

concerned. The volume of the air current used was measured, not by use of an aspirator as is customary, but by weighing the water it evaporated at 25° from a water saturating train described in another place,<sup>1</sup> where also necessary precautions and corrections are referred to. Preliminary experiments having shown that an air speed of half a liter per hour gave saturation, the experiment was continued for 5 days in order to obtain a satisfactorily large loss of weight (5 mg.) from the saturator. On account of fluctuation in the barometric pressure over this period, the suitably weighted mean of many observations of the actual temperature of the saturator tube was employed. This was 99.5°, while the found vapor pressure was 0.102 mm. The vapor pressure for 99.5° as read from the curve given by the previous observations is 0.104, thus showing a degree of concordance rather closer than could be anticipated.

Either the assumptions involved in the application of each of the 2 methods are justified in this instance, or else the error is fortuitously the same for both in direction and amount. Further comment is reserved for a later publication.

#### Summary.

A method has been outlined by which low vapor pressures may be measured by the help of a single McLeod gage. This method is much more expeditious than the gas-current saturation method but, like it, is of accuracy subject to the truth of certain assumptions. Its application, with certain precautions necessary to its use, has been illustrated in the case of T. N. T., whose vapor pressures are here reported for each degree from 82° to 102°.

PRINCETON, N. J.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

### A REVISION OF THE ATOMIC WEIGHT OF ALUMINUM. THE ANALYSIS OF ALUMINUM BROMIDE. PRELIMINARY PAPER.

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The usually accepted atomic weight of aluminum (27.1) is based chiefly on the work of J. W. Mallet,<sup>2</sup> published in 1880. The earlier researches of Davy, Thomson, Berzelius, Mather, Dumas, Tissier, and Terreil regarding this subject were considered carefully in Mallet's paper and therefore need not be detailed here. Those of Isnard and Baubigny are sufficiently described by Clarke,<sup>3</sup> who gives the bibliographical references to

<sup>1</sup> Menzies, *THIS JOURNAL*, 42, 978 and 1953 (1920).

<sup>2</sup> Mallet, *Phil. Trans.*, 171, 1003 (1880).

<sup>3</sup> F. W. Clarke, "Recalculation of Atomic Weights," *Smithsonian Inst. Pub.*, 54, No. 3, 262 (1910).

all the early work. Of course such methods as ignition of aluminum sulfate (Berzelius and Baubigny) or conversion of the metal into nitrate and then into oxide (Tissier and Isnard) are not now acceptable for this purpose. Likewise, the analysis of aluminum halide as it was carried out by Mather<sup>1</sup> and even by Dumas<sup>2</sup> must have given wrong values, because the old method of precipitation and titration of halides was very faulty. The completion of the reaction cannot be accurately ascertained simply by the addition of a standard solution of silver until turbidity is no longer evident. In those days, moreover, no attention was given to the adsorption or occlusion of the dissolved substances by silver chloride in concentrated solutions.

Mallet's work was much more convincing; indeed, it was remarkably good for that time, and received general acclaim. He used 3 methods. First, pure ammonium alum was ignited and the remaining oxide was weighed. Second, aluminum bromide was titrated with a solution of pure silver. Third, metallic aluminum was dissolved in sodium hydroxide solution and (a) the volume of the hydrogen evolved was measured; again (b) the hydrogen set free was oxidized and weighed as water.

The difficulties connected with the first method were recognized by Mallet himself; it is probably impossible to free ammonium alum from traces of hygroscopic water without loss of crystal water. Two series of experiments with this compound were performed and gave for the atomic weight value 27.153 (as recalculated by F. W. Clarke).<sup>3</sup>

The second method was more promising. Aluminum bromide was prepared on a large scale (more than one kg.), no attention being paid to the purity of the factors (aluminum metal and bromine). The bromide obtained was purified by repeated fractional distillation. The arrangement of Mallet's apparatus caused every successive fraction, except the last one, to come into contact with the outside air, causing formation of oxybromide and acid gas. The contamination of the final portion with oxybromide was not necessarily prevented by the last distillation in a current of nitrogen, because the source of nitrogen used by Mallet in his work was not clearly explained and no evidence is given that it was free from oxygen and moisture. Either impurity would tend toward an elevation of the apparent atomic weight. Likewise his method of breaking the tubes containing aluminum bromide would have the same effect; for he opened his tubes in the air of the room; and by this operation, even working quickly (according to our experience) he must have lost hydrobromic acid. The possible errors tending in the opposite direction were

<sup>1</sup> Mather, *Am. J. Sci.*, **27**, 241 (1835).

<sup>2</sup> Dumas, *Ann. chim. phys.*, [3] **55**, 151 (1859).

<sup>3</sup> F. W. Clarke, "The Constants of Nature," Part V, "A Recalculation of the Atomic Weights," p. 264.

less significant, since titration is far more accurate with bromide than chloride, even as formerly carried out, and since the silver employed could hardly have contained an important amount of impurity, having been carefully prepared and fused in a Sprengel vacuum. Hence his value might be expected to be too high. This series of experiments gave the value 27.098.

The experiments designed to determine the amount of hydrogen evolved by the solution of metallic aluminum were less fortunate. Impurity in the metal, hydrogen dissolved in the solution of sodium hydroxide, and the unknown tension of the water vapor of this strong solution were possible sources of error which could not be eliminated by the use of large quantities of substance. This set of experiments gave the value 27.099 for the atomic weight. The modification of this method, in which the hydrogen was weighed as water after oxidation, was subject to some of the same errors, together with others.

Nevertheless, in some respects Mallet's work deserves the commendation which it has received for 40 years. He duly considered many details of accurate weighing, and of precision in chemical operations. Because of the numerical agreement of the results obtained by the different methods, the international committee, having to choose between the value of Mallet and the more recent work of Thomsen<sup>1</sup> (26.99), accepted the former. Nevertheless Thomsen's work (which resembled the third series of Mallet) was more carefully executed than Mallet's. He used larger amounts of material, and weighed the loss of dry hydrogen from his apparatus as well as the oxygen needed to oxidize it. Careful corrections were made for the iron and silica found among the products of the reaction, and for the contraction occurring when the metal is dissolved. The fact that his method stood alone whereas Mallet had 4 more or less confirmatory series, doubtless militated against Thomsen's outcome, as already stated.

The most recent determination of the atomic weight of aluminum was performed by Kohn-Abrest.<sup>2</sup> Impure aluminum (98.68%) was dissolved in hydrochloric acid, the hydrogen evolved was burned by the copper oxide, and the resulting water was weighed. Again, impure metal was converted into oxide. The results were, respectively, 27.25 and 27.23. Kohn-Abrest used methods of an early period (without modern precautions), which are sufficiently characterized by Brauner.<sup>3</sup>

Of all the methods used for the determination of the atomic weight of aluminum undoubtedly the best is the analysis of pure halide, which has

<sup>1</sup> Thomsen, *Z. anorg. Chem.*, **15**, 447 (1897).

<sup>2</sup> Kohn-Abrest, *Bull. soc. chim.*, [3] **33**, 121 (1905).

<sup>3</sup> See Brauner's article in Abegg's "Handbuch der anorg. Chemie," "At. Weight of Aluminum," III, (1), 59 (1906).

been in contact only with pure, perfectly dry nitrogen and has finally been redistilled *in vacuo*. Either the chloride or the bromide is suitable for analysis; the iodide is unstable, forming an explosive mixture with air.

We followed Mallet's example and used the bromide, because its properties are more convenient than those of the chloride. Its lower melting-point ( $93^{\circ}$ ) and relatively lower heat of formation are convenient in both synthesis and purification. The great difference between its melting-point ( $93^{\circ}$ ) and boiling-point ( $265^{\circ}$ ) gave a wide range for digestion of the liquid in a current of nitrogen in order to effect the elimination of bromine and other volatile impurities. Bromine has less tendency to attack glass than chlorine: another advantage. Finally, the small solubility of silver bromide facilitates accuracy in the analysis of the salt. On the other hand, the bromide, of course, has one disadvantage as material for atomic weight determination, the smallness of its content of aluminum magnifies the effect of any error.

#### Preparation of Materials.

**Aluminum.**—The task of preparing this metal in a perfectly pure state presented so many almost insuperable difficulties that we decided to use raw material of only moderate purity, and devote our available time to purifying the bromide made from it. Accordingly the best commercial sample which we were able to obtain was used in the final synthesis: namely, a standard sample of aluminum<sup>1</sup> made available by the Bureau of Standards. As the sample was in the form of a cylinder about 5 cm. in diameter, it was first sawed into thin disks about 3 mm. in thickness. In order to remove any surface contamination (derived from the saw) these disks were set in de Khotinsky cement and turned smooth on a lathe. The polished pieces were then washed in alcohol and cut with clean steel shears into strips about 8 mm. wide. These strips were made the anode in a very dilute solution of sulfuric acid in order to facilitate the removal of a possible trace of iron on the surface, and were then etched with dil. hydrobromic acid, washed many times with boiling distilled water and finally dried in an air-bath at  $120^{\circ}$ . Any trace of remaining iron must have been removed together with bromide of silicon during the fractional distillation which followed, as described below.

**Bromine.**—Ordinary c. p. bromine was twice redistilled from a concentrated solution of pure potassium bromide. The middle portion of the second distillate was allowed to react with a solution of pure potassium oxalate. The potassium bromide thus formed was twice recrystallized. In order to remove any iodine which might be present the solution of potassium bromide was digested and evaporated to dryness twice with a little

<sup>1</sup> According to the analysis made by the Aluminum Co. of America, this aluminum contained 99.71% Al, 0.02% Cu, 0.12% Li, 0.15% Fe (*Circular* of the Bureau of Standards, No. 66).

sulfuric acid and potassium dichromate. Organic matter was removed from the dry bromide by fusion in an electric furnace. From the diluted solution of this fused bromide, the bromine was set free by means of the calculated amount of sulfuric acid and pure potassium dichromate. The bromine thus obtained was dried as usual with calcium bromide and phosphorus pentoxide twice resublimed.

**Nitrogen.**—The nitrogen was generated in an apparatus which is generally used at Harvard. A current of air was passed through concentrated ammonia water, over red-hot copper gauze, through dil. sulfuric acid, over red-hot copper oxide, and once more over red-hot copper. The nitrogen was then thoroughly dried (finally with resublimed phosphorus pentoxide) and when tested with alkaline pyrogallol was found to contain no appreciable trace of oxygen.

**Phosphorus pentoxide** used was resublimed twice in an electrically heated Pyrex tube.

**Silver** employed in this investigation was a preparation made by H. H. Willard, remaining from his work in collaboration with one of us upon the atomic weight of lithium.<sup>1</sup> Samples A and B were employed. The preparation of this silver has been fully described both in the place indicated and in an earlier article,<sup>2</sup> so that further description is unnecessary, except perhaps to state that it was precipitated from silver nitrate by ammonium formate, and fused on lime in a current of hydrogen—all the materials being very pure. The 2 samples (which had been kept more than 10 years in a closed desiccator over fused caustic alkali) were washed in pure ammonia, dil. nitric acid, ammonia again, and much pure distilled water. The clean metal was dried in an electric air-bath at 150°.

**Sulfuric acid and nitric acid** were twice distilled. The nitric acid was nephelometrically tested.

**Potassium dichromate**, C. P., was 3 times recrystallized.

**Potassium oxalate** was prepared by the neutralization of pure oxalic acid by twice recrystallized, C. P., potassium carbonate, the resulting oxalate being recrystallized 3 times.

**Distilled water** was prepared from ordinary distilled water by 2 additional distillations, first from alkaline potassium permanganate solution and secondly from a trace of sulfuric acid.

#### **Apparatus for the Synthesis of Aluminum Bromide.**

Two preliminary trial syntheses (the first with less pure aluminum and bromine) were made to determine the best conditions of working and to study the difficulties to be overcome. The original apparatus was very similar to that used in the final synthesis—but some details of the final

<sup>1</sup> Richards and Willard, *THIS JOURNAL*, 32, 18 (1910).

<sup>2</sup> Richards and Wells, *ibid.*, 27, 472 (1905).

arrangement were added in the light of the experience obtained in these earlier experiments. The final form is illustrated in the diagram. The whole apparatus used for the syntheses and for nitrogen was made of glass and sealed together. Where stopcocks for the gas connections were necessary, vacuum stopcocks were used and were lubricated with viscous syrupy phosphoric acid made by moistening phosphorus pentoxide very slightly with water. The caps in which mercury is generally placed were filled with paraffin which was melted when it was necessary to turn the cock. In the train through which the aluminum bromide was distilled, only magnetic valves were used instead of stopcocks.

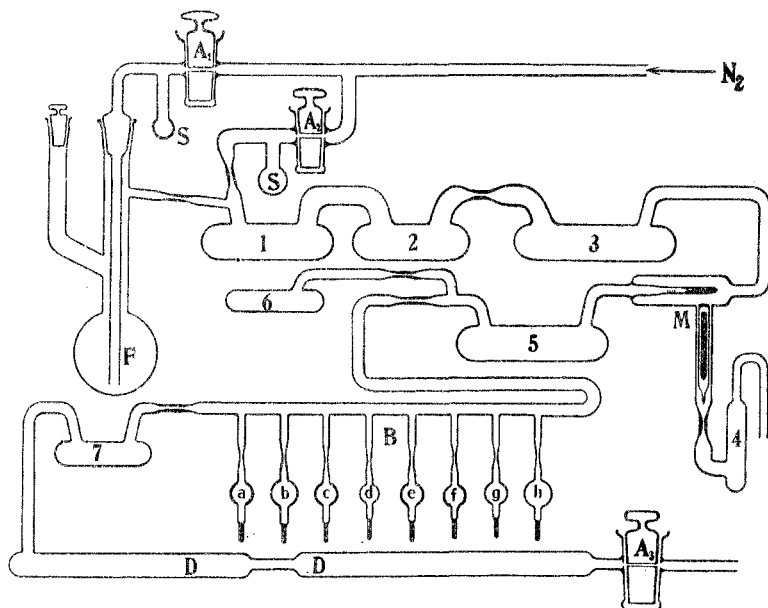


Fig. 1.

The Magnetic Valve *M* in Fig. 1, was a Richards-Craig<sup>1</sup> modification of a device of Briscoe's.<sup>2</sup> A small closed tube containing an iron nail was used as a hammer, actuated by a very strong electromagnet, in order to break the capillary.

**Sampling Bulbs.**—The bulbs used for taking samples were not exactly of the shape used by Baxter and Moore,<sup>3</sup> but were rather like those used by Richards and Craig in an analysis of gallium chloride.<sup>4</sup> They were made of soft glass with heavy walls and had tubes extending on opposite sides. These 2-necked bulbs had the following advantages: first, they

<sup>1</sup> T. W. Richards and W. M. Craig, *THIS JOURNAL*, **41**, 131 (1919).

<sup>2</sup> H. V. A. Briscoe, *J. Chem. Soc.*, **107**, 73 (1915).

<sup>3</sup> G. P. Baxter and C. J. Moore, *THIS JOURNAL*, **34**, 1648 (1912).

<sup>4</sup> *Loc. cit.*

were easily broken at the necks; second, no fine pieces of glass resulted from breaking them, and third, the solution of the substance within them could be controlled easily and the bulb could be drained completely. After washing and steaming the separate parts of the apparatus, they were sealed together with great care.

#### Synthesis of Aluminum Bromide.

The synthesis of aluminum bromide was effected in this apparatus by allowing dilute bromine vapor to react upon metallic aluminum. Thus the violent reaction which results when the bromine is liquid is prevented. The metal had been introduced into the vessels No. 1 and No. 3 before these parts had been sealed to the system. The part of the apparatus comprising Bottle F, Vessels 1, 2, 3, Magnetic Valve M, Vessel 4, and drying tubes (cut off from the sample bulbs by means of the valve M), communicated with the outside air beyond Vessel 4 through a phosphorus pentoxide tube, 2 tubes of calcium bromide and a washing flask with distilled sulfuric acid. This part of the apparatus was dried by moderate heating while a current of dry nitrogen was passed through it. The other part, containing Vessels 5, 6, the series of sampling bulbs, *a* to *h*, Vessel 7, and 2 phosphorus pentoxide Tubes (D,D) with vacuum Stopcock A<sub>3</sub>, was dried by heating and repeated evacuation.

Before starting the reaction, pure dry nitrogen was passed for 2 hours through the stopcock A<sub>1</sub> (Stopcock A<sub>2</sub> being closed), the empty flask F and the first part of the apparatus as mentioned before. After proving that the apparatus was completely filled with pure nitrogen, the flask F was filled with pure bromine in the following manner. The stopcock A<sub>1</sub> was turned off and Stopcock A<sub>2</sub> opened, the nitrogen stream through the reaction tubes, 1, 2, 3, etc., was stopped by closing a stopcock beyond Vessel 4, and its drying system. The stopper in the side arm of Flask F was opened and cold bromine was poured into the flask, which was strongly cooled with a mixture of ice and salt. A counter current of nitrogen prevented the reaction of the bromine vapor with the aluminum and the introduction of outside oxygen while filling the flask with bromine. The side arm was then closed with a well-ground stopper which had been lubricated with phosphorus pentoxide and was firmly secured in place by means of de Khotinsky cement.

Since dry bromine vapor reacts very slowly with aluminum at ordinary room temperatures the vessel No. 1, containing aluminum, was kept at 120° by means of an electric heater. The stopcock A<sub>2</sub> was then turned off and stopcock A<sub>1</sub> opened. The nitrogen thus was bubbled through the bromine in flask F and accordingly carried with it a stream of bromine vapor over the gently heated aluminum. The current of nitrogen was regulated so as to carry only the amount of bromine necessary for convenient speed of reaction. The reaction of bromine with aluminum was

continued 22 hours while the vessels 2 and 3 were kept cool. At the end of this time a sufficient quantity of aluminum bromide had been formed, although quite a quantity of uncombined aluminum was left in tube No. 1. The current of nitrogen was then stopped (by means of  $A_1$ ) and the whole apparatus was allowed to cool.

The flask F, after being cooled, was disconnected from the reaction tubes by sealing the connecting capillary. The contents of Tube 1 were first digested for one hour at  $100^\circ$  in a slow current of nitrogen (Stopcock  $A_2$ ) and then for one hour at  $150^\circ$ . Perfectly clear colorless, strongly refracting liquid aluminum bromide was obtained, the excess of bromine having been removed partly by the reaction with the excess of metal left in the reaction tube, partly by the current of nitrogen.

After digestion, the vessels 1 and 2 were heated electrically while Tube 3 (containing more aluminum) was cooled with ice-water. The bromide was thus distilled in a slow current of nitrogen at a temperature slightly below its melting-point into Vessel 3. About 20 g. was left in the reaction vessel; this residue must have contained the least volatile impurities, if there were such.

After this first fractional distillation the portion in Vessel 3 was digested in a very slow current of nitrogen at  $200^\circ$  for one hour. Without stopping the current of nitrogen the temperature was raised and the first fraction (15–20 g.) of the distillate was distilled over into the cooled vessel 4. Subsequently the whole apparatus was allowed to cool and stopcock  $A_2$  cut off. Tube 3 was cooled with ice, the capillary connecting tubes 2 and 3 was sealed; and tube 4, containing the most volatile impurities, if any, was disconnected from the magnetic valve by sealing the capillary between them. The remainder of the pure colorless bromide to be further fractionated for analysis was treated as follows.

That part of the system comprising Tubes Nos. 5, 6, the sampling bulbs, Tube F and Drying-system D was evacuated through the phosphorus pentoxide tubes; connection was made between this system and vessel 3 by breaking the magnetic valve M, and the apparatus was again evacuated. Next, Tube 3 and the broken magnetic valve were heated electrically while Tube 5 was cooled with filter paper kept wet with ice-water. The temperature was regulated so as to carry on the distillation at as low a temperature as possible. In an oven kept at  $120^\circ$  the aluminum bromide sublimed *in vacuo*, and at  $130^\circ$  distilled very slowly into the cooled vessel 5. About 10 g. was left behind in Tube 3, thus affording another fractionation as regards less volatile impurities. From this Tube 5, now separated from Tube 3 by sealing an intervening capillary, the bromide was distilled fractionally into the several bulbs in which it was subsequently weighed. Tube 5 and that part of the tubes leading to the samp-



ling bulbs<sup>1</sup> above the capillary were incased in a fixed electric oven (kept at 125–135°) which remained in this position during the entire sampling process. The bulbs and capillaries were heated by means of an adjustable oven which could be moved along so as to heat all the bulbs except that in which a sample was being taken. This adjustable oven was kept at the temperature some 75° higher than was the fixed oven above—a precaution which prevented distillation into bulbs other than the one in which a sample was to be collected. The first portion of distillate, collected and sealed in Bulb 6, was rejected. The capillary of Valve M and the capillary connecting Tube 7 and the sample bulbs became plugged with solid bromide—a portion which constituted another fraction, as it was likewise taken from Tube 5.

When a sample bulb had been filled about  $\frac{3}{4}$  full of liquid aluminum bromide, the capillary above it was sealed off with a very small flame. The movable oven was then changed in position so as to cool another bulb, and another sample taken as before. In this manner 8 samples were taken.

#### Method of Analysis.

Each sample bulb (as may be seen from the figure) had on one end a solid rod while on the other end was a capillary, which had been sealed off from the apparatus. This capillary was converted into another solid rod by a small flame. To make proper vacuum corrections the exterior volume of each bulb separately was determined by weighing in water and subtracting this weight from the weight in air, the temperature and pressure being noted. As the specific gravity of single bulbs varied from 1.77 to 2.6, a specially calculated correction for the buoyancy of air for each bulb was used, varying from 0.53 mg. to 0.32 mg. per apparent gram. Each bulb, just before weighing, was scratched with a very sharp razor blade on both ends very near to the solid rods. After scratching it was washed in alcohol, rinsed in distilled water and wiped dry with clean lintless cloth. Before its precise weighing (by substitution) the sample bulb was allowed to remain in a desiccator for several hours.

Great care was necessary in dissolving the sample in water, owing to the great heat of solution and the consequent danger of loss of either bromide or glass. Samples from the first trial synthesis were broken in various ways to determine the best conditions for dissolving the bromide without loss. After the discarding of a number of only partially successful devices, a method was devised which proved altogether satisfactory in that the rate of solution could be adequately controlled and fuming prevented. This method of breaking and solution was used for all the samples analyzed from the final synthesis.

An amount of water, which was roughly sufficient to make a *N* solu-

<sup>1</sup> Vessel 5 and the sampling bulbs were actually in line with each other.

tion with the bromide contained in the bulb to be broken, was placed in a heavy-walled ground-stoppered flask. The water was frozen with a freezing mixture of ice and calcium nitrate, c. p., (all anions precipitated by silver being for safety excluded). The ice thus formed inside the flask was then further cooled by means of solid carbon dioxide and alcohol. This served to cause the ice to contract and break away from the surface of the glass. When the flask was thoroughly cold the scratched, weighed sample-bulb was carefully introduced and allowed to slip down the side of the flask to the ice. After the stopper had been replaced it was covered with chemically clean cloth and tied down. A slight shaking of the bulb against the ice on the sides of the flask was sufficient to break off both ends of the bulb at the scratches. Sufficient ice was melted to allow the solution to go on very slowly and without any fuming. When the reaction seemed to become too rapid the flask was again strongly cooled. The rate of solution was so well controlled that an hour was generally consumed in the solution of each sample.

The stoppered flask was allowed to stand one hour more after completion of solution. The flask was then opened and diluted, a few drops of nitric acid being added to prevent hydrolysis. The diluted solution was filtered very carefully through a weighed Gooch-Munroe hat-form platinum crucible<sup>1</sup> into a precipitating flask. The crucible with the broken bulb after drying in an air-bath was again weighed and the weight of the empty bulb thus ascertained. The solution of aluminum bromide was diluted so as to be about 0.1 *N* and was precipitated with silver solution, using the usual Harvard methods. After precipitation 2 or 3 cc. of distilled nitric acid was added to prevent the hydrolysis of aluminum nitrate formed. The end-point of precipitation was then ascertained with the assistance of the nephelometer.

In order to make sure that no powdered glass should be rubbed off from the stopper of the Erlenmeyer flask this stopper had been very carefully ground, first with fine emery, and finally with rouge. After this treatment, a blank experiment (involving about 10-fold as much rubbing as occurred in an analysis) yielded only 0.01 mg. of glass powder which could be caught by the Gooch-Munroe crucible used for the collection and weighing of the shattered bulb. Hence no correction was needed on this account, when the silver bromide was weighed.

Five samples were analyzed. In one case (Sample *b*) the ratio  $\text{AlBr}_3:3\text{AgBr}$  was determined; in 4 cases (Samples *a, d, e, f*) the ratio  $\text{AlBr}_3:3\text{Ag}$  was ascertained. Sample *c* was accidentally contaminated after opening by a piece of broken glass rod, which could not be separated from the fragments of the bulb. The analysis of this sample was therefore not finished. The complete weighings of a single analysis follow.

<sup>1</sup> T. W. Richards, THIS JOURNAL, 31, 1146 (1909).

Analysis of Bulb No. 1.		G.	G.
Bulb No. 1 in air.....		7.79985	
Correction for vacuum (Sp. gr. 2.215).....		0.00312	
		-----	
Bulb No. 1 <i>in vacuo</i> .....		7.80297	7.80297
Glass of bulb No. 1 in air.....		2.76411	
Corr. for vac. (Sp. gr. 2.6).....		0.00088	
		-----	
Glass <i>in vacuo</i> .....		2.76499	2.76499
		-----	
Aluminum bromide (in vac.).....			5.03798
Silver in air.....		6.11310	
Corr. for vac.....		0.00019	
		-----	
Silver <i>in vacuo</i> .....		6.11291	
Silver added in titration.....		0.00033	
		-----	
Total amount of Ag (in vac.).....		6.11324	6.11324

All weighings were thus corrected for vacuum by the application of the following corrections per gram: Silver, —0.000031; silver bromide, +0.000043; glass, +0.00032. The atomic weight of bromine was taken as 79.916, that of silver as 107.88.

In the following tables the results are summarized.

TABLE I.  
Preliminary Analysis.  
The Ratio of Aluminum and Silver Bromides.  
Weights in Grams.

Sam- ple.	Wt. of AlBr <sub>3</sub> in vac.	Wt. of AgBr in vac. be- fore fusing.	Wt. of AgBr in vac. after fusing.	Corrections ap- plied for AgBr dissolved.	Total amount AgBr.	AlBr <sub>3</sub> :3AgBr.	Atomic weight of aluminum.
2	3.23784	6.84028	6.8397	0.00026	6.83996	0.47337	26.944

TABLE II.  
The Ratio of Aluminum Bromide to Metallic Silver.

Sample.	Sample Ag.	Weight of AlBr <sub>3</sub> <i>in vacuo</i> . G.	Weight of Ag <i>in vacuo</i> . G.	AlBr <sub>3</sub> :3Ag.	Atomic weight of aluminum.
1.....	B	5.03798	6.11324	0.824110	26.967
4.....	A	5.40376	6.55955	0.824105	26.965
5.....	B	3.41815	4.14786	0.824076	26.956
6.....	A	1.98012	2.40285	0.824071	26.954
				-----	
				Average 0.824090	26.960
Total.....		15.84201	19.22350	.....	26.963

The last figure, 26.963, which weights the analyses according to the mass of material employed, is probably the most acceptable outcome of this work. This value is about 0.5% lower than the usually accepted value 27.1. The probable error of the result is very small. Whether or not

there may be a constant error from some entirely unknown cause lurking in the procedure, it is, of course, impossible to say. But there can be no doubt that the outcome is more to be depended upon than Mallet's for the reasons already specified. Moreover, the single preliminary analysis of Table I (in which silver bromide was weighed) not only served as a guide to the amount of silver to be used in the following titrations, but also confirms the others in proving that no important amount of impurity existed either in the silver or bromine—at least as far as a single determination can carry any weight. The fused silver bromide was a clear pale greenish-yellow. The close agreement of all the analyses of the final series shows that the samples used for analysis were chemically identical. The small variations are to be ascribed to the inevitable small errors of experiment.

The value 26.963 indicated by the present research agrees fairly well with Thomsen's 26.99, which also seems to have been more carefully carried out than Mallet's work involving the same process. Accordingly modern evidence seems to show that the atomic weight of aluminum is really less, not more, than 27. Theorists interested in the underlying determining factors of atomic weights and those concerned with the structure of the atom will note with interest that the new value is distinctly nearer a whole number than the old one and that, as just stated, it is rather less than more than this whole number.

We take pleasure in acknowledging our indebtedness to the Carnegie Institution of Washington for financial support in this investigation.

### Summary.

This paper records the synthesis and analysis of pure aluminum bromide. The substance was prepared from very pure bromine and the purest obtainable aluminum. It was digested 3 times in nitrogen at different temperatures and fractionated by distillation twice in nitrogen and twice *in vacuo*. The residue was in each case discarded, as were 2 of the portions first volatilized.

The close agreement of all the 5 analyses shows that the material used for analysis was very nearly, if not quite, homogenous. In the 4 final analyses 15.84201 g. of aluminum bromide required 19.22350 g. of silver for complete combustion, corresponding to an atomic weight for aluminum of 26.963, if silver is taken as 107.88, the current international value.