vapor. Finally, the cover was removed, so that the uncombined iodine escaped from the crucible, and the salt was kept fused, covered with the original crucible cover, until it was certain that all excess of iodine had been eliminated. That no excess of iodine was retained by the silver iodide was readily shown in one experiment with 18 gm. of salt by reheating the salt to its fusing point and reweighing. A loss in weight of only 0.00003 gm. resulted.

After the silver iodide had been weighed it was heated in a current of chlorine. This gas was generated by dropping concentrated hydrochloric acid upon manganese dioxide, and it was purified and dried by bubbling through water and passing through a 3-foot tube filled with beads moistened with concentrated sulphuric acid. Traces of bromine or iodine in the chlorine would have been no disadvantage, and it is inconceivable that it should have contained fluorine. In order to prevent spattering of the fused salt from the crucible, a perforated porcelain disk, which fitted the crucible half-way between the bottom and the top, was placed in the crucible. This disk was always weighed with the crucible.

The chlorine was conducted into the crucible by means of a small hard-glass tube, which passed just through the perforated cover of a Rose crucible, while the apparatus for generating chlorine was constructed wholly of glass with the exception of the joint between this hard-glass tube and the drying tube. The chlorine did not come in contact with the rubber tube used in making the connection tight, however, for the hard-glass tube telescoped into the drying tube for some distance and the joint was sealed with concentrated sulphuric acid. In order to avoid volatilization of the silver salts, the heat applied was very gentle and only sufficient to fuse the mixed halides. Even at this temperature the iodine was rapidly replaced. Heating in chlorine was continued some time after the color of the iodine vapor had ceased to be visible. Then the Rose cover was replaced by the ordinary cover and the silver chloride was kept fused for several minutes, with occasional lifting of the cover, so as to drive off any chlorine which might have been dissolved by the fused salt. Although fused silver chloride, when cooled in chlorine, dissolves this gas very appreciably, no evidence was found that any remained in the solidified salt when it was heated for a short time in air. In one experiment 18 gm. of the chloride after the usual treatment were re-fused in air with a loss in weight of only 0.00002 gm. The same chloride, when fused and cooled in chlorine, gained 5 mg.

It was soon discovered that a porcelain crucible, when used for the conversion of silver iodide into silver chloride, gradually gained in weight. In the first experiment this gain was over 3 mg., and in several subsequent experiments with the same crucible, amounted to slightly less than a milligram in each case. This gain did not take place to the slightest extent when the crucible was heated alone in chlorine, nor after the reaction was complete, for the weight of the crucible and silver chloride very soon became constant. Probably it was due partially to solution of the silver salt in the glaze, as was shown by slight discoloration on the bottom of the crucible. Possibly, however, it was caused by the attacking of the glaze by the "nascent" chlorine and iodine set free in the process, perhaps with evolution of oxygen. At any rate too great an uncertainty existed as to the weight of the crucible at the end of the experiment. Accordingly quartz crucibles were next employed for the same purpose. These crucibles behaved in an ideal fashion, for they remained practically constant in weight through the process. It was only necessary to rotate the crucibles during the solidification of the fused salts in order that the salt might solidify in a thin layer on the sides of the crucible. Neglect to do this almost invariably resulted in the cracking of the crucible.

After the first weighing of the crucible, it was again heated in chlorine for an hour, and again cooled and weighed. In no case did a loss in weight of more than 0.1 mg. take place, showing both that the iodine was completely replaced, and that no silver chloride had volatilized. The following five experiments were completed with quartz crucibles in the manner described. A vacuum correction of + 0.000071 is applied to every apparent gram of silver chloride.[1]

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[1] From the density 5.56 determined by Richards and Stull, not yet published, the weights being assumed to have the specific gravity 8.3.

RESULTS.

Atomic Weight of Iodine. Series IV. AgI : AgCl.

No. of analysis.	Weight of silver iodide in vacuum.	Weight of silver chloride in vacuum.	Ratio. AgI : AgCl.	Atomic weight of iodine. Ag = 107.880. Cl = 35.457
	mg.	*gm.*		
20	9.26856	5.65786	1.638174	126.931
21	6.72058	4.10257	1.638139	126.926
22	11.31822	6.90910	1.638161	126.929
23	10.07026	6.14753	1.638099	126.920
24	13.49224	8.23645	1.638114	126.922
Average			1.638137	126.925

At the time when these experiments were performed, Richards and Wells had not completed their research upon the atomic weights of sodium and chlorine, so that, although these investigators had found that Stas's determination of the atomic weight of chlorine had yielded too low results, the magnitude of his error was still uncertain. Using a value for chlorine intermediate between Stas's and Richards and Wells's final result, the above five experiments in Series IV appeared to agree almost exactly with the results of the first three series of experiments, and accordingly all four series were published. Not long afterwards Richards and Wells's research was completed. Using their final result for the atomic weight of chlorine, 35.457 (Ag = 107.880), as has been done in this paper, Series IV gives a result 0.01 unit higher than the average of Series II and III. The desirability of further investigation of the atomic weight of iodine was evident and new experiments were accordingly begun.

RATIO OF SILVER IODIDE TO SILVER BROMIDE.

In the first place eight experiments were made in which the iodide was heated in a current of air and bromine. The air was purified by being conducted successively over beads moistened with silver nitrate solution, sodium carbonate, and finally concentrated sulphuric acid which had been heated to its boiling point with a small quantity of recrystallized potassium dichromate to eliminate volatile and oxidizable impurities. Four different samples of bromine were employed, each one of which had been thrice distilled from a solution of a bromide, in each distillation the bromide having been made from a portion of the product of the previous distillation. Chlorine must have been completely separated in this way. The presence of iodine in the bromine was of less importance. Nevertheless each sample, while in the form of hydrobromic acid, was freed from iodine by boiling with several small portions of potassic permanganate.

The apparatus for purifying the air and saturating the air with bromine was so constructed that the gases came in contact only with glass. The quartz crucibles were always contained in large porcelain crucibles during the heating in bromine, as well as in the initial fusion of the silver iodide with iodine. Volatilization of the silver halides was prevented by heating very gently at first, at a temperature insufficient to fuse the mixture; then, when the greater part of the iodine had been replaced, till the silver bromide barely fused. Moreover, the crucible was very deep and the current of gases very slow, so that any volatilized silver halides had opportunity to condense upon the cool walls of the crucible.

That no loss from volatilization actually took place was certain for two reasons. In the first place, the weight of the bromide in most cases became constant within a few hundredths of a milligram after once being heated, although subsequently the salt was maintained at a temperature slightly above its melting point for at least an hour. In the second place, the perforated cover and hard-glass delivery-tube for the bromine, when rinsed with ammonia and the solution treated with hydrochloric acid in excess, gave no visible trace of opalescence. Before the salt was allowed to solidify it was maintained above its fusing point in air for a few minutes to eliminate dissolved bromine.

The silver bromide resulting from each analysis was converted into silver chloride by heating in a current of pure dry chlorine as described on page 102. Here also constant weight within a very few hundredths of a milligram was easily obtained, and as before the perforated cover and inlet tube were free from weighable amounts of chloride. It has already been shown that silver chloride and silver iodide, when fused in an atmosphere of the corresponding halogens and then in air, retain none of the halogen. The quartz crucibles remained almost absolutely constant in weight during these experiments. From the ratio between the original silver iodide and the silver chloride the atomic weight of iodine was calculated. All completed analyses are recorded in the tables. Several were lost, owing to breaking of the crucibles. The vacuum correction for silver bromide is assumed to be +0.000041.

RESULTS.

THE ATOMIC WEIGHT OF IODINE. Series V. AgI: AgBr.

No. of analysis.	Sample of bromine.	Weight of silver iodide in vacuum.	Weight of silver bromide in vacuum.	Ratio. AgI : AgBr.	Atomic weight of iodine. Ag = 107.880. Br = 79.916.
		gm.	*gm.*		
25	A	13.65450	10.92087	1.250313	126.924
26	A	17.35521	13.88056	1.250325	126.926
27	B	9.70096	7.75892	1.250298	126.921
28	B	10.27101	8.21480	1.250305	126.922
29	B	9.85684	7.88347	1.250317	126.925
30	C	8.62867	6.90102	1.250347	126.930
31	D	11.92400	9.53699	1.250290	126.919
32	D	7.56930	6.05386	1.250326	126.926
Average				1.250315	126.924

THE ATOMIC WEIGHT OF IODINE. Series VI. AgI: AgCl.

No. of analysis.	Weight of silver iodide in vacuum.	Weight of silver chloride in vacuum.	Ratio AgI : AgCl.	Atomic weight Cl = 35.457.
	gm.	*gm.*		
33	13.65450	8.33536	1.638142	126.926
34	17.35521	10.59453	1.638129	126.925
35	10.27101	6.27004	1.638109	126.922
36	8.62867	5.26732	1.638152	126.928
37	11.92400	7.27923	1.638085	126.918
Average			1.638123	126.924

These two series of experiments confirm with considerable exactness the higher value indicated by Series IV, and lead to the suspicion that owing to certain peculiarities of silver iodide which have already been discussed, the values furnished by the earlier syntheses of silver iodide are too low. Further evidence was therefore sought in new experiments which had as their object the determination of the ratio of iodine to both silver and silver iodide. Agreement between the sum of the weights of the iodine and the silver and the weight of the silver iodide would furnish important evidence as to the accuracy of the methods involved.

RATIOS BETWEEN IODINE, SILVER, AND SILVER IODIDE.

For this purpose iodine was purified as before by thrice converting it into hydriodic acid with hydrogen sulphide, and then heating the hydriodic acid with a slight excess of potassium permanganate which had been freed from chlorine by crystallization. The final product of iodine was distilled once with steam, freed from water by suction upon a porcelain Gooch crucible, and dried as far as possible in a desiccator over concentrated sulphuric acid. It was then sublimed once from porcelain boats in a current of pure dry air in a hard-glass tube, and then a second time from the hard-glass tube into the weighing-tube, which was constructed as described on page 99 of this paper. This weighing-tube remained constant in weight within a few hundredths of a milligram in each experiment, and lost in weight in all only 0.1 mg. in the eight final analyses.

Next, the iodine was dissolved in sulphurous acid, and was then precipitated by adding a solution of a slight excess of pure silver to the solution of hydriodic acid in a precipitating flask. The silver iodide clotted together very rapidly in the presence of the nitric acid and excess of silver, and offered none of the difficulties met when the precipitation is carried out with an excess of iodide, for it may be washed almost indefinitely with pure cold water without showing the least tendency to pass into colloidal solution. The silver iodide was collected upon a Gooch crucible, dried, and weighed. The loss on fusion was determined, and the asbestos shreds in the filtrate were collected. Twelve determinations carried out in this way with solutions varying from tenth to thirtieth normal gave results from 126.87 to 126.92. The variations were finally traced to the carrying down of silver nitrate by the silver iodide; for the more concentrated the solutions during the precipitation and the greater the excess of silver employed, the lower was the observed atomic weight of iodine. The occlusion of silver nitrate by silver halides is well known in the cases of silver bromide and silver chloride, but in these cases it is possible to wash out the occluded salts by oft-repeated treatment with water. The difficulty in removing the silver nitrate in the case of silver iodide is doubtless due to the lesser solubility of this halide.

Similar observations have been made also by Köthner and Aeuer,[1] who found that with fifth normal solutions the carrying down of silver nitrate is very considerable, and that an excess of iodide converts this occluded silver nitrate into silver iodide only very slowly if at all. They found, however, that, if the precipitated silver iodide is washed with ammonia, the greater part of the occluded matter may be eliminated, owing possibly to the slight solubility of silver iodide in ammonia. On account of this newly discovered tendency of silver iodide, it seemed probable that the results of the synthesis of silver iodide from known weights of silver in the early part of this research were somewhat too low; for although the precipitations took place in ammoniacal solution and an excess

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[1] Liebig's *Ann.*, 337, 123 (1904).

of iodine was employed, the fact that the solutions were always very nearly as strong as tenth normal and that the ammonic iodide was poured into the silver nitrate made it probable that occlusion had taken place at least to some extent even here. It is noteworthy that three of these syntheses yielded results as high as 126.926. Similar conclusions are to be drawn concerning the results of the titration of silver and iodine, although in this case precipitation took place in the reverse fashion, *i. e.*, by adding the silver nitrate to the iodide.

Accordingly experiments were carried out for the redetermination of the ratios of silver to silver iodide and to iodine, as well as the new one of iodine to silver iodide, with especial precautions to avoid the error of occlusion by using very dilute solutions and no excess of silver. After the iodine had been weighed, very nearly the exact amount of silver to combine with the iodine was weighed out and dissolved in nitric acid with the usual precautions to avoid spattering. The quantity of iodine used in each analysis was between 3 and 4 gm., and the amount of silver consequently about 3 gm.

The solutions of both silver and iodine were diluted to a volume of 1 liter each, so that the solutions were about thirtieth normal, and then the silver nitrate was added very slowly to the solution of hydriodic acid with constant stirring. The flask in which precipitation was carried out was then shaken for some time, and allowed to stand until the supernatant liquid was clear. This liquid was tested for an excess of iodine or silver in a nephelometer, and if a deficiency of either was found, it was made up and the solution again shaken, until the point was reached where the extremely faint opalescence produced by both hydriodic acid and silver nitrate was equal in both nephelometer tubes. The excess or deficiency of silver was in no case over 0.1 mg., and in most cases much less.

THE ATOMIC WEIGHT OF IODINE. Series VII. Ag: I.

No. of analysis.	Sample of silver.	Weight of iodine in vacuum.	Weight of silver in vacuum.	Ratio Ag:I.	Atomic weight of iodine.
		gm.	*gm.*		
38	A	3.29307	2.79897	0.849958	126.924
39	B	3.70131	3.14584	0.849926	126.929
40	B	3.75640	3.19258	0.849904	126.932
41	B	3.24953	2.76186	0.849926	126.929
42	A	4.12539	3.50639	0.849954	126.925
43	C	3.53165	3.00165	0.849928	126.929
44	C	2.99834	2.54842	0.849944	126.926
45	C	2.00014	1.69991	0.849896	126.933
	Average			0.849930	126.928

Several samples of iodine were employed in these analyses, each one of which had been three times distilled from an iodide as previously described. Three different specimens of silver, purified by different methods, were used. Sample A was a portion of the material used in the early part of this investigation. Sample B was prepared from silver nitrate which had been recrystallized seven times from nitric acid, five times from water, and finally precipitated by ammonium formate. Sample C was precipitated as silver chloride once, electrolyzed once, and finally precipitated with formic acid. All three samples were fused in a current of hydrogen on a lime boat.

In order to determine whether an even more gradual addition of silver nitrate would influence the extent of the occlusion, in Analysis 42 the silver was introduced by means of a large funnel provided with a fine spout.

In one of the foregoing analyses the attempt was made to determine the ratio between iodine and silver iodide by adding an excess of silver nitrate and weighing the precipitate. Although only 5 mg. excess of silver nitrate were added, while the total volume of the liquid was over 2 liters, the precipitate was 1 mg. heavier than it should have been as calculated from the result of the titration, showing that the occlusion of silver nitrate by the silver iodide may take place even after precipitation. In order to avoid this difficulty, in succeeding analyses, the silver iodide was collected without the addition of silver nitrate, after washing with pure water; then the dissolved silver iodide was determined in the filtrate and wash-water, by comparing the precipitates produced by the addition of silver nitrate with those formed in standard solutions of hydriodic acid. As a matter of fact, the filtrates were always found to be practically free from silver iodide, while the wash-water contained from 0.2 to 0.4 of a mg. per liter. This difference in solubility of the silver iodide in the filtrate and wash-waters is probably due to colloidal solubility of this salt in pure water. The loss on fusion of the silver iodide and the asbestos shreds were determined as usual. The almost absolute lack of opalescence in the filtrate when treated with silver nitrate or hydriodic acid is a good proof of the complete absence of chlorine and bromine, since both silver bromide and silver chloride are considerably more soluble than the iodide.

THE ATOMIC WEIGHT OF IODINE. Series VIII. I: AgI.

No. of analysis.	Weight of iodine in vacuum.	Corrected weight of silver iodide in vacuum.	Ratio I:AgI.	Atomic weight of iodine. Ag=107.880.
	gm.	*gm.*		
46	3.75640	6.94911	0.540558	126.927
47	3.24953	6.01135	0.540566	126.931
48	4.12539	7.63201	0.540538	126.916
49	3.53165	6.53348	0.540547	126.921
50	2.99834	5.54680	0.540553	126.924
		Average	0.540552	126.924

Finally, in order to determine the ratio of silver to silver iodide, the filtrate and wash-waters were evaporated to very small bulk, until the greater part of the nitric acid had been expelled, and then the amount of silver in the residue was determined nephelometrically, after dilution to 25 c.c., by adding an excess of hydriodic acid and comparing with standard solutions of silver.

This quantity, which was never more than 0.1 mg., was subtracted from the original weight of silver, and no correction was applied to the weight of silver iodide for the amount dissolved in the wash-water.

THE ATOMIC WEIGHT OF IODINE. Series IX. Ag: AgI.

No. of analysis.	Sample of silver.	Corrected weight of silver in vacuum.	Corrected weight of silver iodide in vacuum.	Ratio Ag:AgI.	Atomic weight of iodine. Ag = 107.880.
		gm.	gm.		
51	B	3.19249	6.94875	0.459434	126.931
52	B	2.76175	6.01108	0.459443	126.926
53	C	3.00189	6.53396	0.459429	126.933
54	C	2.54833	5.54657	0.459443	126.926
			Average	0.459437	126.929

DISCUSSION OF RESULTS.

In the following table are summarized the results from the different series:

Series.	Material.	Result.	Series.	Material.	Result.
I	Ag: AgI	126.899	VI	AgI: AgCl indirect	126.924
II	Ag: AgI	126.913	VII	Ag:I	126.928
III	Ag: I	126.918	VIII	I: AgI	126.924
IV	AgI: AgCl direct	126.925	IX	Ag: AgI	126.929
V	AgI: AgBr	126.924			
	Average, omitting Series I, II, and III				126.926

In computing the atomic weight of iodine from these data, Series I, II, and III should obviously be neglected, since the experiments in these series are superseded by the more accurate ones of Series VII and IX.

In Series IV, V, and VI, the three chief possible errors have been considered and shown to have no effect. Occluded silver nitrate in the silver iodide was eliminated by fusion in iodine; and it was proved both that no volatilization of the halides actually took place and that no halogen was retained by the solidified salt. In Series VII, VIII, and IX, the chief possible error, that of occlusion of silver nitrate by silver iodide, was avoided by sufficiently diluting the solutions before precipitation. That the dilution was sufficient was evident from the agreement of the results of the experiments with the larger and smaller quantities of material, the total volume of the solutions being the same in all cases. Furthermore, the weight of the silver iodide obtained in the analyses recorded in Series VIII was in every case very nearly equal to the sum of the weights of silver and iodine employed (Series VII), which could not have been the case if silver nitrate had been retained by the iodide. Additional evidence upon this point is afforded by the percentages of iodine and silver in silver iodide as given in Series VIII and IX, for the sum of the two percentages is 0.999989, the discrepancy being only a trifle greater than 0.001 per cent. The close agreement of the averages of the last six series makes it certain that no constant error of magnitude still remains undetected in any one of the methods. One is forced, then, to conclude that the average of the last six series, 126.926, represents the atomic weight of iodine within a very few thousandths of a unit.

RATIO OF SILVER BROMIDE TO SILVER CHLORIDE.

It is interesting, also, to compare the weights of silver bromide and silver chloride produced in the same analysis. When this is done the ratio of silver bromide to silver chloride and the atomic weight of bromine computed with the assumed atomic weight of chlorine, 35.457, are found to be identical with the corresponding values subsequently determined by Baxter.[1]

Series X. AgBr: AgCl.

Sample of bromine.	Weight of silver bromide in vacuum.	Weight of silver chloride in vacuum.	Ratio AgBr: AgCl.	Atomic weight of bromine.
	gm.	*gm.*		
A	10.92087	8.33536	1.310186	79.918
A	13.88056	10.59453	1.310163	79.915
B	8.21480	6.27004	1.310167	79.915
B	7.87883	6.01350	1.310190	79.919
C	6.90102	5.26732	1.310158	79.914
D	9.53699	7.27923	1.310164	79.915
Average			1.310171	79.916

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[1] See page 61.

HISTORICAL DISCUSSION.

In discussing the bearing of this investigation upon the results of earlier work by other chemists, the experiments of Millon upon silver and potassium iodates [1] and of Berzelius [2] and Dumas,[3] who converted silver iodide into silver chloride, may be disregarded, since at the time the analyses were made, quantitative analysis was in its infancy. Marignac's [4] value for the atomic weight of iodine, 126.79, obtained from titration of weighed amounts of silver with potassic iodide, and from syntheses of silver iodide from weighed quantities of silver, may be accounted for by the supposition that the iodine used in the experiments was not pure. To explain Stas's [5] low value, 126.79, is a difficult matter. His iodine was purified by two different methods, *i. e.*, by once precipitating or distilling the iodine from a strong solution of potassic iodide, and by precipitation of nitrogen iodide. A third sample was purified by both methods. Since the material purified by each of the two methods gave identical results with that purified by both methods, it is inconceivable that either method of purification should not have been effective. Impurity in the silver or loss of silver iodide are improbable causes of the discrepancy, for the weight of the silver iodide produced was equal to the sum of the weights of the silver and iodine employed. Richards and Wells have recently shown, however, that Stas was not infallible, and in fact was capable of making serious mistakes, such that his value for the atomic weight of sodium was 0.2 per cent too high, and that for the atomic weight of chlorine 0.03 per cent too low, so that it is not at all surprising to find that here also his work was faulty in some undiscovered particular.

Ladenburg's result,[6] when calculated from the true value of the atomic weight of chlorine, becomes 126.988, which agrees very closely with the value deduced in this paper. His determinations were affected by several small errors, so that the close agreement is somewhat the result of chance. In the first place, porcelain crucibles, as has been pointed out before, gain in weight when used for the conversion of silver iodide into silver chloride, so that the weight of the silver chloride is somewhat uncertain. Furthermore Ladenburg did not fuse the silver iodide before weighing it. Although Stas states that silver iodide may be completely dried without fusion, his experiments show a loss in weight on fusion of 0.002 per cent, while the average loss on fusion as given on page 97 is about 0.004 per cent. Moreover, Ladenburg's method of purifying silver iodide, by washing the precipitated salt with ammonia, could hardly be expected to remove last traces of silver chloride and silver cyanide "included" by the precipitate. These errors are all so small that they would not affect the second place of decimals.

Shortly after the publication of the first portion of this research there appeared the complete paper of Köthner and Aeuer upon the same subject.[7] These

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[1] *Ann. de Chem. et de Phys.* (3) **9**, 400 (1843).

[2] *Ibid.*, (2) **40**, 430 (1829).

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

[4] Berzelius' *Lehrbuch*, 5th ed., **3**, 1196.

[5] *Œuvres Complètes*, **1**, 548.

[6] *Ber. d. d. Chem. Gesell.*, **35**, 2275 (1902).

[7] Liebig's *Ann.*, **337**, 123 (1904).

chemists, determined the ratio AgI: AgCl, in eight closely agreeing analyses. One synthesis was made by precipitating a weighed amount of silver with hydriodic acid, and one by heating a weighed amount of silver in iodine. A second paper[1] by the same authors contains a recalculation of their results with a different value for chlorine, and a critical discussion of their own, Ladenburg's, and my work.

In this second paper two main criticisms of my investigation are made. One of these concerns the validity of the conclusion that ordinary iodine does not contain an undiscovered halogen element. This criticism is founded upon a mistaken understanding, however. My experiments were directed to prove the existence or non-existence of an element of *higher* atomic weight than iodine, which, if its properties were those to be expected from the properties of the other members of the halogen family, would have been set free from solutions of its compounds by iodine, and hence would have accumulated in the first fraction of the fractional separation (see page 93). The existence of an unknown halogen of lower atomic weight than iodine was not considered.

Although Köthner assumes the possibility that such an element exists, it is obviously improbable that any halogen of lower atomic weight could have remained in the purified samples of iodine which were employed in my experiments; since those specimens which received even the least purification were thrice distilled from an iodide, the iodide having been made in each distillation from nearly half the iodine from the previous distillation.

In the second place, it is maintained that volatilization of silver halides takes place when silver iodide is heated in a current of chlorine. This is undoubtedly true, unless precautions are taken to prevent the volatilization. Silver iodide is much more volatile at its fusing temperature than silver chloride; and if the original silver iodide is fused before the current of chlorine or bromide is begun, a loss may take place by volatilization or possibly by *spattering*. In my own work, however, fusion of the salt was always avoided until the greater part of the change had taken place. Proof that no volatilization of silver halides actually occurred in my experiments has already been given (page 105). It may be added that the exact agreement of the results of Series V and VI is additional evidence in the same direction; for any loss of silver bromide, which is the most volatile of the three halides, would have tended to raise the results of Series V above those of Series VI.

Köthner's average result in the series AgI: AgCl, when recalculated upon the basis of chlorine 35.457, becomes 126.915. The slight difference between this value and the final result of the research described in this paper may be explained in several possible ways. A perusal of Köthner's paper does not make clear whether or not fusion of the silver iodide took place at the beginning of his experiments, so that it is uncertain whether the gain in weight of the coil of glass

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[1] Liebig's *Ann.*, **337**, 362 (1904).

tubing, which was attached to the reaction tube, was due to volatilized silver halides, or to attacking of the glass by the hot halogens. At any rate, it is hard to believe that 1.5 meter of glass tubing subjected to the long-continued action of mixed chlorine and iodine at 150° should not have altered its weight somewhat. Furthermore, Köthner himself showed that the tube in which the reaction took place was slightly attacked by the fused silver chloride, but the nature of the correction for this attacking of the glass is uncertain. Finally, although the precaution was taken of fusing the silver iodide before the initial weighing, so that the salt must have been free from moisture, it was not fused in an atmosphere of iodine. Hence it is possible that the iodide still contained traces of occluded silver nitrate (or metallic silver). This deficiency in iodine, as well as the possible gain in weight of the apparatus during the experiment, would have lowered the atomic weight of iodine.

As far as Köthner's syntheses of silver iodide from weighed amount of silver are concerned, it need only be said that, even assuming that occlusion was avoided in the synthesis in the wet way, and that in the synthesis in the dry way a single precipitation of the iodine from solution in an iodide had completely removed such impurities as chlorine and bromine, which would have accumulated in the silver iodide during the experiment, the fact that Richards and Wells have shown that silver fused in the air or with borax and saltpetre, according to Stas, must contain oxygen, makes it certain that the results of Köthner's syntheses, 126.919 and 126.904, are too low.

It is interesting to note, however, that Ladenburg's, Scott's, and Köthner and Aeuer's work all afford confirmation that the atomic weight of iodine is undoubtedly much higher than was formerly supposed from Stas's syntheses of silver iodide.

SUMMARY.

The results of the research are, then, as follows:

1. The atomic weight of iodine is found to be 126.926 (O = 16.000 and Ag = 107.880). If silver is taken at 107.870, iodine becomes 126.914.

2. The existence of an element of the halogen family of higher atomic weight than iodine is shown to be improbable.

3. The specific gravity of pure fused silver iodide is found to be 5.674 at 25° referred to water at 4°.

4. The observation by Köthner and Aeuer that under certain conditions silver iodide occludes silver nitrate, and that this occluded salt can not be removed by washing with water, is confirmed.

5. The value of Richards and Wells for the atomic weight of chlorine 35.457 (Ag = 107.880) and Baxter's for the atomic weight of bromine 79.916 are substantiated.

VIII.

A REVISION OF THE ATOMIC WEIGHTS OF IODINE AND SILVER.

THE ANALYSIS OF IODINE PENTOXIDE.

By Gregory Paul Baxter and George Stephen Tilley.

Journal of the American Chemical Society, 31, 201 (1909).
Zeitschrift für anorganische Chemie, 61, 293 (1909).
Chemical News, 100, 259, 261, 274, 286, 310 (1909).

Contributions from the Chemical Laboratory of Harvard College.

A REVISION OF THE ATOMIC WEIGHTS OF IODINE AND SILVER.

THE ANALYSIS OF IODINE PENTOXIDE.

INTRODUCTION.

For some time it has been apparent that Stas's researches upon the atomic weight of silver, upon which the value now in use depends, are somewhat at fault. The need for a redetermination of the ratio of this constant to the atomic weight of oxygen is especially pressing, since silver has been very frequently used as the basis for exact work upon atomic weights, both directly, and also indirectly through its relation to the atomic weights of the halogens in the analysis of metallic halides.

The problem is made difficult, however, by the fact that the only known definite compounds of silver with oxygen are difficult if not impossible to prepare in a pure state, besides containing so small a percentage of oxygen that the experimental error would be greatly magnified in the calculation. All other methods involve the knowledge of the exact ratio of at least one other atomic weight to that of silver or oxygen, the accuracy of the process diminishing with the number of atoms involved. Among the various classes of compounds the analysis of which may afford the desired information, oxides are of especial interest because the knowledge of the ratio of only one atomic weight to that of silver is involved. The difficulty and uncertainty in analyzing metallic oxides[1] make them unsuited for the purpose. The ratios of the atomic weights of silver and the halogens are known with greater exactness than in the case of most elements, hence to determine the ratio of any one of the halogens to that of oxygen will serve the purpose equally well. The only compound of a halogen and oxygen of considerable stability is iodine pentoxide. This substance is, however, quite stable through a fairly wide range of conditions, and its analysis offered enticing possibilities. To be sure, the compound contains only 25 per cent of oxygen, but this disadvantage is in part counterbalanced by the fact that the ratio of the atomic weight of iodine to that of silver is greater than in the case of most elements.

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[1] Richards and Baxter: *Proc. Amer. Acad.*, **35**, 61 (1899); **35**, 253 (1900); *Zeit. anorg. Chem.*, **22**, 221; **23**, 245.

The method actually employed was to reduce to hydriodic acid weighed amounts of iodine pentoxide, and to determine the weight of silver necessary to combine with the iodine. If the ratio of silver to iodine pentoxide, $\frac{2\mathrm{Ag}}{\mathrm{I_2O_5}}$, is multiplied by that of iodine to silver, $\frac{\mathrm{I}}{\mathrm{Ag}}$, the per cent of iodine in the pentoxide is obtained, and thence the ratio $\frac{2\mathrm{I}}{5\mathrm{O}}$.

PURIFICATION OF MATERIALS FOR THE FIRST SERIES OF ANALYSES.

IODIC ACID.

Iodine pentoxide may be readily prepared by dehydration of iodic acid at a comparatively low temperature. Of the various methods for preparing the latter substance, by far the most satisfactory for the present purpose is the oxidation of iodine with fuming nitric acid. The volatile by-products of the reaction, oxides of nitrogen and water, as well as the excess of nitric acid, may be removed by heating, and the acid may be crystallized from aqueous solution.

Iodine was purified for most of the preparations by the methods already described by one of us.[1] These consisted usually in a preliminary distillation of commercial iodine from solution in commercial aqueous potassium iodide. The iodine was then twice reduced to hydriodic acid by hydrogen sulphide and water, and the hydriodic acid was subsequently oxidized by very nearly the theoretical quantity of recrystallized permanganate, with intermediate boiling of the hydriodic acid solution to eliminate cyanogen as hydrocyanic acid.[2] In this way, since only five-eighths of the iodine is set free from hydriodic acid by permanganate, the iodine was three times distilled from a solution of an iodide, the iodide being of greater purity in each succeeding distillation. It has already been shown that three such distillations are sufficient to remove completely chlorine and bromine,[3] so that there can be no question of the freedom of the resulting iodine from those closely related elements. The final product was once distilled with water into a Jena glass flask cooled with running water, and the resulting solid was washed with the purest water upon a porcelain Gooch crucible containing no mat.

Pure fuming nitric acid was prepared by distilling the best commercial product several times, with rejection of the first and last thirds, until the distillate, after dilution, gave no test for chloride with silver nitrate in a nephelo-

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[1] Baxter: *Proc. Amer. Acad.*, 40, 421 (1904); *Jour. Amer. Chem. Soc.*, 26, 1579; *Zeit. anorg. Chem.*, 43, 16. (See page 92.)

[2] Richards and Singer: *Amer. Chem. Jour.*, 27, 205 (1902).

[3] Baxter: *Loc. cit.*; also *Proc. Amer. Acad.*, 41, 73 (1905); *Jour. Amer. Chem. Soc.*, 27, 876; *Zeit. anorg. Chem.*, 46, 36.

meter. A quartz condensing tube was used in these distillations, and the final product was collected in a quartz vessel. In this way the introduction of silica and alkalies from glass vessels was avoided. Fused quartz vessels have already been shown to be essentially insoluble in acid solutions.[1]

The reaction between iodine and fuming nitric acid proceeds slowly at ordinary temperatures, with the formation of oxides of nitrogen and nitro-iodic acid. Heat hastens the reaction and also breaks up the nitro-iodic acid into nitric oxide, iodine, and iodic acid. If the nitric acid is in large excess the iodine is converted into iodic acid without loss, and the iodic acid remains insoluble in the residual concentrated nitric acid. If the iodine is in excess, the reaction proceeds until the nitric acid is so dilute, owing to the production of water in the reaction, as to be without further effect upon the iodine, although the acid is still so concentrated that the iodic acid remains essentially insoluble. Nitric acid of this concentration dissolves considerable quantities of iodine, however.

Since the largest quartz vessel at first available was a 100 c.c. transparent fused quartz flask, the most convenient method for making the iodic acid was found to be to treat a large quantity of iodine in the flask with successive portions of fuming nitric acid. After the introduction of the iodine, nitric acid was distilled directly into the flask through the quartz condenser. The flask was then warmed until the nitric acid was spent. The spent acid was removed as completely as possible by drainage, and was replaced by fresh acid, and the process was repeated until the iodine appeared to be completely oxidized. Dissolved iodine was recovered from the spent acid by dilution. After the removal of the last portion of the acid, the iodic acid was dissolved in the smallest possible amount of the purest water and the solution was evaporated to dryness in a dish of fused quartz in order to expel nitric acid and unchanged iodine, for the removal of nitric acid by crystallization is very slow. During this evaporation the dish was placed upon a large watch glass on a sand bath, and was surrounded by a large bottomless beaker. The dish was further protected by being covered with a bottomless flask, through the neck of which a current of pure dry air was introduced in order to hasten evaporation. The air was freed from organic matter by passing over hot copper oxide in a hard-glass tube, and was purified and dried by means of a solution of potassium hydroxide and solid caustic potash. The purifying apparatus was constructed wholly of glass.

The residue from the evaporation was dissolved in the purest water and evaporated in the quartz dish with the same precautions as above until a film of solid appeared on the surface of the liquid. This solid is not iodic acid, but is probably a compound having less water, since it was necessary to induce the crystallization of the acid itself by inoculation. If left to itself the acid crystallizes very slowly, some days being necessary for the establishment of equilib-

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[1] Mylius and Meusser: *Zeit. anorg. Chem.*, 44, 221 (1905). Baxter and Hines: *Jour. Amer. Chem. Soc.*, 28, 1565 (1906); *Zeit. anorg. Chem.*, 51, 205. (See page 36.)

rium. It is economical, however, to wait until crystallization has ceased, since the solubility of the acid at room temperature is so high, a saturated solution at 20° containing over 75 per cent of acid. The first crop of crystals was drained as completely as possible, usually with centrifugal drainage in a platinum centrifugal machine,[1] and the product was twice recrystallized. On account of the high solubility of the acid and the low temperature coefficient of solubility between 0° and 100° the yields of acid were very small, hence the mother-liquors were worked up for several successive yields of crystals. The thrice recrystallized acid was preserved in a desiccator containing solid caustic potash. It was designated Sample I.

The solutions of iodic acid, as well as the solid substance and even iodine pentoxide made from the acid, possessed to a slight degree a peculiar odor which may be described as "aromatic." This odor persisted through the crystallization although with continual diminution, but was not entirely absent from acid which had been crystallized three times. It was later proved that the odor is not due to the acid itself because after a sufficient number of crystallizations the odor disappears. Furthermore, it was experimentally proved that no appreciable amount of iodine was contained in this vapor, for when a concentrated solution of the acid is boiled no iodine can be detected in the distillate, and when a current of air is conducted over the solid at ordinary temperatures into a solution of sulphur dioxide no iodine can be found in the sulphurous acid solution. Even at high temperatures the pentoxide loses in weight very slowly, 10 gm. losing only 1 mg. at 240° in 4 hours. By far the greater part of this loss is due to decomposition of the pentoxide, for free iodine can be easily detected in the air which has passed over the substance at high temperatures.

The possibility of the presence of metallic impurity in the iodic acid, arising from the action of iodine on the glass of the flask in which it was condensed, was tested by evaporating to dryness the mother-liquor of the last crystallization of the original solution and heating the residue in a weighed platinum boat in a current of pure dry air until the pentoxide was completely decomposed. The boat gained in weight only 0.0006 gm., part of this gain being due to the formation of platinous iodide. Faint tests for sodium and calcium only could be obtained with the residue in the spectroscope.

SILVER.

Silver was purified by methods already found in this laboratory to be effective for the purpose (page 22). A dilute solution of silver nitrate was first precipitated with hydrochloric acid in excess, and the precipitate was thoroughly washed with pure water. The chloride was next reduced by means of invert sugar and an excess of sodium hydroxide, and the metal, after long-continued washing by decantation, was fused upon charcoal. After the buttons had been

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[1] Baxter: *Jour. Amer. Chem. Soc.*, **30**, 286 (1908).

cleansed by scrubbing with sand and etching with nitric acid, they were dissolved in nitric acid and the silver was precipitated as metal by means of ammonium formate made from redistilled ammonia and formic acid. This precipitate in turn was thoroughly washed and the metal was fused in the flame of a carefully cleaned blast lamp in a crucible of lime made from purified calcium nitrate and carbonate. After being cleansed as before, the buttons were electrolyzed and the electrolytic crystals, after being washed and dried, were fused in a current of pure electrolytic hydrogen in an unglazed porcelain boat lined with the purest lime.[1] The resulting buttons were cut into fragments of from 3 to 6 gm. with a fine jeweller's saw, etched with small portions of dilute nitric acid until the acid used in etching was free from iron, and finally the fragments were washed and thoroughly dried in a vacuum at about 400°. Two different specimens of silver were prepared in essentially the same way, Samples A and B.

CONVERSION OF IODIC ACID INTO IODINE PENTOXIDE.

The conversion of the iodic acid into iodine pentoxide was effected by heating the substance in a current of dry gas. At the beginning of the research the hope was entertained that the final product might be sublimed. In no experiment, however, have we been able to detect the least trace of sublimation, even when the pentoxide was heated to the decomposition point. Iodic acid may be made to lose all its water of composition without fusion, and consequently it was to be expected that under these conditions dehydration could be made nearly if not quite complete. T. W. Richards has already pointed out that a solid which loses water of composition without fusion is left in the form of a skeleton, from the innermost interstices of which the water vapor may escape, while, if fusion takes place during drying, a portion of the original salt may be enclosed within an impervious coating of anhydrous salt so that escape of water is impossible.[2]

It is commonly stated that the dehydration of iodic acid takes place in two stages, two-thirds the water being lost below 130° and the remainder at about 200°.[3] The acid itself, if heated rapidly, melts at 110° with the separation of the solid phase $I_2O_5.HIO_3$, although this second phase shows no indication of melting up to the temperature of the second stage in the dehydration. Our earlier experience was not in accordance with the above statements. The acid, when heated to about 110°, lost *all* its water of composition, at this temperature. This was shown conclusively in one experiment by heating a weighed amount of iodic acid for some time at about 110° and then reweighing. The

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[1] Fusion in hydrogen (Baxter: *Proc. Amer. Acad.*, 39, 249 [1903]) is probably safer than fusion in a vacuum, since it eliminates the possibility of the taking up of sulphur by the silver from the rubber ring used in fitting the hollow brass stoppers into the porcelain fusion tube. Richards and Wells have shown that silver fused in hydrogen is certainly as pure as any other.

[2] *Zeit. physik. Chem.*, 46, 194 (1903).

[3] For a discussion of this subject see Groschuff, *Zeit. anorg. Chem.*, 47, 333 (1905).

acid lost the amount of water theoretically necessary for the formation of the pentoxide, and further heating to 300° produced only a negligible diminution in weight. On one later occasion, however, when a comparatively crude specimen of acid was being dehydrated, the second phase unexpectedly appeared, and in all subsequent experiments the same result was obtained, no matter what the source of the iodic acid, or how carefully the apparatus was cleaned before use. This point is additional proof that the second phase is a definite chemical compound. The obvious explanation of the phenomenon is that the laboratory became inoculated with "germs" of the second phase so that its formation was thereafter always induced.

The iodic acid was dehydrated in a platinum boat contained in a hard-glass tube heated by a solid aluminum oven (fig. 4, page 78). When heated with a Bunsen flame, this bath could be regulated in temperature to within one or two degrees without the least difficulty, even without the jacket of asbestos paper which was usually employed. Thermometers placed inside the hard-glass tube and in a cavity in the blocks registered the same temperature within a degree even when the oven was heated to 300°.

At first the air was purified and dried by passing over hot copper oxide in a hard-glass tube, then through two towers containing beads moistened with silver nitrate and caustic potash solutions, respectively, and finally through four towers containing beads moistened with concentrated sulphuric acid to which a small quantity of potassium dichromate had been added in order to prevent any possibility of reduction. The apparatus was constructed wholly of glass with ground or fused joints, rubber and grease being carefully avoided. When heated in a current of air thus purified and dried, even the purest iodine pentoxide became somewhat brown owing possibly to liberation of iodine. The use of electrolytic oxygen in place of air failed to prevent this phenomenon. Finally it was found that if the air was dried more thoroughly, by means of resublimed phosphorus pentoxide, the difficulty could be avoided. The cause of this marked catalytic effect from the minute quantity of moisture which is not absorbed by sulphuric acid was not determined.

The hard-glass tube in which the heating was conducted formed part of a bottling apparatus by means of which the boat could be transferred to a weighing-bottle without exposure to moist air (see fig. 1, page 8). Although precautions were taken to prevent exposure of the substance to moisture before weighing, little danger was to be feared from this source, for in air ordinarily moist the pentoxide absorbs water very slowly. For instance 4.4 gm. of pentoxide, when exposed in the platinum boat to the air of the laboratory for 2 hours, gained only 0.0008 gm.

Even when dried under the most favorable conditions the above-mentioned darkening of the pentoxide took place if the temperature rose much over 250°. Accordingly the temperature was not allowed to pass this point in drying the tstance for analysis. Furthermore, since it was by no means certain that every trace of water could be expelled from the pentoxide at this temperature, and since it seemed probable that the amount of water retained would vary with the temperature and time of treatment, the conditions in the different experiments were made as nearly as possible identical.

The details of manipulation were as follows: The crystals of iodic acid were powdered in a new smooth agate mortar together with a small quantity, about 2 per cent of the weight of the acid, of the phase produced in the first stage in the dehydration. This step was of advantage in catalyzing the first stage in the dehydration, for frequently, when the precaution of thus inoculating the iodic acid was omitted, the temperature reached 130° before dehydration began, whereas when this precaution is taken the water first appears as low as 85°. Since the iodic acid itself melts at 110° when in contact with the phase produced at this temperature, it seemed better to prevent the acid from reaching this temperature until the first stage in the dehydration was past. As a matter of fact, preliminary water determinations in the dried material indicated a slightly larger proportion of water in acid which had not been inoculated with the second phase.

The weighed boat, containing from 6 to 10 gm. of the iodic acid, was next heated in a slow current of air at 90° to 110° until the first two thirds of the water of composition had been given off by the iodic acid and had been expelled from the tube by the current of dry air. The temperature was then raised until the second portion of water was given off. Usually the pentoxide began to form at about 220°. There is no evidence of fusion at this point, even if the temperature rises much above 220° before all the remaining water is expelled. After all the water had disappeared the temperature was raised to 240° and maintained at this point for 4 hours. Then the boat was transferred to the weighing-bottle, allowed to stand in the desiccator with the counterpoise for some time, and was weighed.

DETERMINATION OF IODINE IN IODINE PENTOXIDE.

The analysis of the iodine pentoxide for iodine was effected by dissolving the substance in water, reducing the iodic acid solution to hydriodic acid with a suitable reducing agent, and titrating the hydriodic acid against a weighed amount of silver.

The operation in detail was as follows: After being weighed, the boat with its contents was placed in a large thick-walled flask and immediately covered with about 500 c.c. of the purest water, in which it slowly dissolved. Even when the pentoxide was slightly colored the solution was colorless to the eye and absolutely clear. The weighing-bottle was rinsed with water and the rinsings were added to the main solution in the flask. In a number of early experiments the reduction was accomplished by slowly pouring the dilute solution of iodic acid into a solution of a slight excess of sulphurous acid. Very nearly the theoretical amount of the purest silver was weighed out and dissolved in redistilled nitric acid diluted with an equal volume of water as described on page 12. After the silver was completely dissolved, the solution was diluted with an equal volume of water and heated until free from nitrous acid. This latter precaution was especially necessary, since nitrous acid readily liberates iodine from iodides, while nitric acid has this effect only when hot or rather concentrated. Finally the solution was diluted until at least as dilute as thirtieth normal and was added with constant agitation to the solution of the hydriodic acid which had been diluted to a similar concentration in a large glass-stoppered precipitating bottle. The whole was then thoroughly shaken and allowed to stand until clear. In order to determine whether silver or iodide was in excess, 30 c.c. portions of the solution were tested with silver nitrate and hydriodic acid in the nephelometer. The results of these earlier analyses were extremely unsatisfactory, the end-point changing continuously with time, and an unreasonably large amount of silver was required. This could not have been due to occlusion of silver nitrate by the silver iodide, since it has already been shown by one of us that at concentrations less than thirtieth normal, if very nearly equivalent amounts of silver and iodide are used, the latter difficulty is too small to have an appreciable effect.[1]

The cause of the trouble was finally traced to occlusion of silver sulphate by the silver iodide. Richards and Jones [2] found that silver chloride occludes silver sulphate very markedly and tenaciously, hence it is not in the least surprising to find the same difficulty here. It is to be noted that the concentration of sulphuric acid in these experiments is relatively large, *three molecules* of sulphuric acid being produced in the reduction for every *atom* of iodine. That this difficulty did not appear in the above mentioned researches upon the ratio of iodine to silver, where iodine was reduced with sulphurous acid and the hydriodic acid titrated against silver, is undoubtedly due to the fact that the concentration of sulphuric acid was relatively much lower, only *one* molecule of sulphuric acid being formed in the reduction of one *molecule* of iodine.

A search for a more satisfactory reducing agent than sulphurous acid failed to reveal any substance more promising than hydrazine, for the reduction of iodic acid with this substance yields only hydriodic acid, nitrogen and water.[3] In order to avoid the introduction of undesirable acids, the hydrazine was used in the form of a solution of the hydroxide instead of as a salt. The hydrazine hydroxide was made by distilling either the chloride or the sulphate with a concentrated solution of a considerable excess of sodium hydroxide in a platinum still. The product was then redistilled in the platinum still to eliminate

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[1] Baxter: *Proc. Amer. Acad.*, **41**, 77 (1905); *Jour. Amer. Chem. Soc.*, **27**, 880; *Zeit. anorg. Chem.*, **46**, 41. (See page 107.)

[2] *Pub. Carnegie Institution*, **69**, 73 (1907); *Jour. Amer. Chem. Soc.*, **29**, 837; *Zeit. anorg. Chem.*, **55**, 84.

[3] Brown and Shetterly have shown that no hydronitric acid is formed by the action of hydrazine on iodates or iodine. *Jour. Amer. Chem. Soc.*, **30**, 53 (1908)

possible traces of chlorides, and was preserved in a platinum flask. Even when made from the chloride, the doubly distilled product was absolutely free from chlorides. The approximate concentration of the solution was determined shortly before use by titration against a standard solution of iodic acid or potassium permanganate. Preliminary experiments showed that there is no danger of the reduction of the silver salts by a slight excess of hydrazine in nitric acid solution.

Special pains were taken in the reduction of the iodic acid with hydrazine to avoid any possibility of loss of iodine by volatilization. The solution of the iodic acid was transferred to an 8-liter bottle with a carefully ground stopper, and, after the iodic acid had been neutralized with ammonia, very slightly less than the theoretical quantity of hydrazine hydroxide was added. Since in alkaline solution hydrazine is without effect upon iodic acid, the solution was next made acid by slow addition of nitric acid.

As soon as the neutral point has been passed, iodine is freed by interaction of the hydriodic acid with the iodic acid. Lest any of this iodine be volatilized from the solution before it could be reduced by the hydrazine the nitric acid was introduced at the bottom of the solution through a long funnel. Thus iodine was sure to be completely reduced before reaching the surface of the solution. A specially devised stopper, shown in the accompanying diagram, provided for the escape of the nitrogen through a long column of bulbs, which served to catch spatterings or soluble vapors, if any reached this point. As a further precaution against the escape of iodine a small quantity of sulphurous acid was poured into the bottle through the train of bulbs. This sulphurous acid served also to complete the reduction of the iodic acid. The amount of sulphuric acid formed in this way was not sufficient, however, to produce appreciable occlusion of silver sulphate.

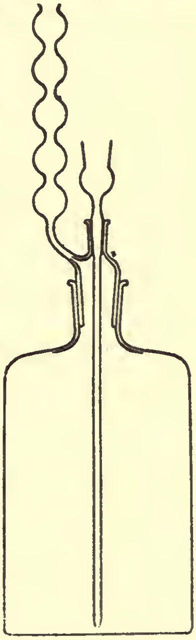

Fig. 5. — Apparatus for reducing iodic acid.

After the reduction and subsequent dilution of the solution to a concentration between thirtieth and fiftieth normal, the hydriodic acid was precipitated with a dilute solution of a weighed amount of silver as before described. On account of the large bulk of the mother-liquor, 6 to 7 liters, the end-point as determined in the nephelometer was somewhat uncertain, especially since it seemed to be complicated by a minute trace of silver iodide held in suspension. Hence, instead of attempting to use exactly the theoretical quantity of silver, an amount was employed a few tenths of a milligram in excess of the required quantity. Then this excess was determined by evaporating the supernatant liquid to a very small bulk, precipitating the excess of silver as silver iodide and determining the silver iodide either gravimetrically upon a Gooch-Munroe-Neubauer crucible, or nephelometrically by comparison with dilute standard solutions of silver.

Before evaporation, the supernatant solution was carefully filtered through the Neubauer crucible and the precipitate of silver iodide was washed by decantation several times with pure water to remove any adsorbed silver nitrate. That washing was able to remove any adsorbed silver nitrate was shown by treating a very carefully washed precipitate of silver iodide resulting from one of the analyses with a solution of silver containing a few tenths of a milligram of silver in 6 liters. After thorough agitation with the precipitate the solution was filtered and evaporated as in the analyses, after washing of the precipitate. Practically all this silver was found in the evaporated solution. Although the silver determined in this way includes the silver iodide *dissolved* in the mother-liquor, the error introduced is very small, the solubility of silver iodide being probably at least as low as 0.0000035 gm. per liter.[1] The platinum boat was not appreciably changed in weight.

DETERMINATION OF MOISTURE IN IODINE PENTOXIDE.

The determination of the water content of the iodine pentoxide when dried under the conditions used in the analyses for iodine, was fully as difficult as the iodine determination, and it was in preliminary attempts to determine the water content that evidence was obtained which led to the adoption of the above precautions for reducing the water content to a constant low value. The method of operation consisted in brief in completely decomposing the pentoxide into iodine and oxygen by heating in a current of dry air, and, after removing the iodine as far as possible by condensation and finally by a layer of hot silver, collecting the water in a weighed phosphorus pentoxide tube. Great pains were taken that the iodine pentoxide should be prepared for the water determinations exactly as for iodine determinations. In order to avoid absorption of water between the heating and the decomposition, the decomposition of the pentoxide took place immediately upon the completion of the heating without interruption of the experiment, the weighing of the pentoxide, which need not be very accurate on account of the low per cent of water, having taken place before the long heating at 240°.

The iodic acid used in the water determinations was not made from either purified iodine or purified nitric acid, and most of it was prepared in glass vessels. However, it was very carefully purified by repeated crystallization from aqueous solution in platinum vessels with centrifugal drainage of the crystals in each case, and gave every outward evidence of great purity. Not only were the final crystals pure white, but the final mother-liquor was colorless. The crystals gave a perfectly clear solution in water and left no appreciable residue when decomposed in the platinum boat.

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[1] Kohlrausch, *Zeit. physik. Chem.*, **50**, 355 (1904).

The platinum boat, containing about 25 gm. of acid which had been inoculated with the second phase, was freed from water by heating at 100°, and then at 220° + in the usual way. It was then bottled and weighed. Next the boat was transferred to a long hard-glass tube very carefully ground into the socket of the bottling apparatus and was heated to 240° for 4 hours in a current of dry air. Toward the end of the heating all of the apparatus beyond the phosphorus pentoxide drying tube was gently heated with a Bunsen flame in order to dislodge any adsorbed water from the inside surface of the glass. Although by far the greater part of the iodine formed in the decomposition condensed in the hard-glass tube, a small quantity of iodine vapor was always carried along by the current of gases.[1] For the absorption of this iodine vapor a small hard-glass tube containing small electrolytic crystals of silver which had been dried by heating to about 400° in a vacuum was carefully ground on the end of the first tube. This silver tube was attached during the decomposition of the pentoxide and was heated to very dull redness. The column of metallic silver was several inches in length, and although considerable silver iodide was produced at the end of the column nearest the decomposition tube, the silver at the other end of the column remained perfectly bright through all the determinations, showing the absorption of iodine to have been complete.

The U-tubes for the absorption of water were provided with glass stopcocks and were filled with phosphorus pentoxide which had been freshly sublimed in a current of oxygen. They were weighed by substitution, with the use of a similar tube as counterpoise. Before being weighed, the tubes were wiped with a damp cloth and were allowed to stand near the balance case for at least an hour. The tubes were weighed with one stopcock open. The balance was provided with a few milligrams of radium bromide of radio-activity 10000 to dispel electrical charges. Under these conditions no difficulty was experienced in weighing the tubes within a few hundredths of a milligram, since they quickly came to constancy in the balance case and retained their weights unchanged for days at a time. Two phosphorus pentoxide tubes were used in the first experiments, but since the gain in weight of the second tube was found to be negligible in all cases where it was used, the second tube was omitted in the later experiments. Still another phosphorus pentoxide tube was placed beyond the weighed tubes as a protection against the back diffusion of moisture. Blank experiments were usually run after the collection of the water resulting from the decomposition. Frequently no gain in weight of the tube in these blank experiments could be detected and in no case did the gain in weight amount to more than 0.1 mg.

The decomposition of the iodine pentoxide was effected by removing the aluminum oven and heating the tube to the temperature of decomposition of the

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[1] Baxter, Hickey, and Holmes, "The Vapor Pressure of Iodine," *Jour. Amer. Chem. Soc.*, **29**, 127 (1907).

pentoxide, about 350°, with a Bunsen burner. Decomposition was conducted as evenly as possible so as to avoid an unduly rapid current of oxygen from the apparatus with consequent incomplete absorption of the water. When decomposition was complete the condensed iodine was heated above its melting-point to set free traces of absorbed moisture. Then the decomposition tube was swept out with a current of dry air and the absorption tube was weighed. In four experiments carried out as above the following results were obtained:

No of analysis.	Weight of I_2O_5.	Weight of H_2O.	Per cent of H_2O.
	gm.	*gm.*	
1	25.0	0.00060	0.0024
2	20.7	0.00032	0.0016
3	26.1	0.00067	0.0026
4	24.6	0.00060	0.0024
Average			0.0023

In addition, several experiments were performed in order to determine the effect of varying the conditions of treatment. In analysis 5 the heating at 240° lasted only one hour, and in analysis 6 the iodine pentoxide was heated for four hours at 260°. In analyses 7 to 11 only a very small quantity of the second phase was used to inoculate the pentoxide; in analyses 7 and 8 the substance was powdered to the same degree of fineness as in the first set of experiments; in analysis 9 the material was very finely powdered, and in analyses 10 and 11 the material was rather coarsely powdered.

No. of analysis.	Weight of I_2O_5.	Weight of H_2O.	Per cent of H_2O.
	gm.	*gm.*	
5	25.5	0.00066	0.0026
6	25.3	0.00062	0.0025
7	24.9	0.00113	0.0045
8	26.8	0.00100	0.0037
9	18.9	0.00077	0.0041
10	21.3	0.00133	0.0062
11	25.0	0.00155	0.0062

The differences in composition of the pentoxide actually observed, even with very widely differing methods of treatment, are so small that there can be no doubt that the slight variations in treatment likely to occur in the course of an analysis could not have had an appreciable effect.

SPECIFIC GRAVITY OF IODINE PENTOXIDE.

In order to find out exactly the buoyant effect of air upon the weight of the pentoxide an accurate knowledge of the specific gravity of the substance was necessary. The density was determined by displacement of kerosene of known specific gravity, by pentoxide which had been prepared as previously described by heating in a small platinum boat. The boat was weighed in a small weighing-bottle, and immediately after the weighing the boat was covered with kerosene in the bottle. The bottle was placed in a small vacuum desiccator and the desiccator was kept exhausted with continual jarring until apparently every trace of air had been displaced from the powder. A special pycnometer stopper [1] was next inserted in the bottle and the pycnometer was set while immersed in a water bath at 25° C.

THE SPECIFIC GRAVITY OF IODINE PENTOXIDE.

Specific Gravity of Kerosene = 0.7655.

Weight of I_2O_5 in vacuum.	Weight of displaced kerosene in vacuum.	Specific gravity of I_2O_5. 25°/4°.
gm.	*gm.*	
5.5136	0.8811	4.790
5.2704	0.8393	4.807
Average		4.799[2]

The vacuum correction for one apparent gram of iodine pentoxide calculated from the above value for the density is +0.000106 gm., the weights being assumed to have the density 8.3.[3] A vacuum correction of −0.000031 was applied for every gram of silver.

A nearly new No. 10 Troemner balance was used in all the weighing. It was readily sensitive to 0.2 mg. The weights were carefully standardized to hundredths of a milligram, by the method described by Richards.[4]

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[1] For details of pycnometer and setting see Baxter and Hines, *Amer. Chem. Jour.*, **31**, 220 (1904).

[2] At 0° Ditte obtained the value 4.487. At 9° Kammerer obtained the value 4.799. Filhol found the density to be 4.250. Dammer. *Handb. der anorg. Chem.*, **1**, 560.

[3] See page 40.

[4] *Jour. Amer. Chem. Soc.*, **22**, 144 (1900).

ADSORPTION OF AIR BY IODINE PENTOXIDE.

Since the pentoxide is formed by a process of double efflorescence, it must be extremely porous, with consequently an unusually large surface with relation to its weight. Hence it might be supposed that such a substance could adsorb appreciable amounts of gases, possibly even air. This question was investigated with iodine pentoxide by determining the difference in weight of the substance in a vacuum and in air.

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 of 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 weighings being carried out with the stopcocks open. Both steps were then repeated with essentially the same results.

Into one of the tubes was introduced about 25 gm. of carefully dried pentoxide and both tubes were completely exhausted. When the tube containing the pentoxide was warmed to about 150° no perceptible quantity of gas was evolved. After the difference in weight of the exhausted tubes had been determined, they were again filled with dry air and weighed, and the process of exhausting the tubes and filling them with air was repeated. In all the weighings the tubes were treated as described in the case of the phosphorus pentoxide tubes.

		gm.
I.	Difference in weight of exhausted tubes	0.01405
I.	Difference in weight of tubes filled with air	0.01395
I.	Difference in air content of tubes	0.00010
II.	Difference in weight of exhausted tubes	0.01415
II.	Difference in weight of tubes filled with air	0.01397
II.	Difference in air content of tubes	0.00018
	Average difference in air content of tubes	0.00014
	Weight of tube with iodine pentoxide	58.6353
	Weight of tube	32.7966
	Weight of iodine pentoxide	25.8387
I.	Difference in weight of exhausted tubes, one containing iodine pentoxide	25.85120
I.	Difference in weight of tubes filled with air at 19° C. and 758 mm.	25.84473
	Difference	0.00647
	Average difference in air content of empty tubes	0.00014
	Air displaced by I_2O_5 at 19° and 758 mm.	0.00633
II.	Difference in weight of exhausted tubes, one containing iodine pentoxide	25.85091
II.	Difference in weight of tubes filled with air at 20° C. and 768 mm.	25.84430
	Difference	0.00661
	Average difference in weight of empty tubes	0.00014
	Air displaced by I_2O_5 at 20° and 768 mm.	0.00647
	The same corrected to 19° and 758 mm.	0.00641
	Average weight of air displaced by I_2O_5 at 19° and 758 mm.	0.00637
	Weight of air displaced by I_2O_5 at 19° and 758 mm. calculated from the density 4.799	0.00649

The agreement in the air displaced as determined experimentally and as calculated from the observed density is as close as could be expected, showing that the vacuum correction determined on page 129 is correct. It is to be noted that if air is adsorbed by the powder the observed weight of air displaced would be less than that calculated from the density. This seems to be actually the case to a very slight degree.

THE RATIO OF SILVER TO IODINE PENTOXIDE.

Series I. By G. S. Tilley.

Sample I of Iodic Acid and Sample B of Silver were Used.

No. of analysis.	Corrected weight of I_2O_5 in vacuum.	Weight of Ag in vacuum.	Weight of AgI.	Corrected weight of Ag in vacuum.	Ratio $2Ag:I_2O_5$.
	gm.	*gm.*	*gm.*	*gm.*	
1[1]	6.06570	3.92046	0.00042	3.92027	0.646234
	9.48035	6.12703	0.00200	6.12611	
2	7.73052	4.99599	0.00077	4.99564	0.646223
3	12.63909	8.16804	0.00058	8.16777	0.646231
4	9.49913	6.13884	0.00094	6.13841	0.646208
5	8.34369	5.39206	0.00008	5.39202	0.646239
6	8.83155	5.70748	0.00071	5.70715	0.646223
7	6.77487	4.37836	0.00071	4.37803	0.646216
	Average				0.646225

The atomic weights of iodine and silver calculated from the ratio of silver to pentoxide depend, of course, upon the ratio of the atomic weights of silver and iodine. The latter ratio has recently been subjected to careful revision by one of us,[2] and has been found to have the value 0.849943. Using this ratio the atomic weight of silver calculated from the above data is 107.847.

This value is highly sensitive to changes in the ratio of silver to iodine, a positive error of 0.01 per cent producing a negative error of 0.03 per cent in the atomic weight of silver. Hence, if the above value of the atomic weight of silver is too low, it might be expected that the ratio of silver to iodine is too high. From Baxter's results it seems certain that the ratio of silver to iodine is at any rate no higher than the value used in our calculations.

The result of the experiments which have been described is unexpected. For although several recent investigations have shown that the atomic weight of silver may be possibly as low as 107.87, referred to oxygen 16.000, no evidence has yet been published which indicated a value as low as the foregoing. Accordingly a new series of experiments was undertaken, similar to the early one, with even greater pains to avoid possible sources of error.

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[1] The first two analyses were inadvertently mixed, and hence are combined in the table.

[2] Baxter: *Proc. Amer. Acad.*, **40**, 419 (1904); **41**, 73 (1905); *Jour. Amer. Chem. Soc.*, **26**, 1577; **27**, 876; *Zeit. anorg. Chem.*, **43**, 14; **46**, 36. See previous paper.

PURIFICATION OF IODIC ACID AND SILVER FOR THE SECOND SERIES OF ANALYSES.

Two new specimens of iodic acid were prepared. In order to determine whether crystallization of the iodic acid alone was sufficient purification, Sample II was made from iodine which had been purified by only a single distillation from solution in an iodide, and then by one from water, while the nitric acid was once distilled through a quartz condenser with no special attempt to remove chlorine. A portion of the iodic acid was prepared in the transparent fused quartz flask as already described. The remainder was made in a large opaque quartz dish nearly one liter in capacity. The inside of this dish had been abraded with sand to break the edges of the bubbles, and had been digested for hours with acid solutions to remove soluble impurities. The combined specimens of acid were crystallized at least ten times in dishes of transparent fused quartz, with centrifugal drainage, until free from the organic odor previously mentioned. In the preparation of this sample the solutions were always heated and evaporated upon an electric stove under a large Victor Meyer funnel, instead of in the special evaporating apparatus previously described.

The second specimen of acid was prepared from iodine resulting from the decomposition of the iodine pentoxide in the water determinations. It was first dissolved in pure sulphurous acid and then set free from solution by distillation with recrystallized potassium permanganate, a little less permanganate than was necessary to set free all the iodine being employed. The product was thus distilled once from a dilute solution of an iodide. Finally the iodine was once distilled from pure water. The nitric acid for this preparation was carefully freed from chlorine by double distillation with a quartz condenser as previously described. The iodine was converted into iodic acid by treatment with the nitric acid in the large opaque quartz dish used for the preparation of Sample II. Before the crystallization of the iodic acid was commenced, the powder resulting from the treatment of the iodine with nitric acid was drained and heated on the electric stove until apparently all nitric acid had been expelled. Then it was heated to 300° in a current of pure dry air in small portions in a platinum boat. The resulting iodine pentoxide was dissolved in water and at least ten times recrystallized in quartz dishes from solution in the purest water, with centrifugal drainage in platinum Gooch crucibles. In spite of the drastic treatment to which the iodine had been subjected before conversion into iodic acid, the mother-liquors of the first crystallization were by no means free from the organic odor previously observed, although nitric acid seemed to have been completely removed. This odor disappeared gradually during crystallization as before, and the final product was free from odor. This specimen is designated Sample III.

Two new specimens of silver were employed. A portion of one had already been used in an investigation upon the atomic weight of lead.[1] This sample was precipitated once as silver chloride, once as metal by ammonium formate, and was finally electrolyzed. It is designated Sample C. Sample D was employed in an investigation upon the atomic weight of bromine.[2] It was first purified in part by precipitation as chloride, in part by precipitation with ammonium formate. The combined material was then subjected to two electrolyses. Both specimens were finally fused in a current of pure hydrogen.

METHOD OF ANALYSES.

The acid was converted into pentoxide exactly as in the first series. Then, after weighing, it was dissolved and reduced with a slight excess of hydrazine as before, and precipitated with a slight excess of silver. After filtration and evaporation of the filtrate the excess of silver was determined gravimetrically as silver iodide in a Gooch-Munroe-Neubauer crucible.

Essentially no change was made in the method of analysis in analyses 8 and 9 except that a slight excess of hydrazine was employed. At this point a tube 50 cm. in length filled with glass pearls was substituted for the column of bulbs in the reduction apparatus, since it was feared that traces of the spray produced by the effervescence during reduction might have been carried through the bulbs by the current of nitrogen disengaged. The pearls were moistened with sulphurous acid before reduction was commenced. This change in the apparatus was without effect, the succeeding five analyses giving results identical with previous ones. In analyses 15 to 17 the method of precipitation was reversed by pouring the iodide solution into the silver nitrate solution. This change also was without effect, hence it is reasonably certain that the dilution of the solutions during precipitation was sufficient to prevent occlusion of perceptible amounts of either iodide or silver nitrate. It is worth pointing out that occlusion of iodide would lower the observed atomic weight of silver, while occlusion of silver nitrate would produce the opposite effect. The occlusion of ammonium nitrate by the silver iodide would of course be without influence upon the final result.

In one analysis, which is not recorded in the table, about one quarter of the iodic acid was reduced by means of sulphurous acid, the ratio of silver to iodine pentoxide in this experiment being somewhat higher than in the other cases, owing doubtless to the occlusion of silver sulphate. In another analysis the attempt was made to precipitate the silver iodide from ammoniacal solution by adding the silver nitrate solution to the slightly ammoniacal solution of the

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[1] Baxter and Wilson: *Proc. Amer. Acad.*, **43**, 365 (1907); *Jour. Amer. Chem. Soc.*, **30**, 187; *Zeit. anorg. Chem.*, **57**, 174. (See page 67.)

[2] Baxter: *Proc. Amer. Acad.*, **42**, 201 (1906); *Jour. Amer. Chem. Soc.*, **28**, 1322; *Zeit. anorg. Chem.*, **50**, 389. (See page 55.)

iodide. Köthner and Aeuer[1] and Baxter have shown that silver iodide formed in ammoniacal solution is freer from occluded matter than when formed in acid solution. This experiment was a failure, for silver was reduced to the metallic state owing to the slight excess of hydrazine.

The question of adsorption of silver nitrate by the precipitate was further tested in several instances by evaporating the wash-waters of the silver iodide separately from the filtrate. In every such case only a mere trace of silver could be detected, even when the precipitate was allowed to stand in contact with the wash-waters for several hours.

No experiments were performed to test for complete reduction of the iodic acid to hydriodic acid, since evidence upon this point is already available. Sammet[2] has recently determined the equilibrium constant for the reaction of iodides upon iodates in acid solution to be as follows:

$$\frac{(H^+)^6.(IO_3^-).(I^-)^5}{(I_2)^3} = 2.8\ .\ 10^{-47} \qquad i.\ e.,\ IO_3^- = \frac{(I_2)^3}{(H^+)^6.(I^-)^5}\ .2\ .8\ .\ 10^{-47}$$

Since after reduction by the hydrazine the concentration of the free iodine approximates zero, and since the concentrations of the hydrogen and iodide ions are fairly large, and since the constant itself is extremely small, it is evident that the concentration of residual iodate must have been vanishingly small.

A few analyses which met with known accidents are omitted from the following table:

THE RATIO OF SILVER TO IODINE PENTOXIDE.

Series II. By G. P. Baxter.

No. of analysis.	Sample of I_2O_5.	Sample of Ag.	Corrected weight of I_2O_5 in vacuum.	Weight of Ag in vacuum.	Weight of AgI from filtrate.	Corrected weight of Ag in vacuum.	Ratio $2Ag:I_2O_5$.
			gm.	*gm.*	*gm.*	*gm.*	
8	II	B	12.09036	7.81397	0.00167	7.81320	0.646234
9	II	B + C	6.29744	4.07015	0.00127	4.06957	0.646226
10	II	A	10.89880	7.04362	0.00092[3]	7.04309	0.646226
11	II	D	9.33895	6.03554	0.00106	6.03505	0.646222
12	II	A	10.15370	6.56194	0.00055	6.56169	0.646236
13	III	D	11.00453	7.11201	0.00130	7.11141	0.646226
14	III	A	7.01649	4.53456	0.00055	4.53431	0.646236
15	III	D	9.33573	6.03362	0.00125	6.03304	0.646231
16	III	D	8.72163	5.63666	0.00103	5.63619	0.646231
17	III	D	9.01524	5.82603	0.00025	5.82591	0.646229
		Average					0.646230

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[1] *Loc. cit.*

[2] *Zeit. physik. Chem.*, 53, 640 (1905).

[3] AgBr.

DISCUSSION OF RESULTS.

The average of this series is higher than that of Series I by less than one one-thousandth of a per cent, the atomic weight of silver calculated from the ratio of silver to pentoxide being 107.850. While it is true that impurity in the iodic acid not containing halogens would tend to lower the observed atomic weight of silver, the close agreement of the two series carried out with material of fairly diverse nature practically eliminates impurity in the iodic acid or silver as the cause of the low resulting value for the atomic weight of silver. Sample I of iodic acid was crystallized only three times from aqueous solution, while Samples II and III were both crystallized at least ten times. It is improbable that any impurity could have passed through the additional crystallizations without appreciable diminution in quantity. It has already been shown that mineral impurities were surely absent even before the crystallization of the acid. Nitric acid could hardly have survived the prolonged heating at 240° even if it had not been completely removed by the many crystallizations of the iodic acid.

With regard to impurities containing halogens other than iodine, it may be pointed out that Samples I and III were prepared from iodine and nitric acid which had been very thoroughly freed from chlorine and bromine, while even in the case of Sample II only traces of chlorine could have been present. Aside from these facts it is decidedly improbable that an oxygen acid of either chlorine or bromine could have been formed and then have accompanied the iodic acid during its purification, for during the heating of the acid both before and after crystallization such impurities would have been either volatilized or destroyed. Impurity of chlorine would probably tend to lower the observed atomic weight of silver on account of the relatively high solubility of silver chloride. For the same reason a trace of chlorine in either the hydrazine or the nitric acid employed in the analysis would have had no injurious effect. Impurity of bromine would produce the reverse effect if present in the form of a compound analogous to iodine pentoxide.

The presence of a halogen of higher atomic weight than iodine, forming an insoluble silver salt, if present as pentoxide would lower the observed atomic weight of silver. The existence of such an element is purely hypothetical, however, and what evidence exists is contrary to such an hypothesis. One of us has recently searched for such an element in vain.[1]

Two other possible contingencies must be considered, the presence of either free iodine or oxides of iodine higher than the pentoxide. Free iodine might result from reduction of the pentoxide during the heating. Such reduction or decomposition actually does take place to an extremely slight extent when the

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[1] Baxter: *Proc. Amer. Acad.*, **40**, 422 (1904); *Jour. Amer. Chem. Soc.*, **26**, 1580; *Zeit. anorg. Chem.*, **43**, 17. (See page 93.)

pentoxide is heated to 240°, for traces of free iodine can be detected in air that has been passed over iodine pentoxide at that temperature. That no appreciable quantity of iodine could remain in the pentoxide was shown by the fact that the solutions of the pentoxide were always absolutely colorless even when concentrated. Furthermore it was found by experiment that a mere trace of iodine could be detected by its color in such a solution. About 0.01 per cent of iodine in the pentoxide would be necessary to raise the observed atomic weight of silver by 0.01 unit.

Iodine heptoxide might result from either the presence of periodic acid in the iodic acid or from auto-oxidation of the pentoxide during the heating. Both possibilities are wanting in plausibility, for it is not at all probable in the light of the known instability of the heptoxide that the latter substance could have withstood the high temperature of heating. 0.025 per cent of heptoxide in the iodic acid would be necessary to lower the observed atomic weight of silver by 0.01 unit.

It is intended to pursue farther the study of iodic acid in this laboratory, by the preparation of this substance by other methods than the action of nitric acid on iodine. Furthermore, since a very exact knowledge of the ratio of the atomic weights of silver and iodine is necessary for the computation of the proportion of iodine in the pentoxide, it is intended to investigate farther the combining proportions of silver and iodine, especially by a method as nearly as possible like that employed in this research.

The results of this research may be briefly summed up as follows:

1. The preparation of pure iodic acid is described.
2. The existence of the compound $I_2O_5.HIO_3$ is confirmed.
3. It is shown that, while iodic acid may be almost completely converted to pentoxide by heating at 240°, a small proportion of water remains, which is constant for definite conditions of heating.
4. It is shown that silver iodide occludes silver sulphate and that sulphur dioxide may not be used as a reducing agent if the iodine is to be precipitated by means of silver.
5. Hydrazine salts are found to be suitable reducing agents.
6. The specific gravity of iodine pentoxide at 25° referred to water at 4° is found to be 4.80.
7. It is shown that iodine pentoxide does not adsorb appreciable amounts of air.
8. The ratio of silver to iodine pentoxide is found to be 0.646230.
9. Upon this basis, if oxygen is assumed to be 16.000, and if the ratio of silver to iodine is assumed to be 0.849943, the atomic weight of silver is 107.850 and that of iodine is 126.891.

IX.

A REVISION OF THE ATOMIC WEIGHT OF CHROMIUM.

THE ANALYSIS OF SILVER CHROMATE.

By Gregory Paul Baxter, Edward Mueller, and Murray Arnold Hines.

Proceedings of the American Academy of Arts and Sciences, **44**, 401 (1909).
Journal of the American Chemical Society, **31**, 529 (1909).
Zeitschrift für anorganische Chemie, **62**, 313 (1909).
Chemical News, 100, 180, 189, 199 (1909).

Contributions from the Chemical Laboratory of Harvard College.

A REVISION OF THE ATOMIC WEIGHT OF CHROMIUM.

THE ANALYSIS OF SILVER CHROMATE.

INTRODUCTION.

The following table[1] gives the results of investigations upon the atomic weight of chromium from the time of Berzelius, recalculated with the use of recent atomic weight ratios upon the basis of silver (107.88) and oxygen (16.000).[2]

Date.	Investigator.	Reference.	Ratio determined.	Result.
1818	Berzelius .	Pogg. Ann. **8**, 22	$Pb(NO_3)_2 : PbCrO_4$	55.95
1844	Peligot . .	Ann. Chim. Phys. (3), **12**, 530	$CrCl_2 : 2AgCl$	52.33
			$2CrCl_2 : Cr_2O_3$	51.58
			$4AgCl : Cr_2O_3$	51.61
1846	Berzelius .	Berzelius' Jahresb., **25**, 46	$BaCrO_4\ BaSO_4$	54.5
1846	Berlin . .	J. prakt. Chem., **37**, 509; **38**, 149	$Ag_2CrO_4 : 2AgCl$	52.65
			$2Ag_2CrO_4 : Cr_2O_3$	52.41
			$Cr_2O_3 : 4AgCl$	52.46
			$Ag_2Cr_2O_7 : 2AgCl$	52.11
			$Ag_2Cr_2O_7 : Cr_2O_3$	52.34
1848	Moberg. .	Ibid., **43**, 114	$Cr_2(SO_4)_3 : Cr_2O_3$	53.42
			$(NH_4)_2Cr_2(SO_4)_4\ 24H_2O : Cr_2O_3$	53.46
1850	Lefort . .	Ibid., **51**, 261	$BaCrO_4 : BaSO_4$	53.04
1853	Wildenstein	Ibid., **59**, 27	$BaCl_2 : BaCrO_4$	53.56
1855	Kessler . .	Pogg. Ann., **95**, 208	$K_2Cr_2O_7 : KClO_3$	52.23
1861	Kessler . .	Ibid., **113**, 137	$K_2Cr_2O_7 : KClO_3$	52.32
			$2K_2Cr_2O_7 : 3As_2O_3$	51.92
1861	Siewert . .	Zeit. gesammte Naturwis., **17**, 530	$CrCl_3 : 3AgCl$	52.05
			$Ag_2Cr_2O_7 : 2AgCl$	52.14
			$Cr_2O_3 : 2AgCl$	52.04
			$Cr_2O_3 : Ag_2Cr_2O_7$	52.05
1884	Baubigny .	Compt. Rend., **98**, 146	$Cr_2(SO_4)_2 : Cr_2O_3$	52.13
1889	Rawson .	J. Chem. Soc., **55**, 213	$(NH_4)_2Cr_2O_7 : Cr_2O_3$	52.09
1890	Meineke .	Liebig's Ann., **261**, 339	$(NH_4)_2Cr_2O_7 : Cr_2O_3$	52.11
			$2Ag_2CrO_4 : Cr_2O_3$	52.10
			$Ag_2CrO_4 : 2AgCl$	52.03
			$4AgCl : Cr_2O_3$	52.14
			$2Ag_2CrO_4\ 4NH_3 : Cr_2O_3$	52.27
			$Ag_2CrO_4\ 4NH_3 : 2AgCl$	51.62
			$4AgCl : Cr_2O_3$	52.14
			$Ag_2CrO_4 : 3I$	52.41
			$Ag_2CrO_4\ 4NH_3 : 3I$	52.05
			$K_2Cr_2O_7 : KHIO_3$	52.14
			$(NH_4)_2Cr_2O_7 : KHIO_3$	52.13

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[1] Clarke, "A Recalculation of the Atomic Weights," *Smith. Misc. Coll.*, 1910.

[2] The following atomic weights are used in the calculation of the older values: Ag = 107.88; Cl = 35.46; Pb = 207.09; N = 14.01; Ba = 137.37; S = 32.07; H = 1.008; K = 39.10; As = 74.96; I = 126.92. The values of Rawson and Meineke are reduced to the vacuum standard; the others are not so corrected.

It has been repeatedly shown, especially in this laboratory, that most of the earlier work upon atomic weights has been vitiated by neglect of certain fundamental precautions. The incomplete drying of solids has been responsible for many of the discrepancies and errors which exist. Neglect of the solubility of precipitates, together with the use of too concentrated solutions during precipitation, so that perceptible inclusion and occlusion took place, undoubtedly have influenced many gravimetric processes. Volumetric processes have been affected by inaccurately prepared standard solutions, as well as the difficulty inherent in measuring exactly large volumes of solution.

In discussing in detail the applications of the above causes of constant error to the individual investigations, at the best it is possible merely to indicate the nature of the difficulties; as a rule it is impossible to estimate the magnitude of the error without repetition of the experimental work. Hence in this paper attention is called only to points in the earlier work which have been experimentally investigated. The uncertainty in most of the previous determinations is emphasized by the lack of agreement in the individual analyses in each series, as well as in the different series.

The choice of method for this investigation was influenced by several considerations. In the first place, the substance to be analyzed must be definite in composition and capable of being either fused or heated to a high temperature in order to insure the elimination of moisture. In the second place, in view of the fact that chromium is hard to handle satisfactorily in a quantitative fashion, the analytical operation should involve the determination of some other element. The halogen compounds, which have been employed very successfully many times, especially in this laboratory, for the determination of the atomic weights of metallic elements, are less suited for use in the case of chromium on account of the difficulty in the complete precipitation of the halogens by means of silver nitrate.

All things considered, the chromates of silver seemed to offer the most promising possibilities on account of the ease with which their silver content may be determined. It is true, in order to determine the ratio of the atomic weight of chromium to that of either silver or oxygen, this method necessitates a knowledge of the exact ratio of the atomic weights of silver and oxygen, knowledge which is still slightly uncertain. The per cent of silver in the compound being known, however, analytical data may be used at any subsequent time for the calculation of the atomic weight of chromium. Furthermore, since the value for the atomic weight of chromium at present accepted depends very largely upon the analysis of silver chromate, a study of this salt with the application of the most modern methods seemed to promise interesting results, and therefore was first taken up. In a following paper is given a description of the analysis of silver dichromate.

PURIFICATION OF MATERIALS.

The laboratory distilled water was twice redistilled, once from alkaline permanganate and once from very dilute sulphuric acid. In both distillations block tin condensers were employed, no cork or rubber connections being necessary.

The preparation of pure neutral silver nitrate for the precipitation of silver chromate followed the lines laid down in previous researches in this laboratory. A large quantity of heterogeneous silver residues was reduced to metallic silver by means of sticks of pure zinc in slightly acid solution. After the silver had been washed with water until free from halogens, it was dissolved in nitric acid, and the solution was filtered. Silver chloride was precipitated from the diluted nitrate by means of hydrochloric acid, and the precipitate of silver chloride was thoroughly washed. From this silver chloride, metallic silver was again obtained by reduction with cane sugar in strongly alkaline solution. After being washed until free from chloride, the metal was again dissolved in nitric acid in a Jena glass flask. By reduction with ammonic formate (prepared from redistilled formic acid and redistilled ammonia), the silver was once more obtained in the metallic state. The crystals were then dissolved in the purest nitric acid, and the nitrate, after concentration of the solution, was four times recrystallized from the purest water in platinum until free from acid. In this crystallization, and in all others, centrifugal drainage in a machine employing platinum funnels as baskets[1] was always used, in order to free the crystals entirely from any adhering mother-liquor, the mother-liquors all being rejected.

Hydrochloric acid was prepared by distilling the commercial chemically pure acid, after dilution with an equal volume of water.

The methods for obtaining pure bromine have been recently tested by one of us,[2] and the processes found suitable for the purpose were employed here. A considerable quantity of hydrobromic acid was prepared by passing a current of pure hydrogen sulphide through a layer of bromine covered with water. The hydrogen sulphide was generated by the action of dilute sulphuric acid on ferrous sulphide, and was thoroughly scrubbed in gas-washing bottles and towers containing water. After the precipitated mixture of sulphur bromide and sulphur had been removed by decantation and filtration, the acid was boiled, with the occasional addition of small portions of recrystallized potassium permanganate. This was done to eliminate any iodine which might have been present.

The hydrobromic acid was then heated with the calculated quantity of recrystallized potassium permanganate, the bromine being condensed in a Jena flask cooled with running water. In this way three-eighths of the bromine remained behind as potassium and manganous bromides, the remaining five-

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[1] Richards: *Jour. Amer. Chem. Soc.*, 27, 110 (1905).

[2] Baxter: *Proc. Amer. Acad.*, 42, 204 (1906); *Jour. Amer. Chem. Soc.*, 28, 1327; *Zeit. anorg. Chem.*, 50, 394. (See page 54.)

eighths being distilled from the solution of these bromides. The greater part of the chlorine was undoubtedly eliminated by this operation, since the original bromine was fairly pure. In order to be on the safe side, however, the bromine was again reduced to hydrobromic acid, and this in turn was changed to bromine as above. From the product the final hydrobromic acid was prepared with hydrogen sulphide. After filtration and distillation, it was preserved in Jena glass.

Chromic acid was prepared from Merck's "Highest Purity Chromic Acid." The material was dissolved in pure water, and the solution was filtered through a Gooch-Munroe-Neubauer crucible with a mat of platinum sponge, a quantity of sandy material being thus separated. The solution was then evaporated to saturation and three times systematically recrystallized in platinum dishes with centrifugal draining, each mother-liquor being used for the crystallization of three crops of crystals on account of the small temperature coefficient of solubility of chromic acid. The mother-liquors from the first crystallization, on testing in the nephelometer, indicated only traces of sulphates and halogens.

Some of the purest commercial potassium chromate, after solution in water, was filtered through a Gooch-Munroe-Neubauer crucible. It was then four times crystallized in platinum, each crop of crystals being centrifugally drained.

PREPARATION OF SILVER CHROMATE.

The point in the investigation requiring the most attention was the preparation of normal silver chromate free from both basic and acid salts. Since the salt can not be crystallized, owing to its slight solubility in water, it is necessary so to regulate the conditions during precipitation that neither acid nor basic salts can separate as distinct solid phases. Even then the *occlusion* of traces of either basic or acid salts is still possible, and it is necessary to form the salt under a fairly wide range of conditions in order to show constancy of composition.

Fortunately data are available which indicate the conditions under which silver dichromate or hydrochromate can exist. Sherrill [1] has recently shown that silver chromate changes into silver dichromate rapidly under a saturated solution in nitric acid more concentrated than 0.075 normal, while silver dichromate changes into silver chromate under a saturated solution in nitric acid less concentrated than 0.06 normal. Some time before, Krüss [2] had shown that silver dichromate is converted into silver chromate by contact with water.

In the light of these facts it is obvious that the solutions of the soluble chromates can safely be employed for the precipitation of silver chromate without the least danger of the precipitation of silver dichromate, and even that the presence of a slight amount of free acid could do no harm.

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[1] *Jour. Amer. Chem. Soc.*, 29, 1673 (1907).

[2] *Ber. d. d. Chem. Gesell.*, 22, 2050 (1889).

Owing to the weak nature of the second hydrogen of chromic acid, the first hydrogen dissociating to the same extent as that of hydrochloric acid,[1] but the second hydrogen having the constant 6.0×10^{-7} at 18°,[2] appreciable hydrolysis of solutions of its salts takes place, to a greater extent the weaker the base with which the chromic acid is combined. Sherrill has found, for instance, that ammonium chromate in 0.05 molal solution is 2.7 per cent hydrolyzed. The basicity of the solutions, on the other hand, will be greater the stronger the base. In order to determine whether this hydrolysis is sufficient to produce precipitation or occlusion of basic chromates, precipitates of silver chromate were formed by means of solutions of both ammonium and potassium chromates. The comparison of precipitates formed in this way will show whether the presence of basic salts is to be feared.

Sample I. — Ammonic chromate was prepared by adding to a solution of the pure chromic acid a slight deficiency of the purest freshly distilled ammonia. The solution was diluted until about tenth normal, and was slowly poured with constant shaking into a solution of an equivalent quantity of silver nitrate of about the same concentration. The dark red precipitate of silver chromate was washed six times by decantation with large portions of water, centrifugally drained to remove as much water as possible and dried at gradually increasing temperatures in an electric oven, finally at 160° for a long time. The dried lumps were then gently ground to a fine powder in an agate mortar in order to facilitate further drying as well as to insure homogeneity. During the addition of the chromate to the silver solution, since the chromate solution was slightly deficient in ammonia, acid accumulated in the silver nitrate solution. Hence each succeeding portion of precipitate was formed under conditions of greater acidity, although the concentration of acid in the solution could never have approached that found by Sherrill to be necessary for the existence of the silver dichromate.

Sample II. — This preparation was practically identical with Sample I, since part of the precipitate obtained as above was washed by decantation with water eight times more, each wash-water being allowed to stand in contact with the precipitate for many hours, and the precipitate being shaken with the wash-water very thoroughly at intervals, in order to leach out any accidentally inclosed or adsorbed soluble salts. The prolonged extra washing evidently was unnecessary, since the results are practically the same as those obtained with Sample I.

Sample III. — This sample was prepared from the four times recrystallized potassium chromate. A quantity of this material in about tenth normal solution was precipitated with an equivalent amount of silver nitrate, equally dilute. The precipitation took place in Jena glass, the silver solution being slowly poured into the chromate, in order to accentuate the effect of the hydrolysis if possible. It will be recalled that in the case of Samples I and II pre-

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[1] Walden: *Zeit. physikal. Chem.*, **2**, 49 (1888).

[2] Sherrill, *Loc. cit.*

pared with the ammonium salt, the chromate was added to the silver solution. The precipitate was then transferred to platinum and washed seven times with the purest water, the chromate being thoroughly agitated with each washing. After the removal of the greater part of the adhering water by centrifugal settling, this sample was dried in a preliminary fashion at 150° and was pulverized in an agate mortar, as in the case of Sample I and II. The salt was soft and crystalline, and greenish black in color.

Sample IV. — A fourth sample also was prepared from recrystallized potassium chromate, which in turn was made from recrystallized chromic acid. In the first place, potassium hydroxide was prepared by the electrolysis of three times recrystallized potassium oxalate, with the use of a mercury cathode and decomposition of the amalgam with pure water in a platinum dish, as in the preparation of potassium hydroxide in an investigation upon the atomic weight of potassium.[1] The solution of the pure hydroxide was added to a solution of three times recrystallized chromic acid, contained in a platinum dish, until the normal chromate had been formed as indicated by the yellow color. From this solution, by three systematic crystallizations, potassium chromate was separated.

The silver chromate was prepared from this material and the purest silver nitrate by slowly adding a six-hundredths normal solution of the chromate to a silver nitrate solution of equivalent concentration, this procedure being the reverse of that used in the preparation of Sample III. By this method of precipitation the solution is maintained as nearly neutral as it is possible to keep it. The dark brownish-red precipitate was allowed to settle in the flask in which precipitation took place. Then, the supernatant solution having been decanted, the silver chromate was transferred to a platinum dish and washed very thoroughly with water. After being freed from water by centrifugal settling, the silver chromate was dried at about 160° in an electric oven, and powdered in an agate mortar.

Since in the case of Sample III the silver nitrate was added to the chromate, while in preparing Sample IV precipitation took place in the reverse fashion, a comparison of the two samples would not only throw light upon the effect of hydrolysis, but also show whether the occlusion of potassium chromate or silver nitrate was to be feared.

DRYING OF SILVER CHROMATE.

The fact that salts dried by prolonged heating at 100°, or at even higher temperatures, usually contain appreciable amounts of moisture, owing to included mother-liquor, is a point which has been overlooked by most earlier investigators,[2] and the oversight throws doubt on much otherwise very careful work. In exact work the residual water must either be corrected for or entirely

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[1] Richards and Mueller: *Pub. Car. Inst.*, 69, 33 (1907); *Jour. Amer. Chem. Soc.*, 29, 645; *Zeit. anorg. Chem.*, 53, 431.

[2] Richards: *Proc. Amer. Phil. Soc.*, 42, 28 (1903).

avoided. The simplest fashion of drying a substance perfectly is to fuse it in a current of dry gas. In the case of the silver chromate, however, this is not practicable, for even at 300° incipient decomposition sets in. Upon attempting to dissolve in nitric acid samples dried in air at that temperature, a slight insoluble residue was always obtained, while heating in a current of oxygen gave no better results. Since the moisture can not be entirely expelled from silver chromate by heating at a moderate temperature, it must be determined by the analysis of separate portions of the substance which have been treated in some definite fashion.

Experiments showed that at temperatures below 225° the salt was not appreciably changed, hence this temperature was chosen as a suitable one at which to heat the salt preparatory to analysis. The silver chromate was therefore always heated in a current of pure dry air for 2 hours at 225°, in order to obtain the separate portions in as nearly as possible the same condition.

The drying apparatus was constructed entirely of glass, rubber connections being especially avoided. A current of air was passed first over red-hot copper oxide to destroy organic matter, then through successive Emmerling washing towers. In the first were beads drenched with silver nitrate solution, in the second with a strong solution of potassic hydroxide containing much potassic manganate, and in the last three with concentrated sulphuric acid. The already very dry air was then passed through a long tube containing resublimed phosphoric anhydride spread over a large surface of glass beads and ignited asbestos. From the drying apparatus the air passed into the tube in which the boat containing the silver chromate was placed.

DETERMINATION OF SILVER IN SILVER CHROMATE.

During the drying of the silver chromate it was contained in a platinum boat which had been weighed, in a weighing-bottle, by substitution for a similar bottle which with its contents displaced the same amount of air as the bottle with the boat. The boat was placed in a hard-glass tube connected by a carefully ground joint with the bottling apparatus.[1] The tube was heated by means of the solid aluminum oven described on page 78. After 2 hours' heating at 225° the boat was transferred to the weighing-bottle and was allowed to stand in a desiccator near the balance for several hours before being weighed.

Next, the weighed quantity of silver chromate was transferred to a 3-liter glass stoppered Jena flask with a carefully ground stopper, and, after the boat and bottle had been cleaned with hot dilute nitric acid and water, the rinsings were poured into the flask and the silver chromate dissolved by the application of gentle heat. If the salt had not been heated above 225°, the solution was absolutely clear. Specimens heated above this temperature always showed more or less turbidity.

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[1] See page 8.

The chromate was next reduced to the chromic state by the addition of a very slight excess of sulphur dioxide which had been freshly distilled into pure water. The slight excess of sulphurous acid was soon oxidized under the combined influence of heat and nitric acid. In analyses 1, 2, 3, 12, 13, and 14 the reduction was effected by means of recrystallized hydrazine sulphate, in order to avoid to a large extent the presence of sulphuric acid, for Richards and Jones[1] found that silver chloride occludes silver sulphate very tenaciously. The two methods of reduction, however, gave essentially identical results.

Since in the reduction of the chromate by hydrazine, nitrogen gas is evolved, the flask in which the reduction took place was protected from loss by spattering by means of a long column of bulbs fitting loosely into the neck of the flask. The solution of hydrazine sulphate was added through a funnel with a long fine stem which extended through the column of bulbs nearly to the bottom of the flask. After the addition of the hydrazine, the reaction was allowed to continue slowly, with occasional shaking, and was completed by heating the solution upon a steam bath for a short time. In the presence of acid a dilute solution of hydrazine is without effect upon silver salts.

After the solution had been allowed to cool, it was diluted to a volume of 1.5 liters, and the silver was precipitated as chloride or bromide by the addition of a very dilute solution of an excess of either hydrochloric or hydrobromic acid. The flask with its contents was shaken thoroughly for a few moments and was then allowed to stand several days, until, the silver bromide having settled, the supernatant solution was perfectly clear.

Since the mother-liquor of the silver halide contained both nitric and hydrobromic acids in excess, the use of a Gooch-Munroe-Neubauer crucible seemed to be attended with danger on account of solution of platinum. Such a possibility has already been pointed out,[2] and an actual loss was found to take place in blank experiments carried out at the beginning of this research. Accordingly the ordinary platinum Gooch crucible with an asbestos mat was used. The asbestos had been carefully cleansed by ignition, and washing first with nitric acid and then with water. The crucible was prepared for weighing before and after filtration of the silver halide in exactly the same way.

The silver halides were washed many times by decantation with dilute hydrochloric acid in the case of silver chloride, and with very dilute hydrobromic acid in the case of silver bromide. The precipitate was then transferred to the weighed crucible and was dried in an electric oven at 170° for at least 16 hours.

In order to correct for the small quantity of moisture retained by the silver halides, each precipitate was transferred as completely as possible to a porcelain crucible and fused. From the loss of weight of the portion of silver salt transferred to the crucible, the amount of water in the entire precipitate was calculated.

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[1] *Pub. Car. Inst.*, 69, 73 (1907); *Jour. Amer. Chem. Soc.*, 29, 831; *Zeit. anorg. Chem.*, 55, 84.

[2] Morse, "Exercises in Quantitative Chemistry," p. 203 (1905).

The small quantity of asbestos, together with a trace of silver bromide which escaped the crucible, was collected by passing the entire filtrate and washings through a small filter. The ash of this filter was treated with nitric and with hydrochloric or hydrobromic acid, then it was reheated and the crucible was weighed. After correction for the ash of the filter, the gain in weight of the crucible was added to the weight of the main mass of silver halide.

Another correction was necessary. The filtrate contained dissolved silver salt, even though an excess of halogen acid was used in the precipitation. The larger part of the dissolved halide is due to the marked solubility in solutions of chromic salts, the amount dissolved increasing with increasing concentration of the chromic salts. Berlin overlooked this correction which was afterwards pointed out by Siewert. Meineke later determined experimentally the quantity of dissolved material, and also proposed the method of separation which was adopted in this work. The entire filtrate of 3 to 4 liters was evaporated to small bulk, nearly neutralized with ammonia, and then the silver was precipitated from a hot solution as sulphide. The precipitate was collected upon a filter paper, which was ignited. The residue was converted to the nitrate by digestion with dilute nitric acid, and the solution was then filtered into a graduated flask, in which it was diluted to known volume. By comparison in the nephelometer of this solution with standard solutions of silver the quantity of silver in solution was determined.

That all dissolved silver was recovered in this way was shown by adding an excess of ammonia to the filtrate of the silver sulphide in one analysis, the hydrogen sulphide having been expelled, and after removal of the chromic hydroxide by filtration, testing the acidified filtrate for silver. None could be detected.

DETERMINATION OF MOISTURE IN DRIED SILVER CHROMATE.

The proportion of moisture in the silver chromate was found by fusing weighed quantities of the salt in a current of pure dry air and collecting the water vapor produced in a weighed phosphorus pentoxide tube. During the fusion of the salt oxgyen is evolved, but since the fusing point is low, there is on danger of volatilization of either silver or chromium compounds.

In order to avoid the necessity of removing the fused silver chromate from a platinum boat, boats of copper foil which had been cleaned and ignited were employed.

It was desirable to determine not only whether the proportion of water could be made constant at any one temperature, but also how much the proportion of water is affected by variations in temperature. Experiments were therefore carried out with silver chromate which had been dried for 2 hours at 200°, 225°, and 300°, in dry air which had been purified as previously described.

After the salt had been dried, a carefully weighed U-tube containing resublimed phosphorus pentoxide was attached to the end of the tube, This U-tube was provided with ground glass stopcocks lubricated with Ramsay desiccator grease. The silver chromate was gradually heated until fusion took place, and a slow current of air was allowed to pass through the system for one half hour in order to make certain that all moisture was carried into the absorption tube. Finally the phosphorus pentoxide tube was reweighed.

Temperature of heating.	Weight of silver chromate.	Weight of water.	Per cent of water.
	gm.	*gm.*	
200°	4.87	0.00097	0.0199
200°	4.74	0.00098	0.0207
200°	4.43	0.00093	0.0210
	Average		0.0205
225°	9.01	0.00136	0.0151
225°	10.85	0.00188	0.0173
225°	10.11	0.00125	0.0124
225°	7.95	0.00105	0.0132
225°	8.23	0.00114	0.0139
	Average		0.0144
300°	3.50	0.00034	0.0097

The pentoxide tube was weighed by substitution with the use of a counterpoise of the same size and weight. Before being weighed both tubes were carefully wiped with a damp cloth and were allowed to stand near the balance case for 30 minutes. Care was taken to equalize the pressure inside and outside the tubes by opening one stopcock immediately before hanging on the balance.

In order to test the efficiency of the drying apparatus, blank experiments were carried out by allowing a slow current of air to pass through the apparatus into the weighed pentoxide tube. The variations in the weight of the tube were never much larger than the probable error in weighing the tube.

As is to be expected, the water content gradually decreases with increasing temperature of heating. The extreme variation with specimens of silver chromate which have been heated at 225° amounts to only 0.005 per cent. Evidently the percentage of residual water is as constant as can be reasonably expected, and the mean can safely be assumed to represent with sufficient exactness the average proportion of water in the salt. Hence from every apparent gram of silver chromate 0.000144 gm. is subtracted.

SPECIFIC GRAVITY OF SILVER CHROMATE.

In order to correct the weight of silver chromate to a vacuum standard, a knowledge of its specific gravity is necessary. This has already been determined by Playfair and Joule[1] and Schroeder,[2] who obtained the values 5.77 and 5.53 respectively. On account of the marked difference between these values, new determinations of the density were made by the displacement of toluol with weighed amounts of salt. The toluol was first dried by stick soda and was then distilled. Its specific gravity at 25° referred to water at 4° was found to be 0.86156. Great pains were taken to remove air from the chromate when covered with toluol by placing the pycnometer in an exhausted desiccator before setting.

THE SPECIFIC GRAVITY OF SILVER CHROMATE.

Weight of silver chromate in vacuum.	Weight of toluol displaced in vacuum.	Density of silver chromate. 25°/4°.
gm.	*gm.*	
5.1584	0.7898	5.628
3.6012	0.5520	5.621
Average		5.625

The following vacuum corrections were applied:

	Specific gravity.	Vacuum correction.
Weights	8.3	
Toluol	0.862	+0.00126
Silver chromate	5.625	+0.000069
Silver chloride	5.56	+0.000071
Silver bromide	6.473	+0.000041

BALANCE AND WEIGHTS.

All weighings were made by substitution upon a nearly new short-armed Troemner balance, easily sensitive to 0.02 mg. with a load of 50 gm.

The gold-plated Sartorius weights were carefully standardized by the method described by Richards,[3] and were used for no other work.

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[1] *Mem. Chem. Soc.*, **2**, 401 (1845).

[2] *Lieb. Ann.*, **173**, 72 (1874).

[3] *Jour Amer Chem. Soc.*, **22**, 144 (1900)

Series I. $2AgCl : Ag_2CrO_4$.

$$\frac{Ag}{AgCl} = 0.752632^{1}$$

No. of analysis.	Sample of Ag_2CrO_4.	Corrected weight of Ag_2CrO_4 in vacuum.	Weight of AgCl in vacuum.	Loss on fusion.	Weight of asbestos	Dissolved AgCl from filtrate.	Corrected weight of AgCl in vacuum.	Ratio $2AgCl : Ag_2CrO_4$.
		gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	
1	II	10.30985	8.90835	0.00063	0.00117	0.00019	8.90908	0.864132
2	II	8.26920	7.14327	0.00063	0.00211	0.00017	7.14492	0.864040
3	IV	6.56679	5.67324	0.00039	0.00136	0.00023	5.67444	0.864111

Average 0.864094

Per cent of Ag in Ag_2CrO_4 . . . . 65.0345

Series II. $2 AgBr : Ag_2CrO_4$.

$$\frac{Ag}{AgBr} = 0.574453^{2}$$

No. of analysis.	Sample of Ag_2CrO_4.	Corrected weight of Ag_2CrO_4 in vacuum.	Weight of AgBr in vacuum.	Loss on fusion.	Weight of asbestos.	Weight of AgBr from filtrate.	Corrected weight of AgBr in vacuum.	Ratio $2AgBr : Ag_2CrO_4$.
		gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	
4	I	2.63788	2.98579	0.00028	0.00056	0.00014	2.98621	1.13205
5	II	2.82753	3.20018	0.00008	0.00060	0.00014	3.20084	1.13203
6	III	2.33454	2.64054	0.00032	0.00220	0.00026	2.64268	1.13199
7	I	1.77910	2.01304	0.00050	0.00144	0.00004	2.01402	1.13204
8	I	2.33198	2.63988	0.00030	0.00034	0.00002	2.63994	1.13206
9	II	3.10402	3.51311	0.00033	0.00094	0.00018	3.51390	1.13205
10	III	2.92751	3.31411	0.00027	0.00033	0.00010	3.31427	1.13211
11	III	4.21999	4.77677	0.00055	0.00126	0.00014	4.77762	1.13214
12	II	5.24815	5.93939	0.00025	0.00170	0.00020	5.94104	1.13203
13	IV	6.24014	7.06401	0.00039	0.00104	0.00018	7.06484	1.13216
14	IV	7.92313	8.96913	0.00083	0.00129	0.00022	8.96982	1.13211

Average 1.13207

Per cent of Ag in Ag_2CrO_4 . . . . 65.0321

Average per cent of Ag in Ag_2CrO_4 . . . . . 65.0333

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[1] Richards and Wells: *loc cit.*

[2] Baxter: *loc cit.*

DISCUSSION OF RESULTS.

In comparing the analytical results, it is to be noted first that the compositions of the different samples agree within less than 0.01 per cent, as the following averages show.

	$2AgBr:Ag_2CrO_4$		$2AgCl:Ag_2CrO_4$
Sample I	1.13205	Sample II	0.86409
Sample II	1.13204	Sample IV	0.86411
Sample III	1.13208		
Sample IV	1.13214		

If anything, Samples I and II show a somewhat lower percentage of silver than Samples III and IV. These samples were made from ammonium chromate which contained a slight excess of chromic acid. This excess of acid accumulated in the solution during the precipitation of the silver chromate, so that the precipitate formed under distinctly acid conditions, although the acidity was not sufficient to present any danger of the formation of dichromate. Samples III and IV, on the other hand, since they were made from potassium chromate, which is markedly hydrolyzed, were formed under distinctly basic conditions, and the precipitation or occlusion of basic salts is to be feared. Such occluded basic salts would tend to raise the percentage of silver in the chromate. However, Sample IV yielded slightly higher results than Sample III, while on account of the method of precipitation the reverse is to be expected; for Sample III was precipitated by adding the silver nitrate to the chromate, while Sample IV was precipitated by adding the chromate to the silver solution, the mother-liquor remaining neutral in both cases. Too much emphasis should not be laid upon the slight apparent difference in the composition of the different samples of salt, since the variations in the experiments with the same sample are as large as the differences between the samples. Hence the average result from the different samples is employed in the final calculations, all the analyses being given equal weight in each series.

In addition to the specimens of silver chromate, the preparation and analysis of which have been described, two other interesting samples were prepared. One was formed by adding a 0.04 normal silver nitrate solution to a solution of chromic acid of similar concentration. On account of the solubility of silver chromate in nitric acid solutions, precipitation was only partial. The precipitate was washed and dried, and upon analysis was found to contain so little silver that the presence of a small proportion of dichromate was certain, a result which is hardly to be expected in the light of Sherrill's experiments.

The second sample was prepared by heating ammoniacal solutions of silver chromate in platinum vessels, the chromate being gradually precipitated as the ammonia was expelled. This material yielded somewhat irregular results, which on the whole indicated too high percentages of silver, and hence the presence of basic salts, a result which could have been predicted from a consideration of the conditions of preparation.

It is to be noted that Series I and Series II yield percentages of silver differing by less than 0.004 per cent, a highly satisfactory agreement, which indicates purity of the halogen acids employed as well as experimental accuracy.

If the percentage of silver in silver chromate is 65.0333, the molecular weight of silver chromate may be calculated from the atomic weight of silver, and from the latter value the atomic weight of chromium by difference. These calculations are carried out with two possible assumed values for the atomic weight of silver, oxygen being assumed to have the value 16.000. It is to be noted that the percentage error in the determination of the molecular weight of silver chromate is multiplied six times in the atomic weight of chromium.

If Ag = 107.880 Ag_2CrO_4 = 331.768 and Cr = 52.008
If Ag = 107.870 Ag_2CrO_4 = 331.737 and Cr = 51.997

Although slightly lower than the previous investigations, these results agree with them as closely as is to be expected, most of the probable errors in earlier work tending to make the results too high.

The more important results of this research may be briefly summed up as follows:

1. Pure silver chromate was prepared.
2. It is shown that silver chromate can not be completely dried without decomposition.
3. The proportion of residual water was determined in salt dried at definite temperatures.
4. The specific gravity of unfused silver chromate is found to be 5.625 at 25° C. referred to water at 4° C.
5. The per cent of silver in silver chromate is found to be 65.0333 by two closely agreeing methods.
6. With two assumed values for the atomic weight of silver referred to oxygen, the atomic weight of chromium is found to have the following values:

If Ag = 107.88 Cr = 52.01
If Ag = 107.87 Cr = 52.00

In the following paper the analysis of silver dichromate is described.

X.

A REVISION OF THE ATOMIC WEIGHT OF CHROMIUM.

THE ANALYSIS OF SILVER DICHROMATE.

By Gregory Paul Baxter and Richard Henry Jesse, Jr.

Proceedings of the American Academy of Arts and Sciences, 44, 421 (1909).
Journal of the American Chemical Society, 31, 541 (1909).
Zeitschrift für anorganische Chemie, 62, 331 (1909).
Chemical News, 100, 213, 228 (1909).

Contributions from the Chemical Laboratory of Harvard College.

A REVISION OF THE ATOMIC WEIGHT OF CHROMIUM.

THE ANALYSIS OF SILVER DICHROMATE.

INTRODUCTION.

In the preceding paper is described a successful attempt to prepare pure silver chromate and to determine its silver content, with the object of throwing light upon the atomic weight of chromium, the value found in this way, 52.01 (Ag = 107.88), being about 0.1 unit lower than the one in common use. The preparation and analysis of silver dichromate were next investigated. Since the proportion of chromium in the dichromate is 50 per cent larger than in the chromate, the effect of experimental uncertainty upon the final result is correspondingly reduced.

Silver dichromate possesses another great advantage over silver chromate for exact work in that it may be readily crystallized from nitric acid solutions, and thus may be freed from impurities included or occluded during precipitation, with the exception of nitric acid and moisture. For, the silver and chromium being present in equivalent proportions during the crystallization, the inclusion of mother-liquor could do no harm. If the concentration of the nitric acid is sufficiently high, there is no possibility of the separation of silver chromate as such during this crystallization, since Sherrill[1] has shown that silver chromate changes rapidly into silver dichromate under nitric acid solutions more concentrated than 0.075 normal. This is primarily due to the low value of the dissociation constant of the second hydrogen of chromic acid, which has been found by Sherrill to be 6×10^{-7}, the solubility product of silver chromate being 9×10^{-12}, and that of silver dichromate being 2×10^{-7}. Sherrill has also investigated the part which the hydrochromate ion plays in the equilibrium relations of chromates and dichromates in solution and has found the following equation to hold:

$$\frac{(Cr_2O_7^{=})}{(HCrO_4)^2} = 75$$

Although obviously the concentration of the hydrochromate ion in dichromate solutions (in a 0.1 molal solution of potassic dichromate fifteen per cent of the salt existing as hydrochromate) is always considerable, the precipitation of the solid phase $AgHCrO_4$ seems not to be possible. Sherrill was not able to find any indication of the presence of this salt in the precipitate formed by adding silver nitrate to chromic acid in nitric acid solution. Furthermore,

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[1] *Jour. Amer. Chem. Soc.*, **29**, 1641 (1907).

since the water content of our material was carefully investigated, the presence of hydrochromate in traces could do no harm; for the latter substance upon sufficient heating would yield dichromate and water according to the following equation:

$$2AgHCrO_4 = Ag_2Cr_2O_7 + H_2O.$$

Although the presence of polychromates other than the dichromate seemed improbable, their absence from our material was shown by crystallizing silver dichromate from nitric acid of different concentrations. Since this variation was without effect, it may be reasonably supposed that more highly acid salts than the dichromates were neither precipitated as solid phases nor occluded.

PURIFICATION OF MATERIALS.

Only slight changes were made in the methods of purifying the materials used in the various preparations of silver dichromate and in the analyses from those described in the preceding paper.

Nitric acid was freed from chlorine by several distillations through a platinum condenser.

Hydrochloric acid also, after dilution, was purified by distillation with a quartz condenser.

Hydrobromic acid was prepared from bromine which had been twice distilled from solution in potassium bromide, the bromide in the second distillation being essentially free from chlorine. The hydrobromic acid was synthesized by passing carefully cleansed hydrogen (made from the lead-sodium alloy "hydrone" and water) through the bromine at about 40° and then over hot platinized asbestos, the acid being collected in pure water. Iodine was eliminated from the acid by boiling with free bromine several times. Finally the acid was redistilled through a quartz condenser three times with rejection of the extreme fractions. The acid, diluted to normal concentration, was kept in a well protected glass bottle.

Silver nitrate was prepared from silver which had been precipitated once as chloride, and then reduced with invert sugar. The nitric acid solution of the fused product was evaporated to crystallization, and the salt was then three times more crystallized from nitric acid solutions, the crystals being drained centrifugally in a centrifugal machine employing platinum Gooch crucibles as baskets.[1] Heating was carried out over electric stoves in order to avoid contamination by the combustion products of illuminating gas, both in this and in all other preparations in this research.

The best commercial potassium dichromate was crystallized four times, once from aqueous solution in Jena glass, and three times in platinum vessels.

Chromic acid was three times recrystallized in platinum vessels as described in the preceding paper.

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[1] Baxter: *Jour. Amer. Chem. Soc.*, 30, 286 (1908).

PREPARATION OF SILVER DICHROMATE.

Silver dichromate was prepared by combining either potassium dichromate or chromic acid with silver nitrate in nitric acid solution in platinum vessels. Precipitation was carried out in fairly concentrated solution, since in the subsequent crystallization of the silver salt from nitric acid solution any included substance was sure to be eliminated. Although the inclusion of nitric acid during the crystallization was to be feared, and was actually found to have taken place, a method was devised for the determination of this nitric acid, together with the moisture retained by the solid.

Sample I. — Silver nitrate and potassium dichromate were dissolved in equivalent proportions in 3 normal nitric acid, the concentration of each salt being about 0.7 normal. The cold silver nitrate solution was added very slowly, with constant vigorous stirring, to the dichromate solution. After the precipitate had been allowed to settle, the mother-liquor was decanted, and the precipitate was centrifugally drained and rinsed with 3 normal nitric acid in the centrifugal machine.

The salt was then five times recrystallized from solution in 3 normal nitric acid with centrifugal drainage after each crystallization. Owing to the slight solubility of silver dichromate in nitric-acid solutions the following scheme of crystallization was adopted. The dichromate was heated with the nitric acid solution upon the electric stove until the acid was saturated with silver dichromate. Then the hot solution was decanted into a dish through a platinum Gooch crucible without a mat of any sort but with small holes, in order to remove particles of silver dichromate either suspended in the solution or floating on the surface. These particles were always of considerable size, so that the resulting solution was clear. After the saturated solution had cooled and had deposited the greater part of its charge of salt, the mother-liquor was continuously used to dissolve fresh portions of salt. About 1 liter of acid was used for the crystallization of about 50 gm. of dichromate. Although by this method the impurities in the original salt accumulate in the mother-liquor, on account of the relatively large volume of the mother-liquor, there was little danger of these impurities being carried into the second crop of crystals. It was shown, for instance, that the mother-liquor from the third crystallization was free from potassium. This mother-liquor was evaporated to small bulk, neutralized with ammonia, and reduced and precipitated with hydrogen sulphide. The filtrate after evaporation and expulsion of the ammonium salts gave no spectroscopic flame test for potassium.

The silver dichromate was not allowed to come in contact with water or any solution except the 3 normal nitric acid solution.

All of the above operations were carried out in platinum vessels.

Sample II. — This sample was made exactly as in the case of Sample I, except that chromic acid was employed instead of potassium dichromate, and that both precipitation and crystallization took place from 0.8 normal nitric acid. The silver dichromate was crystallized five times.

Sample III. — The most dilute nitric acid which was used in the preparation of the silver dichromate was about 0.16 normal, solutions of this concentration being employed in the precipitation and crystallization of Sample III. This sample was made from chromic acid and silver nitrate, and was six times crystallized from 0.16 normal nitric acid.

The chief difference in the purification of the three specimens, aside from the concentration of acid used in their preparation, lies in the fact that Sample I was prepared from recrystallized potassium dichromate and II and III from chromic acid. All three samples were crystallized many times as silver dichromate.

After the final drainage in the centrifugal apparatus, the crystals were dried in an electric oven at 150° for several hours. Then they were powdered gently in an agate mortar and kept in platinum vessels.

DRYING OF SILVER DICHROMATE.

In preparing the silver dichromate for analysis, the complete elimination of moisture by fusion of the salt was impossible, owing to the ease with which silver dichromate decomposes. Even at the comparatively low temperature of the melting point of the dichromate, about 400°, oxygen is given off rapidly, while at temperatures considerably below this point, 300°, and to a very slight extent at 250°, there seemed to be evidence of decomposition, since salt heated to these temperatures did not give an absolutely clear solution in dilute nitric acid. In order to be on the safe side, the drying of the salt took place at 200° C.

The heating of the dichromate was effected much as described in the preceding paper in the case of silver chromate. The salt, contained in a weighed platinum boat, was heated in a current of pure dry air in a hard-glass tube for 4 hours at 200° C., the air being purified and dried by passing over hot copper oxide, solid potassic hydroxide, concentrated sulphuric acid containing dichromate, and resublimed phosphorus pentoxide successively. The oven composed of solid aluminum blocks (page 78) was used, by means of which the temperature could be maintained constant within a very few degrees.

DETERMINATION OF SILVER IN SILVER DICHROMATE.

After the boat had been allowed to cool in the tube, it was transferred to the weighing-bottle by means of the bottling apparatus (page 8), and was reweighed. Then the dichromate was transferred to a flask and was dissolved in hot 0.8 normal nitric acid, the boat and the weighing-bottle being carefully cleansed with nitric acid and the rinsings being added to the main solution. The solution, which was always perfectly clear, was quantitatively transferred to the 3-liter glass stoppered precipitating flask, and at a dilution of about 1 liter was reduced by the addition of a very slight excess of sulphur dioxide. When the solution was cold, a slight excess of hydrobromic acid was diluted to about 800 c.c. and then was slowly added to the silver solution with continual agitation. The flask was stoppered and vigorously shaken. After 24 hours' standing the flask was again shaken, and then was allowed to stand 2 days or more, until the supernatant solution was clear.

Next the silver bromide was washed at least eight times by decantation with pure water and collected upon a weighed Gooch crucible. Then it was dried in an electric oven, first at 100° for 2 hours, then at 175° for about 18 hours. After cooling in a desiccator near the balance for several hours, the weight of the silver bromide was determined.

The use of an asbestos mat in the Gooch crucible made it necessary to collect and determine the fibers detached during the filtration. This was done by passing the entire filtrate and wash-waters through a small filter paper. The paper was ignited in a weighed porcelain crucible, and the ash was treated with nitric acid and then hydrobromic acid to convert a trace of reduced silver to the state of bromide. In order to avoid any danger from adsorption of chromic salts by the filter paper, at the end of the filtration the paper was rinsed with hot dilute hydrobromic acid. The correction for asbestos could have been avoided if it had been possible to employ a Gooch-Munroe-Neubauer crucible with a mat of platinum sponge. It has already been shown, however, in the preceding paper (page 146), that such crucibles lose markedly in weight when exposed to the action even of the dilute aqua regia of the mother-liquors of these analyses.

The moisture retained by the silver bromide was found by fusing the dried salt in a porcelain crucible, the loss in weight on fusion being determined. The fused silver bromide was always light yellow and gave every indication of purity.

As in the preceding research a small quantity of silver bromide dissolved in the filtrate and wash-waters was found by evaporating the combined filtrate and wash-waters until nearly all the excess of acid had been expelled, and then, after slight dilution, precipitating the silver as sulphide. The sulphide was collected on a small paper, the ash of which, after ignition, was treated with nitric acid. The amount of silver thus obtained was found by comparing in a nephelometer precipitates of silver bromide produced in this solution and in very dilute standard solutions of silver.

In analysis 9 the silver was precipitated as silver chloride, the only other difference in the procedure being that the precipitate was washed with dilute hydrochloric acid instead of pure water.

DETERMINATION OF MOISTURE AND NITRIC ACID IN SILVER DICHROMATE.

Silver dichromate which has been crystallized from nitric acid, after being dried at 200°, contains traces of both nitric acid and water. Both of these substances can be expelled from the salt by fusion, although slight decomposition of the salt takes place simultaneously. Since the only readily volatile substance which can be formed by the decomposition of the salt is oxygen gas, the problem of the determination of the moisture and nitric acid consisted in that of absorbing in a quantitative fashion the water, nitric acid, and nitric peroxide formed by decomposition of the nitric acid. This was effected by passing the current of air containing the moisture and nitrogen compounds through two weighed U-tubes, one containing a concentrated solution of potassium hydroxide and solid potassium hydroxide and the other resublimed phosphorus pentoxide. The air current passed first through the potassium hydroxide tube in order that moisture vaporized from the hydroxide might be retained by the pentoxide tube. That the absorption of oxides of nitrogen was complete was shown by the fact that no test for nitric acid could be obtained beyond the phosphorus pentoxide tube either with moist litmus paper or with diphenylamine.

Since the three samples of silver dichromate were crystallized from nitric acid of different concentrations, it was necessary to make separate determinations of the moisture and nitric acid content with each sample. Extreme purity of material was unnecessary, and, as rather large quantities of salt were desired, three samples were prepared from ordinary silver nitrate and potassium dichromate and then were crystallized from nitric acid of the concentrations 3 normal, 0.8 normal, and 0.16 normal, respectively, glass vessels being employed throughout.

Weighed portions of the silver dichromate were heated for 4 hours at 200° in a current of pure dry air exactly as in preparing the salt for the silver analyses. Then the weighed potassium hydroxide and phosphorus pentoxide tubes were attached to the hard-glass tube, with a protection tube containing phosphorus pentoxide at the end. The silver dichromate was gradually heated to complete fusion, and the air current was allowed to pass through the system for 30 minutes in order to make certain that all the vapors expelled from the dichromate were carried into the absorbing tubes. The absorption tubes were then reweighed.

Before the tubes were weighed, they were carefully wiped with a clean damp cloth and were allowed to stand near the balance case for one hour. The tubes were provided with ground glass stopcocks lubricated with Ramsay desiccator grease. During the weighing one stopcock in each tube was open to equalize the air pressure within and without the tubes. In order to lessen the error in weighing, as well as to save time and labor, the tubes were not weighed separately, but together as one system. Counterpoise tubes of the same shape and size were always employed. Blank determinations showed that the air current and manipulation of the tubes caused an increase in weight of 0.00010 gm. in 30 minutes. This quantity is applied as a correction in every case.

In place of a platinum boat a superficially oxidized copper boat was used in these experiments. At the low temperature of fusion of silver dichromate there is little danger of decomposition of nitric acid or oxides of nitrogen by the oxidized copper. It is to be noted that if the nitric acid is decomposed during the experiment according to the following equation:

$$2HNO_3 = H_2O + 2NO_2 + O,$$

and is absorbed by the potassium hydroxide as NO_2, there is a slight loss of oxygen. The proportion of nitric acid present being very small, however, this error could have no appreciable effect on the results.

Sample.	Weight of $Ag_2Cr_2O_7$	Gain in weight of absorption tubes.	$\frac{\text{Gain}}{\text{Wt. of } Ag_2Cr_2O_7}$
I	22.52	0.00448	0.000194
I	20.74	0.00378	0.000177
I	12.25	0.00235	0.000184
Average			0.000186
II	13.13	0.00309	0.000235
II	15.91	0.00317	0.000193
II	21.35	0.00391	0.000178
II	19.60	0.00373	0.000185
Average, rejecting the first determination,			0.000186
III	20.89	0.00353	0.000164
III	19.94	0.00348	0.000169
Average			0.000167

It is somewhat surprising that Samples I and II contain the same proportion of volatile matter. This agrees with the result of the silver determinations, however, the samples proving to be otherwise very similar. As is to be expected, Sample III contains less impurity than either of the other two.

The negative corrections as found above are applied to all the final weights of silver dichromate given in the table of analyses.

SPECIFIC GRAVITY OF SILVER DICHROMATE.

The specific gravity of silver dichromate has been found by Schröder[1] to be 4.669, but on account of the uncertainty of most of the older specific gravity determinations this constant was very kindly redetermined for us by Mr. Victor Cobb. The silver dichromate was precipitated from dilute nitric acid solution and once recrystallized from normal nitric acid. Then it was dried at 200° for many hours. The determination was effected by displacement of toluol of specific gravity 0.86218. Care was taken to extract entangled air from the crystals by exhausting the air from the pycnometer in a vacuum desiccator.

The Specific Gravity of Silver Dichromate.

Weight of $Ag_2Cr_2O_7$ in vacuum.	Weight of toluol displaced in vacuum.	Specific gravity of $Ag_2Cr_2O_7$ $25^\circ/4^\circ$
gm.	*gm.*	
29.308	5.299	4.769
25.330	4.578	4.770

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[1] Liebig's *Jahresb.*, 1879, 31.

The following vacuum corrections were applied:

	Specific gravity.	Vacuum correction.
Weights	8.3	
Toluol	0.862	+0.00126
Silver dichromate . .	4.770	+0.000107
Silver bromide . . .	6.473	+0.000041
Silver chloride . . .	5.56	+0.000071

A No. 10 Troemner balance easily sensitive to 0.02 mg. was used in all the weighings. The gold-plated weights were carefully standardized to hundredths of a milligram by the method described by Richards.[1]

Weighing was always carried out by substitution, with the use of a counterpoise as nearly as possible like the object weighed, both in material, shape and volume.

Series III. $2AgBr:Ag_2Cr_2O_7$.

$$\frac{Ag}{AgBr} = 0.574453^2$$

No. of analysis.	Sample of $Ag_2Cr_2O_7$	Corrected weight of $Ag_2Cr_2O_7$.	Weight of AgBr in vacuum.	Weight of asbestos.	Dissolved AgBr from filtrate.	Loss on fusion.	Corrected weight of AgBr in vacuum.	Ratio $2AgBr:Ag_2Cr_2O_7$.
		gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	
1	II	5.71554	4.97107	0.00024	0.00025	0.00007	4.97149	0.869820
2	II	4.87301	4.23870	0.00019	0.00003	0.00004	4.23888	0.869869
3	II	7.45476	6.48380	0.00034	0.00019	0.00008	6.48425	0.869813
4	III	4.75269	4.13409	0.00020	0.00003	0.00012	4.13420	0.869865
5	III	8.15615	7.09477	0.00022	0.00005	0.00009	7.09495	0.869890
6	III	6.15412	5.35306	0.00007	0.00007	0.00011	5.35309	0.869839
7	I	6.83662	5.94656	0.00030	0.00009	0.00017	5.94678	0.869842
8	I	5.39883	4.69610	0.00027	0.00007	0.00013	4.69631	0.869876
9	III	6.26657	4.16034[3]	0.00018	0.00040	0.00016	4.16076[3]	0.869903[4]
			Average					0.869857
Total . .		55.60829	. . . .				48.37126	0.869854
		Average from Sample I						0.869859
		Average from Sample II						0.869834
		Average from Sample III						0.869874
		Average						0.869856
	Per cent of Ag in $Ag_2Cr_2O_7$, if $2AgBr:Ag_2Cr_2O_7$ = 0.869857 : 1.000000					49.9692		

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[1] *Jour. Amer. Chem. Soc.*, **22**, 144 (1900).

[2] Baxter, *Loc. cit.*

[3] AgCl.

[4] Calculated from the ratio AgBr : AgCl = 131.0171 : 100.0000. Baxter, *Loc. cit.* 4.16076 gm. AgCl $=\!\!\bigcirc\!\!=$ 5.45131 gm. AgBr.

The preceding table gives the results of all the final experiments in the order in which they were carried out. The preliminary analyses, which were defective in various ways, are not recorded.

DISCUSSION OF RESULTS.

The results of the foregoing experiments are as concordant as one can reasonably expect, since the insoluble silver salts are in general difficult to obtain definite in composition.[1] The extreme values differ by only 0.01 per cent, while the averages of the different samples show an extreme difference of less than 0.005 per cent. The composition of the dichromate is evidently not affected by the concentration of the nitric acid from which it is crystallized, since the averages from the different samples do not vary regularly with the concentration of the nitric acid, the average result obtained from Sample II being lower than that of either Sample I or Sample III.

If the per cent of silver in silver dichromate is 49.9692, the molecular weight of silver chromate may be calculated from the atomic weight of silver, and from the molecular weight of the chromate the atomic weight of chromium by difference. These calculations have been made with two values for the atomic weight of silver, oxygen being assumed to have the value 16.000. It is to be noted that the percentage error in the determination of the molecular weight of silver dichromate is multiplied four times in the atomic weight of chromium.

If Ag = 107.880 $Ag_2Cr_2O_7 = 431.786$ and Cr = 52.013
If Ag = 107.870 $Ag_2Cr_2O_7 = 431.746$ and Cr = 52.003

In the following table are given the results of the preceding research upon silver chromate by Baxter, Mueller, and Hines, together with the average of their values and those presented in this paper:

	Baxter, Mueller, and Hines.	Average.
If Ag = 107.880	Cr = 52.008	52.011
If Ag = 107.870	Cr = 51.997	52.000

The agreement of the two independently determined values is highly satisfactory, no matter which value for the atomic weight of silver is assumed, although the higher values for silver give slightly better agreement.

The atomic weights of both chromium and silver may be calculated independently of any assumption except the atomic weight of oxygen from the following equations:

$$\frac{2Ag}{2Ag + Cr + 64} = 0.650333 \qquad \frac{2Ag}{2Ag + 2Cr + 112} = 0.499692$$

to be 52.074 and 107.941 respectively. However interesting these results may be, they have little real significance, since an error of 0.005 per cent in either ratio causes an error of over 0.1 unit in the atomic weights of both silver and chromium.

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[1] Baxter and Coffin: *Proc. Amer. Acad.*, 44, 179 (1909); *Jour. Amer. Chem. Soc.*, 31, 297; *Zeit. anorg. Chem.*, 62, 50. See also preceding paper.

The most important results of this research are as follows:

1. Pure silver dichromate was prepared.

2. It is shown that silver dichromate can not be completely dried without decomposition.

3. It is shown that silver dichromate when crystallized from nitric acid retains traces of the nitric acid.

4. The proportion of moisture and nitric acid in silver dichromate treated in definite fashions was determined.

5. The specific gravity of silver dichromate is found to be 4.770 at 25° C. referred to water at 4° C.

6. The per cent of silver in silver dichromate is found to be 49.9692.

7. With two assumed values for the atomic weight of silver referred to oxygen 16.000, the atomic weight of chromium is found to have the following values:

If Ag = 107.88 Cr = 52.01
If Ag = 107.87 Cr = 52.00

8. If these results are averaged with those previously found by Baxter, Mueller, and Hines, the atomic weight of chromium is found to be as follows:

If Ag = 107.88 Cr = 52.01
If Ag = 107.87 Cr = 52.00

XI.

A REVISION OF THE ATOMIC WEIGHT OF PHOSPHORUS.

THE ANALYSIS OF SILVER PHOSPHATE.

By Gregory Paul Baxter and Grinnell Jones.

Proceedings of the American Academy of Arts and Sciences, **45**, 137 (1910).
Journal of the American Chemical Society, **32**, 298 (1910).
Zeitschrift für anorganische Chemie, **66**, 97 (1910).
Chemical News, 101, 150, 161, 176, 184 (1910).

Contributions from the Chemical Laboratory of Harvard College.

A REVISION OF THE ATOMIC WEIGHT OF PHOSPHORUS.

THE ANALYSIS OF SILVER PHOSPHATE.

INTRODUCTION.

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 discussed by Clarke,[5] Brauner,[6] and others, a few of the more important sources of error are briefly pointed out here.

Schrötter,[7] 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 to 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[8] titrated the trichloride of phosphorus against silver after decomposing the trichloride with water. Since the sample used did not boil at 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. Further-

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[1] *Ann. Chim. Phys.*, **2**, 149 (1816).

[2] C. R., **20**, 1053 (1845).

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

[4] C. R., **33**, 693 (1851).

[5] A Recalculation of the Atomic Weights, *Smith. Misc. Coll.*, 1910.

[6] Abegg, *Handb. der anorg. Chem.*, 1907, vol. 3, part 3, p. 366.

[7] *Ann. Chim. Phys.* (3), **38**, 131 (1853).

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

more 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[1] 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 meagre descriptions of these experiments preclude criticism.

Using Leduc's data for the densities and compressibilities of phosphine and oxygen, Daniel Berthelot[2] has calculated, by the method of limiting densities, the molecular weight of phosphine to be 34.00 and the atomic weight of phosphorus to be 30.98.

Very recently Gazarian[3] 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 0.06 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 moreover Baume[4] 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,[5] which consists in heating calcium phosphate and aluminum together until they react, and then treating the product of this reaction without further purification with water in a gas generator. Matignon

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[1] C. R., 100, 52 (1885).

[2] C. R., 126, 1415 (1898).

[3] *Jour. de Chim. Phys.*, 7, 337 (1909).

[4] *Jour. de Chim. Phys.*, 6, 76 and 86 (1908).

[5] C. R., 148, 167 (1909).

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 0.4 per cent would be sufficient to lower the atomic weight of phosphorus 0.1 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.

From the preceding brief summary it is evident that the uncertainty in the atomic weight of phosphorus is as great as 0.1 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 commercial 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, which has been described in the seventh paper of this collection. 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 remainder 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[3] for the synthesis of silver bromide from a weighed amount of silver was followed in detail. In this experiment 6.02386 gm. of silver yielded 10.48627 gm. 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

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[1] Baxter: *Proc. Amer. Acad.*, 42, 201 (1906); *Jour. Amer. Chem. Soc.*, 28, 1322; *Zeit. anorg. Chem.*, 50, 389. (See page 60.)

[2] Baxter and Tilley: *Jour. Amer. Chem. Soc.*, 31, 201 (1909); *Zeit. anorg. Chem.*, 61, 293. (See page 120.)

[3] Baxter, *Loc. cit.*

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 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 was passed into the solution for several hours. After standing for 24 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 gm. 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 monosilver 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 24 hours, in order to convert occluded acid phosphates into trisilver phosphate. Qualitative tests

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[1] Baxter: *Jour. Amer. Chem. Soc.*, 30, 286 (1908).

for nitrate with diphenylamine and for sodium by the spectroscope showed that all of the first three substances named could be completely washed out.

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 of 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 the phosphate ion ($PO_4^{\equiv}$) is almost completely hydrolyzed to the monohydrophosphate ion ($HPO_4^{=}$), even in slightly alkaline solutions, and since in slightly acid solutions the dihydrophosphate ion ($H_2PO_4^{-}$) acquires an appreciable concentration, the possibility of occlusion must be examined with especial 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 the dihydrophosphate ion to 0.2 per cent of its former value. The concentration of the monohydrophosphate ion remains

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[1] C. R., 103, 1071 (1886). [2] *Jour. Amer. Chem. Soc.*, 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:

$$(H^+)(OH^-) = 0.59 \times 10^{-14} \qquad \frac{(H^+)(PO_4^{\equiv})}{(HPO_4^{=})} = 3\cdot 6 \times 10^{-13} \qquad \frac{(H^+)(HPO_4^{=})}{(H_2PO_4^{-})} = 1.95 \times 10^{-7}$$

essentially unchanged, while the concentration of the phosphate ion is increased seven hundred times. Disodium phosphate doubtless takes a position intermediate between the other two solutions 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 the dihydrophosphate ion must increase greatly at the expense of the 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 the silver ion and on the concentration of the monohydrophosphate or dihydrophosphate ion respectively.

The exact concentrations of the ions during the precipitation can not 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

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

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 1 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 24 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 0.3 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 can not 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 4 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 0.02 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.

DRYING OF SILVER PHOSPHATE.

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 7 hours, and then by means of the bottling apparatus (page 8) it was inclosed 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 aluminum (page 78) 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,[1] 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 0.01 mg. The balance was provided with a few milligrams of radium bromide of radio-activity 10000 to dispel electrical charges generated during the handling of the weighing-bottles with cork-tipped pincers.

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[1] Richards and Jones: *Pub. Car. Inst.*, No. 69, 69 (1907); *Jour. Amer. Chem. Soc.*, **29**, 826; *Zeit. anorg. Chem.*, **55**, 72.

THE DETERMINATION OF SILVER IN SILVER PHOSPHATE.

The platinum boat containing the silver phosphate was transferred to an Erlenmeyer flask of "non-sol" glass of 1 liter capacity and treated with about 30 c.c. 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 c.c. of water was 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 20 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 was 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 c.c. 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 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 gm. 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 1 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 c.c. of water, and treated with an excess of ammonium molybdate reagent with gentle warming. After standing for 3 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 method of precipitation being varied. Disodium phosphate, trisodium phosphate, 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 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 gm. 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 from 4 to 8 gm. 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 0.01 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 gm. of this residue yielded 0.03551 gm. 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 gm. of residue yielded 0.05747 gm. 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 can not 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 is 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.

DETERMINATION OF MOISTURE 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 176.) 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 gm. of silver phosphate were placed in one end of a large silver boat and in the other end about 12 gm. 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 30 minutes. 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 30 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 30 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 pyrophosphate or metaphosphate, would evolve water when fused, although it is possible that occluded acid phosphates might have been converted into pyrophosphate or metaphosphate 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 PHOSPHATE.

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 toluol displaced by a known quantity of salt. The specific gravity of the toluol at 25° referred to water at 4° was 0.8633. Great care was taken to remove air from the salt when covered with the toluol by warming the pycnometer, then placing it in a vacuum desiccator and boiling the toluol under reduced pressure. The salt and toluol were mechanically stirred to assist the escape of air bubbles. This process was repeated several times.

THE SPECIFIC GRAVITY OF SILVER PHOSPHATE.

Weight of silver phosphate in vacuum.	Weight of displaced toluol in vacuum.	Volume of silver phosphate.	Density of silver phosphate. 25°/4°.
gm.	*gm.*	*c.c.*	
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 gm. per gram of salt. Similarly 0.000041 gm. was added for every gram of silver bromide.

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 of 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 gm. respectively (average 0.00025) more than the tube which was later to contain the silver phosphate. After 22.69 gm. 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° C. and 766 mm. was admitted to both the tube containing the silver phosphate and the counterpoise, the counterpoise gained 0.00443 gm. more than the tube. Therefore, the air displaced by the silver phosphate was 0.00443 — 0.00025 = 0.00418 gm. Since 22.69 gm. of silver phosphate of density 6.37 have a volume of 3.56 c.c., the volume of pure air displaced at 25° C. and 766 mm. should weigh 0.00425 gm.[2]

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 gm. more than the tube containing the silver phosphate. Therefore the air displaced by the silver phosphate was 0.00445 — 0.00025 = 0.00420 gm., whereas the weight of air displaced, calculated from the density of the salt, is 0.00426 gm.

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

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[1] Baxter and Tilley: *Jour. Amer. Chem. Soc.*, 31, 214 (1909); *Zeit. anorg. Chem.*, 61, 310. (See page 130.)

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

RATIO OF SILVER BROMIDE TO SILVER PHOSPHATE.

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 1.02727 gm. of silver chloride. Since Baxter found $AgBr : AgCl = 1.31017 : 1.00000$,[1] this analysis indicates that one gram of sample N is equivalent to $1.02704 \times 1.31017 = 1.34560$ gm. 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. $3\,AgBr : Ag_3PO_4$.

No. of analysis.	Sample of Ag_3PO_4	Weight of Ag_3PO_4 in vacuum.	Weight of AgBr in vacuum.	Weight of asbestos.	Dissolved AgBr.	Loss on fusion.	Corrected weight of of AgBr.	Ratio $\frac{3AgBr}{Ag_3PO_4}$.
		gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*	
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	

DISCUSSION OF RESULTS.

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

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[1] *Loc. cit.*

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 very slightly too low, owing to the presence of disilver hydrogen phosphate. The ratio 1.34562, assuming the atomic weight of silver to be 107.880, 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.

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 one gram of silver phosphate yields 1.34562 gm. 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

Baxter, G.P.
Researches upon the
atomic weights of
cadmium.