XXII. *Revision of the Atomic Weight of Aluminum.*

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Need for a redetermination of the atomic weight of aluminum.

There is probably no one of the so-called chemical elements equally abundant in nature with aluminum, and occurring in as numerous compounds, with regard to the atomic weight of which our knowledge has long rested upon so slender a foundation of accurate experiment. The following brief statement includes, I believe, all the determinations of this constant which are on record.

Former Determinations.

1. *Experiments of* Berzelius, 1812.—Berzelius* precipitated a solution of alum by addition of ammonia, dissolved the precipitate in sulphuric acid to saturation, filtered, concentrated the filtrate by evaporation, and threw down aluminum sulphate by alcohol. This salt was well washed with alcohol, to separate as far as possible any excess of acid, and was then heated in a platinum crucible over an alcohol lamp, weighing from time to time, until no further loss of weight occurred. The anhydrous sulphate so obtained was but slowly soluble in water on heating, but left no insoluble residue. 10 grms. of this salt was now raised to a higher temperature in a weighed platinum crucible, and strongly heated as long as any loss of weight could be detected. The residue of loose, light, white alumina found in the crucible weighed 2·9934 grms. Consequently the salt consisted of—

"Sulphuric acid" (SO_3)	70·066	or	100·000
Alumina	29·934	,,	42·722
	100·000	,,	142·722

Several small arithmetical errors have been made in the discussion of this single experiment of Berzelius, upon which for nearly half a century the value assigned to the atomic weight of aluminum may be said to have rested.

In the original paper it is calculated that if 42·722 parts of alumina contain 19·96

* Gilbert's 'Annalen der Physik,' xl. (1812), 260.

parts of oxygen (the atomic weight of sulphur being then taken =201·16—O=100), 100 parts of alumina must include 46·726 parts of oxygen. This last number should be 46·7207. In a later paper* by the same author, it is calculated from the results of the above experiment, that 100 parts of "sulphuric acid" are saturated by 42·7227 parts of alumina, and that the earth contains 46·7047 per cent. of oxygen; the earth is assumed to be Al_2O_3, and consequently the atomic weight of Al is found =171·667 (O=100), or 27·49 (H=1). These numbers, correctly calculated from the percentage of oxygen taken in this second paper, should read 171·167 and 27·39 respectively. Or, if the percentage of oxygen of the former paper, corrected as above, be taken as 46·7207, the atomic weight, for Al_2O_3, will be 171·057 (O=100) or 27·37 (H=1).†

Finally, if BERZELIUS' direct results of experiment be taken, and recalculated with STAS' atomic weights for O (15·96) and S (31·98), the atomic weight of aluminum, its oxide being assumed Al_2O_3, will be 27·237 in reference to that of hydrogen as unity.

BERZELIUS‡ also attempted to obtain a pure hydrate of aluminum by precipitating the sulphate and nitrate with ammonia, but found that highly basic salts only were thrown down. Using the chloride instead, a hydrate was obtained which, after being dried in the sun, gave only water on heating, but there was a little loss from mechanically-carried-over alumina. This sun-dried hydrate left 64·932 per cent. of alumina free from acid. BERZELIUS therefore calculates that 100 parts of anhydrous alumina had been combined with 54 parts of water—this amount of water containing 47·65 parts of oxygen; while the alumina contains, as shown by the above-quoted analysis of the sulphate, 46·726 parts of oxygen. He remarks: "I cannot affirm that either the determination of the amount of water or that of the oxygen in the alumina is sufficiently exact; both are, however, so far so as to sufficiently show us that alumina, like the preceding bases, combines with an amount of water whose oxygen is equal to that of the earth itself."

In the decomposition by heat of aluminum sulphate, as thus used to furnish data from which to calculate the atomic weight of the metal, the following possible sources of error may be noticed:—The hydrate precipitated by ammonia from a solution of (presumably) *potash* alum might carry down with it traces of fixed alkali, and this latter be retained in the sulphate afterwards prepared from the hydrate. The tendency of aluminum to form basic salts suggests the possibility of traces of sulphuric acid being lost in the preliminary drying over the simple alcohol lamp, even at a temperature at which possibly the last traces of water might not have been removed. I have found from my own experiments that a trace of basic sulphate may, on the other hand, be obstinately retained even after prolonged exposure to a very high tempera-

* POGGENDORFF'S 'Annalen der Physik u. Chimie,' viii. (1826), 187.

† A. C. OUDEMANS, Jr. (in his 'Historisch-kritisch Overzigt van de Bepaling der Æquivalent-Gewigten van twee en twintig Metalen;' Leiden, 1853), calculates, from BERZELIUS' figures, Al=171·02.

‡ GILBERT'S 'Annalen,' *loc. cit.*

ture, when it might be assumed that pure alumina alone was left. As BERZELIUS himself says, ignited alumina rapidly absorbs moisture from the air, involving risk of error in determining its weight. Traces of the light pulverulent alumina are liable to be mechanically carried away during the decomposition of the sulphate. It is observable that all these sources of error, except the last, tend in the same direction, to make the atomic weight of aluminum come out too high.

2. *Experiments of* Sir HUMPHRY DAVY, 1812.—In Sir HUMPHRY DAVY's 'Elements of Chemical Philosophy'—published in 1812, the same year in which BERZELIUS' first paper on this subject appeared—it is stated* that no direct researches had then been made on the quantity of oxygen in alumina, but that, from some experiments by the author on the quantity of ammonia required to decompose saturated solutions of alumina in acids, "it would appear that the number representing alumina is about 48, and, supposing it to consist of one proportion of aluminum and one of oxygen, 33 will be the number representing aluminum." The details of the experiments in question are not given, and the combining proportions of all substances having been very imperfectly known at the time—the number 15 is taken above for oxygen—it is needless to say that this passage throws no light upon the exact atomic weight of aluminum.

3. *Experiments of* THOMSON, 1825.—THOMSON† attempted to deduce the number representing this atomic weight from, (*a*) analyses by himself and others of sundry natural aluminous silicates, (*b*) analyses of potassium alum, and (*c*) analyses of hydrates of aluminum. He concluded from all his experiments that the true number for alumina is 2·25 (O=1), and, taking alumina to be AlO, he made Al=1·25. This corresponds to Al=30, if O be assumed =16, and alumina Al_2O_3—a result which can only be viewed as a rough approximation to the truth, since THOMSON's methods were far from accurate, and his experimental results agree but poorly with each other.

4. *Experiments of* MATHER, 1835.—W. W. MATHER,‡ Assistant Professor of Chemistry at the United States' Military Academy, West Point, prepared anhydrous aluminum chloride by WÖHLER's process, dissolved a weighed portion of it in water, added silver nitrate in excess, filtered off, dried and weighed the silver chloride formed, threw down excess of silver from the filtrate by hydrochloric acid, filtered again, evaporated this second filtrate and washings to dryness, ignited the residue, and weighed it as alumina. ·646 grm. of aluminum chloride gave 2·0549731§ grms. of silver chloride (yielding on reduction 1·548161 grm. of silver) and ·2975 grm. of alumina.

* Vol. iv., p. 263, of the 'Collected Works of Sir H. DAVY,' edited by his brother Dr. JOHN DAVY; London, 1840.

† THOMAS THOMSON, M.D., 'An Attempt to Establish the First Principles of Chemistry by Experiment,' vol. i., p. 285; London, 1825.

‡ SILLIMAN'S 'American Journal of Science and Arts,' xxvii. (1835), 241.

§ The seven decimal places are given, notwithstanding the statement by the author himself that his balance could weigh easily $\frac{1}{300}$ grain, and was sensible to $\frac{1}{700}$ grain!

From the amount of silver chloride found and silver obtained from it in this one experiment, and from the atomic weights of silver and chlorine adopted by BERZELIUS and THOMSON respectively, MATHER calculated values for the atomic weight of aluminum ranging from 1·82274 to 1·85430 (O=1, and the formula of the chloride being taken as $AlCl_3$), or 29·16384 to 29·66880 for O=16; but from the amount of alumina obtained and the amount of aluminum therein (the latter deduced from the chloride taken for analysis minus the chlorine found), he calculated the atomic weight for aluminum as 1·3188017 (O=1) for alumina taken as Al_2O_3, or 21·1008272 for O=16. He does not seem to have been struck by the evidence of some error in his own work which these discrepant numbers afford, but suggested that the figures given by BERZELIUS for the aluminum and oxygen in alumina might have been accidentally inverted, which would explain the disagreement between himself and the great Swedish chemist. In reality it is pretty plain that MATHER'S alumina was not pure, either from fixed matter of some kind left behind from the acids and wash water used, or from absorption of moisture before weighing. If his most direct result only be taken as the basis of calculation, namely, the weight of aluminum chloride used and silver chloride obtained from it, using STAS' numbers for chlorine (35·37) and silver (107·66), the atomic weight of aluminum found will be 28·778 for the formula $AlCl_3$.

5. *Experiments of* MALLET, 1857.—In 1857 the writer of this paper attempted to use metallic aluminum, which had not long before begun to be manufactured and sold, for the determination of the atomic weight. At the meeting of the British Association held in that year at Dublin,* he gave a brief account of his experiments, which had been made with the metal of commerce, containing, as he found, only from 93 to 96 per cent. of pure aluminum. The exact nature and amount of the foreign substances present, chiefly iron and silicon, having been determined, the crude metal was dissolved in hydrochloric acid, the solution precipitated by ammonia, and from the amount of alumina left from the precipitate on ignition, after allowing for the impurities, the atomic weight was deduced. The results obtained from a few experiments were not satisfactory enough to warrant any proposal to modify the then received number. The probability that this number needed correction was, however, pointed out, with reasons for such an opinion; the desirability of obtaining for the purpose of new experiments really pure metallic aluminum was noticed; and it was suggested that difficulties connected with the accurate determination of alumina by the method which had just been tried might make it eligible to determine instead the hydrogen given off during the solution of the metal in acid.

6. *Experiments of* DUMAS, 1858.—DUMAS† redetermined the atomic weight in question by dissolving in water known weights of aluminum chloride, and ascertaining the quantity of silver, used as nitrate, which was required in each case for precipitation of the chlorine. The aluminum chloride had been carefully prepared on the large

* 'Report of British Association Meeting at Dublin, 1857: Transactions of Sections,' p. 53.

† 'Annales de Chimie et de Physique' [3], lv. (1859), p. 151.

scale, then sublimed from iron turnings, and re-sublimed from aluminum filings. It sometimes still contained traces of iron. Each specimen to be used was sublimed for the last time from aluminum, in a stream of dry hydrogen, into a small glass tube, which was sealed at both ends before the lamp, and reserved for one of the analytical experiments. Of these there were seven. In each the weight of the sealed tube and its contents was taken, a drawn out end opened, and the weight quickly verified after equilibrium of pressure with the outside air had been thus established; the tube was introduced into water, and after solution of its contents the weight of the empty tube was determined. It does not appear from the published paper how the risk of mechanical loss from violent action of the chloride on the water was guarded against; from my own experiments with the bromide this appears to be a point requiring careful attention. Nor is it stated how the quantity of silver used was determined, whether by weighing the chloride of silver formed, by measuring the volume of a standard solution of silver nitrate, or by weighing off a little less metallic silver than would be required, converting this into nitrate, adding it to the aluminum chloride solution, and completing the precipitation with a measured quantity of dilute standard solution of silver nitrate. Nor is it mentioned how, if at all, the error due to slight solubility of silver chloride in the liquid from which it was precipitated is obviated—a point not ignored by DUMAS, as appears from another part of the same paper,* and afterwards very carefully examined by STAS.

The results of the seven experiments were as follows, the atomic weight or equivalent being calculated for the formula Al_2Cl_3, and on the supposition that Ag=108, and Cl=35·5 :—

				Atomic weight.
I.—1·8786	of Al_2Cl_3	required	4·543 of Ag	=13·74
II.—3·021†	„	„	7·292 „	=13·85 (should be 13·86)
III.—2·399	„	„	5·802 „	=13·73
IV.—1·922	„	„	4·6525 „	=13·68
V.—1·697	„	„	4·1015 „	=13·77
VI.—4·3165	„	„	10·448 „	=13·68
VII.—6·728	„	„	16·265 „	=13·76
		Mean		13·744
		Should be		13·746 or 27·492 for $AlCl_3$

Recalculating this table for the formula $AlCl_3$, and using the atomic weights of STAS for silver (107·66) and chlorine (35·37), the figures of the last column become—

* Page 135.

† Contained traces of iron.

I.	—Atomic weight of Al	=27·447
II.	„ „ „	=27·696
III.	„ „ „	=27·435
IV.	„ „ „	=27·318
V.	„ „ „	=27·522
VI.	„ „ „	=27·327
VII.	„ „ „	=27·489
	Mean	27·462

It is to be remarked that the tendency of the chief causes of error connected with these experiments is in the same general direction. The presence of any iron in the chloride used; the action upon it, though but to a minute extent, of any trace of moisture in the hydrogen in which it was finally sublimed; any loss occurring with the fumes formed on introduction of the chloride into water; and the retention of traces of silver chloride in solution in the liquid from which the main mass of this compound had been thrown down; any or all of these would tend to diminish the quantity of silver chloride obtained, and therefore to make the atomic weight of aluminum appear greater than it really is. In discussing results which we owe to the labours of such experimenters as Berzelius and Dumas, it is of course to sources of error likely to inhere in the method itself that attention should especially be given.

Dumas also tried dissolving aluminum (containing iron and silicon in considerable quantity) in hydrochloric acid, adding nitric acid in excess, evaporating to dryness, igniting and weighing the alumina (and other oxides) left behind. From an analysis of the crude metal employed, so as to allow for the impurities present, and on the basis of three experiments made as above, he calculated the atomic weight as

13·74 (=27·48 for Al_2O_3—O=16)
13·87 (=27·74 „ „ — „)
13·89 (=27·78 „ „ — „)

but he was dissatisfied with these results, having found that the impurities of the metallic aluminum were unequally distributed throughout its mass, and having been unable to obtain the metal in a pure state. He considered the results furnished by the experiments with the chloride as accurate, and concluded that the atomic weight of Al is represented by the number 13·75 (for Al_2Cl_3)—this becomes 27·5 for $AlCl_3$ or Al_2Cl_6.

7. *Experiments of* Tissier, 1858.—Ch. Tissier* prepared aluminum by reducing very pure fluoride of aluminum and sodium—probably cryolite, although this is not stated—by means of purified sodium in a carbon crucible, re-fusing the metal several times in order to free it from any of the flux which might have been retained. No

* 'Comptes Rendus des Séances de l'Acad. des Sciences,' xlvi. (1858), p. 1105.

account is given of the means taken to prepare a carbon crucible free from iron and silicon; and to prevent destruction of the crucible by its material burning away during the fusion at high temperature of the aluminum salt with sodium. The metal was tested for iron by dissolving it in nitro-hydrochloric acid, evaporating to dryness with a large excess of nitric acid, and igniting the residue of alumina, which was observed to be of brilliant whiteness, while the addition of a solution containing a few thousandths of iron sufficed "to colour it very strongly red." Why the much more delicate tests available for iron in the original solution were not used does not appear.

As regards silicon, it is stated that "the solution of the metal by means of hydrochloric acid left no trace of silicon;" no mention is made of the solution having been evaporated to dryness, the residue remoistened with strong hydrochloric acid and dissolved in water in order to see whether silica was left. A portion of the solution obtained with nitro-hydrochloric acid was evaporated to dryness, the residue ignited, and the alumina so left was digested with a strong and boiling solution of ammonium nitrate. This solution was evaporated to dryness, and left a residue of sodium nitrate representing 0·135 per cent. of sodium in the metallic aluminum.

1·935 grm. of this aluminum was dissolved in hydrochloric acid, the solution evaporated with an excess of nitric acid until all chlorine was completely driven off, and the residue heated until the nitric acid was also completely removed and alumina only was left. This alumina weighed 3·645 grms. In the paper recording this single experiment the resulting atomic weight is not calculated, but the author simply points out that the number 14, which he says many chemists adopt as representing aluminum, must be too high, while 13·75, the number assigned by DUMAS, is in all probability accurate. In support of this view it is calculated that, if Al=14, the alumina obtained in the above described experiment should have weighed 3·590* grms.; whereas, with Al=13·75, its weight should have been 3·624 grms. In getting these figures O is taken =8.

But, if the minute quantity of sodium stated to have existed in the metal used be deducted, and allowed for as sodium oxide (aluminate) in the last weighed residue, and if the results obtained be calculated, for alumina $=Al_2O_3$, with STAS' number for oxygen (15·96), the atomic weight of aluminum will be represented by 27·068, a number much nearer to 27 than to 27·5 (13·75×2), the value assumed as most probably correct by TISSIER.

8. *Experiments of* TERREIL, 1879.—Lastly, about a year ago TERREIL† made a determination of the constant in question by passing hydrochloric acid gas over metallic aluminum, collecting and measuring the hydrogen evolved. He placed a known weight of aluminum in a tube of hard glass, the tube wrapped with foil so as to allow of its being made red hot. By one end a stream of well dried gaseous hydrochloric acid could be introduced, while a smaller tube extended from the other end and dipped into a vessel of water.

* This ought to read 3·594.

† 'Bulletin de la Société Chimique de Paris,' xxxi. (20 Fév., 1879), p. 153.

The air was first expelled from the apparatus by a current of dry carbon dioxide, and not until the gas passing through was capable of being completely absorbed by a solution of potash was the hydrochloric acid introduced, this latter itself freed from atmospheric air. The gas escaping from the tube was now collected in a graduated jar, and the temperature of the tube containing the aluminum was raised to a red heat. As soon as hydrogen ceased to come over, the gas in the jar was shaken up with potash to absorb any carbon dioxide which it might contain, and the volume was measured, and reduced by calculation to its equivalent under normal temperature and pressure. The aluminum chloride left in the tube was pulverulent and snow white.

No details are given of the method by which pure metallic aluminum was prepared, although this has been the great difficulty in the way of obtaining accurate results from experiments made with the metal as the starting point, nor is there any record of the tests applied to prove the purity of the metal used. The gas was collected over water, in which hydrogen is not altogether insoluble, and from which more or less of the gases of atmospheric air would be given off into the hydrogen. Nothing is said of the vapour of water, mixed with the hydrogen in proportion depending upon the temperature, having been removed, or its amount calculated and allowed for; though, as it is not likely that so obvious a precaution was neglected, it may be supposed that the potash spoken of as used to absorb any carbon dioxide left was either solid hydrate or so strong a solution as to have also removed most if not all the aqueous vapour.

The results of the single experiment reported were—

Weight of aluminum	·410 grm.
Volume of hydrogen collected at 11° and 768 m.m.	530 c.c.
Corresponding volume at normal temperature and pressure . .	508·2 c.c.
Weight of this hydrogen	·0455 grm.

from which the author calculates

$$·0455 : ·4100 = 1 : 9·01,$$

giving the atomic weight 13·515 (for Al_2Cl_3) or 27·03 (for $AlCl_3$).

In verifying the above calculation I have found as the result of reducing the volume of hydrogen from the given to normal temperature and pressure 514·85 c.c. instead of 508·2 c.c., but this, I am satisfied, arises from the number representing the pressure at the time of experiment being, doubtless by a printer's error, wrongly given as 768 instead of 758 m.m. With the latter figures the result is as recorded in the paper, and of course such atmospheric pressure is more frequently observed than that which appears in the above table.

It is pretty plain that from the researches which have been quoted we may reject those of Davy, Thomson, and Mather as incapable of giving exact results, this being

either admitted by the authors themselves or shown by an examination of their methods and the inconsistency of their conclusions. Our knowledge of the atomic weight under consideration rests therefore upon the investigations of BERZELIUS, TISSIER, and TERREIL, each of whom made one experiment, and those of DUMAS, who made seven.

General results of former determinations.—If all the results be taken as I have re-calculated them, using STAS' atomic weights for the other elements concerned, and equal value be given to all, we shall have the following arithmetic mean—

BERZELIUS	27·237
DUMAS	27·447
,,	27·696
,,	27·435
,,	27·318
,,	27·522
,,	27·327
,,	27·489
TISSIER	27·068
TERREIL	27·030
Mean	27·357

If, however, the results of DUMAS, all depending on repetition of the same process, be viewed as possibly affected by some constant error, and be thrown together, taking into the calculation the mean only of his seven experiments, the general mean will be—

BERZELIUS	27·237
DUMAS (mean)	27·462
TISSIER	27·068
TERREIL	27·030
Mean	27·199

If we separate DUMAS' results, and take the mean of the other three, we get in contrast—

BERZELIUS	27·237
TISSIER	27·068
TERREIL	27·030
Mean	27·112
DUMAS (mean)	27·462

Or, if we throw together only the numbers obtained by TISSIER and TERREIL, which come nearest to each other, we have—

TISSIER	27·068
TERREIL	27·030
Mean	27·049
BERZELIUS	27·237
DUMAS (mean)	27·462

Values now generally adopted for atomic weight of aluminum.

The number adopted in some of the more recent chemical handbooks, reports, &c., may be quoted as follows :—

GMELIN : 'Handbook of Chemistry' (Cav. Soc. Trans.) . . .	27·4
WATTS : 'Dictionary of Chemistry,' First Supplement	27·4
W. A. MILLER : 'Elements of Chemistry,' 4th edit.	27·5
MEYMOTT TIDY : 'Handbook of Modern Chemistry'	27·5
FRANKLAND : 'Lecture Notes for Chemical Students'	27·5
THORPE : 'Quantitative Chemical Analysis'	27·26
'Agenda du Chimiste' (WURTZ' Laboratory, 1879)	27·5
'Annuaire du Bureau des Longitudes, 1876'	27·4
NAQUET : 'Principes de Chimie,' &c., 3e ed.	27·5
FITTICA : 'Jahresb. üb. d. Fortsch. d. Chemie, 1878'	27·4
ROSCOE u. SCHORLEMMER : 'Ausf. Lehrbuch d. Chemie' (Ger. ed.)	27·3
FRESENIUS : 'Anleit. z. quant. chem. Analyse,' 5te Aufl. . . .	27·5
CLASSEN : 'Grundr. d. anal. Chemie' (quant.)	27·3
KOHLRAUSCH : 'Leitfaden d. prakt. Physik,' 2te Aufl.	27·4
MENDELEJEFF : Paper on the "Periodic Law" (transl.) . . .	27·3
J. P. COOKE, Jr. : 'The New Chemistry'	27·5
J. D. DANA : 'System of Mineralogy,' 5th ed.	27·5
E. S. DANA : 'Text-Book of Mineralogy'	27·3

New experiments by the author.

During the last three years I have devoted a large part of my leisure time to a re-determination of this atomic weight, sparing no pains to attain as precise a result as possible, and aiming especially at the discovery, and as far as possible removal, of sources of error connected with the methods employed. The following general principles have been kept in view :—

1. That each process used should be as simple as possible, and should involve as little as possible of known liability to error.

2. That different and independent processes should be resorted to as the means of checking each other's results, even though it may fairly be assumed that one is more advantageous than another.

3. That each process should be carried out with quantities of material differing considerably from each other in successive experiments.

4. That only such other atomic weights should be involved as may be counted among those already known with the nearest approach to accuracy.

The most scrupulous care was taken in the purification and examination of all the reagents used, and as far as possible vessels of platinum or of hard porcelain were substituted for those of glass.

Means and method of weighing employed.—For the weighings an excellent balance, of BECKER'S construction, was employed. It was in perfect order, carefully adjusted (especially as regards centre of gravity of beam with average load to be carried), and would bear safely 200 grms. in each pan, giving when thus loaded a deflection of the index to the extent of $1\frac{1}{4}$ division of the scale over which it moves for a difference of weight of ·0001 grm. All weighings were made by the well-known method of observing the vibrations of the index on either side the position of rest. In one series of experiments *absolute* weights were required, *i.e.*, real equality of weight between the quantities of matter dealt with and the standards of weight with which they were compared; in these cases the method of "double weighing" was made use of, so as to eliminate any error arising from inequality in length of the arms of the balance. In view of this need, in connexion with a part of the research, for absolute weights, directly comparable with those used by REGNAULT in his determination of the density of hydrogen, I applied to my friend J. E. HILGARD, Esq., in charge of the office of the United States' Coast Survey at Washington, for a comparison of a kilogramme with a weight of the same denomination belonging to the Coast Survey, the value of which latter weight is accurately known in terms of the original "kilogramme of the Archives" at Paris. He kindly had this comparison made, and sent me the results in detail, showing that my weight was 8·1 milligrammes heavier than the "star kilogramme" which is the standard of reference at Washington (both *in vacuo*), with an uncertainty of comparison not exceeding ·1 milligramme, while the "star kilogramme" is certified to as agreeing with the normal "kilogramme of the Archives" within 1·1 milligramme. I had already a 10-gramme weight, professedly normal, but, as it turned out, too light by a very minute fraction of its value, and with these two, checked against each other, a full series of comparisons was made of all the other weights to be employed, the specific gravity of each piece being determined before its final comparison as to weight, so that the real values might all be referred to a vacuum by calculation of the buoyancy in air. Determinations of the specific gravity of all materials and vessels which had to be weighed were also made, and, the barometer

and thermometer being observed at the time of each weighing, all weights hereafter mentioned in this paper represent real values *in vacuo*.

Three separate series of experiments were made, by methods to be presently stated. A fourth series was attempted, involving the conversion of metallic aluminum into oxide and determination of the amount of oxygen taken up, but this process was found to be attended with much difficulty from various causes, amongst others from the liability to loss by spirting if the metal were treated with acid in open or small vessels, from the necessity of transfer to such vessels for final ignition if larger ones were at first used, and from the appreciable solubility of the hydrate of aluminum if this were precipitated in order to avoid evaporation of the original solution. The few results obtained in this way agreed generally with those of the other methods, but varied among themselves within unsatisfactorily wide limits, and were manifestly not deserving of equal confidence. Hence the work was not pushed further in this direction.

First series of experiments.

Purification of ammonium alum.—Ammonium alum of commerce was dissolved in water, a very little nitric acid added, and the liquid boiled in large glass beakers by passing in a current of steam. When the solution had become cold a little ammonium ferrocyanide was added—a very small quantity sufficed to throw down the traces of iron present—and a little animal charcoal, previously well boiled with strong hydrochloric and nitric acid and thoroughly washed, was stirred in to aid in the subsidence of the minute amount of very finely divided Prussian blue which had been formed. The clear liquid was after about ten days drawn off, and evaporated until the larger part of the alum crystallised out on cooling. The crystals, of which there was obtained more than a kilogramme, were re-dissolved in hot water, and re-crystallised several times (throwing away all the mother liquors), the last time in a porcelain vessel, and with agitation, so as to obtain a granular crystalline powder, which was washed with cold distilled water.

Re-dissolving in water the so far purified alum, now much reduced in quantity, it became necessary to secure the exclusion of the metals of the fixed alkalies, lest their alums should exist in isomorphous admixture with the pure ammonium alum required. To this end aluminum hydrate was thrown down from the solution by addition of ammonia, using not quite enough of the reagent for complete precipitation. The precipitate was well washed with abundance of water, this tedious process being much expedited by the use of a siphon-filter delivering the liquid drawn off into a large flask connected with a powerful aspirator. The bulk of the precipitate was twice re-dissolved in pure hydrochloric acid (each time avoiding complete solution), thrown down again by ammonia, and again washed.

This hydrate was now dissolved in just the necessary amount of dilute and very carefully purified sulphuric acid, and just the proper amount added of ammonium sul-

phate prepared from the same sulphuric acid neutralised with ammonia. The quantities were determined by bringing the two solutions to known bulks, ascertaining by experiment on a sample of each how much of the respective salts was present, and measuring off the required volumes to be mixed. After concentrating the mixed solution by evaporation it was allowed to crystallise by cooling, and the crystallisation was repeated thrice, each time washing with a little cold water. On the last crystallisation pains were taken to regulate the rate of cooling so that as far as possible uniformly small crystalline grains were formed of about a millimetre in diameter, thus avoiding the liability of large crystals to contain cavities, in which mother liquor might be retained, and on the other hand securing the possibility of seeing with a lens, better than could have been done if the alum were in a still finer crystalline powder, that all the crystals as afterwards used were clear and transparent, and showed no signs of efflorescence.

It should be added that all the aqueous ammonia used as above for the precipitation of aluminum hydrate, and for its reconversion into alum, was recently and carefully prepared from ammonium chloride purified from alcoholic amines by boiling with nitric acid as recommended by STAS,* that the last crystallisations were effected from water which had been, in pursuance of the practice of the same chemist, distilled from potassium permanganate and hydrate, and that for these last crystallisations a large platinum dish was used, and care was taken that the solution was not allowed to boil, nor even to remain for any length of time near the boiling point, since I ascertained that ammonium alum, like simple ammonium sulphate, gradually gives off small quantities of ammonia on continued boiling of a strong solution. The very last crystallisation was carried out with only a sufficient quantity of the alum for a couple of the final experiments.

The salt thus purified was found to be free from any ascertainable content of foreign substances. It gave no trace of coloration in its solution when tested by a ferro-cyanide, tannic acid, &c., and by sulphuretted hydrogen and ammonium sulphide; and spectroscopic examination showed that the fixed alkaline metals and calcium were absent. Silver nitrate gave no indication of chlorine.

Ignition of ammonium alum.—Difficulties connected with this method.—I proposed to ignite a weighed quantity of this alum, whose distinct crystallisation gives it the advantage as to definiteness in the amount of water over the simple sulphate used by BERZELIUS, and to determine the weight of the aluminum oxide left behind, but careful examination of this process showed that two difficulties were to be feared.

In the first place, having rapidly dried the product of the last crystallisation by gentle pressure between folds of smooth filtering paper† free from loose fibre, portions were weighed off and exposed to the air at about 22° C., with the hope that before long a constant "air-dried" weight would be obtained. It had been previously ascer-

* Quoted in FRESENIUS' 'Zeitschrift für analyt. Chemie,' 6ter Jahrg., 4tes Heft., S. 423.

† This had been previously purified by ample washing with acid and water, and well dried.

tained that exposure over sulphuric acid led to large loss of water of crystallisation within a short time. It was found, however, that even in the air loss of weight went on for so long a time that it could not possibly be referred to mechanically adherent water only. It is true that this loss fell off very rapidly after the first hour or so, but it was impossible to decide precisely when it began to affect the water of crystallisation. In order to fully exhibit this I quote the following results obtained from a single large specimen kept very long on hand in a place carefully guarded against dust.

	Grms.
Original weight of alum after one hour's exposure to the air at 22°·5 C.	35·7456
Loss of weight in 1st twenty-four hours	·0088
,, ,, 2nd ,, ,,	·0025
,, ,, 3rd ,, ,,	·0017
,, ,, 4th ,, ,,	·0015
,, ,, 5th ,, ,,	·0010
,, ,, 6th ,, ,,	·0012
,, ,, 7th ,, ,,	·0009
,, ,, 8th ,, ,,	·0011
,, ,, 9th ,, ,,	·0007
,, ,, 10th ,, ,,	·0005

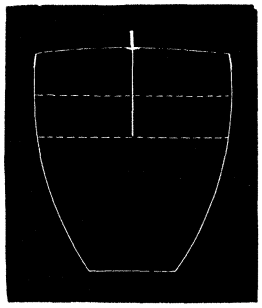
This series of weighings was carried on at longer intervals for six months more; the *monthly* loss was at first ·0087 grm., gradually fell off, became as small as ·0006 grm. in one month of cold weather when the temperature of the room was unusually low, and again rose, with warmer weather, to ·0012 grm. for the sixth and last month for which the weighings were continued. It was further found that, on placing some of the small crystals of the alum in a glass vessel deep enough to prevent mechanical loss, sensible loss of weight could be produced by the heat developed in simply crushing and pulverising the salt with a thick square-ended glass rod used as a pestle, and weighed along with the glass and its contents. While, therefore, it might be assumed as probable that mechanically adherent water would be got rid of within a time during which but a very minute quantity of water of crystallisation would be lost, a slight doubt is thrown over the exact formula of the salt as analysed, in reference to this component. Some of the ignition experiments were made with specimens which had been dried by longer exposure to the air than others, as will be noted hereafter.

In the second place it appeared that a minute trace of basic sulphate was retained by the alumina left after ignition at even a very high temperature. This could not be extracted by water, but was detectable by fusion with sodium carbonate free from sulphur, taking care to use an alcohol flame only. By moistening the alumina with a strong solution of pure ammonium carbonate, re-igniting, and repeating this treatment

a second time, it seemed to be possible to remove this source of error, as out of several specimens thus treated only one afforded a barely detectable trace of sulphate.

Details of method adopted.—The actual experiments on the ignition of the alum were carried out as follows. To render uniform the amount of atmospheric condensation on the surface of the vessel weighed, a very light glass bottle was specially made, with a delicately blown stopper, the latter carefully ground in and fitting quite air-tight; the bottle of a size to contain the platinum crucible in which the ignition was to be effected. The crucible was heated to bright redness, and while still quite hot was placed in a desiccator at some distance above a surface of recently distilled sulphuric acid. When cooled down to the temperature of the balance-room the crucible was as quickly as possible transferred to the weighing bottle, which was at once closed, and the combined weight of bottle and crucible was taken. The stopper was then removed for an instant, the cover of the crucible raised, and the quantity of alum desired, which had been roughly weighed off in a tube, having been poured in, occupying in no instance more than one-third depth of the vessel, cover

Fig. 1.



and stopper were replaced, and a second weighing gave, by the gain upon the first, the exact amount of alum used. Attached to the inner side of the crucible cover was a piece of rather stout platinum wire, which, when the cover was in place, ran down into the crucible in the line of its axis of figure, carrying two little diaphragms of platinum foil perforated with small holes (see fig. 1); such a diaphragm having been suggested and used by DUMAS* in his researches on atomic weights as the means of preventing any loss of solid particles which might otherwise be carried off mechanically from the substance ignited. To avoid inconvenience from the fusion of the alum in its water of crystallisation, and the swelling up of the salt to a bulky, porous mass, the heating was conducted very gradually. The platinum crucible was kept for an hour at 90° C., then for an hour at 100°, for an hour at 110°, another hour at 120°, a like time at 140°, and was then gradually brought to ignition over an argand alcohol lamp. It was then placed inside a larger platinum crucible, resting on a flat bit of unglazed porcelain at the bottom of the latter, and exposed to a gradually increased, and at

* 'Annales de Chimie et de Physique,' *loc. cit.*

last bright yellow heat in a gas furnace of FLETCHER'S construction. This temperature was maintained for a full hour. On cooling down, the smaller crucible was taken out, the cover cautiously raised, and enough of a strong solution of ammonium carbonate introduced to moisten the alumina. Drying gently in a steam-bath, the crucible was re-ignited over an alcohol blast lamp, producing a strong red heat, and the addition of ammonium carbonate, drying, and ignition once repeated. As soon now as the crucible had ceased to be visibly red hot it was placed in the desiccator as at first, allowed to cool down to the temperature of the balance-room, quickly transferred to the weighing bottle, the stopper of which was inserted, and the final weighing was made while the alumina in the crucible was thus protected from absorption of moisture from the air. These experiments were carried out during a period of remarkably steady weather, with very little variation of atmospheric temperature, pressure, or moisture in the balance-room during the whole series.

Direct results of first series of experiments.—The results were as follows :—

A.—Alum dried by exposure to air for 2 hours at 21°–25° C.

I.—	8·2144	grms. of	$(NH_4)_2Al_2(SO_4)_4.24H_2O$ left	·9258	grm. of Al_2O_3.
II.—	14·0378	,,	,,	1·5825	,,
III.—	5·6201	,,	,,	·6337	,,
IV.—	11·2227	,,	,,	1·2657	,,
V.—	10·8435	,,	,,	1·2216	,,

B.—Alum dried by exposure to air for 24 hours at 19°–26° C.

VI.—	12·1023	grms. of	$(NH_4)_2Al_2(SO_4)_4.24H_2O$ left	1·3660	grm. of Al_2O_3.
VII.—	10·4544	,,	,,	1·1796	,,
VIII.—	6·7962	,,	,,	·7670	,,
IX.—	8·5601	,,	,,	·9654	,,
X.—	4·8992	,,	,,	·5528	,,

Second series of experiments.

Preparation and purification of aluminum bromide.—Aluminum bromide was prepared by the action of liquid bromine upon metallic aluminum of commerce, and was afterwards carefully purified. The first action is so violent that without special precaution the process involves some danger. In a first attempt a lump of aluminum weighing 15 to 20 grms. was dropped into a long-necked flask containing a considerable quantity of bromine. There was little action for a few moments, but as soon as it began vivid combustion took place, torrents of bromine vapour were driven forth, and after the flask had cooled the surplus metal was found to have been completely fused and had nearly melted its way through the glass.

By the following arrangement the bromide was prepared in large quantity and without any trouble. About 50 c.c. of bromine was placed in a large untubulated retort of hard Bohemian glass, the neck of the vessel standing vertically upwards, and an elongated piece of ingot aluminum, the upper end of which was firmly tied with aluminum wire to a glass rod, was cautiously dipped into the liquid and withdrawn as soon as violent action began. By alternately lowering and raising the glass rod the lower end of the metal was immersed in the bromine at intervals short enough to keep up the temperature of the latter and make the action practically continuous, while there was no actual ignition, and but little bromine vapour was lost. As soon as a considerable portion of this bromine had become converted into aluminum bromide the further action became manageable. The remainder of the main quantity of metal to be treated was now at once added in lumps of 10 to 20 grms. each; a long tube funnel with a glass stop-cock near the upper end was introduced into the neck of the retort, and liquid bromine was allowed to drip in at just such a rate as to keep up steady but not inconveniently violent action, taking care to keep the metal always covered. When the pieces of metal had nearly disappeared the supply of bromine was stopped, about 30 grms. more of aluminum was added in filings, the contents of the retort were digested for 4 hours at about 230° C., and the fluid portion was then decanted off from the insoluble residue into another (tubulated) retort. Most of the silicon was left undissolved as a brown amorphous powder. Most of the iron was converted into ferric bromide, which, during the continued heating, was in part broken up, leaving ferrous bromide instead. A little copper derived from one sample only of the aluminum used, was of course converted into bromide also.

More than a kilogramme of crude aluminum bromide being thus prepared, it was purified by repeated fractional distillations at carefully regulated temperature, using as a receiver in each case the retort to be next employed, and adding each time, except the last, a few grammes of aluminum filings. About a sixth of the whole amount was each time first distilled off and rejected as liable to contain silicon bromide, a little of this compound actually occurring in the earlier distillations; and another sixth was left behind, in order to retain the iron, which was separated with greater difficulty. After five distillations the bromide was obtained perfectly colourless, and boiling steadily at 263°·3 C. under 747 m.m. pressure. Specimens were dissolved in water, and carefully examined for iron, silicon, copper, and other conceivable impurities, but none could be found. As an additional precaution, the last distillation was effected in a slow stream of pure nitrogen, so as to avoid any formation of oxide or oxy-bromide of aluminum, the propriety of this being suggested by BERTHELOT'S recent results* as to the thermic relations of aluminum to oxygen and the haloids, and the distillate was collected in three successive portions, the results of whose analysis will be separately given further on; they go to show that these three portions were sensibly identical. The individual specimens of pure bromide required were collected in little tubes of thin,

* 'Bulletin de la Société Chimique de Paris,' 20 Mars, 1879, p. 263.

hard glass, previously closed in at one end, carefully dried, and sealed at the other as soon as the tube was nearly filled, the fused bromide having been introduced through a miniature tube funnel to avoid smearing the upper end of the collecting tube, and a new, perfectly dry funnel used each time. The weight of each collecting tube had been taken beforehand, and the piece of glass drawn off in sealing being washed, dried, and weighed, the weight of the sealed tube itself was known, the difference between this and the total weight of tube and contents giving the amount of bromide.

Experiments to determine the amount of bromide in this compound by precipitation with a silver solution have the advantage over those of DUMAS, above quoted, upon the chloride that, as STAS has shown,* silver bromide practically does not share with the chloride of this metal the slight solubility in the exactly neutralised liquid from which precipitation has been effected which renders difficult an exact determination of the amount of silver needed. Pursuing in general the course so carefully examined by STAS, the following were the details of the method employed.

Preparation of pure metallic silver.—Pure metallic silver was prepared by dissolving in nitric acid nearly pure silver already on hand, diluting largely, precipitating with pure hydrochloric acid, digesting the precipitate with aqua regia, washing thoroughly, and reducing the purified chloride in the liquid way with sodium hydrate (from metallic sodium) and invert-sugar (from perfectly pure and well crystallised cane-sugar boiled with dilute hydrochloric acid). The metal, after having been carefully tested, was fused by a jet of purified hydrogen mixed with rather less oxygen than necessary for perfect combustion. To avoid the necessity for any cutting up afterwards with steel tools, the pulverulent metal was divided into a number of little lots of various weight, and these were supported upon the surface of little blocks made by compressing pure sugar charcoal (from cane-sugar quite free from heavy metals) made into a paste with pure cane-sugar syrup and gradually drying and heating to redness.† The fused silver thus obtained was examined for occluded oxygen, following the method of DUMAS‡ in his recent experiments. It was supported upon a thin layer of pure lime in a hard glass tube, and heated to moderate redness in a SPRENGEL vacuum. The amount of oxygen given off was less than that obtained by DUMAS, doubtless owing to the fact that his silver was fused under nitre and borax, while mine was, as just stated, melted on a surface of carbon with no flux. He obtained at the rate of 57 c.c. of oxygen (for 0° C. and 760 m.m.) per kilogramme of silver, and in other experiments, prolonging notably the time of fusion, as much as 158 c.c. and 174 c.c. I obtained but 34·63 c.c. per kilogramme, and in another experiment made by Mr. SANTOS, then a student in this Laboratory, the silver having been fused upon ordinary wood charcoal, but 30·12 c.c. was given off. All the silver used in the atomic weight determinations

* 'Comptes Rendus,' 73, 998. 'Annales de Chimie et de Physique' [5], 3, 289.

† This form of support had the advantage that if any particles of carbon should be mechanically enclosed in the silver they would be readily seen on solution of the latter in nitric acid.

‡ 'Comptes Rendus,' 86, 65. 'Chem. Centralblatt,' 27 Febr., 1878, S. 138.

was, in separate portions, heated in the SPRENGEL vacuum as long as any gas was expelled, and, having been treated with pure hydrochloric acid to remove any possibly adhering particles of lime, the granules were finally washed with pure water, dried, and kept for use in a glass stoppered bottle. An approximate calculation having been made of the quantity of silver which would be required to precipitate each of the specimens of aluminum bromide, an amount less than this by something under a decigramme was dissolved in nitric acid in a strong flask closed with a stopper, which was carefully opened when cold, and the contents were somewhat further diluted with water. The amount of specially purified nitric acid used was apportioned so as to leave the smallest possible excess after solution of the metal.

Precipitation of silver bromide—Details of method used.—To avoid the danger of losing aluminum bromide when it was brought in contact with water, the action being quite violent and attended with dispersion of white fumes, each one of the sealed thin glass tubes containing the bromide was, when the time came for using it, cautiously marked with transverse scratches at intervals of about half-an-inch by means of a writing diamond, and a strong glass bottle with a very well ground stopper having had a sufficient quantity of pure water placed at the bottom, the tube was broken across at the uppermost scratch, above the surface of the bromide, the empty point was dropped into the bottle, and the rest of the tube carefully lowered by means of a loose fitting spiral of platinum wire held sideways, so as to rest by the closed end on the bottom of the bottle without allowing the water to reach the bromide until the stopper had been inserted and tied down. By now gently inclining the bottle the water was brought very gradually into contact with the aluminum bromide, without dangerously violent action and without possibility of loss.

As soon as solution was complete and the bottle had cooled down the stopper was removed, any liquid adhering to it washed back into the bottle, and a stout glass rod with square end was used to gently crush the tube to small fragments, as otherwise its contents could not have been brought fairly into contact with the silver solution, since the interior of the tube would have become plugged up with silver bromide. The scratches previously made upon the glass rendered it easy to break it up without any splashing, and the rod was then well washed with pure water allowed to run directly into the bottle. The silver nitrate solution destined for this particular specimen was now washed out of the flask in which it had been shortly before prepared into the bottle containing the bromide, the stopper was again inserted, and the bottle was vigorously shaken as in the usual GAY-LUSSAC silver assay. The precipitation of the bromine was completed with a very carefully adjusted solution of silver nitrate, containing 1 milligramme of silver per cubic centimetre, and delivered from a burette* reading clearly to $\frac{1}{20}$th c.c. The correspondence in capacity of the burette and measuring flask used was well ascertained. It was at first intended to

* This burette was simply drawn down to proper bore at the bottom, and the flow of the liquid was regulated by the admission of air through a well ground stop-cock at the top.

use, for some at least of the experiments, *an excess* of silver, filter off the silver bromide formed, and determine silver in the filtrate by VOLHARD'S method* with a standard solution of sulpho-cyanate; but this plan was abandoned as less simple, and probably requiring further investigation in regard to inherent sources of error and limits of accuracy. The completion of the reaction was therefore ascertained simply by very cautious addition of the standard silver solution until all trace of turbidity ceased, verifying the result by counter test with a drop of very dilute solution of potassium bromide. By letting the bottle stand for a little while after each addition of silver solution and shaking, and then tilting it to one side so as to bring the upper portion of the liquid above the line it had before occupied on the glass, letting the new drop fall gently in, an exceedingly slight cloud was easily seen.

It should be added that the silver globules and the tubes of aluminum bromide, after final cleansing and drying, were handled only with forceps, so as to avoid any risk of traces of chlorides being taken up from the fingers, and due attention was given to the freedom of the laboratory atmosphere from hydrochloric acid or chlorine in other volatile forms.

Direct results of second series of experiments.—The results of the experiments made in this way were—

A.—Aluminum bromide from first portion of last distillate.

I.—	6·0024	grms. of $AlBr_3$ required	7·2793	grms. of Ag for precipitation	
II.—	8·6492	,, ,,	10·4897	,,	,,
III.—	3·1808	,, ,,	3·8573	,,	,,

B.—Aluminum bromide from second portion of last distillate.

IV.—	6·9617	grms. of $AlBr_3$ required	8·4429	grms. of Ag for precipitation.	
V.—	11·2041	,, ,,	13·5897	,,	,,
VI.—	3·7621	,, ,,	4·5624	,,	,,
VII.—	5·2842	,, ,,	6·4085	,,	,,
VIII.—	9·7338	,, ,,	11·8047	,,	,,

C.—Aluminum bromide from third portion of last distillate.

IX.—	9·3515	grms. of $AlBr_3$ required	11·3424	grms. of Ag for precipitation.	
X.—	4·4426	,, ,,	5·3877	,,	,,
XI.—	5·2750	,, ,,	6·3975	,,	,,

Third series of experiments.

Preparation of pure metallic aluminum.—A further supply of pure aluminum bromide having been made as above described, it was used to prepare metallic aluminum by reduction with sodium.

* FRESENIUS' 'Zeitschrift für analyt. Chemie,' 18ter Jahrg., 2tes u. 3tes Heft., S. 271.

With a view to render the bromide more manageable while in contact with the air, it was decided to unite it with an alkaline chloride, as the aluminum and sodium chloride is used in the ordinary process of DEVILLE, and in order to keep down the melting point, a mixture of both potassium and sodium chlorides was employed. The two alkaline salts were separately purified, carefully tested, well dried in platinum vessels, mixed in the proportion of one molecule of each, the mixture fused in lots of about 250 grms. in a platinum dish over a gas furnace, poured out into another such dish standing on a block of cold iron, the thin cake gently crushed to a coarse powder while still warm in a mortar of hard glazed porcelain (from which, it was afterwards proved by examination, no silica was taken up), and the pulverised product kept until needed in a well stoppered bottle. Separate portions of the purified aluminum bromide having been in the last distillation collected in tared glass flasks and weighed, a quantity of the above mixture of alkaline chlorides was weighed off for each corresponding to 1 molecule (K+Na)Cl for 1 molecule $AlBr_3$, and the flask having been heated until the bromide was fused, the potassio-sodic chloride was cautiously added. Very marked rise of temperature occurred, so that in a first attempt, using considerable quantities of the materials and mixing them abruptly, since such an effect had not been foreseen, the flask was violently cracked, and torrents of aluminum bromide vapour were driven off. This evolution of heat is interesting as evidence of chemical combination taking place, not only between two chlorides or two bromides, but between a chloride and a bromide. The fused mass was on cooling crushed to small fragments and coarse powder and preserved in a well-stoppered bottle. The precaution was not omitted of testing for any evidence of impurity derived from the flasks or mortar, but with negative result. The material thus prepared did not fume in the air, was sufficiently slow in taking up atmospheric moisture to be managed without difficulty, and fused on re-heating to about 130° C. The sodium to be used in decomposing it was in large ingots, which when needed were wiped to remove naphtha, the outer crust cut off with a knife, the large pieces roughly weighed, and the proper quantity rapidly cut up into small fragments without again moistening with naphtha.

The great difficulty in the way of obtaining pure metallic aluminum consists in obtaining crucibles of suitable material, especially such as shall not yield either iron or silicon. M. TISSIER* seems to have been more fortunate than I in the use of carbon vessels. The crucibles of hard carbon which I had on hand, purchased in Germany, contained both the above-named impurities, which were taken up in no small quantity by the aluminum; and I failed in sundry attempts to make crucibles of purer carbon, or to use this substance as a lining, the carbon either burning away, crumbling up, or permitting the fused materials to pass through its pores or through cracks in the mass. I at last succeeded in adapting to my purpose alumina itself, sufficiently cemented together by sodium aluminate. I was indebted to HENRY

* 'Comptes Rendus,' *loc. cit.*

PEMBERTON, Esq., Vice-President of the Pennsylvania Salt Manufacturing Company at Natrona, Pennsylvania, and to W. N. RICHARD, Esq., of the same works, for an abundant supply of aluminum hydrate, such as is thrown down by a stream of carbon dioxide from solution of sodium aluminate in the process of making soda from cryolite. This was not absolutely free from iron, but one lot contained traces only of this metal, insufficient, as it turned out, to contaminate the aluminum to be made in contact with it. The hydrate was strongly heated in well covered crucibles until it ceased to give off water; the alumina which was left required then to be guarded from the air, as it readily took up moisture again. All attempts to use it mixed with water and any unobjectionable cementing material to a plastic mass failed from excessive shrinkage and crumbling, but by mixing it in the dry state with dry sodium aluminate better results were obtained. The sodium aluminate had to be specially prepared, as that made (for soap boilers' use) at Natrona from cryolite contained too much iron. The dry mixture was pressed into wooden moulds, and three or four crucibles thus made having been very slowly and cautiously heated up in a gas furnace, stood fairly the necessary temperature of the reduction of aluminum, although they were very fragile. On the whole, however, it was found best to use a highly aluminous BEAUFAYE crucible, with a thick lining of this mixture of dry alumina and sodium aluminate well rammed in and very gradually heated. There were some failures from cracking of the crucibles or linings, and whenever the slightest contact of the metallic aluminum with the outer crucible occurred, silicon and generally iron were sure to be found in the metal. With successful prevention of this by an adequately thick and perfectly continuous lining there was much difficulty in securing a sufficiently high temperature in the interior, since the conducting power for heat of the alumina linings seemed to be quite low. This led to much loss of sodium by combustion, and but a very small yield indeed of really pure aluminum was secured. When the crucible had been heated up ready for the reduction, a small quantity of the pulverised mixture of potassium and sodium chlorides was thrown in; soon afterwards the aluminum bromide (which had been fused with the alkaline chlorides) with the proper quantity of sodium was introduced,* and as soon as the violent reaction was over a further portion of the mixed alkaline chlorides.

Only the large, well-fused globules of aluminum were picked out; these were refused once or twice before a blowpipe flame upon a support of alumina, to free them from any possible remains of the flux; any trace of oxide was detached by acting slightly upon the surface with pure hydrochloric acid, and the globules were then well washed with water, and dried by a gentle heat. Specimens cut from different portions of the globules were carefully tested, particularly for silicon, iron, sodium, and

* Aside from the question of expense there is some advantage in using aluminum bromide for making the metal, on account of the low melting-point of the sodium bromide which is left. CARNELLEY'S recent determinations (Chem. Soc. Journ., July, 1878, pp. 279, 280) make the melting-point of sodium bromide 708° C., while that of the chloride is 772°, and that of the fluoride above 902°.

potassium; and a sufficient quantity of the metal for the intended experiments was found to yield no appreciable trace of impurity. The surface of the specimens to be used which had touched the cutting pliers was again cleansed by acid and water. This pure aluminum did not differ much in physical character from the ordinary metal of commerce; it seemed, however, to be somewhat whiter, was distinctly softer, and had a little higher density, the mean of three closely-agreeing determinations made at 4° C. giving the number 2·583 as referred to water at the same temperature.

Production of hydrogen by aluminum, and measurement of the gas.—Details of method used.—The pure metal was used for the determination of its atomic weight by acting upon a known weight of it with a strong solution of sodium hydrate and determining the amount of hydrogen evolved. The advantage of using an alkali rather than hydrochloric acid, as in TERREIL'S experiment above quoted, lies in the non-volatility of the former, only vapour of water having to be separated from the hydrogen, while sulphuric acid is not available on account of the resistance to its action of aluminum. In 1863 Fr. SCHULZE* proposed to measure the volume of hydrogen given off by the action of an alkaline solution on commercial aluminum as the means of approximately deciding on the comparative purity of different specimens. The nature of the reaction was established by preliminary experiments, which proved to me that normal sodium aluminate alone is formed, so that each atom of aluminum liberates three atoms of hydrogen. The sodium hydrate was prepared from metallic sodium, and was used in the form of a solution so strong as scarcely to lose a sensible amount of water by the passage through it of a dry gas at common temperature—such an alkaline solution, so far as strength is concerned, as would be used to absorb carbon dioxide in an organic analysis. The quantity taken for each experiment was but a few cubic centimetres, and but little beyond the exact amount required for the solution of the metal; a small excess was, however, always allowed, so that the action might not become very languid towards the end. This strong alkaline solution was prepared with water which had been boiled to expel air, and the solubility in it of hydrogen was ascertained to be so small that any correction on this account would have fallen within the limits of inevitable error, and might be safely neglected.

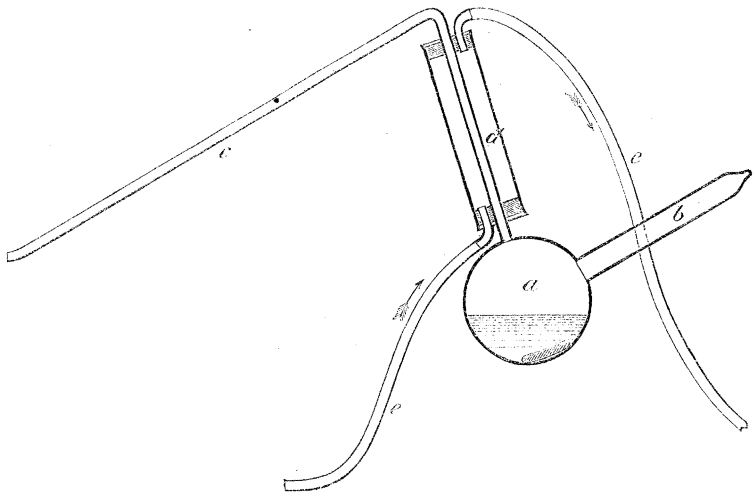
To secure accurate measurement of a somewhat large volume of hydrogen, two stout flasks were selected, one holding about a litre and the other about half as much, and with narrow necks of rather more than usual length; and on the necks a simple millimetre scale was marked. One of these flasks having been carefully filled with mercury and inverted over the mercurial trough, the hydrogen was collected in it, such a quantity of aluminum being used in each experiment as previous trials had shown would yield gas enough to bring the level of the mercury within the range of the scale on the neck. To thus obtain such a volume of gas as could be accurately measured in the narrow part of the flask it was necessary to note in advance roughly the prevailing

* FR. SCHULZE, "Die gasvolumetrische Analyse," S. 18, quoted in v. WAGNER, 'Jahresbericht,' u. s. w., 1864, S. 23.

temperature and pressure, and to take advantage of a time when these were not undergoing much change. The level of the mercury having been noted on the millimetre scale, the corresponding volume was afterwards determined by calibration with mercury, weighed in in portions of about half a kilogramme.

The little piece of apparatus used for the solution of the aluminum is shown in fig. 2, in which (*a*) represents a glass bulb of about 65 m.m. diameter; (*b*) a tube connected therewith, originally open at both ends, and about 12 m.m. diameter and 175 m.m. long, but afterwards reduced in length to about 100 m.m. by drawing off and sealing, as shown in the figure; (*c*) is the much smaller tube for carrying off the gas produced; (*d*) is a water jacket like that of the common LIEBIG'S condenser, formed by a piece of larger tube surrounding the ascending limb of (*c*), and put in place before (*c*) was bent; while (*e*, *e*) represent small indiarubber tubes for circulating a current of water through (*d*).

Fig. 2.



Each experiment was made as follows: The proper quantity of strong solution of sodium hydrate, its volume accurately measured, having been introduced into the bulb by means of a little tube funnel passed through (*b*), taking care to leave the surface of the latter clean, the aluminum (usually in a single piece of elongated shape) was passed into (*b*), held nearly horizontal, so that the metal did not slip down into the bulb, but rested 40 or 50 m.m. from it. (*b*) was now drawn off and sealed with a well-rounded end. The bulb was touched for a moment or two with the hand, so as to expel a very little air, and the outer end of the small tube (*c*) was introduced into the mercury of the trough, taking care that (*b*) was still kept in such a position as to prevent the aluminum coming in contact with the alkaline solution. After a sufficient lapse of time for the apparatus to have acquired the temperature of the room, the barometer and thermometer and the difference of level of the mercury in the trough and in (*c*) were read off;* so that, knowing the volume of alkaline solution introduced

* All readings were of course made from a distance with the aid of a small telescope.

and of aluminum (the latter from its weight), calibration of the bulb and tubes after the experiment was over completed the data necessary to determine the volume of air which the apparatus contained at the beginning. The aluminum was now made to slide down into the bulb, the end of the gas-delivery tube (*c*) having been brought under the mouth of the measuring flask. Over-rapid evolution of hydrogen and any considerable rise of temperature were prevented, partly by tilting the bulb so that the little piece of aluminum rested against one side and exposed but a part of its surface to the action of the liquid, and partly by cooling the outside of the bulb with water; while, on the other hand, it sometimes became necessary to gently warm the liquid towards the end of the experiment. To guard against more than traces of aqueous vapour being carried away with the hydrogen, a current of ice-water was kept up through (*d*). As soon as the last of the aluminum had disappeared, leaving the liquid quite clear, (*c*) was brought up into a nearly vertical position, and the apparatus left to itself until the temperature of the room had been attained. The barometer and thermometer, height of mercury in (*c*) above that in trough, and level of mercury in neck of measuring flask (after the last traces of moisture had been removed from the hydrogen by means of a stick of caustic potash), with its height above that in trough, were now read and recorded. Lifting (*c*) straight up from the trough, the mercury in this tube was got out by running a wire up and down in it, and inverting it, the whole of the remaining space in (*a*), (*b*), and (*c*) was filled up with alkaline lye of the same strength with that already contained, this liquid being run in from a graduated burette through a slender tube funnel, and the volume used noted, so as to show how much liquid had been already present. The apparatus being now emptied, washed out, and calibrated (with water, instead of mercury, on account of the difficulty of getting the interior quite dry), the volume of gas remaining in it at the close of the experiment was had from the difference between the total capacity (to the level of the mercury in (*c*)) and the volume of liquid which the bulb had contained at the close of the experiment, these taken together with the data for pressure and temperature.

On account of slight rise of temperature during the solution of the metal, the volume of hydrogen left in the bulb and tubes was always less than the air in the same at the beginning; and, after reduction to normal temperature and pressure, the difference had to be subtracted from the volume of gas collected in the flask.

In order to connect the weight of the aluminum with the weight of the hydrogen, the latter being obtained from its observed volume and REGNAULT'S determination of its density, it was necessary that the weight of the metal should be absolute, or in terms of equal value with those used in REGNAULT'S researches; hence, as has been already stated, the weights used were such as had had their real value determined, and the precaution of double weighing was applied. The quantities of metal used being small, the centre of gravity of the balance beam was so adjusted as to give great sensitiveness.

In calculating the weight of the hydrogen from its volume, the difference in the

value of the force of gravity at Paris and at the University of Virginia had to be taken into account. In view of the difference of latitude and elevation above the sea this constant is, in C.G.S. units,

For Paris.	980·94
For University of Virginia . . .	979·95

and, applying the difference in nominally normal pressure at the two places, REGNAULT'S value for the weight of a litre of hydrogen at 0° C. and 760 m.m., ·089578 grm., becomes ·089488 grm.

In the experiments made in this way the only assignable cause of constant error, tending to affect in a particular direction the atomic weight deduced from them, seems to be the retention in solution of traces of hydrogen by the alkaline liquid in the bulb. The tendency of this is, of course, to make the atomic weight of aluminum appear greater than it should be, but I am satisfied that the possible extent of such error must be excessively minute, inappreciable within the limits of error of observation.

Direct results of first set of third series of experiments.—The results obtained were as follows :—

A.—Hydrogen by volume at 0° C. and 760 m.m.

I.—	·3697	grm. of Al	gave	458·8	c.c. = ·04106	grm. of H.
II.—	·3769	,, ,,		467·9	,, = ·04187	,,
III.—	·3620	,, ,,		449·1	,, = ·04019	,,
IV.—	·7579	,, ,,		941·5	,, = ·08425	,,
V.—	·7314	,, ,,		907·9	,, = ·08125	,,
VI.—	·7541	,, ,,		936·4	,, = ·08380	,,

Second set of experiments of third series.—Hydrogen collected and weighed as water. —Details of method used.—As the collection and accurate measurement of larger quantities of hydrogen would be difficult from the great weight of mercury to be dealt with, while it seemed desirable to repeat these experiments with a larger amount of aluminum, an arrangement was adopted for burning the hydrogen and weighing it as water.

A bulb like that described above was used for the reaction between the aluminum and solution of sodium hydrate, another small tube (which may be designated as (x)) being connected, however, with the bulb, for the purpose of sweeping out air at the beginning of the combustion and the remainder of the hydrogen at the end by a current of other gas. The gas from the delivery tube (c) was carried through a series of four drying tubes, containing in the former two pumice stone soaked with pure sulphuric acid of full strength, and in the other two well dried asbestos and loose, woolly phosphorus pentoxide; thence it passed through a long combustion tube, filled for the first two-fifths with pure, finely granular cupric oxide, which had been recently ignited, and for two-fifths more with turnings of electrotype copper oxidised on the

surface, while the last one-fifth of its length remained at first unoccupied, to be filled later as will be described; the vapour of water being finally collected beyond this combustion tube in a single light drying tube of calcium chloride, one of sulphuric acid on pumice, and one of phosphorus pentoxide.

The whole of the apparatus having been put together, with the exception of the three final drying tubes, for which at first a single unweighed calcium chloride tube was substituted, with sodium hydrate solution in the bulb, and metallic aluminum in the tube (b), a slow stream of carefully purified and well dried air was passed through from (x) for some time, while the combustion tube was heated to low redness. Having allowed it to cool down to the temperature of the room, the stream of air from (x) was replaced by one of dry nitrogen; a plug of soft copper turnings with bright unoxidised surface was introduced into the further end of the combustion tube, so as to fill up the unoccupied fifth of its length, and it was again brought to and kept at a red heat. After the nitrogen had passed through at this temperature for about twenty minutes, the three drying tubes for the collection of the water to be formed, having been standing for some time in the balance case, were accurately weighed, and connected with the further end of the combustion tube, the previously used and unweighed calcium chloride tube being removed. The tube (x) having been closed, the tube (b) was now tilted so as to make the aluminum slip down into the alkaline liquid, and as in the experiments already described, the rate at which the hydrogen was evolved was controlled by inclining the bulb so as to vary the extent of surface of the metal attacked, and by cooling the outside of the bulb with water.

As soon as the metal was all dissolved, nitrogen was again introduced by (x) to sweep out the remaining hydrogen, limiting the quantity of the former gas to such an amount as was thought necessary for this purpose. This nitrogen was then in turn replaced by pure and dry air, which was passed through the apparatus until the surface of the copper which had been reduced was reoxidized, this being done to avoid any risk of occluded hydrogen being retained, while the nitrogen had served to obviate the danger of explosion. The drying tubes were then finally removed from the further end of the combustion tube, and weighed after exposure to the atmosphere of the balance case long enough to permit the surface of the glass attaining a constant condition. In both weighings the reduction to equivalent weights *in vacuo* was duly attended to, the weights and densities of all the materials making up the drying tubes and their contents having been previously ascertained. The last tube of the set was weighed separately, as was the last of the drying tubes connected with the reaction bulb, and it was found that, there being no increase of weight on the part of either of them, the absorption of aqueous vapour was sensibly complete.

Although all the precautions I could think of were taken in these experiments, the well known difficulty of absolutely excluding moisture, of which every joint to the apparatus becomes a possible source, so that in ordinary organic analysis the amount of hydrogen found may be expected to come out rather above than below the truth,

leads to the suspicion that such constant error as may have been involved tended in this direction, and if so that the resulting atomic weight would be made to appear somewhat too low. The extent of error from this cause, however, if it existed at all, must have been extremely small.

Direct results of second set of experiments of third series.—The results of these last experiments were—

B.—Hydrogen weighed as water.

I.—2·1704	grms.	of Al gave	2·1661	grms.	of H_2O.
II.—2·9355	,,	,,	2·9292	,,	,,
III.—5·2632	,,	,,	5·2562	,,	,,

Calculation of results.

In calculating the atomic weight of aluminum from the data furnished by the above described experiments, the atomic weights assumed for the other elements involved are those which result from the researches of STAS and the previous investigation by DUMAS and STAS of the composition of water, namely—

O=15·961 S=31·996 N=14·010

In regard to silver and bromine a difficulty arises from the fact that the relation between these elements was determined by STAS with metallic silver which, as DUMAS* has pointed out, contained in all probability occluded oxygen. It appears from DUMAS' experiments and from mine, that the quantity of oxygen which may be so retained varies with the conditions under which the metal is fused, and it is impossible now to ascertain precisely how much was present in that used by STAS, while the correction to be applied on this account, though small, is not inappreciable in its effect upon the atomic weight of the aluminum. Omitting to extract in the SPRENGEL vacuum the occluded oxygen from the silver used in my experiments would not have secured identical condition of the silver with that of the metal used by STAS, since the circumstances of fusion and cooling would probably not have been altogether the same, and it seemed best to use silver fully purified in this respect, so that my results might be directly comparable with any obtained in the future, since this source of error once pointed out ought not to be hereafter neglected. I have therefore used as the atomic weights of silver and bromine the numbers obtained by STAS (from his experiments on silver bromide and bromate), recalculated on the assumption that the metal employed by him would have yielded 57 c.c. (reduced to 0° C., and 760 m.m.) or 82 mgrm. of oxygen per kilogramme, this being the quantity obtained by DUMAS from silver treated as nearly as possible as was in all likelihood that which STAS employed. This has the advantage of reducing the remaining error to that only which depends on the *difference* between the real amount of oxygen which was

* *Loc. cit.*

present and that assumed in such calculation, instead of leaving the whole resulting from using STAS' numbers uncorrected, my silver having had the oxygen removed, while his had not been so treated. The atomic weights adopted then for these two elements are—

Ag=107·649 Br=79·754

Calculated results.—The following are the values obtained for the atomic weight of aluminum from the different series of experiments, with the probable (mean) value resulting from each set, the difference from this mean of each individual experiment, and the probable error of the mean itself calculated in the usual way by the method of least squares:

First series.

A.			B.		
Experiment.		Diff. from mean.	Experiment.		Diff. from mean.
I.	Al=27·029	−·011	VI.	Al=27·114	+·018
II.	,, 27·043	+·003	VII.	,, 27·095	−·001
III.	,, 27·055	+·015	VIII.	,, 27·107	+·011
IV.	,, 27·068	+·028	IX.	,, 27·067	−·029
V.	,, 27·005	−·035	X.	,, 27·096	·000
Mean	,, 27·040		Mean	,, 27·096	
Probable error of mean result		±·0073	Probable error of mean result		±·0054

Second series.

A.			B.		
Experiment.		Diff. from mean.	Experiment.		Diff. from mean.
I.	Al=27·035	+·001	IV.	Al=27·028	+·005
II.	,, 27·021	−·013	V.	,, 26·993	−·030
III.	,, 27·046	+·012	VI.	,, 27·036	+·013
			VII.	,, 27·028	+·005
			VIII.	,, 27·030	+·007
Mean	,, 27·034		Mean	,, 27·023	
Probable error of mean result		±·0049	Probable error of mean result		±·0052

C.

Experiment.		Diff. from mean.
IX.	Al=26·999	−·019
X.	,, 27·034	+·016
XI.	,, 27·021	+·003
Mean	,, 27·018	
Probable error of mean result		±·0069.

Third series.

A.			B.		
Experiment.		Diff. from mean.	Experiment.		Diff. from mean.
I.	Al=27·012	+·007	VII.	Al=26·995	+·005
II.	,, 27·005	·000	VIII.	,, 26·999	+·009
III.	,, 27·022	+·017	IX.	,, 26·977	−·013
IV.	,, 26·988	−·017			
V.	,, 27·006	+·001			
VI.	,, 26·996	−·009			
Mean	,, 27·005		Mean	,, 26·990	
Probable error of mean result		±·0033	Probable error of mean result		±·0046

In view of the gradual loss of water which, as has been shown, crystallised ammonium alum undergoes on exposure to the atmosphere, I feel that of these various sets of experiments, B of the first series is entitled to least confidence, and the considerable difference between its results and the others leads me to favour its rejection. On the other hand, I am inclined to attach most weight to series 3, A, since the method used was very simple in principle, the determination of one of the two quantities concerned was rendered very exact by the great volume occupied by the hydrogen, the comparison was made directly with the standard element in our system of atomic weights and not through the intervention of any other substance whose atomic weight must be assumed, and the agreement of the results among themselves is particularly good, as shown by the probable error of the mean being the smallest reached.

General mean of results.—The general mean from all of the thirty experiments, if all be included in the calculation, is Al=27·032, with a probable error for this mean of ±·0045.

If series 1, B, be excluded, the mean of all the remaining twenty-five experiments is Al=27·019, with a probable error of ±·0030. The third decimal having no positive value, we may take Al=27·02. If integer numbers be used for O, N, C, Na, &c., Al=27.

All the experiments which I have made are reported, except three or four in which there was manifest failure, as by accidental loss of material to a visible extent, and which were on that account not completed.

The general result adds, I trust, aluminum to the, unfortunately still limited, list of those elementary substances whose atomic weights have been determined within the limits of precision attainable with our present means of experiment.

*Bearing of final result upon "*PROUT'S *law."*

It is interesting to observe that this result also adds one to the cases already on record of the numbers representing carefully determined atomic weights approaching closely to integers, and leads to a word on the reconsideration of "PROUT'S law." The recent researches of Mr. LOCKYER, not unsupported by evidence drawn from other sources, have tended to suggest the possibility, at least, that the forms of matter which as known to us under ordinary conditions we call elements may be susceptible of progressive dissociation at enormously high temperature, and, under circumstances in which this supposed state of dissociation admits of being spectroscopically observed, some of the characteristic features in the spectrum of what is usually known to us as hydrogen become in a very remarkable degree prominent. If such dissociation may really occur, and if the atoms of hydrogen as commonly known to us form either the last term, or any term not far removed in simplicity from the last, in the progressive breaking up of other forms of matter, it is obvious that "PROUT'S law," or some modification of it, such as was many years ago suggested by DUMAS, *must* be true, the atomic weights of all the other so-called elements must be multiples of that of hydrogen, or multiples of that fraction of the hydrogen atom which may result from the dissociation of this body itself. If such fraction be very small as compared with the effect of the inevitable errors of experiment, the experimental verification or refutation of the law will prove impossible, but if it be considerable, as for instance one-half of the commonly known hydrogen atom, or one-fourth, as assumed by DUMAS, the question admits of practical examination.

Well deserved attention has for some years past been given to the labours of STAS in this direction, and his main result is no doubt properly accepted, if stated thus, that the differences between the individual determinations of each of sundry atomic weights which have been most carefully examined are distinctly less than their difference, or the difference of their mean, from the integer (or one-half or one-fourth unit which PROUT'S law would require.

But the inference which STAS himself seems disposed to draw, and which is very commonly taken as the proper conclusion from his results, namely, that PROUT'S law is disproved, or is not supported by the facts, appears much more open to dispute.

It must be remembered that the most careful work which has been done by STAS and others only proves by the close agreement of the results that *fortuitous* errors have been reduced within narrow limits. It does not prove that all sources of *constant* error have been avoided, and indeed this never can be absolutely proved, as we never can be sure that our knowledge of the substances we are dealing with is complete. DUMAS' late observations on the occlusion of oxygen by metallic silver constitute an illustration of this, some of the best of STAS' results being thereby undeniably vitiated, though probably to but a minute extent.

Of course one distinct exception to the assumed law would disprove it, if that exception were itself fully proved, but this is not the case.

As suggested by MARIGNAC and DUMAS, anyone who will impartially look at the facts can hardly escape the feeling that there must be some reason for the frequent recurrence of atomic weights differing by so little from accordance with the numbers required by the supposed law.

As the question stands at present, the following 18 atomic weights are the only ones which may be fairly considered as determined with the greatest attainable precision, or a very near approach thereto, and without dispute as to the methods employed—

*Oxygen	15·961
*Nitrogen	14·010
Chlorine	35·371†
Bromine	79·757†
Iodine	126·541†
*Sulphur	31·996†
*Potassium	39·042
*Sodium	22·987
*Lithium	7·005
Silver	107·667†
Thallium	203·655‡
*Aluminum	27·019
*Carbon	11·97
*Phosphorus	30·96
Barium	136·84
Calcium	39·90
*Magnesium	23·94
Lead	206·40

If now we discard altogether DUMAS' assumption of multiples of ·5 or ·25, and consider simply the indications afforded of PROUT'S law in its original form, we may safely take the first decimal place of each of these numbers as quite freed from the influence of *fortuitous* errors, while the second decimal is nearly so in many instances. It appears that out of the 18 numbers, 10 (those to which an asterisk is prefixed) approximate to integers within a range of variation less than one-tenth of a unit. What then is the degree of probability that this is purely accidental, as those hold who carry to the extreme the conclusions of BERZELIUS and STAS? Since there are

† STAS' numbers, uncorrected for occlusion of oxygen by silver.

‡ CROOKES' number modified by taking O=15·961 instead of 15·96.

five intervals of ·1 each between any integer and the ·5 which divides it from the next higher (or lower) integer, the result is given by the expression

$$5^{-18}\left[1+\frac{\lfloor 18}{\lfloor 17}\times 4+\frac{\lfloor 18}{\lfloor 16\ \lfloor 2}\times 4^2+\frac{\lfloor 18}{\lfloor 15\ \lfloor 3}\times 4^3+\ldots\ldots\frac{\lfloor 18}{\lfloor 10\ \lfloor 8}\times 4^8\right]$$

and the probability in question is found to be only equal to 1 : 1097·8.

Of course this result might be easily varied by assuming other limits of precision as marking accordance with the law within the range of possible constant error, but this example seems to be based upon not unfairly assumed ground in this respect, and seems sufficiently to illustrate the point that not only is PROUT'S law not as yet absolutely overturned, but that a heavy and apparently increasing weight of probability in its favour, or in favour of some modification of it, exists and demands consideration.