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A REVISION OF THE ATOMIC WEIGHT OF ANTIMONY. THE ANALYSIS OF ANTIMONY BROMIDE.

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Introduction.

It requires only a cursory glance at the earlier reports of the International Committee on Atomic Weights to learn that the value in the tables to-day for the atomic weight of antimony rests on no secure basis. It was put forth in 1903¹ as a compromise between Cooke's work on the bromide,² pointing to 120.0, and the work of Cooke³ and of Schneider⁴ on the sulfide and the work of Friend and Smith⁵ on tartar emetic, the three latter giving values ranging from 120.22 to 120.55.

Careful examination of the papers dealing directly with the analytical problem shows that the uncertainty is much greater actually than the above would indicate. Disregarding the work of Berzelius,⁶ from which he selected the number 129, as well as the earlier work of Kessler,⁷ which he himself later corrected for known errors, the other determinations group themselves into two main divisions approximating 120 and 122. Thus Dexter⁸ (1857), Dumas⁹ (1859), and Kessler¹⁰ (1860), obtained 122.46, 121.83 and 122.08–122.33, respectively, on the basis of which the number 122 was generally adopted. Schneider¹¹ (1856), however, had analyzed a native sulfide of antimony, the data pointing to the number 120.55, and Cooke¹² (1877–81) made a laborious study including syntheses of antimony trisulfide and the estimation of halogen in the trihalides of antimony, which was so convincing that it immediately established the lower value, 120.

Cooke's last data on the ratios, $\text{SbBr}_3 : 3\text{Ag}$ and $\text{SbBr}_3 : 3\text{AgBr}$, presented a concordance of results unknown to chemical analysis of that day, and are credited by Brauner¹³ with introducing the modern era of atomic weight determinations.

¹ THIS JOURNAL, **25**, 2 (1903); *Z. physik. Chem.*, **42**, 634 (1903); *Proc. Chem. Soc.*, **19**, 2 (1903); *Ber.*, **36**, 5 (1903).

² *Proc. Am. Acad. Arts. Sci.*, **15**, 251 (1880); *ibid.*, **17**, 1 (1881).

³ Cooke, *Proc. Am. Acad. Arts. Sci.*, **13**, 1–37 (1877).

⁴ Schneider, *Pogg. Ann.*, **97**, 483; and **98**, 293 (1856); *J. prakt. Chem.*, **22**, 131 (1880).

⁵ Friend and Smith, THIS JOURNAL, **23**, 502 (1901).

⁶ Berzelius, *Pogg. Ann.*, **8**, 1 (1826).

⁷ Kessler, *ibid.*, **95**, 204 (1856).

⁸ Dexter, *ibid.*, **100**, 563 (1857).

⁹ Dumas, *Ann. chim. phys.*, [3] **55**, 175 (1859).

¹⁰ Kessler, *Pogg. Ann.*, **113**, 134 (1860).

¹¹ Schneider, *ibid.*, **97**, 98, 293, 483 (1856).

¹² Cooke, *Proc. Am. Acad. Arts. Sci.*, **13**, 1 (1877); *ibid.*, **17**, 1 (1881).

¹³ Brauner, Abegg's "Handbuch d. anorg. Chem." [III] **3**, 558 (1907).

The electrochemical studies of Pfeiffer¹ (1881) and of Popper² (1886)—generally regarded as discredited by the work of Cohen, Collins and Strengers³—gave 122.36–121.36 and 121.20, respectively. Bongartz⁴ (1883), from a complex process, derived the value 120.64 from the ratio, $2\text{Sb} : 3\text{BaSO}_4$, and—last in the field of ostensible atomic weight studies—Friend and Smith⁵ obtained the value 120.43 from the ratio $\text{KSbOC}_4\text{H}_4\text{O}_7 : \text{KCl}$.

From the time of Becker's "Digest of Atomic Weight Determinations" (1880) down to Brauner's article in Abegg's "Handbuch" (1907), Cooke's work on the bromide of antimony so prejudiced the reviewer that the discussion of the original papers was decidedly uncritical and at times inaccurate as to facts. Compare, as a case in point, the easy dismissal of the work on antimony chloride (Dumas, 121.83; Cooke, 121.84) on the basis of Cooke's first suggestion of some oxychloride in the material studied,⁶ with the fact that Cooke offered two different explanations for these high numbers,⁷ neither of which was adequately supported by his own experimental data.⁸

The controversy as to the atomic weight of antimony was not settled by the adoption of the present value in the tables. It is true that Henz,⁹ Vortmann and Metzl,¹⁰ Kolb and Formhals,¹¹ Hallmann¹² and others, studying quantitative methods for antimony, found the present value satisfactory; but Youtz,¹³ Beckett,¹⁴ and Von Bacho,¹⁵ presented data pointing to a distinctly higher atomic weight, and Treadwell¹⁶ expressed the belief that the older number, 122, was nearer the truth than the new one.

This last opinion was undoubtedly based on the analytical work of Beckett, done in Treadwell's laboratory. In chief part, Beckett prepared a very pure sample of antimony trisulfide and obtained data for the ratios $\text{Sb}_2\text{S}_3 : 2\text{Sb}$, $\text{Sb}_2\text{S}_3 : 3\text{BaSO}_4$, and $\text{Sb}_2\text{S}_3 : 4\text{I}$, corresponding to the atomic

¹ Pfeiffer, *Ann.*, **209**, 174 (1881).

² Popper, *ibid.*, **223**, 153 (1886).

³ Cohen, Collins and Strengers, *Z. physik. Chem.*, **50**, 308 (1904).

⁴ Bongartz, *Ber.*, **16**, 1942 (1883).

⁵ Friend and Smith, *THIS JOURNAL*, **23**, 502 (1901).

⁶ See Brauner, *loc. cit.* Clarke, Recalculations of the Atomic Weights.

⁷ *Proc. Am. Acad. Arts Sci.*, **13**, 70 (1877); *ibid.*, **17**, 22 (1881).

⁸ *Loc. cit.*

⁹ Henz, *Z. anorg. allgem. Chem.*, **37**, 6 (1903).

¹⁰ Vortmann and Metzl, *Z. anal. Chem.*, **44**, 526 (1905).

¹¹ Kolb and Formhals, *Z. anorg. allgem. Chem.*, **58**, 189 (1908).

¹² Hallmann, Vergleichende Untersuchungen ü. Methoden. d. quant. Antimonbest., *Inaug. Dis.*, Aschen, 1911.

¹³ Youtz, *Z. anorg. allgem. Chem.*, **37**, 337 (1903).

¹⁴ Beckett, Beitrag Best. d. Antimons. *Inaug. Dis.* Zürich, 1909.

¹⁵ Von Bacho, *Monatsh.*, **37**, 106 (1916).

¹⁶ Treadwell, "Kurzes Lehrbuch anal. Chem.", 5th ed., **2**, p. 563, retained in the 6th ed.

weight values 121.54, 121.66 and 122.08, respectively. This work, while carried on with few of the refinements of atomic weight practice, bears internal evidence of being a very good quantitative study and favors an atomic weight of antimony somewhat less than 122.

It is with such a background that the preparation of antimony tribromide was undertaken and determinations carried out of the ratios $\text{SbBr}_3 : 3\text{Ag}$ and $\text{SbBr}_3 : 3\text{AgBr}$, using modern methods of preparing the materials and modern technique in carrying out the analytical processes.

Preparation of Materials.

The preparation of pure bromine and pure silver as auxiliary standards followed methods well known in atomic weight work. Separation of crystals from mother liquor was accomplished by centrifugal drainage, and electrical heating was resorted to wherever practicable.

Pure Bromine.—In brief outline the process for bromine was as follows. A high grade of commercial bromine was dissolved in a conc. solution of calcium bromide and distilled therefrom. Then the procedure followed that given by Baxter, Moore and Boylston,¹ except that the removal of iodine was accomplished by the two steps of boiling off an excess of bromine added in forming potassium bromide from the oxalate and of crystallizing out the potassium bromide rather than evaporating the solution to dryness.

Pure Silver.—Silver from students' cyanide analyses was precipitated with ammonium sulfide, dissolved in nitric acid, precipitated in dil. solution with hydrochloric acid, then converted to metal by the method of Buckner and Hulett.² The silver was then fused in air on a pure lime support and the process to this point repeated. It was then carried through the later purification process as outlined by Baxter, Moore and Boylston, including formate precipitation, electrolytic deposition and fusion in electrolytic hydrogen

Accessory Reagents.—Reagents used in the analytical work or incidental to the preparation of pure bromine and silver were purified and handled with a care proportional to the purity of the bromine and silver themselves.

Water was redistilled with block-tin condenser from alkaline permanganate solution, first allowing it to simmer for several hours and then discarding a moderate first fraction.

Nitric Acid.—Ordinary c. p. nitric acid was treated with a crystal of sodium chlorate, then carefully distilled, using a quartz condenser and collecting the middle third. This, by careful test, was shown to be free from iron and chloride and was preserved by sealing up in resistance glass

¹ Baxter, Moore and Boylston, *THIS JOURNAL*, **34**, 259 (1912).

² Buckner and Hulett, *Trans. Am. Electrochem. Soc.*, **22**, 372 (1912).

flasks that had been thoroughly soaked in the usual chromic acid cleaning solution and then well rinsed and steamed.

Calcium Bromide.—A solution for dissolving the bromine was prepared according to the following reaction. $\text{CaCO}_3 + \text{HCOOH} + \text{Br}_2 = \text{CaBr}_2 + \text{H}_2\text{O} + 2\text{CO}_2$. A high grade of precipitated calcium carbonate was treated with diluted, redistilled formic acid, using slightly less than one gram molecule of formic acid to one of calcium carbonate; then bromine was added carefully in slight excess, and the solution boiled, filtered, and evaporated to such a volume that it was nearly saturated with respect to calcium bromide.

Potassium oxalate was twice recrystallized from water. In the final product careful tests for iron and chlorine were negative.

Kahlbaum's *potassium permanganate*, "Zur Analyse," and freshly fumed *sulfuric acid* gave negative tests for halogen and so were used directly.

Phosphorus pentoxide was sublimed in a current of oxygen and found by test with silver ammonia nitrate to be free from reducing material.

Hydrochloric acid and *ammonium hydroxide* were purified by distillation.

Cane sugar was precipitated from solution by freshly distilled alcohol and found, on ignition, to leave an unweighable residue.

Ammonium formate was prepared by careful neutralization of formic acid that had been distilled from silver formate.

The preparation of the pure *lime support* followed essentially the details given by Richards and Wells.¹

Pure *hydrogen* was generated by electrolysis of sodium hydroxide solutions in all-glass apparatus with nickel gauze electrodes, drying being effected by a long tube of solid sodium hydroxide.

Tartaric Acid.—Careful tests of Kahlbaum's chemically pure tartaric acid showed that it was satisfactory for use without further purification. Preliminary experiments were undertaken to see if hydrofluoric acid might not be used in place of the usual tartaric acid as a solvent for the antimony bromide. It was found that antimony bromide dissolves readily in hydrofluoric acid, that no considerable excess of the acid is required, and that such a solution may be diluted largely without precipitation. But, due to the action of the hydrofluoric acid on the glass, the solution underwent slow decomposition with precipitation of antimony oxybromide. Neutralization of the acid solution failed to give it the desired stability, so further attempts in this direction were abandoned and tartaric acid was finally adopted.

Pure Antimony.

Purification of Antimony Compounds.—Fractional distillation of antimony bromide as a means of separation from lead, copper, iron, tin

¹ Richards and Wells, *THIS JOURNAL*, 25, 481 (1905).

and arsenic was studied, using a commercial preparation to which small amounts of these metals were added separately in the form of bromides, and the material distilled into small glass bulbs as receivers. Two small fractions were collected first, then the bulk of the antimony bromide distilled off and the residue examined. Lead, copper and iron were completely retained in the distilling flask, while tin was found largely in the first fraction and was completely removed by the time $\frac{1}{4}$ of the material had distilled over. The method proved unsatisfactory in the case of arsenic, positive tests being obtained on the residue even after $\frac{3}{4}$ of the antimony bromide had been discarded.

In the course of this work a modified distilling flask was developed with the receiver attached at the top by means of a ground glass joint. This avoided the usual dead space which reduces the effectiveness of separation by fractional distillation.

A second method studied for the purification of antimony compounds was the recrystallization of tartar emetic. Using centrifugal drainage and working on a moderate scale it was found that small amounts of copper, iron, tin and arsenic, introduced as chlorides—except arsenic, which was introduced as dipotassium, hydrogen, orthoarsenate—were rapidly removed in the mother liquors. Lead, however, after reduction to a certain small value, was found in about equal amounts in successive crops of crystals.

It was at first intended to use recrystallization of tartar emetic, followed by decomposition with heat as a means of obtaining the metal, which might then be converted to the bromide and subjected to a process of fractional distillation. At this time, however, the work of Groschuff¹ became available, and this appeared so promising that further study on the difficulties of the suggested method was abandoned.

Kahlbaum's antimony trioxide² was dissolved in fairly concentrated hydrochloric acid, filtered through hardened filter paper and treated with chlorine from a cylinder of the liquefied gas till oxidized to antimony pentachloride. This solution was evaporated on a water-bath until very concentrated, then saturated with dry hydrogen chloride (prepared by dropping conc. hydrochloric acid into conc. sulfuric acid and washing with sulfuric acid) and finally cooled to less than 0°. Under these conditions the compound $\text{HSbCl}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ separates out in fine crystalline form. These crystals were collected on a Büchner funnel, then placed in a porcelain evaporating dish, a little water added and the dish placed on the water-bath until a clear solution was obtained. By repeating the earlier

¹ Groschuff, *Z. anorg. allgem. Chem.*, 103, 164 (1918), recommending the method of Weinland and Schmid. *Ibid.* 44, 43 (1905).

² Quantitative analysis of the trioxide using the method of Groschuff for concentrating impurities revealed the following impurities: S, 0.005%; Sn, 0.002%; Cu, 0.001%; Fe, 0.015%; Pb, 0.004%; As, 0.001%.

process a new crop was formed which was drained centrifugally in platinum cups and recrystallized 4 times. These crystals were then worked up in separate lots as follows: they were dissolved in water, diluted largely and heated on a water-bath to complete the hydrolysis, collected on a Büchner funnel, washed copiously with hot water, then transferred to an evaporating dish and twice evaporated to dryness with nitric acid to remove the last trace of chloride. Tests for chlorine on this material were negative.

Recovery of the Metal.—Metallic antimony was recovered from this preparation, after ignition to the oxide, in two ways, (a) heating in hydrogen; (b) fusing with sodium cyanide.

Preliminary experiment had shown that antimony oxide may be satisfactorily reduced to the metal by heating in hydrogen providing a temperature is maintained slightly below the melting point of the trioxide. If the trioxide melts it becomes coated over with the metal in such a way as to be rather effectively protected against further reduction. At the lower temperature the reduction proceeds rather slowly, but it may be carried out in such a way as to require little attention so that the time

used was not a serious objection. There was prepared a cylindrical bomb of iron (see Fig. 1) about 75 mm. deep and 75 mm. in diameter, large enough to receive a fair-sized crucible. A cover was carefully ground and polished so as to fit nearly gas-tight, clamps being arranged for fastening on the cover, which was provided with two 20 cm. lengths of small iron tubing to serve as inlet and outlet tubes. The outlet tube was fitted with a small hard-glass tube bent so as to be out of the way of the crucible and reaching nearly to the bottom of the bomb. The inlet tube came merely to the lower edge of the cover. The whole fitted nicely into a pot furnace wound to give temperatures ranging up to 750–800°.

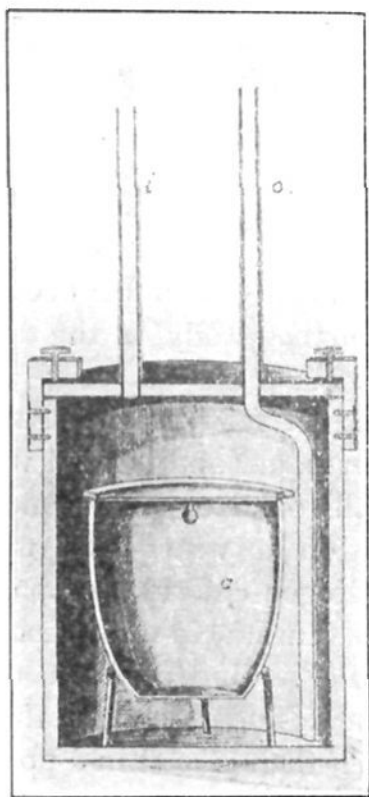


Fig. 1.—Apparatus used for reduction of antimony oxide in hydrogen. *i* = inlet tube for hydrogen; *o* = outlet tube; *c* = crucible for antimony oxide.

The hydrogen used for the reduction was compressed electrolytic hydrogen. This was passed first through a long tube of freshly heated charcoal to remove traces of hydrocarbon;¹ second, a glass tube heated to dull redness to convert any oxygen to water, a

¹ Roscoe and Schorlemmer, "Treatise on Inorganic Chemistry," 4th ed., I, p. 153.

calcium chloride tube, and finally through a phosphorus pentoxide tube for drying.

In carrying out the reducing process a crucible was filled reasonably full of the antimony oxide, placed on a low triangle in the bomb, covered with an inverted quartz cover, then the cover fastened on and the bomb placed in the pot furnace. Hydrogen was next turned on and finally the furnace heated to a temperature of approximately 500° . After about two days, which, under the conditions as standardized, was sufficient for a satisfactory reduction of the oxide to metal, the temperature was raised to about 650° , high enough to melt the antimony, and then the furnace permitted to cool down. Bright buttons of antimony with a few dark specks on the surface were obtained. The specks were removed mechanically, the buttons pounded up in a clean agate mortar and then reheated in hydrogen to $400\text{--}450^{\circ}$ for final drying. This latter was done immediately before the material was to be used for the synthesis of the tri-bromide.

In the reduction of the oxide in hydrogen it was noticed that the porcelain crucible was blackened, the stain thus produced not being removed by soaking in nitro-hydrochloric acid. Consequently contact with porcelain was avoided and one bath of the oxide was reduced to metal using a quartz crucible, and another was reduced on a support of pure lime similar to that used in the preparation of pure silver. In the second case the support, for obvious reasons, underwent considerable disintegration; but, nevertheless, effectively kept the antimony from contact with the crucible. The two specimens of antimony were labelled, respectively, Preparations I and II.

For the second method of reducing the oxide a high grade commercial sodium cyanide was recrystallized 4 times from water using centrifugal drainage, and dried over sodium hydroxide. The resulting material was free from iron and chloride. This was mixed intimately with the oxide in a tall porcelain beaker, then heated in the electric furnace for several hours at slightly above the melting point of antimony. After cooling, the button of antimony was cleaned mechanically, fused in hydrogen, then pounded up in an agate mortar and dried in hydrogen when needed.

Antimony Bromide.

Construction of Apparatus.—The attempt to prepare antimony bromide in such a way as to use the Harvard bottling method was soon abandoned, because the volatility of this compound when slightly above its melting point and its hygroscopic character both make fusion in an atmosphere of dry hydrogen bromide a method of doubtful value for the conversion of traces of oxide or oxybromide to bromide. To test this point a sample of antimony bromide was moistened slightly, then treated for several hours at just above the melting point with hydrogen bromide.

On distilling off the antimony bromide the residue left was distinctly greater than that given by another portion of the dry bromide distilled directly.

The next attempt was in the direction followed by Baxter, Moore, and Boylston,¹ in the work on phosphorus, involving preparation of the tribromide, fractional distillation, and collection of the middle portion in a series of sampling bulbs—all in an inert atmosphere in all-glass apparatus. The first construction followed their general design, except that a separate bulb was added at the beginning from which the bromine could be distilled on to the antimony, and the preparation chamber consisted of an inclined tube lying in an aluminum block oven,² keeping the antimony bromide molten and drained off and exposing fresh surface of metal to the action of the bromine.

Vacuum was obtained at first by a Cenco-Nelson 2-phase pump, later replaced by the "Hyvac," an oil-immersed pump capable of maintaining a vacuum of 0.003 mm.

Nitrogen for drying the apparatus and for establishing an inert atmosphere was prepared from commercial compressed nitrogen containing 0.5% oxygen. The removal of oxygen by the method described by Badger³ was discarded when it was observed that the resulting gas had a slight reducing action. Instead the oxygen was absorbed by copper turnings heated to a dull red. The purifying and drying train was completed by a 60 cm. tube of soda lime, 3 Emmerling towers of sulfuric acid and a tower of phosphorus pentoxide. No reducing effect was noted in the gas thus obtained and careful test showed it to be free from oxygen.

During the course of preliminary runs to get acquainted with both the apparatus and the process, certain mechanical difficulties were encountered with the trap arrangement used in discarding the first fraction of the distillate. On due consideration it was felt that first fractions could be discarded nearly as effectively by setting aside the first 2 or 3 bulbs into which material was condensed, and further, that with antimony and bromine carefully purified the chief danger was from moisture, which could be avoided better by proper drying precautions than by discarding a special fraction. Therefore the trap and separate series of discard bulbs were omitted. At the same time there were added at the other end of the sampling bulbs 2 U-tubes, one containing metallic antimony, which, at 100°, effectively absorbed any traces of bromine that were carried past the preparation chamber, the second, phosphorus pentoxide to ensure complete drying of any gases which might come into the bulbs from that direction.

¹ *Loc. cit.*

² Baxter and Tilley, *THIS JOURNAL*, 31, 206 (1909).

³ Badger, *J. Ind. Eng. Chem.*, 11, 1052 (1919).

In one of the earlier experiments it was discovered, on sealing off an empty bulb with a full one and distilling the antimony bromide out of the latter, that the residue left was unexpectedly large. To study this further, a sample of antimony bromide was moistened with a drop of water, then placed in the first of a series of 10 well-dried bulbs, the system evacuated and sealed, and the material distilled from one bulb to the next, sealing off each residue as obtained. The residues decreased in amount but were fairly marked in the first three bulbs.

Cooke had suggested the possibility of any oxychloride of antimony distilling over in part with the chloride. It seemed as if something of that sort might be the case here. The following experiment, however, pointed to moisture as being the probable source of the residues. Phosphorus pentoxide was added to some antimony bromide and the above study repeated. In the first distillation some chemical reaction took place, but in the second bulb there was no visible residue. From this time on the drying temperature was raised to at least 250° and the time extended to a minimum of 24 hours. With these precautions the amount of residue became uniformly slight. In two cases distilling off 4 or 5 g. of antimony bromide left 0.09 mg. and 0.08 mg., respectively, approximately 0.002%. For comparison, Cooke's residues from the bromide averaged 0.028%, even though he maintained a high enough temperature to feel justified in assigning the formula $Sb_4O_5Br_2$ to the residue.

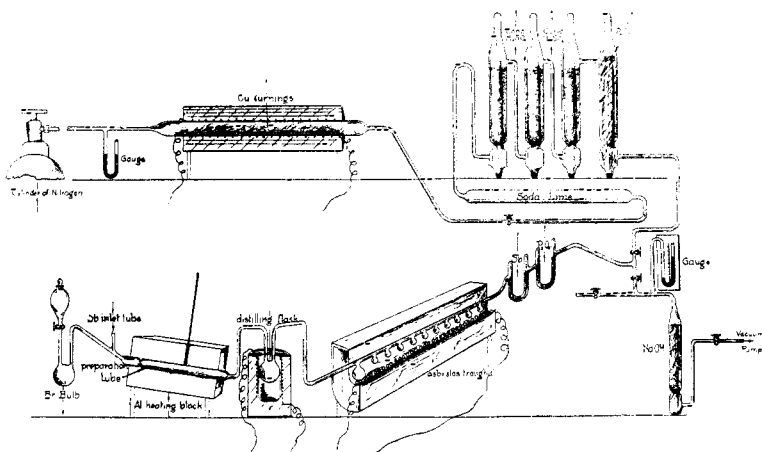


Fig. 2.—Apparatus used for preparation of antimony bromide.

The apparatus as finally developed is represented semi-diagrammatically in Fig. 2. Heating arrangements were provided to give temperatures up to 300° . The bromine bulb and connecting tubes were heated with the Bunsen flame. The sampling bulbs and antimony U-tube were sus-

pended in a movable asbestos trough on the bottom of which lay a close coil of nichrome wire.

Preparation of Samples.—Next was prepared a preliminary series of bulbs to study the analytical process, using for this purpose Kahlbaum's metallic antimony and a good grade of bromine which had been distilled from calcium bromide solution and dried, first with sulfuric acid, and finally with phosphorus pentoxide. The manipulation as finally used in the preparation may well be given in some detail. With the different parts of the apparatus cleaned, dried and sealed together, leaving a small dropping funnel attached to the bromine bulb and an open tube at the upper end of the preparation tube for the introduction of antimony, the apparatus was heated to approximately 300° while a current of dry nitrogen was passed through it for 24 to 36 hours. The preparation tube was then allowed to cool, powdered metallic antimony—freshly dried and cooled in hydrogen—was poured into the preparation chamber and the inlet tube sealed off. The heating was continued for several hours longer, then the preparation tube cooled to 120 – 130° , the sampling bulbs and antimony U-tube reduced similarly and the bromine bulb cooled to room temperature. With the stopcock of the dropping funnel closed and a steady stream of nitrogen maintained, one of the stopcocks was opened to the air so as to obtain atmospheric pressure in the apparatus. Then a little phosphorus pentoxide was placed in the dropping funnel and an amount of dry bromine run in such as would leave several grams of antimony unacted upon. Avoiding introduction of air, the bromine was run into the bulb and the dropping funnel sealed off. Next a large beaker of water was raised under the bromine bulb until the latter dipped well into the water and heat applied till a temperature of 50° to 55° was obtained. This distilled the bromine slowly enough so that it was quite fully taken up by the antimony, only traces getting into the next portion of the apparatus during the latter part of the operation. When the distillation was started the stopcock leading to the air was closed, the nitrogen shut off and the process carried on at ordinary pressure in nitrogen. With 20 to 25 g. of antimony and 10 to 12 cc. of bromine, it required 10 to 15 hours for the synthesis of the antimony bromide. The bromine bulb was then sealed off, the temperature raised to 150 – 160° and the materials allowed to digest for 8 to 12 hours longer. In this way all trace of bromine color disappeared and the melted antimony bromide became light amber-colored. Occasionally slight evidence of action in the antimony U-tube was observed; frequently none was visible.

The preparation tube was next cooled to 130 – 140° , the distilling flask, sampling bulbs and U-tube kept at about 100° and the apparatus then evacuated until the antimony bromide started to distil over into the flask. The heating trough was then permitted to cool down while the

bulk of the antimony bromide was distilled out of the preparation tube. Nitrogen was then carefully admitted to stop the process and to lessen the chance for accident when the preparation tube was sealed off. With the latter done, the apparatus was again evacuated and heat applied until the antimony bromide had largely distilled into the first bulb of the chain. The distilling flask was then sealed off, the apparatus evacuated to a pressure of about 1 mm.—until the antimony bromide, slightly above the melting point, showed signs of distilling—and then the series of bulbs sealed off from the antimony U-tube. This left the bulbs as a single unit which could now be suspended in the heating trough and easily shifted along to cool the bulbs successively, starting at the end opposite the one containing the antimony bromide. Thus, as the material was distilled, successive fractions were obtained, and practice made it possible to regulate the size of these fractions in a satisfactory way.

Further preparations of antimony bromide included two final series using pure bromine and antimony reduced from the oxide by hydrogen, and one final series using pure bromine and antimony reduced from the oxide by fusion with sodium cyanide.

In using Preparations I and II of antimony by hydrogen, it was noticed that the residues in the preparation tube after distilling off the bromide were quite different. The one from antimony reduced in quartz was bright and clean, the other, where the oxide had been reduced on a lime support, being contaminated with a brownish amorphous substance. The preparations of the bromide, however, were both highly lustrous white products of identical appearance. They constituted the material for Series B and Series D, respectively.

In the first preparation of bromide from metal reduced by cyanide, it was found that the final material had a brown tinge. With the series of bulbs still intact the material was melted and poured back into the large bulb and the distillation repeated. The distillate was visibly lighter in color and a black residue was left in the bulb. This process was repeated several times until no further improvement could be noticed. The material still having a faint straw color, the small bulbs were sealed off in groups of two. The bulbs were warmed and the antimony bromide poured into one of them from which about $\frac{2}{3}$ was distilled back into the other. The residue was distinctly dark in color. The final distillate not being entirely white, it was not regarded as satisfactory for final analysis.

Another preparation was made from the same antimony, except that the metal was first kept melted for several hours in a current of hydrogen, with the thought that this might remove, or render harmless, impurities evidently derived from the cyanide fusion. It may be noted, parenthetically, that the usual method of purifying metallic antimony, follow-

ing fusion of the oxide with sodium cyanide, is to maintain the antimony molten for a period of many hours under a layer of the oxide. This was purposely omitted here since it was desired to keep the material as free from oxide as possible and it is not improbable that metallic antimony dissolves the oxide to some slight extent. The antimony bromide prepared from this batch of metal was better than the previous lot, but it still showed a faint color even after repeated redistillation.

The next attempt—the last which could be tried without repeating the earlier process of purifying antimony—added the further precaution of digesting the antimony bromide in the preparation tube for several hours at only slightly below the boiling point under atmospheric pressure, a temperature at least 75° higher than formerly used, or than is needed for any subsequent distillation. It was felt that in this way a decomposition of the objectionable impurity might be accomplished in such a way that gaseous products might still be gotten rid of and non-volatile products retained in the earlier residues. These hopes were rewarded by obtaining a series of samples barely distinguishable from those of Series B and D; so these were labelled Series C and used for final analysis.

Analysis of Antimony Bromide.

With the materials thus at hand, there was started a study of the usual volumetric determination of the ratio of antimony bromide to silver, using the nephelometric end-point, and, further, of the gravimetric determination of the ratio of antimony bromide to silver bromide.

Balance and Weighing.—The balance used was a new Troemner No. 10, easily sensitive to 0.02 milligram. The weights were a set of gold-plated brass weights with platinum fractionals, calibrated by the Bureau of Standards, and carefully rechecked with one another, using the Harvard method. By the method of counterpoises and substitution it was easily possible to check ordinary weights to within 0.02 mg., and, even with a glass vacuum weighing bottle of approximately 50 cc. external volume and weighing slightly over 50 g., extreme errors did not exceed 0.05 mg. for individual weighings. A small amount of radium bromide was kept in the balance case to prevent the objects weighed from retaining electric charges.¹

Vacuum corrections were applied, using the following table, based on average conditions of temperature and pressure (density of air = 0.001173 g.).

Table of Corrections.

Substance.	Mg. per gram.
Silver.....	—0.0285
Silver bromide.....	+0.041
Glass.....	+0.332
Sample in bulb.....	—0.140

¹ Baxter and Tilley, *THIS JOURNAL*, 31, 212 (1909).

For the determination of the density of brass weights used and of the glass from which the bulbs were blown, as well as to avoid determining the volume of each individual bulb, a weighing bottle¹ with well polished and tightly fitting cap, and with stopcock attachment for vacuum connection, was used. By placing object and evacuated weighing bottle on the balance pan and comparing with a counterpoise similar in material and size, a certain difference in weight was obtained. By placing the object in the weighing bottle, evacuating, and comparing again with the counterpoise a certain other difference in weight was obtained, the variation representing the buoyant effect of the air. By observing the temperature and pressure at the time, the volume of the object could be calculated and the density of the material determined. In the case of the samples of antimony bromide only the direct weighing *in vacuo* was needed since this made it unnecessary to apply a correction for buoyancy of the air, other than that exerted on the brass weights. The weight was obviously obtained by comparing the evacuated weighing bottle empty with the evacuated weighing bottle containing the sample and subtracting from this the vacuum correction for the weights used.

As evidence of the accuracy with which the weight *in vacuo* may thus be determined a piece of glass rod was weighed in air, its volume determined by displacement of water and a vacuum correction calculated, the weight thus found being compared with that obtained by the method outlined.

(a)	Apparent weight in air.....	3.17303 g.
	Vacuum correction.....	+0.00105
		3.17408
	Weight <i>in vacuo</i>	3.17408
(b)	Direct weighing <i>in vacuo</i> wts.....	3.17448 g.
	Correction.....	-0.00044
		3.17404
	Weight <i>in vacuo</i>	3.17404

The weight of the sample in the bulb having been obtained, the bulb was placed in a tall, narrow, thick-walled beaker and covered with a freshly prepared and filtered solution of tartaric acid, allowing 3 to 4 g. of acid for each estimated gram of antimony bromide. Using a heavy platinum rod, the bulb was then broken, the rod thoroughly rinsed and removed, and the solution allowed to stand with frequent agitation until all of the antimony bromide had dissolved, an additional time of 6 to 12 hours being allowed to complete solution. The broken glass was then filtered out, being washed 3 times by decantation with dil. tartaric acid solution and then 10 to 12 times with water before transferring to the filter. Following ignition and cooling, the weight of the glass was found and this subtracted, after correction to vacuum, from the weight given, to obtain

¹ Renard and Guye, *J. chim. phys.*, **14**, 57 seq. (1916).

the weight of the antimony bromide. The empty space in the bulb introduced no appreciable error, since the bulbs were well evacuated.

The use of filter paper to retain the glass, with correction after ignition for the ash of the paper, was given up when it was found that the ash of a single 9 cm. paper of one brand of "ashless" filters might run as high as 0.4 mg., that even with the best grades the ash of papers from different parts of the package might vary as much as 0.05 mg., and that there was no obvious relation between the weight of the filter paper and that of the ash.

A platinum-sponge filtering crucible was next tried and found entirely satisfactory. With reasonable attention to the conditions of drying the crucible before and after filtering, it was found possible to check its weight regularly to within 0.02 mg. When the crucible became clogged with the fine glass particles it was easily cleaned by soaking in hydrofluoric and nitric acids, followed by washing with hydrofluoric acid and then copiously with water.

Methods of Analysis.—With the weight of the samples known, the usual Harvard refinements¹ on the method of Pelouze were carried out. Assuming a value for the atomic weight of antimony, an amount of silver was weighed out corresponding to slightly less than the sample under examination. This was dissolved in pure dil. nitric acid in Jena Erlenmeyer flasks provided with refluxing bulbs, the reaction being carried out slowly, and the temperature being raised finally to remove the nitrous fumes.

In filtering out the glass, the filtrate had been collected in 3-liter Erlenmeyer precipitation flasks provided with well-polished glass stoppers. To the solution, diluted to about 0.1 *N* concentration with respect to bromide ion, was added the silver nitrate solution, carrying out this operation at night under red light. All processes of transfer of materials, filtering and washing, taking test portions, etc., involved in the analysis of the samples, took place under the cover of a large sheet of glass fastened over the desk adjacent to a vertical pane which diminished drafts from the side.

With the silver nitrate solution added, the flask was warmed slightly by the hands, then the stopper inserted, and the flask shaken vigorously for several minutes. It was then wrapped carefully in a black cloth as protection from the light during the day. The solution was shaken occasionally during 36 hours and permitted to settle for 10 to 12 hours, then samples were taken for nephelometric examination. According to the conditions observed, dilute standard solutions of silver nitrate and of potassium bromide were used to make up any slight deficiency of silver or bromide ion. The shaking process was repeated and the solution

¹ Described in detail by Richards and Wells. *THIS JOURNAL*, 27, 502 *seq.* (1905).

again tested 2 days later. With equivalence of silver to bromide finally obtained—a condition in which 2 equal portions of the solution develop equal opalescence when treated with equivalent excess of silver nitrate and potassium bromide, respectively—corrections were applied for all adjustments required, including material removed in the sampling, and weights were obtained representing the ratio $\text{SbBr}_3 : 3\text{Ag}$.

To the above solution was then added about 50 cc. of 0.1 *N* silver nitrate solution. The flask was shaken for a short time and allowed to stand for 3 or 4 days with occasional agitation. The clear solution was then poured through a platinum-sponge filtering crucible, the precipitate of silver bromide washed 15 times with approximately 1% nitric acid and finally transferred to the crucible with this same solution under hydrostatic pressure. After rinsing twice with water, the precipitate was dried overnight at 180°, cooled and weighed. The bulk of the precipitate was transferred to a quartz crucible, weighed, fused with cover on in an electric furnace, cooled and reweighed, and the loss on fusion calculated to the basis of the total weight of dried silver bromide. The crucible in which the silver bromide had been dried was conveniently cleaned by treatment with powdered zinc in slightly acid water, then rinsed thoroughly, and treated successively with nitric acid, and ammonium hydroxide. It was then washed copiously and dried. Meanwhile the precipitation flask was treated with 25 cm. of ammonium hydroxide, allowed to stand overnight, then rinsed out, the rinsings being diluted to a known volume and tested for silver ion by comparison with a standard similarly prepared. A correction for silver bromide in the flask was thus obtained. The weight of the silver bromide, with proper correction for material retained in the precipitation flask, for loss on fusion, and for adjustments of the solution in the volumetric determination gave a basis for calculating the ratio $\text{SbBr}_3 : 3\text{AgBr}$.

Preliminary Studies.—Using the introductory preparation of antimony bromide derived from Kahlbaum's antimony, the above analytical process was studied. This series of bulbs had totaled 7, so, discarding the first and last, there were 5 bulbs representing in numerical order the middle portion of the preparation.

The volumetric determination ran smoothly after it had been found by experience that an external standard had to be set up to determine with reasonable accuracy the concentration of bromide ion in the solution. The use of such external standard was adopted at the start in accordance with general practice.¹ But the idea suggested itself that there is an inevitable error in adjusting concentrations of the various materials in such a way as to duplicate the conditions present in the solution being examined. And as a means of avoiding such error it seemed feasible to

¹ Richards and Wells, *Am. Chem. J.*, **31**, 242 (1904); Richards, *ibid.*, **35**, 512 (1906).

take two portions of the solution, treating one with silver nitrate and the other with an equivalent amount of potassium bromide and then match opalescence by adding to the weaker one sufficient silver ion or bromide ion as the case might be. Then if the original solution showed deficiency of silver ion the amount of silver ion added to the tube containing potassium bromide in matching the other tube would give a basis for estimating how much silver ion should be added to the solution in the flask. That this scheme did not work may be seen in the following data concerning one of the determinations.

SUCCESSIVE ADDITIONS OF SILVER ION CORRESPONDING TO INDICATIONS IN
TEST SOLUTIONS.

Date.	
2-19-20.....	+0.40 mg. Ag
2-24-20.....	+0.40
2-27-20.....	+0.40
3-2-20.....	+0.20
3-4-20.....	equilibrium

In attempting to account for this unexpected behavior, a brief study of the effect of tartaric acid on the determination of silver ion and of bromide ion was undertaken. The results may be summarized as follows. Tartaric acid does not affect appreciably the determination of small amounts of silver ion. It does, however, affect the determination of small amounts of bromide ion, the effect, strangely enough, decreasing with decreasing concentration of bromide ion. So, while the above scheme did not work satisfactorily for the determination of bromide in amounts ranging over 0.25-0.30 mg. per liter, yet for the lower concentrations corresponding to a saturated solution of silver bromide the nephelometric end-point was shown to be reasonably accurate.

The volumetric data on the preliminary series is given in the following table, the bulbs being analyzed in the order in which they were collected.

TABLE I.—ANALYSES OF ANTIMONY TRIBROMIDE FROM KAHLBAUM'S ANTIMONY.

	Wt. sample.	Wt. silver.	Ratio SbBr:3Ag.	At. wt. antimony.
I.....	2.54052	2.27493	1.11675	121.675
II.....	3.86859	3.46507	1.11645	121.577
III.....	4.07278	3.64722	1.11668	121.651
IV.....	3.80772	3.40997	1.11664	121.638
V.....	4.72332	4.23070	1.11644	121.574
	<hr/>	<hr/>	<hr/>	<hr/>
		Average	1.11663	121.623

The atomic weight of antimony is calculated on the basis of $\text{Ag} = 107.880$, using Baxter's ratio $\text{Ag} : \text{AgBr} = 0.57445^1$ as an intermediate step.

The gravimetric determinations of the antimony ratio in the preliminary series were all unsatisfactory for various causes which were systematically

¹ Baxter, *THIS JOURNAL*, 28, 1322 (1906).

eliminated. In earlier analyses, black spots in the fused silver bromide frequently showed inaccuracy in the composition of the precipitate, and heating such a precipitate in chlorine to convert any silver bromide and metallic silver to silver chloride gave variable results indicating the presence of small amounts of other volatile material, probably antimony compounds.

With errors in manipulation corrected, it seemed desirable to test the method and gain additional experience by carrying out a few analyses on material of known composition. For this purpose some of the potassium bromide was used that had been prepared in one of the last steps of purifying bromine. A sample was dried by fusing in platinum, then dissolved in water, diluted to one liter, and a solution of 15 g. of tartaric acid added. Then the usual determinations of the ratios, potassium bromide to silver and potassium bromide to silver bromide were carried out. The results follow.

Wt. KBr = 6.01916; Wt. Ag = 5.45519; Wt. AgBr = 9.49639. Ratio KBr : Ag = 1.10336; Ratio KBr : AgBr = 0.63387. Ratio Ag : AgBr = 0.57445.

By comparison with the following ratios by Richards and Mueller,¹ $\frac{\text{KBr}}{\text{Ag}} = 1.10319$; $\frac{\text{KBr}}{\text{AgBr}} = 0.63373$; and with the ratio by Baxter, Ag : AgBr = 0.57445, it may be seen that the material contained slightly less than the required amount of bromine, unless, indeed, the tartaric acid present was preventing an accurate determination of bromide by either the volumetric or the gravimetric method. Also the ratio of silver required to silver bromide obtained checked exactly that obtained by Baxter in determining the atomic weight of bromine. The fused silver bromide was a clear amber-colored mass.

To check up still more closely the possible effect of tartaric acid two more of the volumetric determinations were carried out on potassium bromide, tartaric acid being present in one case and absent in the other. The samples were dried first by fusion in nitrogen.

	1. Tartaric acid absent.	2. Tartaric acid present.
Wt. KBr.....	3.34853	3.54828
Wt. silver.....	3.03532	3.21617
Ratio KBr/Ag.....	1.10319	1.10326
Wt. AgBr.....	5.59914
Ratio KBr/AgBr.....	0.63372 ^a
Ratio Ag/AgBr.....	0.57440

^a Fused AgBr not clear.

In the case of No. 1 a slight mechanical loss of silver bromide spoiled the gravimetric determination, but the silver bromide was nevertheless dried and fused in quartz to determine its appearance. As a further check

¹ Richards and Mueller, THIS JOURNAL, 29, 652, 654 (1907).

on the purity of the amber mass the silver bromide was then fused in chlorine.

Wt. silver bromide.....	5.01673
Wt. final residue.....	3.82902
Ratio.....	1.31019
Correct ratio AgBr : AgCl.....	1.31018 (determined by Baxter).

The exact agreement of the volumetric ratio with that of Richards and Mueller may have been somewhat fortuitous, but the data have distinct bearing on the purity of the silver. The close check of the ratio of silver bromide to silver chloride with that of Baxter, favored as it is by the fact that no transfer of material is involved in its determination, gives evidence of the purity of the silver bromide.

Furthermore, it appears from No. 2 that there may be some slight effect of tartaric acid in rendering the determination of bromide inexact, though the material was not prepared and handled throughout with the care required to assign positive significance to the difference between the two ratios 1.10326 and 1.10319, which vary from each other by less than 7 parts in 100,000. Nor is there the concordant series of analyses that would be required to establish such a difference. At its maximum, assigning full weight to the earlier determination where less care was taken to protect the material during the drying process, the error would not be over 1 part in 10,000.

Qualitative testing of dilute bromide solutions in the nephelometer failed to reveal corroborating data.

It is of interest that in recent work on the atomic weight of tin¹ in which the chloride and the bromide were prepared and analyzed by methods similar in principle to the one here used, mention is made of the possibility of interference due to tartaric acid, but it is dismissed as improbable. The close agreement of the work of Brauner and Krepelka and that of Briscoe with that of Baxter and Starkweather² establishes the fact that any error from such source must be very small.

Since a further testing out of this point would need to be supplemented by a series of tests concerning the possible influence of antimony on the nephelometric end-point if experimental completeness were to be attained, while the error in the accepted atomic weight of antimony is of gross rather than microscopic magnitude, it seemed not illogical to leave such refinements for later study.

Concerning the gravimetric determination of the ratio of potassium bromide to silver bromide in the presence of tartaric acid, it may be noted that the numerical value checks Mueller's work closely, but the fused mass

¹ Briscoe, *J. Chem. Soc.*, 107, 76 (1915); Brauner and Krepelka, *THIS JOURNAL*, 42, 924 (1920).

² Baxter and Starkweather, *Proc. Nat. Acad. Sci.*, 107, 76 (1915); *THIS JOURNAL*, 42, 905 (1920).

was not clear, distinct dark patches being present. This had been associated by experience with an overweight of precipitate, so the data are chiefly of value in showing the readiness with which slight impurity in the silver bromide can be recognized by obvious defects in the fused mass.

With further experience thus accumulated, with every confidence in the purity of the silver and the bromine, and with renewed assurance as to the accuracy of the volumetric determination, attention was turned to the analysis of the three carefully prepared series of antimony bromide samples.

The manipulation involved in the final analyses was not altered in any essential detail from that already described in connection with the preliminary series. The greater uniformity of results is due, undoubtedly, to increased skill in manipulation acquired during the earlier work. The slightly higher value may well be due to purer materials being combined in the preparation of these final series.

Final Analyses.—Series B and D were prepared from antimony obtained by reducing the oxide in hydrogen. Series C was prepared from antimony obtained by fusing the oxide with sodium cyanide.

TABLE OF FINAL ANALYSES.
Summary of Series B (by hydrogen).

Sample No.	Weight.	Wt. Ag.	Ratio I SbBr ₃ :3Ag.	At. wt. Sb from R I.	Wt. AgBr.	Ratio II SbBr ₃ :3AgBr.	At. wt. Sb from R II.	Ratio Ag:AgBr.
I	4.17410	3.73672	1.11705	121.771	6.50517	0.641659	121.774	0.57442
III	4.97693	4.45524	1.11710	121.787	7.75589	0.641697	121.775	0.57443
IV	5.97344	5.34702	1.11715	121.803	9.30873	0.641703	121.759	0.57441
V	5.65589	5.06310	1.11708	121.781	8.81443	0.641663	121.756	0.57441

Average 1.117095 121.786 0.641680 121.766 0.574418

Summary of Series C (by cyanide).

I	3.64686	3.26462	1.11709	121.784	5.68301	0.641713	121.784	0.57445
III	3.64435	3.26258	1.11701	121.758	5.67970	0.641645	121.746	0.57443
IV	3.35749	3.00574	1.11703	121.765	5.23284 ^a	0.641619 ^a	(121.731)	0.57440 ^a
V	2.92082	2.61469	1.11712	121.794	4.55149	0.641728	121.793	0.57445

Average, 1.117063 121.777 0.641679 121.764 0.574433

Summary of Series D (by hydrogen).

I	3.39050	3.03541	1.11699	121.752	5.28506 ^a	0.641525 ^a	(121.678)	0.57434 ^a
II	4.32024	3.86739	1.11709	121.784	6.73334 ^a	0.641619 ^a	(121.731)	0.57436 ^a
III	4.70518	4.21221	1.11703	121.765	7.33279	0.641663	121.756	0.57443

Average 1.117037 121.767 0.641602 121.722 0.574377

^a Silver bromide showed dark specks when fused.

Average of 11 vol. det. = 121.777.

Average of 11 grav. det. = 121.753.

Average of 8 grav. det. = 121.768.

Average of 11 vol. det. and 11 grav. det. = 121.765.

Average of 11 vol. det. and 8 grav. det. = 121.773.

Series B was from Preparation I of antimony (reduced in quartz). A total of 7 bulbs was collected, the first and last being discarded. The numbers in the series represent the bulbs in the order in which they were filled. No. 2 was spoiled in the analysis.

Series D was from Preparation II of antimony (reduced on a lime support). A total of 9 bulbs was collected. No first sample was discarded. The numbers in the series represent the bulbs in the order in which they were filled. No. 2 was lost in the analysis.

Series C was from Preparation III of antimony. A total of 10 bulbs was filled, Nos. 5 and 6 being lost in sealing up. No first sample was discarded. The numbers in the series represent the bulbs in the order in which they were filled.

It is noted that the volumetric result on each sample is checked more closely by the corresponding gravimetric result, when the fused silver bromide was clear, than by the other volumetric results within the series. Therefore, it seems proper to refer the small variations among the different samples, less to the analytical process following the filtering of the solutions, than to slight deviations in accuracy of weighing, in accuracy of applying vacuum corrections and in accuracy of the whole manipulation from the breaking of the bulb to the washing of the glass.

It is customary to attempt to reduce the magnitude of individual errors to one part in 100,000. Assuming that the volumetric determinations are slightly more accurate than the gravimetric determinations, it is to be observed that the maximum variation among the ratios calculated for $\text{SbBr}_3 : 3\text{Ag}$ is from 1.11715 (maximum) to 1.11699 (minimum), a variation of 14.3 parts in 100,000. With the complexity of manipulation involved in the analytical procedure, this may be regarded as representing a concordance comparing favorably with other atomic weight work of the present day.

The mean of Series B varies from that of Series D by 5.2 parts in 100,000, while the average of Series B and D varies from the mean of Series C by only 0.27 part in 100,000.

In calculating atomic weights from analytical data of the halide to silver or silver halide type, it is to be noted that variation in the ratio is multiplied by the valence of the metal. The 11 volumetric determinations average 121.777 with a so-called "probable error" of 0.003, while the 8 acceptable gravimetric determinations average 121.768 with a "probable error" of 0.004.

The average from 11 volumetric and 8 gravimetric determinations is 121.773, the most probable atomic weight of antimony.

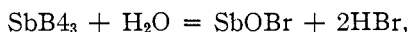
Note on Cooke's Bromide.

Since the number assigned as the atomic weight of antimony has for many years been based on the work of Cooke in which a material, given

the formula SbBr_3 , was analyzed for bromine; it is peculiarly of interest that in the work here reported a material of the same assigned formula has been studied. Careful examination of Cooke's paper makes it evident that the difference must be assigned chiefly to the compositions of the materials studied rather than to later refinements of the analytical process. Cooke's method of preparation included repeated distillation from metallic antimony, several recrystallizations from carbon disulfide, and repeated fractional distillation. In the last work this product was twice sublimed in a current of carbon dioxide. In the earlier work the recrystallized material was analyzed. The average results were the same, though the variations were large in the earlier work. The description of the whole process, however, shows that all handling of material involved exposure to air and that, in the earlier part of the preparation, there was considerable opportunity for the absorption of moisture. Furthermore, while the carbon dioxide used in the process of sublimation is described as "absolutely dry," careful search fails to reveal the use of drying agents other than sulfuric acid followed by calcium chloride. Nor is any statement made as to method of drying, distilling flasks, receivers, etc. Aside, therefore, from carbon disulfide, used in the recrystallization, the chief difference between the preparation by Cooke and that just described would appear to lie in the relative exposure to moisture.

In the work just completed, probably greater care has been taken in the drying of the initial materials and apparatus than has been described in the recent work on the halides of phosphorus and of tin where the results of analyses have been regarded as entirely trustworthy.

It may be worth while to suggest a way in which moisture might account for the difference obtained. Assuming the reaction



and knowing the readiness with which complex bromides are formed, it is possible that the process of crystallization and distillation may leave a product containing a small amount of hydrobromic acid. During the sublimation this may again condense with the crystals in the receiver; or from incomplete drying of the carbon dioxide, a trace of moisture interacting with the molten antimony bromide may supply extra hydrogen bromide such that the amount retained by the sublimate is the same as that in the original material.

Direct comparison of the bromine content to correspond to the two values for the atomic weight gives the following:

Atomic weight.	% bromine.
120.0	66.643
121.77	66.317

Difference, 0.328

If this difference is assumed to be due to the cause suggested the material studied by Cooke had the approximate composition, 99% SbBr_3 , 1% HBr .

Summary.

In an all-glass apparatus, 3 preparations of antimony were combined with bromine, the resulting product twice distilled under a pressure of 5 to 10 mm. while gaseous materials could yet be removed, then distilled a third time under less than one mm. pressure into a series of small bulbs which were sealed off from each other as individual samples. From the time the pure dry materials were placed in the apparatus till the bulbs were broken under tartaric acid solution, only inert gases came into contact with the preparation. The resulting product was analyzed for bromine in two ways; first, by finding the amount of silver equivalent to the sample in the usual way; second, by adding excess of silver nitrate, then filtering out and weighing the silver bromide. Precautions taken and corrections applied include all described within recent years in similar work. In eleven analyses a total of 46.76580 g. of antimony bromide required 41.86463 g. of silver and formed 72.88245 g. of silver bromide. The ratios are 1.117074 and 0.641611, from which the respective values for the atomic weight of antimony would be 121.799 and 121.755. If for the antimony bromide to silver bromide ratio samples C-IV, D-I and D-II are omitted since in these cases the fused silver bromide did not give a clear mass, the weights would be 35.69757 g. of antimony bromide to 55.63121 g. of silver bromide, corresponding to an atomic weight of 121.767. The ratios of silver to silver bromide are 0.574413 and 0.574427, according to whether the imperfect silver bromide determinations are included or omitted. Baxter's determinations of this ratio gave 0.57445. Averaging the volumetric results for the 11 samples with the gravimetric results for 8 samples, the most probable atomic weight for antimony (assuming $A_g = 107.880$) becomes 121.773.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE MASS EFFECT IN THE ENTROPY OF SOLIDS AND GASES.

By WENDELL M. LATIMER

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The Third Law of Thermodynamics, by means of which the entropy of a substance may be calculated from specific heats, has made possible the determination of free energy changes in chemical reactions from thermal data alone. However, the difficulties involved in the accurate measurements of specific heats at low temperatures are so great as to make highly desirable some method of calculating the entropy of a substance from other physical quantities. Many attempts in this direction have been made. A large number of these, including the determination