LI.—*On the Atomic Weight of Gold.*

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ALTHOUGH gold is not usually regarded by chemists as one of the "rare" elements, it is remarkable that few atomic weights have been more imperfectly determined than that of this metal. This may be partly due to the circumstance that gold and its compounds have hitherto played a comparatively unimportant part as chemical reagents, and that the value of its atomic weight enters but seldom into chemical calculations. An additional reason may be found in the experimental difficulties with which such a determination is surrounded, owing to the unstable character of gold compounds in general. It is of course desirable that this, like every other stoichiometrical constant, should be known with the greatest attainable precision in view of the far wider question than that of mere chemical equivalence with which the chemical philosophy of to-day deals. In the special case of gold, there is the further reason that the position of this metal in the system of the chemical elements, as determined by Mendeléeff's law, would seem to require a distinctly higher value for the atomic weight than is usually assigned to it. For these reasons, therefore, we were induced to undertake the revision of the atomic weight of gold, which forms the subject of the present communication.

Shortly after the publication by Dalton of his first table of atomic weights, attempts were made independently by Proust and Oberkampff in 1806 (*Gehlen's Journ.*, 1, 487) to determine the relation of gold to oxygen from the analysis of gold monoxide. Similar experiments were also made by Dalton, but the numbers obtained by all those observers were, as might be expected, not very concordant. Indeed, in the "New System of Chemical Philosophy," Dalton remarks "that the weight of an atom of gold is not easily ascertained because of the uncertainty in the proportions of the elements forming the compounds into which it enters. It is probably not less than 140 nor more than 200 times the weight of an atom of hydrogen." ("A New System of Chemical Philosophy," Part II, p. 250.)

The first approximately accurate determination of the atomic weight of gold was made by Berzelius in 1813 (*Kgl. Vetensk. Acad. Handl.*, 1813, p. 185; details taken from Sebelien's "*Beiträge zur Geschichte der Atomgewichte*"). A neutral solution of auric chloride was digested for several days with a weighed quantity of mercury, in

amount equal to about half that of the gold present, until the whole of the mercury was apparently dissolved. The precipitated gold was collected and weighed and afterwards strongly heated to expel the small quantity of mercury which invariably amalgamated with it; the volatilised mercury being collected and its weight subtracted from that originally taken. On the basis of Sefström's determination of the ratio between oxygen and mercury, Berzelius found from the two experiments which he made that $\text{Au} = 1242.05$ and 1249.65 ($\text{O} = 100$). From the relation $\text{Au}_2 : \text{O}_3 = 100 : 12.040$, Berzelius concluded that the mean value of $\text{Au} = 1246$. Taking $\text{H} = 1$, this value gives for $\text{Au} 198.8$. If $\text{Hg} = 199.6$, the two experiments give respectively $\text{Au} = 196.0$ and 197.3 .

Pelletier (*Ann. Chim. Phys.*, **15**, 5), who first prepared aurous iodide, attempted to determine the atomic weight of gold by heating that salt and weighing the residue, which he regarded as pure gold. From the relation $100 \text{ gold} : 51.515 \text{ iodine}$, he found the value of $\text{Au} = 235.6$. This abnormally high value doubtless arises from the instability of aurous iodide: the salt cannot be dried without loss of iodine, and decomposes even on exposure to light.

Javal (*Ann. Chim. Phys.*, **17**, 337), by heating auric oxide, Au_2O_3 , prepared by adding baryta-water to a solution of auric chloride, obtained the relation $\text{Au}_2 : \text{O}_3 = 100 : 11.909$, whence $\text{Au} = 201.0$. Even higher values were given by Figuier (*Ann. Chim. Phys.*, **19**) from the analyses of the chloro-aurate of sodium. The gold was separated by means of sulphuretted hydrogen and the sodium chloride in the filtrate recovered by evaporation, the total chlorine in the double salt being determined in a separate portion by precipitation with silver. No numerical details of the analysis are given. The percentage composition of the salt is stated as 69.3 AuCl_3 , 14.1 NaCl , and $16.6 \text{ H}_2\text{O}$, whence Figuier deduces the value $\text{Au} = 248.6$. But from the relation $\text{NaCl} : \text{AuCl}_3 = 14.1 : 69.3$, the real value to be deduced from Figuier's numbers is 168.

In 1844, Berzelius (*Berz. Jahr.*, **25**, 41) again determined the atomic weight of gold by reducing chloro-aurate of potassium in hydrogen, weighing the residue, treating the mass with water, and weighing the gold. As these experiments have afforded the results upon which the usually accepted value for Au is based, it may be advisable to give the numerical details of the estimations.

The numbers are as follows:—

	Double salt taken.	Residue.	Potassium chloride.	Gold.
	grams.	grams.	grams.	grams.
I	4·1445	2·9775	0·8185	2·159
II	2·2495	1·61625	0·44425	1·172
III	5·1300	3·6360	1·01375	2·67225
IV	3·4130	2·45125	0·6740	1·77725
V	4·19975	3·01975	0·8295	2·1880
	—	—	3·7800	9·9685

From the relation $\text{KCl} : \text{Au} = 3·78 : 9·9685$ we find that $\text{Au} = 196·2$ ($\text{H} = 1$).

In 1850, Levol (*Ann. Chim. Phys.* [3], **30**, 59) sought to determine the atomic weight of gold by dissolving a known weight of the metal in aqua regia and expelling the nitric acid from the chloride by repeated evaporation with hydrochloric acid, and reducing the aqueous solution by means of sulphur dioxide.

The sulphuric acid in the filtrate was then estimated as barium sulphate. As the result of two experiments, Levol found that 1 gram of gold was equivalent in the above equation to 1·782 grams of barium sulphate, whence he deduced the value $\text{Au} = 195·9$. Taking Stas's numbers for the molecular weight of BaSO_4 , the value becomes 195·5.

Julius Thomsen found that hydrogen bromo-aurate,

contained 32·11 per cent. of gold and 52·00 per cent. of bromine, from which he concludes that Au is probably about 197 (*J. pr. Chem.*, 1876, **13**, 345).

It must be obvious that much of the discrepancy between the results of the foregoing observations can only be due to the very unstable nature of the gold compounds employed. On the other hand, some of the quantitative methods are bad in principle, and even with the most careful manipulation would be quite incapable of affording accurate values. The best methods would seem to be those of Figuier, and more especially of Berzelius; but, on reflection, it appeared to us unlikely that a mere repetition of the Swedish chemist's experiments, even if made with all the resources of modern quantitative analysis, would furnish us with more trustworthy numbers. A careful consideration of the properties of such gold compounds as seemed suitable induced us to hope that the *bromo-aurate of potassium* might

prove to be well adapted to our purpose. A number of specimens of this salt were therefore prepared by various methods and repeatedly crystallised. It was found that the ratio of the auric bromide to the potassium bromide in the double salt was perfectly constant even after five and six crystallisations. The salt, too, is easily decomposed, and at temperatures far below that at which potassium bromide volatilises. We doubt, however, whether the salt can be wholly dehydrated by heating, without loss of bromine; hence, as will be seen below, our method of analysis was so devised as to obviate the necessity of drying the salt. We found that the mixture of finely divided gold and potassium bromide could be weighed in a covered porcelain crucible without risk of error from hygroscopic moisture, and there was no difficulty in separating the last traces of the alkaline bromide by treatment with hot water. Samples of gold so washed, dried at 140–150°, and weighed, showed no loss of weight after being heated for two or three hours to the highest temperature of a muffle furnace.

These preliminary points being satisfactorily settled, we arranged the following plan of work:—An unweighed quantity of the bromoaurate (say from 12 to 15 grams) was placed in a large porcelain crucible, previously weighed against a precisely similar crucible, and then heated for some hours at a temperature gradually increasing to about 160°, after which it was still more strongly heated over a small Bunsen flame. The auric bromide readily parts with its bromine, and with due care there is no risk of loss by decrepitation or by the potassium salt being mechanically carried away with the escaping bromine. The tare is of course heated in precisely the same way, both crucibles, in fact, being treated from first to last in the same manner. The decomposed salt was then weighed, and the salt again heated in order to ascertain that the weight was constant.

By treatment with hot water, the potassium bromide was separated from the gold, the solution being drawn over by the method of reverse filtration which one of us has already employed in the course of the experiments which served to fix the atomic weight of titanium (*Chem. Soc. Journ.*, Trans., 1885, **47**, 108). The washed gold was then heated in a muffle in a porcelain crucible, and weighed against a similar crucible similarly treated and used as a tare. The ratio of the weight of the gold to that of the potassium bromide afforded one value for the atomic weight of gold.

A second value for Au is got by comparing the weight of the washed gold with that of the silver which would be required to precipitate the whole of the bromine in the solution of potassium bromide.

And lastly, a third value is found by comparing the weight of the

washed gold with the weight of the silver bromide formed in the second series of observations.

Two balances were made use of in the course of the determinations, a long-beamed instrument by Oertling, and a short-beamed instrument by Wolters, for the loan of which we are indebted to Dr. Hodgkinson. The weights were of gilded brass by Standinger; they were the set already used by one of us in the determination of the atomic weight of titanium, and had been previously compared amongst themselves and their errors determined by the method of vibrations. The weighings were made by the method of vibrations, the balances being placed in a room set apart for the purpose.

The corrections employed for reduction to a standard atmosphere were as follows:—

Per gram of gold	=	− 0.00010
„ potassium bromide	=	+ 0.00031
„ silver bromide	=	+ 0.00006
„ silver	=	− 0.00002

The method adopted for the preparation of the silver was identical with that already described in the memoir “On the Atomic Weight of Titanium” (*loc. cit.*). It consisted in reducing purified silver chloride by means of hot solutions of pure soda and milk-sugar in silver vessels, treating the reduced silver with ammonia, washing with distilled water, and fusing on a support of “brasqued” lamp-black.

The fusion was made at the lowest possible temperature, and as the metal cooled it was surrounded by a faintly luminous flame in order to diminish the chance of the occlusion of oxygen. There can, however, be little doubt that the error due to this cause is much less than the observations of Dumas would seem to imply. Mallet, in the course of his experiments on the determination of the atomic weight of aluminium, found only about 30 c.c. of oxygen per kilo. of silver, and more recently van der Plaats (*Beiblätter, Ann. Phys. Chem.*, **10**, 579) observed that silver prepared by Stas's method lost no weight on being heated in a vacuum or in a stream of hydrogen or carbon monoxide.

Professor Roberts-Austen, who has in many ways shown a very practical interest in our work, was good enough to compare the silver thus prepared with the standard trial plate used in connection with the coinage. He reported that after very careful assays, two from each of the four sample buttons sent, it appeared safe to conclude that the silver in question had a standard fineness of 999.5, the trial plate being taken as 1000.0.

The method of preparing the pure silver for this plate is described in the “Report of the Deputy Master of the Royal Mint” for 1873.

It was identical with that recommended by Stas, depending upon the reduction of an ammoniacal solution of a silver salt by means of ammoniacal cuprous sulphite, and the purity of the metal was tested by distillation in a lime crucible by the aid of the oxyhydrogen blow-pipe. It is the practice in the Mint to regard the fineness of the trial plate as 999.9 compared with silver prepared by Stas himself. On the basis of these comparisons, we have assumed that 1 gram of the metal employed by us contained 0.9994 gram of real silver.

The gold was prepared from old assay cornets, by dissolving them in nitrohydrochloric acid, evaporating to get rid of excess of nitric acid, diluting with a large quantity of distilled water, and allowing it to stand for some weeks to remove traces of silver. It was then precipitated by well-washed sulphurous acid gas, and the spongy precipitate repeatedly boiled with distilled water till every trace of chlorine was removed. The cornets used were those obtained from the check assays, and consisted originally of pure gold.

The gold used, after preparation, was assayed against the trial plate at the Mint. Taking the trial plate as 1000, this gold is 999.93. The trial plate itself is not so pure as it was before rolling, being reduced from 1000 before rolling to 999.95 after rolling. Consequently the purity of the gold used as compared with the original trial plate is 999.88.

Of this trial plate, Professor Roberts-Austen states in the Mint Report, that he has never been able to obtain from any source gold in a greater state of purity. In its preparation, special care was taken to remove traces of platinum* by treating the dissolved gold with alcohol and chloride of potassium.

The pure potassium bromide was prepared from the potassium bromide made according to the Pharmacopœia. It was found to be absolutely free from iodine, and was treated to remove any possible traces of chlorine by dissolving in water and adding sufficient absolute alcohol to produce a slight precipitation of the KBr. The solution was then filtered and evaporated, and the bromide allowed to crystallise out. These crystals, drained of mother-liquor, were dissolved and again partially precipitated with alcohol. The crystals obtained from the second filtration were drained, dried, and heated over a Bunsen in a porcelain crucible.

The bromine was prepared from the purified potassium bromide by

* The effect of any trace of platinum, if present, would be to lower the atomic weight. The double bromide of potassium and platinum is a sparingly soluble salt. Platinum present in the gold used for assaying, is revealed at once by the appearance and behaviour of the button of alloy obtained in cupelling, even though only present in minute quantities. No indications of its presence have been observed in assaying this gold at the Mint.

distilling it with pure chromic acid and pure sulphuric acid. The bromine thus obtained was carefully redistilled. It still contained a little water, but this was immaterial.

In order to prepare the potassium bromo-aurate, a weighed quantity of gold with its equivalent of potassium bromide was placed in a stoppered bottle; a large excess of bromine and a considerable quantity of water were next added, and the stopper inserted and tied down.

At first, the reaction between the gold and the bromine was sufficiently vigorous to heat the contents of the bottle; afterwards it proceeded more slowly, and was completed in about 36 hours. When the gold had completely dissolved, the solution was evaporated down, the double salt allowed to crystallise out, and the crystals drained thoroughly from mother-liquor. After the third crystallisation, the well-drained crystals were considered sufficiently pure for the atomic weight determination.

Series I. Au : KBr.

The potassium bromo-aurate, contained in a large porcelain crucible of known weight, was gently heated, at first in an air-bath and then over the rose of a Bunsen burner until bromine was no longer evolved. As soon as the weight was constant, the mass was treated with hot water and the solution of potassium bromide was drawn over by reverse filtration into a bottle which could be closed by a well-fitting stopper. The gold was left as a loosely coherent cake of a brownish-yellow colour. It was readily washed, and there was no difficulty in removing the last traces of the potassium bromide. The gold was then dried in the air-bath and heated to bright redness in a muffle.

The results of the several estimations are seen in Table I.

TABLE I.

Wt. of Au + KBr.	Wt. of Au.	Wt. of KBr.	At. wt. Au (H=1).
9.92441	6.19001	3.73440	196.88
7.64672	4.76957	2.87715	196.90
6.63872	4.14050	2.49822	196.86
5.77784	3.60344	2.17440	196.85
5.89941	3.67963	2.21978	196.89
7.33952	4.57757	2.76195	196.86
8.60480	5.36659	3.23821	196.85
8.27939	5.16406	3.11533	196.89

Series II. Au : Ag.

The weight of the potassium bromide obtained in the several estimations being known, an amount of silver—slightly less than that

required for its total decomposition—was weighed out into a $\frac{1}{4}$ -litre flask and dissolved in the minimum quantity of nitric acid of sp. gr. 1.21. The solution was effected at the lowest possible temperature, so as to exclude the possibility of loss by portions being mechanically carried away in the gaseous products. The solution was then heated to expel the last traces of the lower oxides of nitrogen, diluted with water, and transferred to the bottle containing the potassium bromide. The liquid, made turbid by suspended silver bromide, was violently shaken until clear, and the last traces of the bromide were precipitated by the addition of a solution of silver nitrate of known strength (1 c.c. = 0.0010818 gram silver). The operation was carried out in substantially the same manner as that described by Stas, the room being illuminated by red light only. The results of this series of experiments are seen in Table II.

TABLE II.

Weight of gold.	Weight of silver.	At. wt. Au (H = 1).
6.19001	3.38451	196.90
4.76957	2.60896	196.82
4.18266	2.28830	196.78
4.14050	2.26415	196.88
3.60344	1.97147	196.78
3.67963	2.01292	196.81
4.57757	2.50334	196.87
5.36659	2.93608	196.78
5.16406	2.82401	196.87

Series III. Au : AgBr.

The precipitated silver bromide obtained in the preceding series of experiments was then transferred to a weighed porcelain crucible, the solution of the potassium nitrate being removed by reverse filtration in the manner already described (*loc. cit.*). The crucible containing the well-washed bromide, together with the small platinum rose and disc of filter-paper, was heated at first to about 90—100° and afterwards at about 160° until its weight was constant. In some of the experiments, the bromide was fused after a constant weight had been found at 160° and again weighed, but no alteration sufficiently large to affect the second decimal place in the atomic weight was ever perceived. Silver bromide can be thoroughly dried by sufficiently prolonged heating at 160°.

The results of the several weighings are seen in Table III.

TABLE III.

Weight of gold.	Weight of silver bromide.	At. wt. Au (H = 1).
6·19001	5·89199	196·89
4·76957	4·54261	196·77
4·18266	3·98288	196·81
4·14050	3·94309	196·79
3·60344	3·43015	196·88
3·67963	3·50207	196·91
4·57757	4·35736	196·88
5·36659	5·11045	196·80

The total weight of the silver bromide obtained from the several determinations given in Series III is 34·76060 grams: it was formed from 19·96973 grams of metallic silver employed in the preceding series. Hence $\text{Ag} : \text{AgBr} = 1 : 1·74072$.

From Marignac's experiments (*Bibl. Univ. Genève*, **46**, 360) it would appear that—

$$\text{Ag} : \text{AgBr} \dots\dots\dots 1 : 1·74077$$

Stas (*Nouv. Rech.*, p. 158, 1865) found the ratio—

$$\text{Ag} : \text{AgBr} \dots\dots\dots 1 : 1·74081$$

The close accordance of our results with those of Stas and Marignac is at once a proof that the correction applied to the silver was perfectly valid, and that the silver bromide and hence the bromo-aurate from which it was derived was practically free from chlorine.

Calculation of the Results.

The value of Au has been calculated from each experiment in order to show the agreement among the various observations. Instead of simply taking the mean of the several results it is better to deduce the final results from the aggregate weights of the gold, potassium bromide, silver and silver bromide: in this way the influence of the large quantities employed is directly felt.

We take from Stas the following ratios of Ag, Br, K, O, and H:—

Ag	6·7449
Br	4·99634
K	2·44523
O	1
H	0·06265

On the basis of these numbers we may thus summarise the results of the various observations :—

Series I. (8 Experiments).

Au : KBr	37·49137 : 22·61944
„	1·65748 : 1
Au : O	12·3343
Au : H	196·876

Series II. (9 Experiments).

Au : Ag.....	41·67403 : 22·79374
„	1·82831 : 1
Au : O	12·3318
Au : H	196·837

Series III. (8 Experiments).

Au : AgBr.....	36·50997 : 34·76060
„	1·05033 : 1
Au : O	12·3322
Au : H	196·842

On the assumption that these values have equal weight, the final value from the whole 25 experiments becomes—

	Au.	Diff. from mean.
Series I.....	196·876	+ 0·024
„ II.....	196·837	— 0·015
„ III.....	196·842	— 0·010
Mean	196·852	
Probable error of one series.....		± 0·014
Probable error of result.....		± 0·0082

A considerable proportion of the determinative work connected with this investigation had been accomplished, when there appeared in the *Ber. deut. chem. Ges.* for February, 1887, a paper by H. Gerhard Krüss on the same subject (20, 205). We had originally contemplated extending our observations so as to include a direct comparison of the atomic weights of gold and silver, and a determination of the ratio of gold to cyanogen in aurous cyanide. The results we had been able to obtain from the potassium bromo-aurate agreed so closely with those of Krüss that it seemed useless to prolong the inquiry. Krüss also made use of potassium bromo-aurate, but his method of treating the salt differed somewhat from that employed by us. Krüss assumed

that the double salt could be obtained absolutely anhydrous by heating, without loss of bromine, and further that it was so slightly hygroscopic that it could be weighed without risk of absorbing moisture. As we had doubts on both these points, we so arranged our plan of work that it was unnecessary either to dry the double salt or to know its weight. The presence of moisture in the bromo-aurate in no degree affected the determination of the ratios upon which our values of Au depended. Krüss obtained four values for Au from his analyses of the bromo-aurate. A weighed quantity of the double salt was reduced, in some cases by heating in a current of hydrogen, and in others by treatment in aqueous solution with sulphurous acid. From the relation of the weight of the gold to (1) that of the double salt taken; (2) to the loss of weight in hydrogen; (3) to the total weight of bromine weighed as silver bromide and obtained as such by adding silver nitrate to the aqueous solution of the double salt after reduction with sulphurous acid; (4) to that of the potassium bromide obtained by dissolving out the potassium bromide after heating the double salt in hydrogen, Krüss obtained the following values:—

				Au (H = 1).
I.	Au : KBr, Br ₃	(9 experiments)		196·741
II.	Au : Br ₄	(5 „)		196·743
III.	Au : Br ₃	(4 „)		196·619
IV.	Au : KBr	(4 „)		196·620

The results of I, II, and III would be affected by any moisture in the salt or by any loss of bromine in dehydrating. The values from IV are alone directly comparable with our own, as they may be regarded as obtained from unknown weights of the bromo-aurate. The weight of the potassium bromide in Krüss's observations was, however, determined after the evaporation of the aqueous solution of the salt, and not, as in our case, by subtracting the weight of the gold from that of the double salt after decomposition by heat. Hence any moisture left in the salt after evaporation would tend to lower the atomic weight of Au.

The lower value of Au obtained by Krüss from the analyses of the gold potassium bromide agrees, however, with the results of his analyses of a neutral solution of auric chloride prepared by decomposing by warm water, auro-auric chloride obtained by Thomsen's method, weighing the gold (after reduction with sulphurous acid), and the chlorine as silver chloride. From the relation Au : Cl₃, Krüss obtained Au = 196·594. This value would, of course, be affected by any free chlorine left in the double chloride after treating the finely divided metal with that gas. In Krüss's experiments, the occluded chlorine was removed by aspirating dry air over the product and then

allowing it to stand over soda-lime for some time before decomposition with water.

From the results of all his observations, Krüss adopts 196.64 as the most probable value for Au—a difference of 0.21 from the mean value obtained by us.

We cannot conclude this communication without expressing our acknowledgments to Professor Roberts-Austen and to Messrs. Rigg and Bailey, of the Royal Mint, for the assistance they have rendered us throughout the course of this investigation.