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Revision of the Atomic Weight of Gold

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XIII. *Revision of the Atomic Weight of Gold.*

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UNTIL lately gold ranked among the elementary substances of which the general properties had been well ascertained, but in regard to the atomic weights of which our knowledge was least satisfactory. That this constant should be determined as accurately as possible for gold was desirable in view of its bearing on the precise place assigned the metal in the "periodic" classification of the elements based on the ideas of NEWLANDS, ODLING, MENDELEJEFF, and L. MEYER. Furthermore, an exact knowledge of the atomic weight of gold might be conveniently applied in the determination of the atomic weights of some of the other elements. A practical laboratory reason for desiring to possess a trustworthy value for this constant was also presented by the facility with which gold compounds of many organic substances may be prepared, and the ease with which their composition may be ascertained by simple ignition in the air and weighing of the residual gold, the results leading to a knowledge of molecular composition when the atomic value of the weight of the metal obtained is assumed to be known.

For the last three years and a half I have been occupied, during a large part of such time as has been available for original work, in devising and carrying out experiments aiming at the redetermination of the constant in question. The difficulties met with have been greater than were at first looked for, and have led to much time and labour being consumed in attempts to overcome them. About two years ago, when this work was already well under way but still in progress, there appeared the results of experiments aiming at the same end, by KRÜSS in Germany and by THORPE and LAURIE in England—experiments made with the care and accuracy of modern methods, and apparently deserving of much confidence. My own work, however, was continued, as we cannot have too many careful independent determinations of atomic weights by different workers, and as I had used to a considerable extent other processes than those on which the newly published determinations were based, while the chemists named had employed, in the main, one and the same method. A preliminary notice of my work was read in the Chemical Section of the British Association at the Manchester meeting of 1887. The details of my experiments and the results which I have reached are now laid before the Royal Society.

Earlier Determinations of the Atomic Weight of Gold.

In the work of L. Mulder, 'Historisch-kritisch Overzigt van de Bepalingen der Æquivalent-Gewigten van 24 Metalen,' Utrecht, 1853, and in the recent papers of Krüss and of Thorpe and Laurie, there are abstracts of reports upon a number of experiments by chemists of the earlier part of this century bearing on the value to be assigned to the atomic weight of gold, such as those of Proust,* Richter,† Dalton,‡ Thomson,§ Oberkampf,‖ Pelletier,¶ Figuier,** and Javal;†† but of these none deserve any attentive consideration at the present day, the methods used having in some cases been such that accurate results could not be expected from them, and the actual figures obtained in other cases differing so widely from each other that no importance can be attached to them.

Before the year 1887 but two chemists—Berzelius and Levol—had published the results of experiments furnishing fairly admissible data for calculating the atomic weight in question.

A. *Experiments of* Berzelius, 1813.‡‡—The method adopted was the precipitation of a solution of auric chloride by metallic mercury, determining the quantities of mercury dissolved and gold thrown down. In the original paper but a single experiment is reported, but later the author appears to have made a second,§§ so that for the two Meyer and Seubert, in their recalculation of the atomic weights of the elements,‖‖ give as the sums of the amounts of mercury and gold found to be equivalent to each other 24·240 grm. of the former and 15·912 grm. of the latter. Taking these quantities to represent the ratio between the weights of three atoms of mercury and two atoms of gold, we have for the weight of the single atom of the latter (H = 1)

If we assume Hg = 199·8 (L. Meyer and Seubert‖‖). . 196·73
" " " 199·712 (F. W. Clarke¶¶). . . . 196·65

This method recommends itself as advantageous on several grounds, and the experiment deserves repetition as soon as the atomic weight of mercury becomes

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* 'Journal de Physique,' vol. 62, 1806, p. 131; 'N. Gehlen, Journal,' vol. 1, 1806, p. 477.

† 'Schweigger, Journal,' vol. 7, 1813, p. 43.

‡ 'New System,' part 2, 1810, p. 253.

§ 'First Principles,' vol. 1, 1825, p. 440.

‖ 'Annales de Chimie,' vol. 80, 1811, p. 140.

¶ 'Annales de Chimie,' vol. 15, 1820, pp. 5, 113.

** 'Annales de Chimie,' vol. 19, 1821, p. 177.

†† 'Annales de Chimie,' vol. 17, 1821, p. 337; 'Schweigger, Journal,' vol. 33, 1821, p. 238.

‡‡ 'Stockholm, Kgl. Vetensk. Akad. Handl.,' 1813, p. 185.

§§ Berzelius, 'Lehrbuch,' vol. 3, p. 1212, str. 70.

‖‖ Lothar Meyer u. Karl Seubert, 'Die Atomgewichte d. Elemente aus d. Originalzahlen berechnet,' Leipzig, 1883, p. 191.

¶¶ "The Constants of Nature," 'Smithsonian Miscellaneous Collections,' Washington, D.C.

known with greater certainty than at present. But until this condition is fulfilled the result for gold cannot be depended upon as of the first rank in exactness. In any renewed attempt to apply this method several questions would have to be examined as to the precise nature of the solution used, and of the reaction itself.

[BERZELIUS[*] also precipitated gold by means of a known quantity of phosphorus from a solution of the chloride used in excess, and his results, as calculated by F. W. CLARKE,[†] lead to the atomic weight 195·303 for gold; but this process appears ill adapted to give very exact results, even in such hands as those of the great Swedish chemist, and the value obtained is certainly too low in the light of more modern researches.]

B. *Experiments of* BERZELIUS, 1844.[‡]—In these experiments potassium auri-chloride, which, it was found, could not be completely dried without loss of chlorine, was ignited in hydrogen, and the residue was treated with water to dissolve potassium chloride, the quantity of which was determined, as well as that of the metallic gold left undissolved. Five experiments were made, and the aggregate amounts obtained of potassium chloride and gold were 3·7800 grm. and 9·9685 grm. respectively. These figures, if we assume K = 39·03 and Cl = 35·37, give for the atomic weight of gold 196·20, the lowest result from one of the individual experiments being 196·11, and the highest 196·27.

Among possible sources of error in this process we may note as deserving consideration the conceivable retention by the potassium auri-chloride of hydrogen auri-chloride, and the difficulty of directly determining with accuracy the potassium chloride extracted by water. The former would lead to a higher result for gold than should be obtained; the latter might either give too low a result in consequence of imperfect drying, or too high if there were partial loss by volatilization, either during the ignition in hydrogen or in subsequently recovering the potassium chloride from solution. The quantities of material used were smaller than is probably desirable.

C. *Experiments of* LEVOL, 1850.[§]—A weighed quantity of gold was dissolved as auric chloride, the metal reduced from the solution by means of sulphur dioxide, and the sulphuric acid formed was determined as barium sulphate. In two experiments, reported as giving exactly the same result, 1 grm. of gold gave 1·782 grm. of barium sulphate. Hence, if Ba be taken = 136·86, S = 31·98, and O = 15·96, we have for the atomic weight of gold the number 195·86.

Of the sources of error to which this method is liable probably the most important are atmospheric oxidation of sulphurous to sulphuric acid and imperfect washing out of soluble compounds of barium from the barium sulphate. Both would tend to give too low a result for gold.

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[*] BERZELIUS, 'Lehrbuch,' 5. Aufl., vol. 3, p. 1188.

[†] "The Constants of Nature," 'Smithsonian Miscellaneous Collections,' Washington, D.C.

[‡] BERZELIUS, 'Lehrbuch,' 5. Aufl., vol. 3, p. 1212.

[§] 'Annales de Chimie,' [3], vol. 30, p. 355.

For all these earlier experiments details are wanting as to the exact mode of purification of the gold and other materials used, and in the weighings there appears to have been no correction introduced for atmospheric buoyancy; the results doubtless represent apparent, not absolute, weights.

[There is also to be quoted the statement of JULIUS THOMSEN,* that he found in hydrogen brom-aurate ($AuBr_3.HBr.5H_2O$) 32·11 per cent. of gold and 52·00 per cent. of bromine, from which he concluded that Au = probably about 197. Taking Br = 79·76, and calculating from the ratio of Br_4 : Au, the number is 197·01.]

Recent Careful Determinations of the Atomic Weight of Gold.

A. *Experiments of* GERHARD KRÜSS, 1886.†—The author has described in detail the means resorted to for the preparation of pure metallic gold, and especially for its separation from silver and the metals of the platinum group, with an account of the spectroscopic examination of the gold employed. He has then given a full account of:—*a.* His determinations of the gold and chlorine (the former reduced by a stream of sulphur dioxide; the latter precipitated and weighed as silver chloride) in a neutral solution of auric chloride, prepared by the action of water on the so-called auro-auric chloride (Au_2Cl_4),‡ itself prepared by the direct action of chlorine on metallic gold; *b.* Like determinations of gold and chlorine in sublimed auric chloride, made by direct action of the elements on each other with careful regulation of the temperature; *c.* Determinations of the gold in a weighed quantity of potassium auri-bromide ($KAuBr_4$), the metal in some experiments reduced from a solution of the salt by sulphurous acid, in others reduced from the dry salt by heating in a stream of hydrogen; *d.* Determinations of the gold and bromine (the former thrown down by sulphurous acid; the latter precipitated as silver bromide) in the same salt, potassium auri-bromide; *e.* Determinations of the loss of weight (representing 3 atoms of bromine for 1 of gold) undergone by heating potassium auri-bromide gradually to 320° C., towards the end in a stream of hydrogen; *f.* Determinations of the quantity of potassium bromide recovered from the residue left in the experiments of *e* by treatment of this residue with water, separation of the metallic gold, careful evaporation of the liquid, and final cautious heating of the potassium bromide over a free flame. In the experiments of series *a* account was taken of the somewhat different processes of purification of the gold used, but, no corresponding differences

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* 'Journ. Prakt. Chem.,' vol. 13, 1876, p. 345.

† 'LIEBIG's Annalen,' vol. 238, p. 30; and separate publication, G. KRÜSS, 'Untersuchungen über das Atomgewicht des Goldes,' München, 1886.

‡ KRÜSS has in a later paper ('Berichte Deutsch. Chem. Gesell.,' vol. 20, p. 2634) denied the existence of auro-auric chloride as a definite compound, but admits that the substance so described by JULIUS THOMSEN yields on treatment with warm water a solution of pure neutral auric chloride, with separation of metallic gold.

being observable in the results obtained, no further record was made in the remaining series of the history of the gold used in these.

After correction of the weighings for atmospheric buoyancy in such cases as seemed to the author to involve a correction worth noticing, the following results were calculated from the figures obtained, these figures agreeing in general closely with each other in each series :—

Series *a*.	Mean of	8	experiments.	Atomic weight of	gold	= 196·622
,, *b*.	,,	4	,,	,,	,,	= 196·143
,, *c*.	,,	9	,,	,,	,,	= 196·741
,, *d*.	,,	5	,,	,,	,,	= 196·743
,, *e*.	,,	4	,,	,,	,,	= 196·619
,, *f*.	,,	4	,,	,,	,,	= 196·620

Leaving out the results of series *b* on the ground of the very small quantity of sublimed auric chloride available, and the considerable discrepancy of one of the results (that in which most material was used) from the rest, the author calculates from the remaining 30 experiments the general mean 196·669 ; but, taking into account the greater or less closeness of agreement of the figures obtained by the several methods, he comes to the conclusion that 196·64 may better be assumed as the true atomic weight of gold. In these calculations Ag was assumed = 107·660, Cl = 35·368, Br = 79·750, and K = 39·040.

As regards possible sources of constant error in Krüss's experiments, it may be observed that—

1. In series *b* very small quantities of sublimed auric chloride were used—the whole amount available for all four experiments being only about seven-tenths of a gramme—and it is probable that a little free chlorine may have been physically retained by the chloride in spite of the long-continued passage over it of dry air. The experiment in which the largest quantity of material was used gave the atomic weight = but 194·79. On these grounds the author himself excludes the series from consideration in calculating his general mean.

2. In series *c*, *d*, and *e* the evidence is pretty strong, but perhaps not conclusive, to show that potassium auri-bromide can be rendered absolutely dry by exposure to air in a vessel containing phosphorus pentoxide, either at ordinary or higher temperatures, without, at the same time, undergoing any loss of bromine. The attainment of constant weight by the salt does not positively prove the entire removal of water. If moisture were retained the atomic weight of gold found would be brought out lower than it should be.

3. Krüss himself observed that in all cases in which he dissolved potassium auri-bromide in water a small residue of metallic gold was left, and, determining in a single experiment the amount of this (about ·05 per cent.), he used it as a corection for all

his results. As pointed out by THORPE and LAURIE[*] this partial decomposition of the salt was probably due to the action of dust from the air. If the results obtained from the solution were used, without any correction, to establish the atomic weight of gold, the tendency would of course be to a value lower than the truth. Although the correction introduced is small, it can hardly be supposed that it should be taken as constant in amount in all the experiments.

4. In series *e* it may be questioned whether traces of potassium bromide may not have been volatilized at the highest temperature used, or the residual potassium bromide may not have, to a small extent, exchanged bromine for oxygen while heated in air (before the use of the stream of hydrogen), the latter change being one to be guarded against whenever haloid salts are strongly heated in the presence of free oxygen. The tendency in both cases would be to a lower atomic weight for gold.

5. In series *f* there was risk of slight loss of potassium bromide during filtration and evaporation of its solution, and during exposure of the salt to the heat of a free flame, when there might possibly have been again slight replacement of bromine by oxygen, thus causing the atomic weight sought to come out too high, or else, on the other hand, risk of imperfect drying, which would give too low a value for the atomic weight in question.

On the whole it seems probable that the tendency of most of the constant errors to be suspected in connection with KRÜSS's experiments—experiments carried out with remarkable patience, skill, and apparent freedom from merely "fortuitous" errors—was in the direction of an atomic weight for gold somewhat below, rather than above, the true value.

B. *Experiments of* THORPE *and* LAURIE, 1887.[†]—In these experiments potassium auri-bromide was used, and determinations were made :—*a*. Of the weight of the residue left on heating the salt over a Bunsen flame till bromine ceased to be given off (this residue consisting of metallic gold and potassium bromide), and the weight of the gold left by such residue after all potassium bromide had been washed out of it by water; *b*. Of the weight of silver necessary to be added as nitrate to the solution of potassium bromide obtained in *a* in order to just precipitate the bromine present; *c*. Of the weight of the silver bromide so precipitated. All suitable experimental precautions seem to have been taken, and the weighings were corrected for atmospheric buoyancy. The individual results in each series agreed with each other even more closely than in KRÜSS's research.

The results obtained were as follows, using in calculation the numbers Ag = 107·66, Br = 79·75, and K = 39·03 :—

Series *a*.	Mean of 8 experiments.		Atomic weight of gold	= 196·876
,, *b*.	,, 9	,,	,, ,, ,,	= 196·837
,, *c*.	,, 8	,,	,, ,, ,,	= 196·842

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[*] 'Chem. Soc. Journ.,' Dec., 1887, p. 866.

[†] 'Chem. Soc. Journ.,' June, 1887, p. 565, and Dec., 1887, p. 866.

The general mean of these values, giving equal weight to the different series, is 196·852.

As regards possible sources of constant error specially belonging to these experiments, it is to be noticed—

1. There is an advantage, as observed by the authors themselves, over the greater part of the experiments of Krüss in the nature of the relations employed not requiring that the potassium auri-bromide should be perfectly dry, the exact quantity of the original salt not needing in fact to be known.

2. In series *a* it is conceivable that there might have been slight volatilization of potassium bromide, or interchange in it to a small extent of bromine for oxygen, during the heating of the original salt, or retention of traces of potassium bromide by the metallic gold when washed—the latter but little probable. Any of these defects, if existing, would cause the method to give a higher value for Au than the true one.

3. In series *b* the probability seems to be in favour of not quite the whole of the original potassium bromide being actually used, and minute loss of silver solution having perhaps occurred, so that rather more of this solution was counted as used than the true quantity. If so, the former defect would tend to raise, the latter to lower, the atomic weight of gold.

4. In series *c*, in view of the evidence adduced to prove complete drying of the silver bromide, it is more likely that its weight as obtained was below, rather than above, the truth. Hence we should suspect, if any constant error exist, that it would rather tend towards an unduly high value for Au.

On the whole, there seems to be less reason to fear sources of constant error of any considerable amount in connection with the experiments of Thorpe and Laurie than with those of Krüss, and the drift is in the opposite direction, tending rather to give too high than too low a value for the atomic weight to be determined.

It should be mentioned that Krüss* has claimed that in the potassium auri-bromide used by Thorpe and Laurie there was probably as much free gold as he considered to exist in the salt used by himself, and on this assumption has calculated that the three series of experiments by the English chemists should, if corrected on this account, lead to the numbers 196·616, 196·559, and 196·575 respectively for Au. From this conclusion the latter chemists altogether dissent,† and express their confidence that in none of the preparations used by them was there free gold sufficient to account for the difference between their own results and those of Krüss.

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* 'Berichte Deutsch. Chem. Gesell.,' vol. 20, p. 2365.

† 'Chem. Soc. Journ.,' Dec., 1887, p. 868.

General Results of Former Determinations most deserving Confidence.

These recent researches, unquestionably by far the most valuable up to the present time, give us, when taken separately and together, the following values for the atomic weight of gold :—

1.	General mean of 5 series by KRÜSS, as calculated by himself .	196·640
2.	,, ,, 3 series by THORPE and LAURIE, as calculated by themselves . . . . ,	196·852
3.	,, ,, 1 and 2, giving equal value to each	196·746

Difficulties to be overcome in Determining the Atomic Weight of Gold.

Besides the special difficulties connected with each method which may be adopted, the determination of any high atomic weight with a degree of accuracy which enables the result to be accepted to a given decimal place is clearly a much less easy matter than would be the attainment of an apparently equal degree of precision for an atomic weight represented by a small number. In obtaining the atomic weight of lithium, the first with which, many years ago, I had any personal experience, a difference of unity in the first decimal place corresponded to about $\frac{1}{70}$th of the whole value considered to be correct. In getting the atomic weight of aluminum, worked on later, a like difference represented approximately $\frac{1}{270}$th of the whole value. But, in the case now considered, of the atomic weight of gold, unity in the first decimal place means but about $\frac{1}{1970}$th of the whole value. So that, looking at the matter in this light, it may be said that a degree of precision is demanded more than seven times as great as in the case of aluminum, and twenty-eight times as great as in the case of lithium.

There is also to be noticed, as the most obvious *general* difficulty to which all methods for determining the atomic weight of gold are more or less exposed, the instability of compounds of this metal ; not merely the ease with which complete decomposition occurs, with separation of free gold, but the much more insidious and less easily detected trouble arising from the comparative ease with which aurous pass into auric compounds, and the reverse.

New Experiments by the Author.

The general difficulties just alluded to, and the special points to be investigated in regard to each method of determination tried, have demanded much time and work, and I cannot feel even now that all has been done that is desirable and possible ; but the experiments projected have been so far completed as to seem to justify publication, and I am not likely soon to be able materially to extend them.

General Principles kept in View.

The improvements made of late years in manipulative methods and apparatus have tended to reduce very much the magnitude of what are commonly called "fortuitous" errors in our quantitative determinations of matter, and to increase greatly the accuracy of such determinations. Probably no modern work has had more influence in this direction than the classic researches of STAS on certain atomic weights—the precautions taken by him, and his remarkable manipulative skill, causing his results to bear almost the same relation to those of his immediate predecessors as did those of BERZELIUS to the work of the chemists of his earlier day. No one nowadays would undertake the determination of an atomic weight of one of the better known elements without taking such elaborate precautions as practically ensure pretty close concordance of results, when obtained by the same method, applied in the same hands. In the present state of the question of atomic weights and improvements in their determination, advances in mere delicacy of manipulation and success in merely securing close agreement of results by the same method are not alone sufficient. It cannot be too much insisted upon that we need, besides, well-directed and laborious investigation of possible sources of *constant errors*, and the adoption of means to guard against them. Careful preliminary study is required, in a general way, of the precise nature of each reaction employed, and how it may be influenced by the conditions of the experiment. We learn more and more of late that many of the reactions—perhaps it should rather be said all of the reactions—which have been generally supposed to be of the simplest nature are in reality complex.

The following are among the general principles which seem to be most important, as tending to greater accuracy and trustworthiness in atomic weight determinations; they have been in part stated in the author's earlier paper on the atomic weight of aluminum :—

1. In purifying the materials used, both the element of which the atomic weight is to be investigated (or any special compound containing it) and all substances used to react thereupon, resort should in all cases be had to "fractional" methods, assuming materials to be pure only when earlier and later fractions give no signs of any constant difference in the results which they yield.

2. Different and independent processes should be applied to the determination of the same atomic weight, and the results used to check each other. It is desirable that as many such different processes be applied as can be devised, provided each be reasonably free from apparent sources of error, even though it be usually impossible to properly assume that all are equally advantageous in this respect, and therefore of equal value. In the comparison of results obtained it should be noticed whether a given method tends on the whole to yield results probably higher or lower than the truth, though it may be gravely doubted whether the practice is commendable of

attempting any numerical estimate of relative value, by so-called "weighting" of the results in calculation.

3. In connection with each process there should be careful study of the reactions depended upon for the final determination of an atomic weight, looking especially to the possibility of the occurrence of secondary or subsidiary reactions.

4. Each process adopted should be as simple as possible, both in the nature of the chemical reaction or reactions and in the known liability to merely manipulative errors.

5. Each process should be carried out with, in some experiments larger, and in others smaller, quantities of material. But, on the whole, the quantities used should be kept within such limits as are most likely to admit of most accurate determinations being had under the conditions of the special process.

6. In the reactions depended upon only such other elements should be concerned as may be counted among those of which the atomic weights are already known with the nearest approach to exactness.

7. It is particularly desirable that, if possible, the atomic weight to be investigated shall be, by at least one process, compared directly with that of hydrogen, now almost universally taken as the basis for the whole list of the elements. It is remarkable for how very few of the elementary substances—not more than three or four—this direct comparison has been accurately made.

8. In the greater number of the processes available for atomic weight determinations the comparison with hydrogen must perforce be made indirectly. When this is the case, it is desirable that as few other elements as possible, the assumed atomic weights of which will have to be taken into account, shall be involved in each single reaction depended upon.

9. In selecting *different* processes to be applied to the determination of the atomic weight of a given element, in order that the results may check each other, it is desirable that, not the same, but as many different other elements as possible, shall be concerned in the several reactions, provided all such elements count amongst those of which the atomic weights may be considered in the first rank as to the accuracy with which they are known.

Means and Methods of Weighing Employed.

These were in the main the same as those which I had in former years used in determining the atomic weight of aluminum.

The balance chiefly used, made by Becker, was carefully cleaned, and all its parts adjusted, especially as to the position of the centre of gravity for each load to be used. A second balance by the same maker, of larger size, capable of taking a load of a kilogramme in each pan, was employed in weighing certain of the solutions experimented on, and was in like manner carefully adjusted and tested. All weighings were made by observation of the oscillations of the index on either side of the position of rest. A difference of ·0001 grm. with the smaller balance, and ·0002 grm. with the larger instrument, was easily and distinctly observable with any load which the research required.

The same kilogramme weight was made the basis of a comparison with all my other weights which had been before used in the same way. This had been compared at Washington with the "star kilogramme" of the United States Coast Survey, the value of which is known in terms of the original "kilogramme of the Archives" at Paris. All the smaller weights were carefully rechecked against this and against each other, and their real values ascertained as referred to a vacuum. The necessary determinations were made of the specific gravity of all materials and vessels which were to be weighed, and the barometer and thermometer were read at the time of each weighing, so that all weights recorded in this paper represent real values *in vacuo*. In order to reduce to a minimum errors due to varying deposition of hygroscopic moisture, vessels of like material, shape, and size with those used to contain substances to be weighed were used as tare.

History and Mode of Purification of the Gold used in this Research.

Most of the metal needed was prepared by myself, with precautions presently to be mentioned; a part was obtained, as "proof gold," from the United States Mint at Philadelphia; another part from the United States Assay Office at New York; and a single specimen of English "trial plate" gold from the Royal Mint in London.

1. *Purification of Gold by the Author.*—It may fairly be concluded from the general history of the gold of commerce that the impurities most to be suspected, and most requiring special precautions for their removal, are silver and the metals of the platinum group. My preliminary experiments led me to believe that the greatest difficulty in the way of obtaining perfectly pure gold consists in getting rid of the last traces of silver, the chloride of this metal not being quite insoluble in a solution of auric chloride. For the removal of silver, I have chiefly depended upon evaporation of the gold solution with a little hydrobromic acid, followed by large dilution with water, and long continued clearing by subsidence. As regards the platinum metals, my results agreed substantially with those of HOFFMANN and KRÜSS,[*] but I have been inclined to lay some stress on reduction of the gold from its solution *with exclusion of light*, and on *fractional* reduction, using only the middle portion thrown down. I avoided altogether the use of ferrous salts as reducing agents, in view of the difficulty of preparing them in large quantity with assurance of their purity, and the trouble of thoroughly washing the precipitated gold. For the final precipitation of the gold formic acid seemed to offer real advantages; its volatility admits of easily getting it

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[*] 'LIEBIG'S Annalen,' vol. 238, p. 66.

free from any metallic contamination, and the reduction is more easily effected than with oxalic acid.

Starting with United States gold coin, it was first heated to bright redness in a muffle, as a precaution against the presence of any traces of mercury, and to remove any grease, &c., from the surface, and then dissolved in a mixture of pure hydrochloric and nitric acids in the right proportions. The solution was evaporated with excess of hydrochloric acid nearly to dryness, the auric chloride redissolved in a considerable quantity of water, and the solution allowed to settle for four or five days. The greater part of the clear liquid, drawn off with a syphon, and filtered through very fine siliceous sand,* was again evaporated nearly to dryness, adding towards the end a few drops of pure sulphuric acid, in case of the conceivable, though unlikely, presence of such traces of lead as this might reveal; much pure water was added, the solution again cleared by subsidence for several days, and the greater part of the clear liquid again drawn off and filtered. This solution was now rendered pretty strongly acid with hydrochloric acid, and fractionally precipitated by sulphurous acid (SO_2 was evolved from sodium sulphite), at as low a temperature as possible, and *in the dark*, putting aside the first and last portions of the metal thrown down, and reserving for further treatment the (largest) middle portion. The gold thus obtained was well washed with water, boiled with nitric acid alone, again washed, boiled with hydrochloric acid alone, again washed, dried, and heated strongly with fused acid sulphate of potassium in a porcelain crucible, boiled with dilute hydrochloric acid, and then with water. The metal was redissolved in aqua regia, the solution evaporated nearly to dryness, with addition of pure hydrobromic acid towards the end, very largely diluted with water, and allowed to stand for two days, well protected from dust, before again syphoning off as much of the clear portion as could be safely removed without risk of disturbing the remainder at the bottom, using a conical precipitating jar with greatest diameter below, and filtering the liquid through siliceous sand as before. The evaporation with hydrobromic acid was repeated twice more, and the clear solution—allowed the last time to stand a month before being syphoned off and filtered—was then reduced, once with oxalic acid (neutralizing the liquid with pure sodium hydroxide from the metal), once (after re-solution) with sulphurous acid, and once with formic acid, washing the reduced metal well each time before redissolving in aqua regia. In the first and second of these reductions a little of the metal first and last thrown down was rejected, and in the final reduction with formic acid the first portion precipitated, about one-fifth of the whole, was reserved for use, labelled A, *a*, the middle portion, about three-fifths, was labelled A, *b*, and the last portion, the remaining one-fifth, was also preserved for use, marked A, *c*, so that it might be seen whether any difference in the character of the metal could be detected in the

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* The sand was carefully purified beforehand by boiling with nitric and hydrochloric acid, thorough washing with water, and heating to redness in the air.

atomic weight determinations. All of these fractions received a very thorough final washing with water.

Such part of the purified metal as was to be used in the preparation of gold compounds was not fused, but was heated in a glazed porcelain tube to moderate redness in a Sprengel vacuum. A small part of the metal used in the free state, and desired in compact form, was fused in a perfectly clean Beaufaye crucible with a little acid sulphate of potassium and borax, the button flattened, boiled with strong nitric and then strong hydrochloric acid, thoroughly washed with water, and, finally, heated in the Sprengel vacuum. Throughout the long process of purification, and especially towards its close, the most scrupulous care was taken to exclude dust, and to prevent grains of sand from the bottoms of beakers or any other impurities getting into the precipitated gold, upon which the acids used would not act, so as to obviate the risk of merely mechanical contamination, which, if overlooked, might lead to that being weighed as part of the gold which was, in fact, foreign to it.

2. *Purification of "Proof Gold" obtained from the United States Mint at Philadelphia.*—I owed to the kindness of Mr. J. B. ECKFELDT, Chief Assayer to the Philadelphia Mint, a liberal supply of the "proof gold" used in checking the gold assays there made, and he furnished me the following statement of the manner in which this purest metal is prepared, under his directions:—"The best cornets from the gold assays selected and dissolved in aqua regia. Solution evaporated, with additions of HCl, to nearly crystallization, diluted largely with water, and allowed to stand for three or four weeks. About seven-eighths of the solution drawn off from the silver chloride, and passed through several thicknesses of various filters. Solution somewhat concentrated, and alcohol and potassium chloride added, allowed to stand for some time (precip. traces of platinum*), and carefully filtered. Gold precipitated by addition of pure ferrous sulphate. Reduced gold washed repeatedly in boiling HCl, until washings show no iron, then well washed in pure water. Gold dissolved, and solution evaporated to crystallization, with repeated additions of hydrobromic acid,† diluted, and again allowed to stand for some time; filtered. Through the solution was passed pure SO_2 until all the gold was reduced; washed. Gold again dissolved, evaporated with HCl, diluted, and oxalic acid added, and heated, until all gold is down. Melted in white clay crucible with potassium chlorate and nitrate, afterwards with pure sodium carbonate and borax." Mr. ECKFELDT also informed me verbally that the proof gold thus purified is cast into a small bar in a perfectly clean and bright cast-iron mould; the bar is boiled in nitric acid, washed and dried, rolled between fine

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* The platinum of South American native gold, and of scrap gold from dentists, is at the Philadelphia Mint separated solely by alloying with enough silver, and dissolving out the latter metal with nitric acid. The platinum dissolves with the silver.

† I had, many months before, independently adopted and used hydrobromic acid to remove traces of silver more effectually than by hydrochloric acid, when I learned from Mr. ECKFELDT that he had thus habitually employed it.

steel rolls quite free from grease, and the strip finally cleaned for use with hot hydrochloric and then nitric acid.

In a letter of later date he wrote, "In preparing the 'proof' I seldom make over 10 oz. in one lot; from 8 to 10 oz. is the usual amount. There is comparatively little trouble in making 999·9 fine, but beyond that it is rather troublesome; and it seems that, with all the care, the final result is sometimes a little in doubt."

The fine gold received from the Philadelphia Mint is designated as B in this paper, in connection with the experiments in which it was used.

3. *Purification of "Proof Gold" obtained from the United States Assay Office at New York.*—Dr. H. G. TORREY, Chief Assayer in this office, was obliging enough to let me have several samples of his finest proof gold, used in checking the regular assays in his department. He informed me that this proof gold was independently prepared at New York, but was occasionally compared with that of the Philadelphia Mint. He furnished the following brief statement as to its preparation—"The process used in preparing the gold is to dissolve 'cornets' (or gold from assays) in nitro-hydrochloric acid, and after filtration precipitating by oxalic acid, and after thorough washing melting under borax. The operation is conducted with the utmost care throughout."

The gold from this source is designated as C in this paper.

4. *Gold from the "Trial Plate" of Fine Gold of the English Mint.*—Professor ROBERTS-AUSTEN, Chemist to the Royal Mint, was so kind as to let me have a specimen of a few grammes of gold cut from the trial plate of the pure metal prepared by him in 1873. In its preparation use was made of potassium chloride and alcohol to separate any platinum present in the original material, a long period of subsidence was allowed for the deposit of any silver chloride from the solution, and the whole process was applied on a large scale, resulting in the purification of some 70 ounces of fine gold, of which Professor ROBERTS-AUSTEN himself has said: "I have not been able to prepare, or to obtain from any source, gold of greater purity, even in small quantities." It seems, however, that the apparent standard of this gold was slightly reduced in rolling, the finished plate being counted as 999·95 fine in comparison with the same gold before rolling. A memorandum given me by Professor ROBERTS-AUSTEN states that this trial plate gold is 999·98 fine as compared with the purest gold obtained by STAS for the Belgian Mint.

This specimen of English trial plate gold is designated as D in the present paper.

All the samples of gold received from others—B, C, and D—were, before using them, carefully boiled in nitric acid to remove any possible traces of silver or other metal derived from the shears used in cutting the plates. They were also previously well washed with ether, to remove any grease, and afterwards with pure water, and were finally heated to redness in the Sprengel vacuum.

It may be remarked, in advance, that I have not been able to trace any probable connection between the history of the several samples of gold used and the values obtained for the atomic weight of the metal. Within the limits of accuracy attained, the results appear to have been sensibly the same by each method for all the gold used. Nor is there apparent in the results of KRÜSS, or those of THORPE and LAURIE, any evidence of a difference fairly traceable to the nature of the metal employed by them.

A considerable part of the gold prepared by myself was, after having once served for a determination of the atomic weight, redissolved and reprecipitated, and was afterwards more than once used in subsequent determinations, and yet no sign was obtained of any resulting influence upon the later values of the atomic weight as obtained, evidence being thus furnished of the purity, not only of the gold itself, but of the reagents used to act upon it, so far as any contamination of the metal was concerned. It may, therefore, be concluded with reason that the gold used in these experiments was of uniform character, and uniformly free from any known impurities, to such an extent, at any rate, as to sensibly change the results obtained.

It is to be noted that the only known elements having higher atomic weights than that of gold are mercury, thallium, lead, bismuth, thorium, and uranium. The presence of any of these in the gold experimented on, even in traces too minute to weigh, is in a very high degree unlikely. The presence of any other element or elements than these would, for analogous compounds, tend to lower the value obtained for the atomic weight of gold; so that, in considering the chances of error due to the nature of the metal used as gold, we should be inclined to say that the risk was rather in the direction of too low than too high a result being reached. But, if the possibility be observed of compounds not analogous being erroneously compared, the contrary error will be seen to be possible. Thus, in case the composition of an auric haloid salt obtained from a given amount of metallic gold should be examined, if any unsuspected silver were present there would be required for the same amount of the halogen three atoms of silver instead of one atom of gold, and, therefore, the apparent weight of gold as compared with that of the halogen would be increased instead of diminished, and a higher value obtained for the atomic weight sought.

General Precautions Observed in the Experiments for Determination of the Atomic Weight.

All the reagents used were prepared or purified by myself, and most carefully tested for any traces of such impurities as might reasonably be suspected, and as could affect their application to the purpose in view. Particular care was bestowed upon the examination of the distilled water, acids, and other materials used in large quantity. To remove organic matter from the water required, it was distilled from a small amount of potassium permanganate and sulphuric acid.

Scrupulous care to exclude atmospheric dust was observed. In the evaporation of some of the gold solutions the process was carried out in a glass bottle of considerably larger capacity than the volume of liquid to be treated, furnished with a well ground-glass stopper of special construction, as shown in figs. 1 and 2, the latter representing the stopper in place. Air, purified by passing through a red-hot tube, then through a solution of potassium permanganate and sulphuric acid, and dried by passing through concentrated sulphuric acid and over solid potash, was introduced by the tube *a*, which went down to near the level of the liquid to be evaporated, while this air, charged with vapour of water from the liquid, was withdrawn through the tube *b* by means of a water-jet pump; the bottle was moderately heated by immersion to the greater part of its height in a water bath.

Fig. 1.

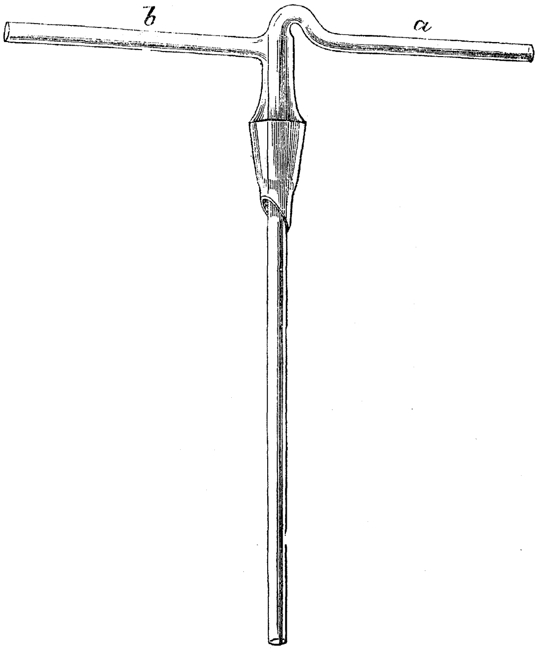
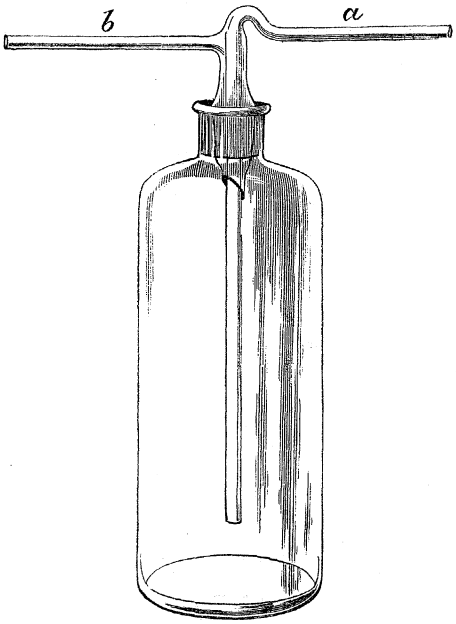


Fig. 2.



In filtering the gold solutions no paper or other organic material was used, but fine white siliceous sand, previously boiled in nitric and hydrochloric acids, washed with water, and well ignited to burn off any organic matter, was substituted, supporting it on coarser sand and larger fragments of quartz, similarly purified, and the whole arranged so as to prevent the possibility of any sand grains being mechanically carried into the filtered liquid. Vessels of hard glass and Berlin porcelain were employed. Care was taken to work in a clean laboratory atmosphere, free from gases or vapours which might affect the materials dealt with.

First Series of Experiments.

A neutral solution of auric chloride was prepared by cautiously heating auric chloride, made, as suggested by Julius Thomsen, by the direct action of pure chlorine upon finely divided metallic gold, until such an amount of chlorine had been given off that on treating the residual material with moderately warm water, metallic gold only remained undissolved, which was then filtered off. This neutral solution having been rendered uniform by agitation, two approximately equal portions of it were weighed off, using, of course, stoppered vessels to prevent evaporation during the weighing. From one of these portions the gold was thrown down in the metallic state by pure sulphurous acid with the aid of heat, carefully collected, well washed, dried, ignited in a Sprengel vacuum, and weighed. To the other portion there was added the carefully prepared solution in a minimum of nitric acid of an accurately weighed quantity of pure silver, a little more than equivalent to the chlorine present, the liquid and precipitate digested together for a considerable time with gentle warming in a stoppered glass flask, well agitated from time to time, and the precipitate (of silver chloride, containing also the gold) filtered off upon siliceous sand, and thoroughly washed, avoiding throughout the decomposing influence of light. The clear filtrate was nearly neutralized with pure sodium hydroxide (from metallic sodium), evaporated down to a small bulk, using the vessel represented in fig. 2 (p. 410), and finally the remaining silver was determined (with all the needful precautions of the silver assay) by means of a weighed quantity of a weak solution of pure hydrobromic acid standardized against pure silver. This mode of determining chlorine by means of silver and hydrobromic acid was suggested to me in a letter, of the 27th January, 1887, with which I was favoured by M. STAS,[*] who advocates it as the most exact process available. The pure silver required was prepared in the same way as that used in my experiments on the atomic weight of aluminum,[†] and was heated in the Sprengel vacuum to remove all occluded gas. The hydrobromic acid was prepared as directed by STAS in his published paper—"De la détermination du rapport proportionnel entre l'argent, les chlorures et les bromures."[‡]

In reporting the results obtained, the quantity of gold stated is that actually weighed, but the quantity of silver corresponding thereto has, for the sake of simplicity, been given as that required for an exactly equal quantity of the auric chloride solution, while, as stated above, the quantity of liquid weighed off was very nearly, but not exactly, equal to that from which the gold was thrown down, the difference being allowed for in calculation.

With this explanation the results of the first series of experiments were as follows :—

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[*] In this letter M. STAS says, "Je me permets de vous recommander l'emploi de l'acide bromhydrique pour la précipitation de l'argent resté dans un liquide après une double décomposition opérée à l'aide d'un *chlorure* et d'un sel d'argent. On réussit à condition que l'eau mère renferme un excès d'argent dont le poids est le triple du métal qui peut rester en solution à l'état de chlorure d'argent."

[†] 'Phil. Trans.,' 1880, p. 1020.

[‡] 'Mémoires de l'Acad. Royale des Sciences de Belgique,' vol. 43, 1882.

Experiment.	Character of gold used.	Gold.	Silver required to precipitate Cl.
		grm.	grm.
I.	A, *a*	7·6075	12·4875
II.	A, *b*	8·4212	13·8280
III.	B	6·9407	11·3973
IV.	A, *c*	3·3682	5·5286
V.	C	2·8244	4·6371

In regard to conceivable sources of error connected with this method, it is to be observed that, in preparing the original auric chloride solution, if there should be any reaction between this gold salt and the water, leading to the formation of traces of hydrogen auri-chloride and precipitation of a little auric oxide or hydroxide, which might escape observation in admixture with the metallic gold left undissolved, the tendency would be to lower the atomic weight found for gold. If, by reaction between this residual metallic gold and the auric chloride solution, any traces of aurous chloride were produced and taken up by the solution of the higher chloride, the effect would be to raise the apparent value of the atomic weight.*

If, in the reaction of the silver solution upon that of auric chloride, *partial* withdrawal of chlorine should lead to the formation of any traces of aurous chloride, precipitated along with the chloride of silver, and not afterwards decomposed during the digestion of the precipitate with the remaining solution, the resulting error would also be in the direction of too high an atomic weight. The probability of the last supposition is diminished by an excess of silver for the whole amount of chlorine present having been added at once. It is not very likely that any one of these defects actually belongs to the method and affects its results to a sensible extent. Of the three I should be more inclined to suspect the possibility of the second than either of the two others.

Second Series of Experiments.

A neutral solution of auric bromide was prepared by a like process to that used in making the auric chloride of the first series: acting upon pure metallic gold with pure bromine (prepared with the precautions recommended by STAS), evaporating the solution to dryness out of reach of dust, cautious heating of the residue, re-solution of auric bromide, and filtration from undissolved metallic gold.

Two nearly equal portions of the solution were accurately weighed off, and treated as described above: in one reducing the gold to the metallic state and determining its weight; treating the other with a small excess of silver in solution as nitrate, filtering off the precipitate, concentrating the filtrate with the precautions already described, and determining in it the excess of silver by means of hydrobromic acid.

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* These two remarks apply, of course, also to KRÜSS's first series of experiments.

Reducing the amounts of silver actually used to the corresponding quantities for portions of auric bromide solution exactly equal to those from which in each case the gold was obtained, the results in six experiments stood as follows :—

Experiment.	Character of gold used.	Gold.	Silver required to precipitate Br.
		grm.	grm.
I.	A, *b*	8·2345	13·5149
II.	A, *c*	7·6901	12·6251
III.	B	10·5233	17·2666
IV.	A, *a*	2·7498	4·5141
V.	C	3·5620	5·8471
VI.	A, *b*	3·9081	6·4129

In these experiments the sources of constant errors which suggest themselves as possible are essentially similar to those for the first series; but, if any such really exist, there is, of course, the likelihood of some difference being introduced by the substitution of bromine for chlorine. Hence the desirability of multiplying experiments in this modified form.

Third Series of Experiments.

For these experiments potassium auri-bromide was prepared with great care from an excess of metallic gold treated with bromine and potassium bromide, purified in accordance with STAS's suggestions, and the double salt five times recrystallized. The last crystallization was conducted fractionally, in closed vessels, with special care to exclude dust, by gradual but pretty rapid cooling with agitation, and the earlier and later portions separated out were kept apart in after use.

For each atomic weight determination an unweighed quantity of this potassium auri-bromide was dissolved in water, the solution rendered uniform by agitation, and divided into two nearly equal parts, which were severally weighed with accuracy, and in one the gold reduced to metal as in the experiments of the first and second series, and in the other the total bromine precipitated by silver solution as before, the comparison being made once more between the weight of the gold and that of the silver equivalent to the bromine (in this case representing 4 atoms) existing in the double bromide.

Again stating the quantities of silver corresponding to portions of the auri-bromide solution exactly equal to those used in determining the gold, the following were the results obtained :—

Experiment.	Character of gold used.	Fraction of crystallized auri-bromide used.	Gold.	Silver required to precipitate Br.
			grm.	grm.
I.	A, *b*	First	5·7048	12·4851
II.	A, *b*	Second	7·9612	17·4193
III.	B	First	2·4455	5·3513
IV.	B	Second	4·1632	9·1153

Of the tendencies to constant error which may be imagined in connection with the experiments of the first two series, and which have been noticed above, the first may probably be considered as not applying to the method pursued in this third series, while the second and third might still be applicable. But the superior stability of the double salt constitutes an advantage in its favour, and, as it formed the chief material for the experiments of KRÜSS and of THORPE and LAURIE, a comparison with their results is desirable, the mode of treatment pursued by me in ascertaining the composition of the salt not having been quite the same as that used by these chemists.

Fourth Series of Experiments.

A weighed quantity of trimethyl-ammonium auri-chloride [$N(CH_3)_3HAuCl_4$] was decomposed by heating in the air, and the weight of the residual metallic gold determined. This trimethylamine salt was selected because the base is of simple and well established constitution, and may with reasonable probability be counted upon as obtainable in a state closely approaching purity, and because the gold salt is easily crystallized, possesses a considerable degree of stability, and contains approximately half its weight of gold, so as to offer the most favourable chance of determining with accuracy the ratio between the metal left behind and the sum of the remaining constituents driven off on ignition. Although its use in fixing the atomic weight of gold involves the atomic weights of three other elements—carbon, nitrogen, and chlorine—all three of these constants deserve to be ranked amongst those already known with the nearest approach to precision at present attainable.

In order to obtain pure trimethyl-ammonium chloride, the impure commercial salt, derived from the *vinasse* of beet-root sugar making, was used, first setting free and distilling off a considerable quantity of trimethylamine and condensing at about the right temperature, and subsequently purifying the product by HOFMANN's method of treatment with ethyl oxalate and renewed distillation. The purified trimethylamine was several times fractionally distilled, and the portion of correct and most constant boiling-point finally neutralised with pure hydrochloric acid. The concentrated solution of trimethyl-ammonium chloride was now precipitated by a strong solution of auric chloride, the mother liquor decanted off, and the gold salt redissolved in hot water, and recrystallized several times. The bright yellow crystalline powder was dried, first over sulphuric acid and afterwards over phosphorus pentoxide, until it ceased to lose weight; towards the end of the drying the temperature of the vessel was raised to about 50° C. Preliminary experiments seemed to indicate the probable existence of this salt crystallized with a single molecule of water, but most of that prepared contained no constituent water, and it appeared easy to attain complete drying without any decomposition of the salt itself. Throughout its treatment the salt, which was not in any high degree hygroscopic, was well guarded from dust and from any possible decomposing effect of light.

The portion of the salt to be used in each experiment was contained in a small glass-stoppered weighing flask, which was removed just before it was needed from the phosphorus pentoxide desiccator, the stopper having been inserted; the flask was weighed, the greater part of its contents transferred quickly to a weighed porcelain crucible, the stopper at once replaced, and, the flask being again weighed, the quantity of gold salt taken from it was found by difference.

In order to avoid mechanical loss by spattering on igniting the crucible and its contents, the auri-chloride lying together at the bottom of the crucible was covered by a layer, nearly a centimetre deep, of clean, carefully purified, and just previously well-ignited siliceous sand, the weight of this sand being known by taking it from a weighing flask in which it had been cooled over phosphorus pentoxide, and noting the loss of weight of this flask. In applying heat to the crucible and its contents it was found necessary to heat gently for a long time, raising the temperature slowly, in order to prevent extensive charring at the bottom. Then, before the temperature had become too high, but after a considerable part of the volatile matter had been driven off, the sand was carefully stirred in with the remaining material so as to produce pretty uniform mixture, in order that the gold might not undergo partial welding together at a higher temperature, which might have led to wrapping up particles of carbon and their protection from combustion. In this operation a very small porcelain stirrer was used, as a platinum wire would have welded on and taken up some of the metallic gold; the weight of this stirrer was determined in advance, and checked after use. Finally, the contents of the crucible were submitted to very careful and prolonged heating to moderate redness, with free access of air and occasional cautious stirring, so as to burn away every trace of carbon. After cooling in a desiccator, the crucible and its remaining contents were weighed, giving the weight of the residual gold by subtraction of the weights of the crucible itself and the siliceous sand. As an additional safeguard against any particles of carbon left unburned escaping detection, the gold was afterwards dissolved out with aqua regia, and the white sand carefully looked over with a lens.

The results of five experiments thus conducted were as follows:—

Experiment.	Character of gold used.	Character of gold salt used.	Salt ignited.	Residual gold.	Loss by ignition.
			grm.	grm.	grm.
I.	A, *b*	Earlier crop of crystals .	14·9072	— 7·3754	= 7·5318
II.	A, *b*	Middle „ „ „ .	15·5263	— 7·6831	= 7·8432
III.	A, *b*	Last „ „ „ .	10·4523	— 5·1712	= 5·2811
IV.	C	Middle „ „ „ .	6·5912	— 3·2603	= 3·3309
V.	C	Last „ „ „ .	5·5744	— 2·7579	= 2·8165

In these experiments the most probable source of error may be fairly taken as arising from the presence of traces of methyl-ammonium or dimethyl-ammonium aurichloride with the trimethyl-ammonium salt. I know of no direct evidence that any such impurity was present, and the absence of any such evidence in the results from the earlier as compared with the later crops of crystals rather tells against the supposition of its presence, but one cannot feel certain of its entire absence. If present, its effect would be to raise the atomic weight obtained for gold. It is also conceivable that there may have occurred volatilization of gold to a minute extent as auric chloride, in accordance with the observation of KRÜSS that this salt may be sublimed in small quantity at moderate temperatures in a stream of chlorine; but, there being no such stream of chlorine in these experiments, and on the contrary the decomposing action of the hydrogen of the trimethylamine salt, this does not seem likely; the effect would, of course, be to raise the atomic weight obtained for gold. Another possible cause of error might consist in imperfect drying of the gold salt used, but the constancy of weight attained on drying renders it unlikely that any other than extremely minute error should come of this, though not altogether excluding the possibility of its occurrence; its tendency would, of course, be to lower the atomic weight obtained. Any trouble from hygroscopic moisture on the surface of the porcelain crucible and sand was, I think, satisfactorily guarded against by the use of a corresponding tare crucible, and by more than one weighing after a near approach to the true figures had been obtained, the crucibles having meanwhile been restored to the desiccator and kept therein for some time. The precautions taken seemed to afford sufficient protection against any merely mechanical loss during the ignition.

Fifth Series of Experiments.

In these experiments an attempt was made to determine the ratio between the weights of metallic gold and metallic silver deposited by the passage of one and the same electric current successively through solutions of the two metals. The simplicity and accuracy with which the direct weighings may be made seemed to present decided advantage, but various difficulties were encountered, and, after the expenditure of a very large amount of time and labour upon the method, it cannot be said, on the whole, to have satisfied me with its results.

While taking due note of the recent literature on the subject of the quantitative electro-deposition of metals from their solutions, especially the reports of work by A. Classen,[*] Lord Rayleigh and Mrs. Sidgwick,[†] Dr. Gore,[‡] Thos. Gray,[§] and W. N. Shaw,[||] the author of the present paper made for himself a somewhat extended preliminary examination of the effect of varying conditions on such depositions, so far at least as seemed to be required for his immediate purpose.

The general arrangement of apparatus adopted consisted of a horizontal strip, 4 mm. thick, of vulcanite, or hard vulcanized india-rubber, about 26 cm. long by 3 cm. wide, near each end of which and in the middle of the width were two small holes, through which passed short bits of brass rod, each having attached to it above a binding screw, and below a forceps-like clip, which could be opened by pressure on two little outside studs, but closed firmly, on release of this pressure, by the elasticity of the metal. In these clips were supported the plates of metal to be immersed in the electrolysed solutions, and to serve as anode and cathode terminals respectively, there being two pairs of such plates, one pair near each end of the vulcanite strip, with four corresponding binding screws. The electric current passed from the first binding screw through one of two metallic solutions—as, for instance, that containing gold—between the first pair of plates, consisting of the same metal as that in this solution, then from the second binding screw to the third (at the other end of the vulcanite strip) by a stout copper wire above, and then through the second of the two solutions—as, for instance, that of silver—between the second pair of plates, consisting again of the same metal as that in the solution in which they were immersed, thus reaching the fourth and last binding screw, the first and last binding screws being, of course, connected by wires with the terminals of the galvanic cells used to develop the current. Fig. 3 shows the disposition in question. The source of the electric current was for the most part galvanic cells of the Meidinger pattern, but in some of the experiments small Daniell cells, and also a Clamond thermo-electric battery, were used. The lower parts of the clips were heavily electroplated with the same metal as that in the solution to which they respectively belonged, in order to avoid any risk of contamination of the solution, in case there should be spattering or accidental immersion, even for a moment, of any part of the clip.

It was decided to place the plates vertically in the liquids, but to make the vertical height small in proportion to width, so as to preserve as far as possible a uniform condition of the solution in depth. The form adopted for the plates was that of fig. 4, the shaded part of the surface being coated with hard paraffine, with a view to

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[*] A. Classen, 'Quantitative Chemische Analyse durch Electrolyse,' 2te aufl., Berlin, 1886.

[†] 'Phil. Trans.,' 1884, p. 411.

[‡] 'Nature,' March 16, 1882; Feb. 1 and Feb. 15, 1883.

[§] 'Phil. Mag.,' Nov., 1886, p. 389; and March, 1888, p. 179.

[||] 'Phil. Mag.,' Feb., 1887, p. 138.

preventing the strip by which the anode plate was suspended from its clip being cut across by solvent action at the surface of the liquid. This coating of paraffine was put on after the plates were first weighed, and carefully removed before the second weighing. The four plates for each experiment were of equal size as to length and breadth; in most of the experiments the immersed surface (of one side) measured about 25 square centimetres, though in some cases plates of double this size were used. The thickness was the same for plates of the same metal, but those of the different metals to be compared were made to differ in thickness to such an extent as to allow for the different rate of solution to be expected of the anode plate. I was indebted to the kindness of Mr. Eckfeldt, of the Philadelphia Mint, for having plates of "proof" gold and silver specially rolled for me, with all necessary precautions as to perfect cleanliness of the rolls, &c., so as to obtain the determinate thicknesses desired.*

Fig. 3.

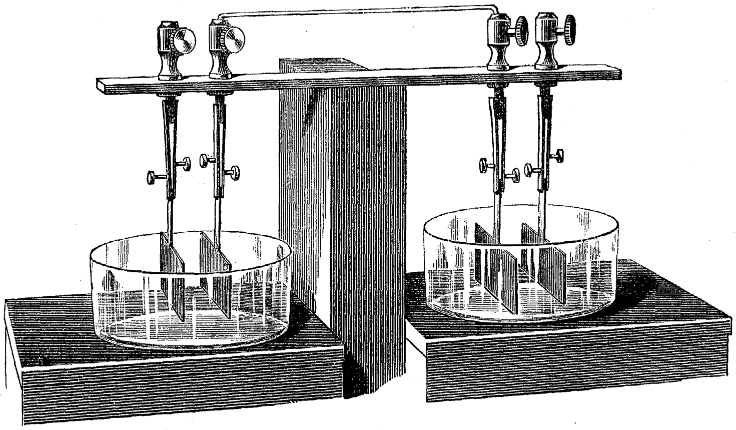
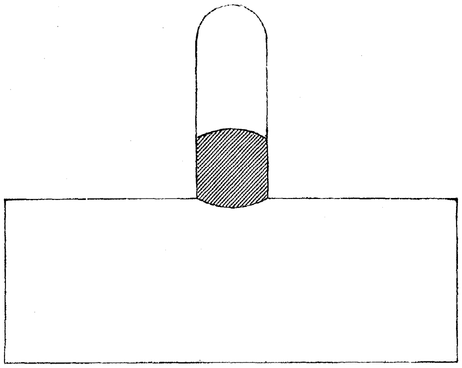


Fig. 4.



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* Mr. Eckfeldt informed me that his method of preparing the proof silver used for these plates was as follows:—" Nitrate of silver from the gold assay parting is, after careful filtering, precipitated with

By heating in a Sprengel vacuum I found traces of oxygen in the rolled silver plates, and extremely minute traces of gas, apparently also oxygen, were likewise obtained from the gold plates, before either had been used.

The middle of the vulcanite strip was supported at a suitable height, so as to allow of equal immersion of the two pairs of plates in their respective solutions, which were contained in small vessels of good hard glass, free from lead. Care was taken to keep the vulcanite strip dry, so that there should be no practical defect of insulation between the two plates of each pair; the necessity for this precaution having been shown in some of the very early preliminary experiments with copper plates, using a wooden supporting strip; some puzzling results being traced back to a little accidental moistening with sulphate of copper solution of the part of the strip between one pair of plates, while those of the other pair were well insulated as to the strip from which they hung.

In all the experiments the two pairs of plates, previously ignited in the Sprengel vacuum, cooled, and weighed, were placed in position in the clips, the distance between the parallel surfaces of the plates of each pair being the same, and in most of the experiments measuring about 2·5 cm., and connection was made with the terminals of the galvanic cell or cells used before immersion of the plates in the metallic solutions. All four plates were immersed at the same moment, and at the end of the experiment were in like manner lifted out of the solutions at the same moment, before the current had been broken. They were immediately introduced into one after another of several portions of distilled water, before removal from the clips, thorough washing, heating in the Sprengel vacuum, and final weighing.

A preliminary course of experiments was carried out with plates of pure electrotype copper (both pairs) in solutions of cupric sulphate, in order to test the effects, if any, of the following differences in the conditions of the two electrolysis cells compared.

1. *Effect of Difference in the Degree of Concentration of the Two Solutions.*—The solution in one of the two vessels in which the plates were immersed being made to contain but one-tenth the proportion of cupric sulphate existing in the other, acidification and all other conditions being the same for both, only a very minute difference was found between the quantities of copper deposited in the same time on the two cathode plates, and the difference was not invariably in the same direction. The tendency however, seemed on the whole to be toward a slightly larger amount thrown down

hydrochloric acid, and the chloride of silver, after a thorough washing with pure water, is dried and reduced in the melting pot with pure carbonates of soda and potash and carbon in the shape of wheat flour, the melting being done in a clay crucible. The resulting silver bar is then dissolved in dilute nitric acid, and after standing some time filtered, precipitated, and reduced as before; then remelted with the addition of pure nitrate of potash and borax. This generally gives a bar somewhat brittle (crystalline in fracture). It is then remelted, and stirred with a pine stick, and chloride of ammonium added; when the chloride has disappeared the metal is poured. I find this method more satisfactory than any other I have tried."

from the stronger than from the weaker solution. In every case there was decidedly more copper dissolved from the anode than was deposited on the cathode plate.

2. *Effect of Difference in Acidity of Two Solutions, otherwise of the Same Strength.*—With the same proportion of cupric sulphate in both solutions, one was made to contain but one-tenth as much free sulphuric acid as the other; all other conditions remained the same for both. As before, the difference of result was insignificant, and somewhat variable in direction, with an apparent tendency towards a very slightly greater deposit on the cathode plate in the less acid as compared with the more acid solution. As before, there was in every case a distinctly greater loss of copper from the anode than gain on the cathode plate, especially in the more acid solution.

3. *Effect of Difference in Temperature of the Two Solutions.*—The proportion of cupric sulphate and of free acid being the same for both solutions, and all other conditions the same, one of the two, however, being maintained at 72°, 47°, or 37° C., while the other was at 2° C., thus establishing a difference in temperature of 70°, 45°, or 35° respectively, there was distinctly in every instance rather more copper thrown down on the cathode plate in the colder than in the warmer solution. The loss of weight of the anode plate was always greater than the gain at the cathode, and the difference in this respect was greater in the warmer than in the colder solution.

4. *Effect of Difference in the Size of the Plates.*—All other conditions being the same in both the electrolysis cells, the plates in one were made to present but one-fourth the surface of those in the other, so that the "current density" was proportionally increased in the former. Under these circumstances there was a constant, though but small, difference in the amount of copper deposited on the two cathodes, the quantity being greater on the cathode plate with smaller surface. The tendency seemed to be towards a greater excess of metal removed from the anode over that deposited on the cathode plate in the case of the larger plates, as compared with the smaller.

5. *Effect of Difference in the Distance between the Plates.*—The plates of both pairs being equal in size, and all other conditions being uniform, the plates in one of the two electrolysis cells were placed at a distance apart only one-fifth that intervening between those of the other pair. It was not clear that any constant difference of result could be detected, but the tendency seemed to be rather toward a very slightly greater deposit on the cathode plate in the case in which the plates were farther apart as compared with that in which they were nearer together. There was no recognisable difference in the proportion of metal dissolved off from the anode plate.

Similar experiments were made with two pairs of plates of pure silver, thus checking the results obtained with copper, and contrasting the behaviour of one at least of the less chemically alterable metals with that of the more easily alterable copper. It was intended to make a set of similar experiments also with gold plates only, but the available supply of pure gold in the form of rolled plates was not sufficient for the numerous experiments required. The silver solution used was one of potassium argento-cyanide, and the substitute for the free sulphuric acid of the copper experiments was an excess of potassium cyanide. The results obtained were essentially similar to those of the copper experiments, the effect of difference in temperature between the two solutions being, however, less decided, and the slight effect of difference in the size of the plates ("density of current") less constant and distinct.

In all the preceding experiments it was found that the most constant results under otherwise similar conditions were obtained by using feeble currents rather than those of greater strength, especially in the case of the silver solutions. There seemed, however, to be a limit to this. On the whole, the most satisfactory results were obtained (both in these preliminary experiments, and in those aiming at the atomic weight determination) with currents not exceeding $\frac{1}{100}$th of an ampère per square centimetre of surface of (one side of) the opposed plates, and in some cases a current but one-fifth of this maximum was used.

Having in view the indications afforded by the preliminary experiments, it was determined to use tolerably strong solutions of the metals to be deposited, with not more than a moderate excess of free acid, or, in the case of the double cyanide solutions, excess of potassium cyanide, to maintain the same temperature in both the electrolysis cells and to have this temperature as low as possible (about 2° C.), and to have the plates of the two metals to be compared equal in size, and at equal distances apart, using a weak electric current, and keeping watch over its strength by means of an ordinary hydrogen voltameter in the circuit.

In the actual experiments on the deposition of gold as compared with silver it was originally proposed to use a solution of potassium auri-cyanide against one of potassium argento-cyanide, with the expectation that 3 atoms of silver would be thrown down for 1 atom of gold. But the first attempts made showed clearly that this reaction could not be obtained. The comparison as to gain in weight of the gold and silver cathode plates gave results leading to an atomic weight for gold impossibly high if the silver deposited were taken to represent 3 atoms, and much too low if it were taken to represent but 1 atom. Hence it appeared that the potassium auri-cyanide had been partially, but not completely, reduced to auro-cyanide by the action of the current, and an intermediate result obtained as to the equivalent quantity of silver between that due to the one or the other gold salt if exclusively present.

A change was therefore made to the auro-cyanide in the preparation of the solution to be electrolysed. A pure form of potassium cyanide was prepared with the aid of alcohol, and carefully tested as to the absence of any metal capable of deposition from the watery solution on electrolysis. Auric chloride was precipitated by ammonia, the fulminating gold, after washing, dissolved in a strong solution of this potassium cyanide with the aid of heat, and the auro-cyanide crystallized out by cooling. The crystals were washed, redissolved in water, aurous cyanide separated from the solution by evaporation with hydrochloric acid, and the crystalline powder after cautious washing again dissolved in potassium cyanide solution, using for the purpose the barely necessary amount of the solvent liquid, but afterwards adding a further quantity, so as to have potassium cyanide in excess. Potassium argento-cyanide was prepared by precipitation of a solution of pure silver in nitric acid with the purified potassium cyanide, washing the precipitate, and re-solution with the aid of the necessary quantity of potassium cyanide, of which finally a moderate excess was added. The solutions of the gold and silver salts were made of equivalent strength, for the most part at the rate of 7 grm. of metallic gold for each 100 c.cm. of solution, and an approximately corresponding amount of silver, taken atom for atom. Both solutions received the same excess of potassium cyanide, generally equal to one-half of that already present in the double salt, but in some of the experiments it was found necessary to add yet more during the electrolysis in order to preserve the purely metallic character of the surface of the plates. As an additional security against admixture of auri-cyanide with the auro-cyanide of the gold solution, it was subjected for some time to electrolysis with unweighed gold plates immersed, these being reversed two or three times in position, just before the introduction of the weighed plates for a quantitative experiment. A number of attempts were made to substitute for the solution of potassium auro-cyanide one of sodium auro-thio-sulphate, of potassium or sodium auri-chloride, and of simple auric chloride, in the last two cases employing at the same time a solution of silver nitrate, but these efforts led to no success.

In many of the experiments made with the double cyanide solutions the cathode plates, both of gold and silver, after removal from the electrolysis cells and thorough washing, were found to curl up on being heated, the deposit, which in these cases was rather hard and brittle, swelling up in a remarkable way, with formation and bursting of little blebs or minute bubbles of the metallic surface, and parting off to some extent of the deposit from the original plate underneath. When the heating was carried out in the Sprengel vacuum small but quite appreciable amounts of hydrogen were found to be given off, having been occluded in the metal deposited. It seemed necessary to throw aside the results in all cases in which this condition of the deposit was well marked. Other experiments were vitiated by the gold deposit not being thoroughly compact, and still others by the surface not being clearly metallic, aurous cyanide making its appearance from the solution. It was hoped that in the experiments, free from apparent defect, any irregular behaviour of the gold solution at first might be got rid of by continued electrolysis, with reversal of the anode and cathode plates when necessary, until the ratio of gold to silver deposited should become constant; but confidence in this was greatly shaken when an instance occurred, followed afterwards by others, of sudden change in this ratio, attended with much less loss from the anode gold plate than the gain of the opposed cathode plate, pointing to deposition of gold from the auro-cyanide with simultaneous formation of auri-cyanide in the solution.*

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* HITTORF ('POGGENDORFF, Annalen,' [4], vol. 16, p. 523), in the simultaneous electrolysis of gold and

Altogether but five experiments made in this way yielded results which seemed worthy of being used to determine the atomic weight of gold, and it is of course unsatisfactory to know that these were selected out of a much larger number, mainly because, while not known to be in any way vitiated by apparent defects, they lead to values for the atomic weight in question close to those obtained by other methods and other experimenters. It is possible that this near approach to agreement may merely result from a balance of errors in opposite directions, which taken separately would have caused the experiments to be rejected. Some other experiments, under apparently similar conditions, gave figures for the atomic weight differing from those reported by one or two whole units.

These only admissible results are the following :—

Experiment.	Character of gold in solution.	Character of gold in plates.	Gold deposited.	Silver deposited.
			grm.	grm.
I.	A, *b*.	B	5·2721	2·8849
II.	,,	,,	6·3088	3·4487
III.	,,	,,	4·2770	2·3393
IV.	,,	,,	3·5123	1·9223
V.	,,	,,	3·6804	2·0132

Aside from other difficulties liable to be encountered in carrying out this electrolytic method, the two most important sources of possible inherent error which suggest themselves are the occlusion of hydrogen by the metallic deposit and the instability of the atomicity of gold in the solution electrolysed.

The separation of hydrogen on the cathode plate, whether in bubbles (which may be avoided by proper regulation of the current) or occluded by the metal (which does not seem to be completely avoidable with any current, although the amount of occluded gas was extremely small in a number of my experiments), must be ascribed to decomposition, simultaneous with that of the cyanide of gold, either of water or, more probably, of cyanide of potassium, with secondary action of the potassium on the water. In either case, it is by no means clear that the proportion of current giving rise to this liberation of hydrogen can be counted upon as the same in the gold solution and in that of silver; and hence, even though it be fairly assumed that FARADAY'S principle of equivalent electrolysis by the same current is strictly correct for the *ensemble* of chemical actions in the two cells, the portion of current actually concerned in depositing gold or silver only in each of the respective cells may conceivably not be

silver solutions, the gold as potassium auri-chloride, obtained results which showed that this metal was deposited at the rate of 1 atom for 3 of silver. Calculating on this basis from his two experiments, the atomic weight of gold comes out = 196·311 and 194·197; for silver = 107·66.

In one experiment of my own, using sodium auri-chloride, the result showed that the gold was thrown down for the most part as a triad, but partly as a monad, element.

quite the same, so that the weights of the two metals thrown down may not be strictly equivalent.* It was, therefore, deemed important to work with feeble currents, and, while heating all the plates in a Sprengel vacuum before weighing, to reject the results of all those experiments in which the quantity of gas thus discharged amounted to more than the merest trace. But, if the source of error in question still exist at all, it might affect the atomic weight of gold in comparison with that of silver, either by making the former appear higher or lower than the truth.

The source of error most to be feared, however, in connection with the application of this electrolytic method to the determination of the atomic weight of gold, is the uncertainty of having all the gold throughout the process in the form of potassium auro-cyanide in the solution, in view of the transition observed to auri-cyanide during electrolysis, although change in the opposite direction occurs with even greater ease. Each of the two salts appears to admit of electrolytic decomposition, and the presence of any traces of the auri-cyanide, in which the gold has triad character, while the calculation is based on the supposed presence of monad gold only would, of course, tend to make the atomic weight of the metal appear lower than the truth.

Sixth Series of Experiments.

These experiments consisted merely in the further application of electrolysis to the deposition of metallic gold from a solution of potassium auro-cyanide, comparing the weight of the metal thrown down, however, not with the weight of silver, but with the volume of hydrogen gas liberated by the action of the same current, the object being to thus secure, with an assumed knowledge of the density of hydrogen, a direct comparison of the atomic weight of gold with that of the element most generally taken as the basis of the numerical constants in question.

A cell containing the same solution of potassium auro-cyanide as was used in the

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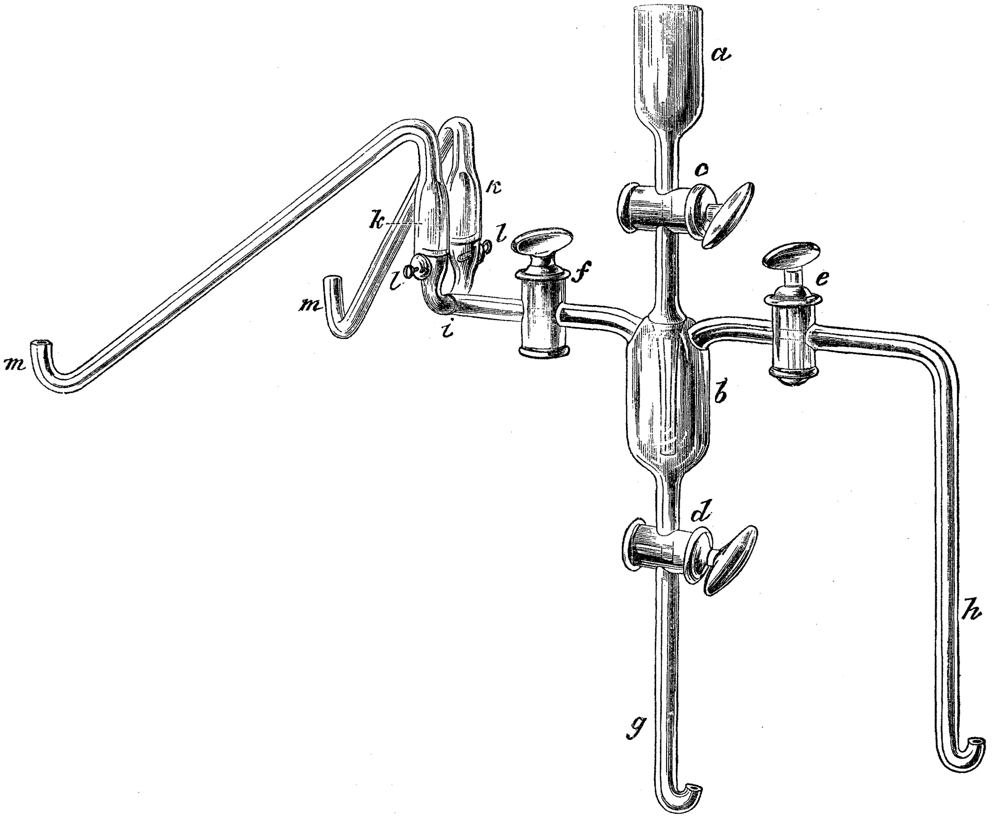
* As bearing on the question of the simultaneous decomposition of two electrolytes in the same solution, the following results may be recorded of an experiment made with a solution of mixed zinc and copper sulphates, with excess of potassium cyanide, the anode plate being of brass and the cathode plate of platinum, and an analysis made of the proportions of the two metals in the anode plate, in the solution as first taken, and in the alloy deposited on the cathode plate and subsequently dissolved off from it by means of nitric acid.

Proportion of copper to zinc.	In the brass anode plate.	In the solution electrolysed.	In the alloy deposited on the cathode plate.
Copper	68·74	13·81	73·34
Zinc	31·26	86·19	26·66
	100·00	100·00	100·00

Different results would undoubtedly have been obtained by substituting some other metal for one of those taken.

fifth series of experiments, and having immersed in it a pair of plates of "proof" gold, as already described, was employed for the deposition of the gold. The same current which traversed this cell was passed through a hydrogen voltameter of special construction,* made of glass, in a single piece, the general character of which will be seen from fig. 5.

Fig. 5.



When this instrument was to be prepared for use, it was cautiously heated pretty strongly in an air-bath to remove the film of moisture and air from the internal surface, drawing dry air through by means of an aspirator. Clean mercury, previously heated, was then poured in through the funnel *a*, going down to nearly the bottom of the cylindrical vessel *b*, until this vessel—about 30 mm. in diameter and 60 mm. in height—was completely filled, and also the tubes and stop-cocks *c*, *d*, *e*, and *f*, each of these in succession being opened to allow escape of air, and afterwards closed; *f* was a three-way stop-cock, which could either be made to open communication between the parts of the tube on either side of it, or to simply close this tube, or to close this tube and establish communication between the vessel *b* and the outside air through the base of the stop-cock; it was in this last-named way that air and surplus mercury were allowed to escape, filling the tube between *b* and *f* with mercury, but not allowing of any of the

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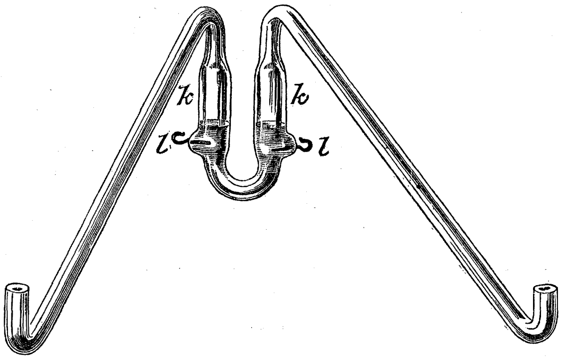
* This piece of apparatus—an excellent specimen of skilful glass-blowing—was made, from drawings furnished by me, by Mr. Emil Greiner, of 63, Maiden Lane, New York.

metal going further along the tube towards *i*. The stopcock *c* was closed, with the tube on which it was situated completely full of mercury, and leaving surplus mercury in the funnel *a*. In filling *b* and its connected tubes care was taken to leave no visible bubbles of air. Pure water mixed with one-twelfth its weight of pure sulphuric acid was boiled for some time in a small flask to expel all dissolved air, keeping up the volume by additions from time to time of water kept boiling in a second flask; the lower turned-up end of the tube *h* was then immersed in the dilute acid, and the lower end of *g* in a cup of mercury; on opening the stopcocks *e* and *d* mercury ran out from *g*, and the dilute acid came in through *h*, filling about half full the cylinder *b*. Closing *d* and *e*, opening *c*, and keeping up a supply of mercury in the funnel *a*, *f* was now turned so as to force out through the base of this stopcock the little mercury in the tube behind it, and fill this tube with the acidulated water. Then *f* was turned so as to allow of this acidulated water being forced on to the bend *i* and into the two little voltameter tubes *k* and *k*, filling these about one-third full. While these tubes were being thus filled the extremities of the delivery tubes *m* and *m* were in communication with a Sprengel pump, so that they were very nearly exhausted of air. The stopcock *f* having been closed, *e* was opened, and by suitable tilting of the apparatus, and running in of mercury from the funnel *a*, nearly all of the acidulated water from *f* backwards was expelled through the tube *h*. A repetition of the procedure by which the cylinder *b* had been partially filled with acidulated water now served to partially fill it with well-boiled and still hot distilled water to which no acid had been added. The two delivery tubes *m* and *m* were severally detached from the Sprengel pump, after allowing (by a special separate arrangement of tubes with stopcocks) hydrogen to enter one of the two and oxygen the other, and when thus filled the ends of these two tubes were dipped under mercury, and the two platinum wires, *l* and *l*, sealed into the voltameter tubes were connected by the little rings on their outer ends with the terminals of the galvanic cells whence the electric current was to be derived, taking care, of course, to connect to the negative pole the wire of the tube already filled in its upper part with hydrogen, and to the positive pole the wire of the oxygen tube. Viewed from the front, the two voltameter and delivery tubes presented the appearance shown in fig. 6. The little voltameter tubes *k* and *k* had an external diameter of about 12 mm. and a length of 40 mm. The platinum wires, *l* and *l*, serving as electrodes were 1 mm. in diameter, and extended beyond the interior surface of the glass (into which they were sealed) for only 3 mm. in length. They could be well covered, and the voltameter tubes filled to one-third their capacity, with only about 2 c.cm. of the acidulated water. By careful tilting of the apparatus laterally it was found to be possible to so regulate the pressure of mercury at the ends of the delivery tubes, and therefore the gaseous tension in the two voltameter tubes, that the acidulated water was not forced over from the one to the other, which, had it occurred, would have allowed admixture of the two gases; this required constant watching, however, and there was needed from time to time a little tapping of the apparatus to get rid of the effect of irregular adhesion of the liquid to the walls of the voltameter tubes.

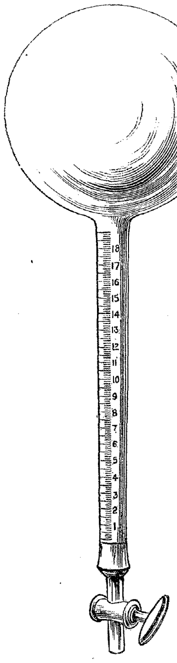
Fig. 6.



It will be seen that, with the arrangement described, the electrolysis could be effected of acidulated water, thoroughly deprived in advance of dissolved air, and in quantity so small as to be capable of retaining in solution but infinitesimal quantities of the hydrogen and oxygen electrolytically separated. As the decomposition proceeded, the quantity of liquid in the voltameter tubes could be maintained constant by opening the stopcock *c*, with a supply of mercury in the funnel *a*, and then cautiously opening *f*, so as to feed forward a little of the air-free water from the cylinder *b*, thus leaving the proportion of acid unaltered. The surface presented by the platinum wire electrodes was so small as to allow of occlusion of the gases to only an extremely minute extent, and both the hydrogen and oxygen were allowed to escape for some time before any was collected for measurement.

The hydrogen only was collected and measured. I had hoped to apply this form of voltameter to a more exact determination of the relative volumes of hydrogen and oxygen derived from water by electrolysis than is possible with the voltameters of more common construction. But I have not yet seen my way to getting over the difficulties connected with the presence of ozone, hydrogen dioxide, BERTHELOT'S persulphuric acid, or other by-products in the oxygen gas evolved at the positive pole. If this could be accomplished, a useful contribution might possibly be made to the question, revived and worked upon of late by several chemists, of the exact atomic weight of oxygen. The vessel for collecting and measuring the hydrogen, shown in fig. 7, consisted of a spherical globe of tolerably stout glass, with a capacity of about 250 c.cm., having a neck of about 1 cm. internal diameter, and 22 cm. long. This neck had etched upon it a simple linear scale of millimetres. At the mouth it was fitted with a well ground perforated glass stopper, forming part of a glass stopcock with an outer orifice of about 1 mm. bore. The exact capacity of the whole globe and neck was ascertained by heating it in an air-bath to remove air and moisture condensed on the interior surface, drawing dry air through with an aspirator, then filling the globe with heated mercury, allowing it to cool to an accurately noted temperature, immersing the body of the globe in an outer vessel of mercury so as to prevent extension or flexure of the glass by the weight of the contained metal, filling up to the very mouth with mercury, inserting the stopper with the stopcock open, thus forcing out through its orifice the last of the air, closing the stopcock, removing from the orifice tube, by an iron wire, the drop or two of mercury remaining in it, and then emptying the flask, and carefully weighing in successive portions the mercury which it had held. The hydrogen from the voltameter was collected in this flask, without its stopper, the flask having been previously filled with mercury, with the needful precautions for removal of all air, and inverted over a mercury trough. In each experiment the process of electrolysis was arrested when the hydrogen had filled the body of the globe and reached to a point rather more than half way down the length of the neck, the gold plates being of course withdrawn at the same moment from their cell of gold solution, set away to soak in distilled water, and afterwards thoroughly washed, dried, heated in the Sprengel vacuum, cooled, and weighed. The portion of hydrogen collected was dried by successive balls of fused potash introduced and withdrawn by means of platinum wire. The neck of the flask having, in advance of the collection of hydrogen, been passed through a cork, this was used to close the mouth, placed downwards, of a vessel through which a stream of water was caused to flow rapidly from the pipes supplying the University buildings. The atmospheric temperature of the day on which the electrolysis experiment was made having been such as not to differ too much from the temperature of the water from the pipes, the gas occupied such a volume after effectual exposure to this latter temperature that

Fig. 7.



the mercury marked a point somewhere within the length of the neck, which point was noted by the millimetre scale, the thermometer immersed in the flowing water, and the barometer and its attached thermometer being read at the same time. It remained only to insert the stopcock stopper under the mercury of the little mercury trough, close the stopcock, withdraw the flask from the trough, reject the drop or two of mercury from the stopcock orifice by means of a wire, remove the portion of mercury left in the neck of the flask, and weigh it carefully. Its weight, with consideration of its temperature when the stopcock was closed, gave the volume of the portion of the flask not occupied by hydrogen, and this, subtracted from the whole volume of the interior of the flask, as found by the original calibration, gave the volume, under known conditions of temperature and pressure, of the hydrogen which had been collected. From two calibrations at different temperatures a correction was obtained for the expansion of the glass of the flask, but it was hardly necessary to take this into account, in view of the small limits within which temperature varied in all the experiments made.

But three experiments carried out by this method led to results which seemed worthy of confidence. These results were as follows:—

Experiment.	Character of gold in solution.	Character of gold in plates.	Gold deposited.	Hydrogen liberated.	
				Vol. at 0° C. and 760 mm.	Weight.
			grm.	c.cm.	grm.
I.	A, *b*	C	4·0472	228·64	·02053
II.	A, *b*	C	4·0226	227·03	·02039
III.	A, *b*	C	4·0955	231·55	·02079

In calculating the weight of hydrogen from its observed volume, REGNAULT's value for the weight of a litre of this gas at 0° C. and 760 mm. was taken as the basis. The correction, of which Lord RAYLEIGH not long since pointed out the need—namely, for the compression of the vacuous glass flask by atmospheric pressure—was adopted from the experiments of J. M. CRAFTS ('Comptes Rendus,' vol. 106, p. 1662); and his corrected value, ·08988 grm., was still further corrected for the difference in the force of gravity at Paris and at the University of Virginia (in C. G. S. units, 980·94 : 979·95), giving as the value to be used ·08979 grm.

The electrolysis of the water was carried on very slowly, so as to keep the density of the current low with such small electrodes as were used. Nevertheless, as the hydrogen voltameter required constant watching, it became necessary to bring the whole time of an experiment within moderate limits, and hence a considerably stronger current was used than in the simultaneous deposition of gold and silver in the fifth series, this circumstance being less favourable to the satisfactory deposition of the gold. It would have been desirable to use a larger flask, and to collect a greater volume of hydrogen ; but this, on account of the time required, would have made an experiment exceedingly troublesome and difficult.

In the work of this series the same unsatisfactory need for selecting only such results as came fairly close to the figures expected, and rejecting several others on the ground of very considerable departure therefrom, and the same sources of possible constant error in regard to the gold deposit present themselves which have already been noticed under the head of the fifth series. As regards the hydrogen, one is led to consider possible diffusion of hydrogen and oxygen between the two little voltameter tubes, and slight imperfection in the drying of the hydrogen obtained. The former would, on the whole, probably tend to diminish the volume of gas collected, and hence to raise the apparent value of the atomic weight of gold. The latter would have the opposite tendency. That neither can have had more than an extremely minute influence was fairly proved by testing a part of the hydrogen obtained, on the one hand by passing it through a red-hot glass tube, and on the other by submitting it to more extended drying by contact with phosphorus pentoxide both before and after such heating ; in neither case was there appreciable change of volume.

Notwithstanding the desirability of comparing the atomic weight of any other element directly with that of hydrogen, the difficulty is not to be overlooked of doing this for an element having so high an atomic weight as that of gold. There is a manifest objection to the necessity of dealing with such minute quantities of hydrogen as those concerned in these experiments. A very small error in the determination of the hydrogen greatly affects the value found for an atomic weight nearly two hundred times as large. It is true that the measurement of the volume of the hydrogen admits of being made with such precision as to leave room for but an extremely minute error in the corresponding weight, yet this measurement is not one of *limitless* delicacy, particularly if the difficulty be properly appreciated of ascertaining with certainty the precise temperature of the gas at the time its volume is read. Moreover, in measuring the volume of the gas, and thence deducing its weight, there is need not merely for a knowledge of changes of temperature and pressure, but for *absolutely* correct readings of the barometer and thermometer, so that there must usually be a degree of hesitation in accepting the readings of even fairly standard instruments, when temperature and pressure come to be placed in comparison with these conditions as affecting the results of REGNAULT for gaseous density. Nor can the results of that great physicist be assumed as themselves free from all possible need of further correction.

The error of direct comparison with so small an atomic weight as that of hydrogen is, however, after all only *masked* by substituting an *indirect* comparison through some larger atomic weight, since the assumed value of the latter is uncertain within limits which depend upon *its* comparison with the atomic weight of hydrogen.

Seventh Series of Experiments.

In pursuance of the attempt to connect directly the atomic weight of gold with that of hydrogen, metallic zinc was prepared as nearly as possible in a state of purity, and, a known quantity of the metal having been dissolved in dilute sulphuric acid, the amount of hydrogen evolved was determined by volume. A solution of pure auric chloride or bromide was then treated with a known quantity of the same zinc, more than sufficient for the complete precipitation of all the gold present; the excess of zinc was dissolved by dilute sulphuric acid, and the volume of hydrogen given off was determined. The precipitated gold was carefully collected, washed, dried, ignited, and weighed. The difference between the volume of hydrogen which the zinc gave when thus partly used to replace a known quantity of gold and the volume which it would have given if replacing hydrogen alone represented, of course, the volume of a quantity of hydrogen equivalent to the gold precipitated and weighed. From this volume, under known conditions of temperature and pressure, the weight of the hydrogen was calculated on the basis of REGNAULT's results for the density of the gas, after application of the needful corrections, as in the sixth series of these experiments.

In a preliminary notice of my work read before the Chemical Section of the British Association at the Manchester meeting of 1887, it was pointed out that the method just described has certain advantages in principle. It does not require that the weight of the gold salt in solution be known, so that all difficulties in regard to drying such salt without decomposition are disposed of. It does not depend upon a knowledge of the atomic weight of the halogen in combination with gold, or upon a knowledge of the atomic weight of zinc. It does not even require that the zinc be of assured purity, provided only it be uniform in character, so that a given weight of it can be trusted to yield always the same quantity of hydrogen, and there be no impurities present capable of interfering with the collection of the whole of the precipitated metallic gold in a state of purity. The chief difficulty consists in the accurate ascertainment of the total volume of hydrogen evolved from the solution of a satisfactorily large quantity of zinc; when the gold solution comes to be used, as the volume of hydrogen given off on solution of the *surplus* zinc may be made quite small, its measurement becomes both easy and exact.

The pure zinc required was obtained by fractionally distilling in a Sprengel vacuum some very nearly pure metal from the Bertha Zinc Works, in South-western Virginia, using a long combustion-tube of hard Bohemian glass, and substantially the same arrangement of apparatus as that described by MORSE and BURTON* in connection with their work on the atomic weight of zinc. The original metal was found, by an analysis in the laboratory of the University of Virginia, to contain less than ·04 per cent. of foreign matter, almost solely consisting of lead and iron. It was four or five

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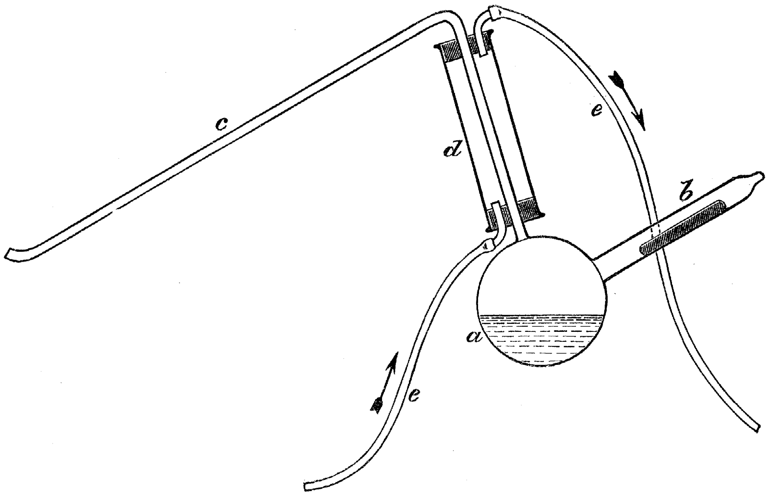
* 'American Chemical Journal,' vol. 10, p. 312. Tubes of glazed porcelain, closed at one end, had been specially procured for use in thus distilling zinc, but it was found that they were quite unnecessary.

times redistilled *in vacuo*, rejecting each time about one-third of the quantity treated. The process is easily carried out, and in the final product, completely soluble in dilute sulphuric acid without visible residue, no trace of detectable impurity could be found.

For the evolution of hydrogen on solution of this zinc in acid the little piece of apparatus represented in fig. 8 was used, the same that I had used in my work of several years ago on the atomic weight of aluminum.* The description formerly given of the details of an experiment with this apparatus may be repeated with but trifling change of language. A rather more than sufficient quantity of diluted sulphuric acid, its volume accurately measured, having been introduced into the bulb *a* by means of a little tube-funnel passed through the tube *b*, the outer end of which was originally open, taking care to leave the surface of *b* clean, the metallic zinc, in a single piece of elongated shape, and having a little bit of slender platinum wire wrapped round it, was passed into *b*, held nearly horizontal, so that the metal did not slip down into the bulb, but rested 40 or 50 mm. from it; *b* was now drawn off in the lamp flame, 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 zinc coming in contact with the dilute acid. 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 dilute acid introduced and of metallic zinc (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

Fig. 8.



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* 'Phil. Trans.,' 1880, p. 1026.

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

piece of zinc 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 zinc 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. To guard against more than traces of aqueous vapour being carried away with the hydrogen, a rapid current of ice-water was kept up through *d*.

As soon as the last of the zinc 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 and the height of the mercury in *c* above that in the 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 solution of zinc sulphate and free acid 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 having been 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.

The dilute acid was saturated with pure hydrogen just before being used (and in the experiments with auric chloride or bromide the main portion of water holding this salt in solution was similarly treated), and a preliminary experiment showed that there was but an extremely minute difference between the amount of gas removable from such liquid by heating in a Sprengel vacuum and from that containing zinc sulphate after the solution of the metal; so that, practically, the question of retention of gas in solution by the liquid might be neglected.

The sulphuric acid was diluted to 25 per cent. by weight, only a small bit of platinum wire was wrapped round the zinc, and the temperature of the bulb was not allowed to rise beyond about 20° C. Thus the risk of evolving other gaseous products than hydrogen*—as hydrogen sulphide or sulphur dioxide—was avoided, and on testing for these impurities the hydrogen collected no traces of them were found.

The measuring flask used to collect the hydrogen was of the same character as that used for the experiments of the sixth series, but of much larger size, holding

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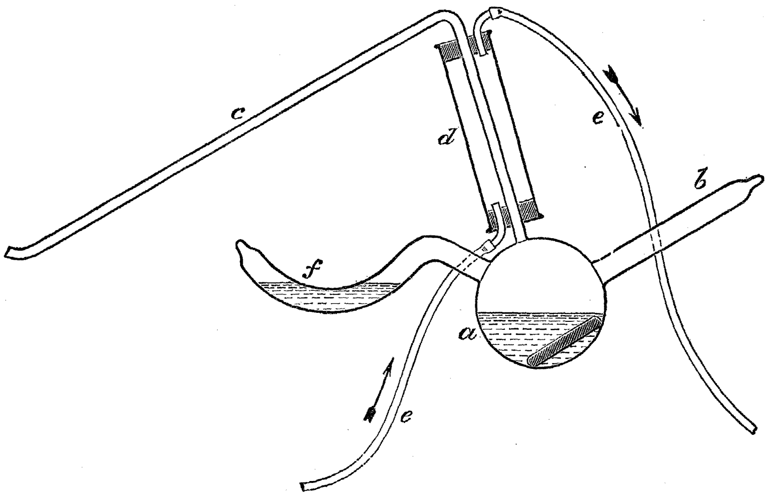
* MUIR and ADIE: "On the Interaction of Zinc and Sulphuric Acid," 'Chem. Soc. Journ.,' Jan., 1888, p. 47.

about a litre. The quantity of zinc taken for each experiment was calculated to give a volume of gas which, under the conditions of temperature and pressure of the day, would bring the mercury to somewhere near the middle of the neck, and the gas, previously dried by balls of fused potash, was measured after the temperature had been rendered as nearly as possible fixed by the circulation round the outside of the flask of an active stream of water from the laboratory supply pipes. 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 that of the air in the same at the beginning; and, after reduction to normal temperature and pressure, the difference had to be subtracted from the gas collected in the flask.

In the experiments with auric chloride or bromide the quantity of hydrogen given off on solution of the *surplus* zinc was so small that it could be easily measured in a little gas tube, the same method of double calibration with mercury being used as for the larger volumes. In these experiments the bulb used had a second side tube, *f*, as shown in fig. 9, to hold the sulphuric acid, while *a* contained the aqueous solution of the gold salt; this acid was already somewhat diluted, and was introduced into *a*, after complete precipitation of the gold, very gradually, so as to avoid any considerable rise of temperature. The quantity of water used was such as to make the whole volume of liquid very nearly the same in the experiments with zinc alone and in those with zinc and the auric salt. Care was taken to ascertain, after measurement of the hydrogen, that it had been effectually freed by the potash balls not only from moisture, but from any traces of hydrochloric acid formed and carried over.

Fig. 9.



In order to connect the weight of the zinc with that of the hydrogen produced by its solution, 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 on the density of hydrogen; hence, as has been already stated, the weights used were such as had had their real values 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 same value for the weight of a litre of the gas was assumed as has been already stated, viz., ·08979 grm., being the result of REGNAULT'S determinations, with the correction pointed out by Lord RAYLEIGH and numerically estimated by CRAFTS, and further corrected for the force of gravity at the University of Virginia.

The haloid salts of gold were prepared as for the experiments of the first and second series, and the careful filtration of their solutions was followed by long continued standing at rest before the portions required were gently drawn off for use. Great care was taken in removing the last traces of precipitated gold from the bulb—to facilitate which the connected tubes were all cut off short—and in repeatedly washing the metal, first with dilute sulphuric acid, then with pure hydrochloric acid, and, finally, with water, before drying, heating (in the Sprengel vacuum), cooling, and weighing.

The results obtained by this method were much freer from irregularity, and much more satisfactory, than those of the electrolytic experiments. All are reported, except one or two cases obviously vitiated by mechanical defects of manipulation, and, in consequence, not carried out to the end.

Experiments with Zinc alone.

Experiment.	Zinc dissolved.	Hydrogen obtained, at 0° C. and 760 mm.		Hydrogen, at 0° C. and 760 mm., for 1 grm. of zinc.
	grm.	c.cm.		c.cm.
I.	2·6990	922·64	Equivalent to	341·85
II.	2·6771	915·33		341·91
III.	2·7029	924·20		341·93
IV.	2·7117	927·51		342·04

Or a total amount of 10·7907 grm. of zinc gave 3689·68 c.cm. of gas,* equivalent to 341·93 c.cm. of hydrogen for 1 grm. of zinc. This value was adopted in calculating the fifth column of the following table.

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* These figures represent an atomic weight for zinc = 65·142, taking the weight of a litre of hydrogen at 0° C. and 760 mm. as ·08979 grm., and assuming the zinc used to have been absolutely pure, and the quantity of hydrogen collected to have been strictly equivalent to it; neither of the two latter assumptions is essential to the use made in this paper of the experiments. REYNOLDS and RAMSAY in their recent paper ('Chem. Soc. Journ.,' Dec., 1887, p. 854) on the atomic weight of zinc arrive at a somewhat higher value, on the basis of a like comparison of the weight of the metal with the volume of hydrogen liberated by it, but they assume the weight of the litre of hydrogen under normal temperature and pressure as ·0896 grm., which must be considered too low in view of the recently applied correction of Lord RAYLEIGH.

Experiments with Gold Salt and Zinc.

Experiment.	Character of gold used.	Character of gold salt.	Gold precipitated	Hydrogen, at 0° C. and 760 mm.		Hydrogen equivalent to gold.	
				Corresponding to total zinc.	Obtained from residual zinc.	Vol. at 0° C. and 760 mm.	Weight.
			grm.	c.cm.	c.cm.	c.cm.	grm.
I.	A, *b*	$AuCl_3$	10·3512	1779·44	—23·34	=1756·10	=·15768
II.	A, *b*	$AuBr_3$	8·2525	1428·99	—28·61	=1400·38	=·12574
III.	A, *b*	$AuCl_3$	8·1004	1393·43	—18·56	=1374·87	=·12345
IV.	C	$AuCl_3$	3·2913	582·82	—24·18	= 558·64	=·05016
V.	C	$AuBr_3$	3·4835	606·20	—15·27	= 590·93	=·05306
VI.	D	$AuBr_3$	3·6421	643·31	—25·20	= 618·11	=·05550

In considering possible causes of constant error in the experiments of this last series it seems most likely that they would affect the exact determination of the weight of the precipitated gold, either by mechanical loss of some minute particles of the metal, tending to lower the atomic weight, or by incomplete washing out of the zinc salt, with an influence in the opposite direction. Any failure to remove the last traces of moisture from the hydrogen was, I think, effectually guarded against, at any rate within such limits as would have sensibly affected the resulting atomic weight; and any error due to retention of hydrogen in solution by the liquid must also have been inappreciably small, in view of the precautions taken and the close similarity of conditions in the experiments with zinc alone and with zinc and the auric salt.

Calculation of Results.

In calculating the atomic weight of gold from the data furnished by the experiments which have been described, I have thought it best to conform to the most general usage of those who have been working on questions of this sort of late years, so as to facilitate comparisons with the results of others. Hence, although the atomic weight has been calculated separately from the figures of each experiment reported, the value deduced from each series has not been taken as the arithmetical mean of the separate results, nor has the probable error of these or of the mean been calculated by the method of least squares, as was done in my paper on the atomic weight of aluminum, but, instead, the general result for each series has been obtained, as in the calculations of MEYER and SEUBERT, from the aggregate quantities of the materials employed, though I am by no means convinced that this mode of reckoning is in all cases sound in principle, giving, as it does, weight to each experiment in proportion to the quantity of material employed.

The atomic weights assumed for the other elements involved are those which have been most generally accepted in calculations of this kind, based for the most part on the experiments of STAS, and representing, with greatest probability, the values as at present known to us. They are as follows :—

H = 1.
Ag = 107·66.
Cl = 35·37.
N = 14·01.
C = 11·97.

Calculated Results.

The following are the values obtained for the atomic weight of gold from the different series of experiments :—

FIRST Series.

$(Ag_3 : Au : : 322{\cdot}98 : x.)$

Experiment.	Silver.	Gold.	Atomic weight of gold.	
	grm.	grm.		
I.	12·4875	7·6075	196·762	
II.	13·8280	8·4212	196·694	
III.	11·3973	6·9407	196·688	Lowest value
IV.	5·5286	3·3682	196·770	Highest value
V.	4·6371	2·8244	196·723	
	47·8785	29·1620	196·722	

SECOND Series.

$(Ag_3 : Au : : 322{\cdot}98 : x.)$

Experiment.	Silver.	Gold.	Atomic weight of gold.	
	grm.	grm.		
I.	13·5149	8·2345	196·789	
II.	12·6251	7·6901	196·731	Lowest value
III.	17·2666	10·5233	196·843	Highest value
IV.	4·5141	2·7498	196·746	
V.	5·8471	3·5620	196·756	
VI.	6·4129	3·9081	196·828	
	60·1807	36·6678	196·790	

THIRD Series.

$(\mathrm{Ag}_4 : \mathrm{Au} :: 430{\cdot}64 : x.)$

Experiment.	Silver.	Gold.	Atomic weight of gold.
	grm.	grm.	
I.	12·4851	5·7048	196·772
II.	17·4193	7·9612	196·817 Highest value
III.	5·3513	2·4455	196·799
IV.	9·1153	4·1632	196·685 Lowest value
	44·3710	20·2747	196·775

FOURTH Series.

$(\mathrm{N(CH_3)_3HCl_4} : \mathrm{Au} :: 201{\cdot}40 : x.)$

Experiment.	Loss by ignition of trimethyl-ammonium auri-chloride.	Gold.	Atomic weight of gold.
	grm.	grm.	
I.	7·5318	7·3754	197·218
II.	7·8432	7·6831	197·289 Highest value
III.	5·2811	5·1712	197·209
IV.	3·3309	3·2603	197·131 Lowest value
V.	2·8165	2·7579	197·210
	26·8035	26·2479	197·225

FIFTH Series.

$(\mathrm{Ag} : \mathrm{Au} :: 107{\cdot}66 : x.)$

Experiment.	Silver.	Gold.	Atomic weight of gold.
	grm.	grm.	
I.	2·8849	5·2721	196·747
II.	3·4487	6·3088	196·945 Highest value
III.	2·3393	4·2770	196·837
IV.	1·9223	3·5123	196·709 Lowest value
V.	2·0132	3·6804	196·817
	12·6084	23·0506	196·823

SIXTH Series

(H : Au : : 1 : x.)

Experiment.	Hydrogen.	Gold.	Atomic weight of gold.	
	grm.	grm.		
I.	·02053	4·0472	197·136	
II.	·02039	4·0226	197·283	Highest value
III.	·02079	4·0955	196·994	Lowest value
	·06171	12·1653	197·137	

SEVENTH Series.

(H_3 : Au : : 3 : x.)

Experiment.	Hydrogen.	Gold.	Atomic weight of gold.	
	grm.	grm.		
I.	·15768	10·3512	196·941	
II.	·12574	8·2525	196 894	
III.	·12345	8·1004	196·851	
IV.	·05016	3·2913	196·848	Lowest value
V.	·05306	3·4835	196·956	Highest value
VI.	·05550	3·6421	196·865	
	·56559	37·1210	196·897	

General Mean of Results.

If each of the foregoing series of experiments be represented by the result calculated from the aggregates of material used, and if equal weight be attached to the results of all the methods, the general mean derived from the whole of the 34 experiments will be as follows :—

First series	196·722	Lowest value.
Second series	196·790	
Third series	196·775	
Fourth series	197·225	Highest value.
Fifth series	196·823	
Sixth series	197·137	
Seventh series	196·897	
General mean	196·910	

The results of the fifth and sixth series, obtained by electrolysis, are, I am convinced, much less entitled to confidence than any of the others. If these two be excluded, the general mean of the remaining series will be **196·882,** a number differing but little from the mean of all.

The highest value is that derived from the fourth series—ignition of trimethyl-ammonium auri-chloride. It has been seen that the individual results of this series agree fairly well with one another, and, when examined in connection with the facts as to the different crops of crystals of the salt used, do not seem to present any evidence of want of uniformity in the material. But, as it may still be suspected that traces of dimethyl- or of monomethyl-ammonium auri-chloride may have been present, and have caused the apparent value of the atomic weight of gold to come out higher than the truth, if we exclude also this series, the general mean of the remaining four will be **196·796.**

Finally, if for the sake of comparison with the results of KRÜSS and of THORPE and LAURIE the general mean be taken for the first three series only, in which auric chloride and bromide were examined, the result is **196·762**—intermediate between the general means of the two previous researches, but rather nearer to that derived from the work of THORPE and LAURIE than of KRÜSS.

It will be observed that, although there is pretty close agreement among the means of results obtained by altogether different methods, this agreement is not so close as that presented by the results of the nearly similar methods pursued in the first three series. This cannot but suggest the probability of there being still sources of minute errors inherent in the methods themselves, and not dependent upon mere imperfections of manipulation in carrying these methods out. Although there is thus to be noticed a slight tendency on the part of each method to yield high or low figures severally, with the exception of the results of the fourth series there does not appear to be any considerable reason to see in the values obtained confirmation of the special suspicions in connection with each method which have been stated. There is no clear evidence of any difference in the results which can be traced to the history of the particular samples of gold used; a larger number of somewhat low results seem to have been yielded by the metal designated as (C)—*i.e.*, obtained from the United States Assay Office at New York—than by the others, but the difference is not marked or constant enough to warrant any trustworthy conclusions as to the character of this material.

Concluding Remarks.

The atomic weight of gold as deduced from the experiments reported in this paper is entirely in accord with the place occupied by the metal in MENDELEJEFF's "periodic" classification of the elements, but this is equally true of the slightly different values obtained by KRÜSS, and by THORPE and LAURIE, and the only difficulty at one time apparent as to this point—namely, the relative positions of gold on the one hand and of platinum, iridium, and osmium on the other—has been removed, not by any change in the atomic weight of gold, but by changes affecting the values to be assigned the three other metals, as these values have been determined by SEUBERT.* It is very desirable that, in order to a fuller and more exact examination of the Mendelejeff table of the elements, there be accomplished as soon as possible a general revision of the atomic weights of *all* the elements of well determined individuality, so many of which are still very imperfectly known.

As to any bearing of the results of the present paper on the so-called hypothesis of PROUT,† the general mean of all my results, or even the general mean with exclusion of the values obtained by electrolysis, approaches the integer number 197 rather more nearly than does the final number arrived at by THORPE and LAURIE, and still more nearly than does that considered by KRÜSS to express the final result of his experiments. If the results of the fourth series be also rejected, my general mean will be nearer the integer than is the KRÜSS number, but not quite so near as that of THORPE and LAURIE. I feel that somewhat greater confidence may be placed in my own work, simply on the ground of its involving the use of more completely different and independent methods—a principle which I believe to be of the first importance in any attempts at increased accuracy in the determination of atomic weights.

At the same time, as has already been pointed out, this work seems to me to furnish some probable evidence that not all inherent defects of method have been eliminated. Whether or not such defects may exist to an extent sufficient to account for the remaining difference between the value obtained and the integer multiple of the atomic weight of hydrogen there does not seem to be ground on which to express a positive opinion. But this research does not supply any clear evidence contradictory of such a possibility.

On this point, and generally on the attainment of what is sometimes rather too easily spoken of as the greatest possible accuracy in the determination of an atomic weight—particularly of an element for which the value is as high as that for gold—any one who actually works in a conscientious way at such determinations will be pretty sure to feel more strongly the difficulty of the task, and to express himself with more caution, than do some compilers of results in assuming at any time that the last word has been spoken.

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* 'Berichte Deutsch. Chem. Gesell.,' vol. 11, p. 1770; vol. 14, p. 868; vol. 21, p. 1839.

† Soon after the publication of my paper on the atomic weight of aluminum, I was criticised by a writer of abstracts for the German Chemical Society on account of my use of the expression "PROUT'S law," amazement being indicated that I should have called the "hypothesis" of PROUT a *law*. If this writer had noticed my use of inverted commas, and still more what was said in the course of two or three pages of the paper, he would have seen that the use of the expression "PROUT'S law" was by no means equivalent to assuming this to be "a law of nature."