richs,[1] Dubreuil[2] and Leduc.[3] The electrochemical equivalents of oxygen and hydrogen have been studied by Lehfeldt.[4] On the silver voltameter and coulometer there are elaborate papers by Duschak and Hulett,[5] and by Smith, Mather and Lowry.[6] In the latter research the electrochemical equivalent of silver is fixed at 1.11827 mg. per coulomb.

In the International Table, published in this JOURNAL for March, there is a serious misprint. Zn should be **65.37** instead of 65.7.

WASHINGTON, D. C.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF ARSENIC.

PRELIMINARY PAPER—THE ANALYSIS OF SILVER ARSENATE.

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Below is a summary of the previous work upon the atomic weight of arsenic,[7] the results obtained by the several investigators having been recalculated with the use of the following atomic weights:[8] O = 16.000; Ag = 107.880; Cl = 35.457; Br = 79.916; S = 32.07; K = 39.096; Na = 22.977; Cr = 52.01; Pb = 207.09.

1816	Thomson,	*Schweigger 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 two-tenths of a unit in the averages of the five series.

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[1] *Chem. Zent.*, 1908 (1), 1240; *Compt. rend.*, **146**, 971; **147**, 797, and **147**, 1302.

[2] *Compt. rend.*, **147**, 627, 856, and 1300.

[3] *Ibid.*, **147**, 972.

[4] *Phil. Mag.* [6], **15**, 614.

[5] *Trans. Amer. Electrochem. Soc.*, **12**, 257

[6] *Phil. Trans.*, **207**, A, 545.

[7] Clarke, A Recalculation of the Atomic Weights; Smith, Misc. Coll., Constants of Nature, Part V, p. 213 (1897). For an excellent critical discussion of previous work, by Brauner, see *Abegg's Handbuch der anorganischen Chemie*, **3** (2), 491 (1907).

[8] Richards, *Jour. chim. phys.*, **6**, 130 (1908).

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 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.

Purification of Materials.

Silver 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 a temperature of 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.

Sample B.—This sample was made from disodium arsenate which had been recrystallized five times in platinum vessels. Silver arsenate was precipitated with a solution of this salt without the addition of ammonia.

Sample C.—Commercial C. P. arsenic trioxide was recrystallized three times from dilute hydrochloric acid solution, and, after being rinsed with water and centrifugally

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[1] Washburn calculates from Walden's conductivity measurements the constant for the first hydrogen of arsenic acid to be $4.8.10^{-3}$. THIS JOURNAL, 30, 35 (1908). The constants for the second and third hydrogens are probably lower than those of phosphoric acid, $2.1.10^{-7}$ and $3.6.10^{-13}$. *Ibid.*, 30, 38.

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 metarsenic acids to be converted as completely as possible into orthoarsenic 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.

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 triammonium 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.

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.

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.

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, three 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.[2]

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

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[1] Baxter, THIS JOURNAL, 30, 286 (1908).

[2] Baxter, *Ibid.*, 28, 1322 (1906).

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 grams of silver bromide were obtained from 6.02386 grams of the purest silver. This ratio of silver bromide to silver of 100.0000 to 57.4452 is in close agreement with the most probable value, 100.0000 to 57.4453.[1]

Hydrochloric Acid.—A solution of this 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.

Water.—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 flask.

Utensils.—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 management the attacking of the quartz could be wholly prevented. The vessel used to contain the arsenate was a quartz tube nearly two centimeters 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.[2] 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 seven and eight hours at 250°. 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

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[1] This Journal, 28, 1322 (1906).

[2] *Ibid.*, 29, 833 (1907).

tube connected with an apparatus for furnishing a current of pure dry air. The hard glass tube was heated by means of an oven made of two solid aluminum blocks.[1] 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 three towers filled with beads moistened with concentrated sulphuric acid, and finally through a tube filled with resublimed phosphorus pentoxide. The apparatus was constructed wholly of glass, with ground joints.

After being heated, the quartz tube was transferred to a desiccator and 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.

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 considerable arsenic, which could not be completely removed even by keeping the silver chloride fused in the current of hydrochloric acid for as long as eight 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 eight hours to the action of the hydrochloric acid gas, next to heat the salt gently below its fusing point for from ten to fifteen hours, and finally to keep it barely fused for from five to ten 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 fifteen 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.

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[1] Baxter and Tilley, THIS JOURNAL, **31** 201 (1909)

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.

The U-tube beyond the quartz tube 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,[2] by means of which the boat could be transferred to the weighing bottle in which it was always weighed without exposure to moist air. 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 nitric acid of density about 1.15. Then the solution was carefully transferred to a large glass-stoppered precipitating flask and diluted to a volume of about one liter. A slight excess of either hydrochloric or hydrobromic acid was diluted to about six hundred cubic centimeters, 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, dried, and weighed. The moisture retained by the precipitate was determined by fusion in a porcelain crucible and the asbestos mechanically detached from the Gooch crucible was collected upon a small filter. Dissolved silver halides in the filtrate and wash waters were determined nephelometrically after evaporation to small bulk.[3]

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

[2] Richards and Parker, *Ibid.*, **32**, 59 (1896). See also THIS JOURNAL, **31**, 16 (1909).

[3] For details concerning these operations see Richards and Wells, THIS JOURNAL, **27**, 515 (1905); Baxter, *Ibid.*, **28**, 1329 (1906).

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.

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 gram, 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.

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.

Weight of silver arsenate. Grams.	Weight of insoluble residue. Gram.	Weight of silver. Gram.	Per cent of silver.
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 third determination also was made with a sample of salt which had been exposed to bright light for three 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.

The Determination of Moisture in Silver Arsenate.

T. W. Richards[1] and others have called 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 cannot 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

[1] *Z. physik. Chem.*, **46**, 196 (1903).

the salt in a current of pure dry air and collecting the water vapor in a weighed phosphorus pentoxide tube. Of course great pains was 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 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 seven and eight hours at 250° 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-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 point 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 twenty-five minutes with the hottest flame of the blast lamp, being then completely fused, and was further heated for thirty-five 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.

Since it seemed possible that the hard glass tube itself, when heated nearly to fusion, might give off traces of water vapor,[1] two blank determinations were made by heating the empty hard glass tube in exactly the same way as in the water determinations.

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[1] W. A. Noyes has suggested that moisture may diffuse through the viscous glass. THIS JOURNAL, **29**, 1725 (1908).

These determinations showed a gain in weight of the pentoxide tube of 0.00022 and 0.00037 gram respectively, the average being 0.00030 gram. 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 one hour. The observed gain in weight of the absorption tube was 0.00048 gram. A negative correction of 0.00030 gram was applied in each water determination.

Weight of silver arsenate. Grams.	Weight of water. Gram.	Weight of water per gram of salt.
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

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

The 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 toluene displaced by a known quantity of salt. The toluene was first dried by means of solid sodium hydroxide 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 was 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. Grams.	Weight of displaced toluene in vacuum. Gram.	Specific gravity of silver arsenate 25°/4°.
5.1690	0.6688	6.662
5.6729	0.7350	6.652
	Average........	6.657

The following vacuum corrections were applied:

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

Balance and Weights.

All weighings were made upon a nearly new short-armed Troemmer balance, easily sensitive to one fiftieth of a milligram with a load of fifty grams.

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

SERIES I.

$3AgCl : Ag_3AsO_4$.

No. of analysis.	Sample of Ag_3AsO_4.	Corrected weight of Ag_3AsO_4 in vacuum. Grams.	Weight of AgCl in vacuum. Grams.	Residual $AsCl_3$. Gram.	Volatilized AgCl. Gram.	Corrected weight of AgCl in vacuum. Grams.	Ratio $3AgCl$: Ag_3AsO_4.
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. Grams.	Weight of AgCl in vacuum. Grams.	Weight of asbestos. Gram.	Dissolved AgCl from filtrate. Gram.	Loss on fusion. Gram.	Corrected weight of AgCl in vacuum. Grams.	Ratio $3AgCl$: Ag_3AsO_4.
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. Grams.	Weight of AgBr in vacuum. Grams.	Weight of asbestos. Gram.	Dissolved AgBr from filtrate. Gram.	Loss on fusion. Gram.	Corrected weight of AgBr in vacuum. Grams.	Ratio $3AgBr$: Ag_3AsO_4.
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

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[1] Ag: AgCl = 0.752632: 1.000000. Richards and Wells, THIS JOURNAL, **27**, 459 (1905).

[2] Ag: AgBr = 0.574453: 1.000000. Baxter, *Ibid.*, **28**, 1322 (1906)

SERIES IV.

$3AgCl : Ag_3AsO_4$.

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

Average of all analyses in Series V and VI............. 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. Grams.	Weight of AgBr. in vacuum. Grams.	Weight of asbestos. Gram.	Dissolved AgBr from filtrate. Gram.	Loss on fusion. Gram.	Corrected weight of AgBr in vacuum. Grams.	Ratio $3AgBr : Ag_3AsO_4$.
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

Discussion of Results.

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 two thousandths of a 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	$(NH_4)_3AsO_4$		

It is to be expected that the basicity due to hydrolysis would be most marked with Samples F and G, less in the case of Samples A and E, still less with Sample D, and least in the case of 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. Some uncertainty exists as to this ratio, hence calculations have been made upon the basis of several possible values for silver, oxygen being assumed to have the value 16.000. 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 six one-hundredths of a per cent. in the atomic weight of arsenic.

	Series I and II.	Series III.
If Ag = 107.930, As =	75.026	75.017
If Ag = 107.880, As =	74.961	74.953
If Ag = 107.850, As =	74.923	74.914

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

If Ag = 107.930 As = 75.021
If Ag = 107.880 As = 74.957
If Ag = 107.850 As = 74.918

The atomic weight of arsenic will be further investigated in this laboratory.

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 cannot be completely dried without fusion.

4. The specific gravity of unfused trisilver arsenate is found to be 6.66 at 25°/4°.

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

6. With several 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 = 107.93 As = 75.02
If Ag = 107.88 As = 74.96
If Ag = 107.85 As = 74.92

A grant from the Carnegie Institution of Washington has been of great assistance in the pursuit of this investigation. We are also indebted to the Cyrus M. Warren Fund for Research in Harvard University for much indispensable platinum apparatus.

CAMBRIDGE, MASS., November 24, 1908.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 160.]

THE CALCULATION OF THE CRITICAL TEMPERATURE OF AN ASSOCIATED LIQUID FROM SURFACE TENSION RESULTS.

BY J. LIVINGSTON R. MORGAN.

Received December 26, 1908.

Theoretical.

According to Ramsay and Shields[1] liquids may be divided into two great classes. One of these, the so-called *non-associated* liquids, following the law

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[1] *Z. physik. Chem.*, 12, 433–75 (1893).