CLXIII.—*A Revision of the Atomic Weight of Tantalum. Determination of the Ratios* $TaBr_5 : 5Ag : 5AgBr$ *and* $TaCl_5 : 5Ag : 5AgCl$.

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THE accepted value for the atomic weight of tantalum is based on results which are not in satisfactory agreement. Marignac (*Arch. Sci. phys. nat.*, 1866, **26**, 89), who was the first to employ purified materials, used the double fluorides of tantalum with potassium and with ammonium, R_2TaF_7, to determine the ratios $2K_2TaF_7 : Ta_2O_5$, $K_2TaF_7 : K_2SO_4$, $K_2SO_4 : Ta_2O_5$, and $2(NH_4)_2TaF_7 : Ta_2O_5$, and calculated therefrom values which ranged from 182·66 to 183·55, giving as a mean, Ta = 182·98. Hinrichson and Sahlbom (*Ber.*, 1906, **39**, 2600) carried out five determinations of the ratio $2Ta : Ta_2O_5$ by observing the gain in weight of known amounts of the metal when heated in a stream of oxygen; values ranging from 180·60 to 181·72 were obtained for Ta, the mean being 181·02 ± 0·09. Van Haagen (Thesis, University of Pennsylvania, 1909) sought to fix the ratio $2TaBr_5 : Ta_2O_5$ by weighing the pentoxide formed from the hydrolysis of a known weight of the pentabromide; eight determinations gave values ranging from 183·10 to 183·42, the mean being 183·28 ± 0·09. Chapin and Smith (*J. Amer. Chem. Soc.*, 1911, **33**, 1497) redetermined the ratio $2TaBr_5 : Ta_2O_5$, and calculated Ta = 181·69—181·94; mean 181·82 ± 0·04. Balke (*ibid.*, 1910, **32**, 1127) conducted eight determinations of the ratio $2TaCl_5 : Ta_2O_5$, finding Ta = 181·45—181·60; mean 181·52 ± 0·02. Later, Sears and Balke (*ibid.*, 1915, **37**, 833) concluded that determinations of the ratio $2TaCl_5 : Ta_2O_5$ were untrustworthy owing to serious sources of error. They therefore attempted to find the ratio $TaCl_5 : 5Ag$, and from three series of determinations found Ta = 181·77, 181·31, and 181·03, which gave on combination the general mean 181·29 ± 0·20. The poor agreement between the three series of results was later explained by Balke (*ibid.*, 1917, **39**, 1852) as being due to uncertainty arising out of the analytical procedure employed, and he concluded that tantalum pentachloride was unsuitable for use in atomic-weight determinations (see p. 1289).

All the figures given above are on the basis of the recalculated data published by F. W. Clarke (" A Recalculation of the Atomic Weights," 1920), who summarised the situation thus : " So far as present evidence goes it seems probable that the atomic weight of tantalum is somewhere near 181 with an uncertainty of at least half a unit." This remark is equally applicable now, for no fresh evidence has appeared. In 1912, the International Committee on Atomic Weights gave the value of tantalum as 181·5, which is still used by the German (*Ber.*, 1930, **63**, 1) and American (*J. Amer. Chem. Soc.*, 1929, **51**, 653) Chemical Societies, but in 1929 the Chemical Society (J., 216) changed it to 181·3, the value deduced by Clarke (*op. cit.*) from the results of Sears and Balke (*loc. cit.*).

Purification of Materials.

Water.—The distilled water of the laboratory was redistilled from a faintly alkaline, dilute permanganate solution and then redistilled in an all-silica still and condenser. The purified water was found by nephelometric test to be halogen-free and was collected and stored in stoppered Pyrex flasks.

Nitric Acid.—Merck's " pure " acid was redistilled in an all-silica still and condenser, and the middle fraction, which was found to be halogen-free, was collected and similarly stored.

Oxalic Acid.—" A.R." Material supplied by the British Drug Houses, Ltd., was used directly, since it dissolved completely in water and was also free from iron as well as halogens.

Chlorine.—The source of this gas was a cylinder of the liquid supplied by the Imperial Chemical Industries, Ltd., and stated to contain only a trace of bromine. The gas was passed through an all-glass apparatus in which it was first dried by sulphuric acid contained in four wash-bottles, then freed from possible traces of hydrogen chloride by passage through two tubes containing ignited lime, as recommended by Hönigschmid (*Z. anorg. Chem.*, 1927, **163**, 315), and finally dried by passage through two tubes containing phosphoric oxide.

Bromine.—This had been prepared free from chlorine and iodine by Willard and McAlpine's method (*J. Amer. Chem. Soc.*, 1921, **43**, 799) and was from a stock prepared for an earlier work. Removal of traces of hydrobromic acid was effected by keeping it over calcium oxide as recommended by Hönigschmid and Zintl (*Annalen*, 1923, **433**, 217).

Argon.—The gas from a steel cylinder of compressed argon was purified in an all-glass apparatus by bubbling through sulphuric acid and passing successively over soda–lime, hot copper and copper oxide, hot magnesium ribbon, and finally again over hot copper oxide and copper; it was then stored in galvanised-iron holders. As it was not considered necessary for this work to free it completely from nitrogen, it was passed through the purification train only once.

Sodium Chloride.—Kahlbaum's " pure " salt was reprecipitated twice from a filtered aqueous solution by passage of hydrogen chloride, and the product was recrystallised from water and fused in a platinum basin.

Potassium Bromide.—Kahlbaum's " pure " salt was recrystallised twice from water, the crystals being drained centrifugally and fused in platinum.

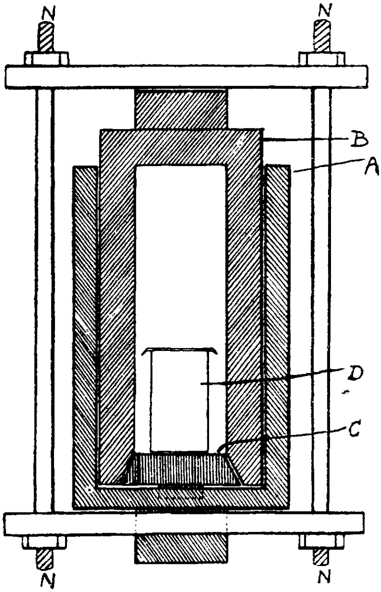
Silver.—This was obtained from a stock prepared for an earlier work by following the method of Richards and Wells (*J. Amer. Chem. Soc.*, 1905, **27**, 472), and fused on a magnesia support in a vacuum.

Preparation of Tantalum.—Although tantalum of a high degree of purity is commercially available, no details are to be found in the literature regarding the conditions governing its preparation in a pure state. Von Bolton (*Z. Elektrochem.*, 1905, **11**, 45), who achieved a purity of 99%, merely mentions that he used a " modification " of the process by which Berzelius (*Pogg. Annalen*, 1825, **4**, 10) and Rose (*ibid.*, 1856, **99**, 60) had been unable to obtain metal of more than 58% purity; he effected further purification by fusing the compressed powdery material in a vacuum arc furnace. Spitzin and Kaschtanoff (*Z. anorg. Chem.*, 1929, **182**, 207) state that their attempts by an improved Berzelius–Rose method yielded metal of only 95% purity. Since it appears that very pure tantalum cannot be prepared by other methods of reduction (*e.g.*, Moissan, *Compt. rend.*, 1902, **134**, 211; Goldschmidt, *Z. angew. Chem.*, 1898, **11**, 823; Ruff and Thomas, *Z. anorg. Chem.*, 1925, **148**, 18; Muthmann, Weiss, and others, *Annalen*, 1904, **337**, 387; 1907, **355**, 62), and as it was not considered feasible to study electrolytic methods (*e.g.*, Bouhard, French Patent, 1907, 377931; Weintraub, U.S.P. 1910, 947983), it was decided to investigate the Berzelius–Rose method under improved conditions which included those indicated by Balke (*Chem. Met. Eng.*, 1922, **27**, 1272; **28**, 560). Briefly, it consisted in the preparation of the metal by the fusion of potassium tantalifluoride with sodium under conditions which minimised the formation of oxides of tantalum and sodium tantalate.

The starting material was the double fluoride obtained from Merck as well as Kahlbaum. Both the specimens contained nearly 1% of silica and small traces of iron, manganese, titanium, and niobium. Removal of silica was effected by treatment with sulphuric acid as described by Balke (*J. Amer. Chem. Soc.*, 1905, **27**, 1142). The silica-free preparation was purified according to Meimberg and Winzer's method (*Z. angew. Chem.*, 1913, **26**, 157), and finally recrystallised by cooling from its saturated solution at 100° in 5% hydrofluoric acid, all the crystallisations being done in platinum basins. The crystals were transferred to a stout gutta-percha suction funnel and freed as far as possible from mother-liquor, after which they were centrifuged in a cylinder of platinum gauze. They were dried over caustic potash in a vacuum desiccator and preserved in small cardboard boxes lined with filter paper.

The reduction process. This had to be carried out in the absence of air and moisture; otherwise, oxides of tantalum and sodium tantalate would be formed in considerable quantities, and the removal of even small traces of oxide from the metal can be accomplished only by heating at a very high temperature—probably above 1500°—in a high vacuum. The bomb employed for the process is shown diagrammatically in Fig. 1. It consisted of a thick steel cylinder (A) open at the top and having a recess at the bottom to take the solid steel piece (C), the top of which was turned to fit accurately a conical taper in the hollow steel vessel (B). A trace of oil on the taper was enough to secure good fitting when the bolts (N, N) were tightened. The clearance between A and B was about 1 mm., so that they could be welded together in case the tapering joint proved unsatisfactory. The reaction vessel D, made from a sheet of the purest commercial molybdenum, seemed to resist attack during the reaction.

FIG. 1.



The actual manipulation during an experiment was as follows. The shell A containing the block C and the reaction vessel D was dried by being heated whilst a stream of argon passed through it. Pure freshly dried potassium tantalifluoride (50 g.) and Merck's sodium (18 g.), freshly cut into small pieces under dry benzene, were alternately transferred in small quantities to the reaction vessel while a stream of argon was circulating in the shell. The reaction vessel was then covered with its lid, the vessel B kept in position, and the bolts tightened. The bomb was now heated by burners and kept at a dull red heat for about an hour; its lower portion was then cooled quickly by a jet of water while two tubes were delivering argon near its top. After cooling to room temperature, the bomb was opened and the contents of the reaction vessel, which still contained some free sodium, were transferred in small quantities to water (300 c.c.) contained in a large platinum basin, whereupon most of it disintegrated to a black powder, the few lumps remaining being crushed with a clean steel rod.

Purification of the crude metal. The powdery material in the dish was washed five or six times by decantation with cold water and then several times with dilute alcohol (25%), as recommended by Rose (*loc. cit.*), until the removal of soluble salts was practically complete. It was then digested with three successive portions of hot nitric acid (*d* 1·20), well washed with water, digested twice with hot hydrochloric acid (1 : 1), again washed with water, and finally dried in a stream of argon at about 300°. The dried powdery material was found to contain 97·9% of free tantalum. The powder was compressed into pellets, each weighing nearly 5 g., in a nickel–steel die at pressures ranging from 20,000 to 30,000 lb. per sq. in. and the pellets were freed from gas by 10 hours' heating at about 1000° in a vacuum of 10^{-4}—10^{-5} mm. They were then heated inductively in a vacuum furnace in a crucible of pure thoria, a current of 180 amps. at 7000 volts and 490,000 cycles being used. The vacuum maintained was about 10^{-5} mm., and temperatures of 1700—1800° were reached. After this treatment the pellets were found to have sintered to a hard mass with a platinum-grey lustre, and oxidation experiments showed them to contain 99·2% of free tantalum. The remaining 0·8% was deemed to be tantalum oxide, since a spectrographic study of the metal did not reveal the presence of foreign metals.

The Method of the Determinations.

The method consisted in the preparation of the chloride and the bromide of tantalum by direct union, their purification by distillation and sublimation in a vacuum, and collection in sampling bulbs which were evacuated and then sealed for analysis. The bulb containing the halide was weighed and then broken under a dilute solution of ammonia whereby all the halogen was converted into the ammonium halide, which could be transferred to another vessel for halogen estimation. The insoluble tantalic acid, formed by the hydrolysis of the sample, and the glass fragments resulting from the breaking of the bulb were then digested with a hot solution of oxalic acid, whereupon all the tantalic acid went into solution. The glass pieces that remained were weighed in order to obtain the weight of the sample originally in the bulb. The estimation of halogen was carried out both nephelometrically and gravimetrically by the method of Richards as adopted by Hönigschmid. The ratios $TaBr_5 : 5Ag : 5AgBr$ and $TaCl_5 : 5Ag : 5AgCl$ so obtained enabled the calculation of the atomic weight of tantalum on the assumption that the values for silver, bromine, and chlorine were 107·880, 79·915, and 35·457 respectively.

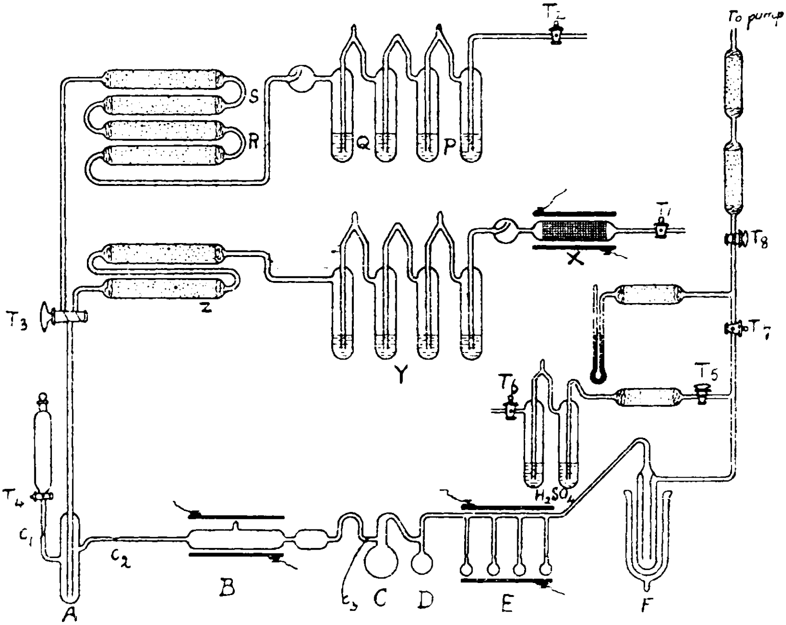
The analytical part of this work, including weighings, was carried out in special rooms which were free from acid fumes and were illuminated only by ruby light.

Balance and Weighing.—The weights were standardised by the method of Richards (*J. Amer. Chem. Soc.*, 1900, **22**, 144), and the weighings performed in a room which was maintained by electrical heaters at a constant temperature of 20° ± 0·1°. The balance employed was of the special type made by Oertling with a beam of invar-steel which was protected by an aluminium partition and provided with a prism and mirror device to enable movements of the beam to be noted with a lamp and scale fixed at a distance of 2 m. from it. The weighings were done by the method of counterpoise and substitution, and the weights so obtained were corrected for errors due to inequality of weights and reduced to vacuum. Successive weighings of the same object usually agreed to 0·01 mg. and never differed by more than 0·02 mg.

The Distillation Apparatus.—This resembled the apparatus devised by Willard and McAlpine (*loc. cit.*) and is shown diagrammatically in Fig. 2. It consisted of a bubbler (A) into which bromine could be introduced through a side tube and separating funnel, a tube (B) in which powdered tantalum could be kept heated, the distillation bulbs (C and D), and the system of sampling bulbs (E). The three-way tap T_3 served to introduce either argon or chlorine into the apparatus. Argon entered from a gas-holder through the tap T_1, and passed over copper gauze kept at 500—550° in X, through sulphuric acid in Y, and phosphoric oxide in Z; whereas chlorine entered through the tap T_2 and, after bubbling through a strong solution of potassium permanganate in P and sulphuric acid in Q, passed over ignited lime in R and phosphoric oxide in S. A continuous flow of either gas through the apparatus could be maintained by keeping open T_1 or T_2 and also T_3, T_5, and T_6 while the other taps were kept closed. With taps T_7 and T_8 open and all the others closed, the apparatus could be evacuated by a mercury-vapour pump working in conjunction with a " Hyvac " pump. The trap F, which was cooled in liquid air, served not only to freeze bromine or chlorine, which would otherwise pass into the pumps, but also to minimise diffusion of mercury vapour into the apparatus. All the taps in the apparatus were lubricated with metaphosphoric acid.

The Preparation of Tantalum Bromide.—The parts A to E of the apparatus were kept at 300—350° and thoroughly dried and freed from air by alternate evacuation and filling with argon, the process being repeated 5 or 6 times. Then, with a stream of argon flowing through the apparatus, the tip of the side tube attached to *B* was broken to introduce 7—8 g. of finely powdered tantalum, which had been previously dried in a current of argon. The tube was now sealed off and the apparatus evacuated and refilled with argon, thus ensuring the total absence of air and moisture from the system. Through some phosphoric oxide, which was kept in the separating funnel, somewhat more than twice the quantity of bromine necessary to react with the tantalum taken was run into the bubbler *A*, entry of air being prevented by closing the tap of the funnel while there was still about 1 c.c. of bromine in it. The constriction c_1 was then sealed. The furnace surrounding the tube *B* being kept at 650—700°, a beaker of water at about 55° was placed under the bubbler, and a slow stream of argon bubbled through, carrying bromine vapour to the hot tantalum in *B*. The initial formation of the bromide was immediate, although it continued slowly, much bromine escaping combination. By suitably warming the tube connecting *B* and *C*, and keeping *C* and *D* cool, most of the bromide was collected in *C*; some of it, however, went into *D*, and a small quantity was carried still farther in a thin cloud by the gas stream. At the same time, some drops of bromine collected in *C* and *D* and

FIG. 2.



also in some parts of the system E. When enough of the bromide had been prepared, the argon supply was stopped and the preparation tube B allowed to cool. The apparatus was then sealed at the constriction c_2, heated at 100—110°, and evacuated so as to remove all free bromine. The constriction c_3 was now sealed and the tube B removed. With the pump in continuous operation, the bulb C was kept at about 300° in order to drive most of the bromide into the bulb D, which was kept cool. The constriction (not shown in the diagram) in the tube connecting C and D was then sealed. The sublimation of the bromide from D into the bulbs E was effected by suitable movement of the furnace, which was maintained at about 300°. With the vacuum pump in continuous operation the bulbs were finally sealed for analysis.

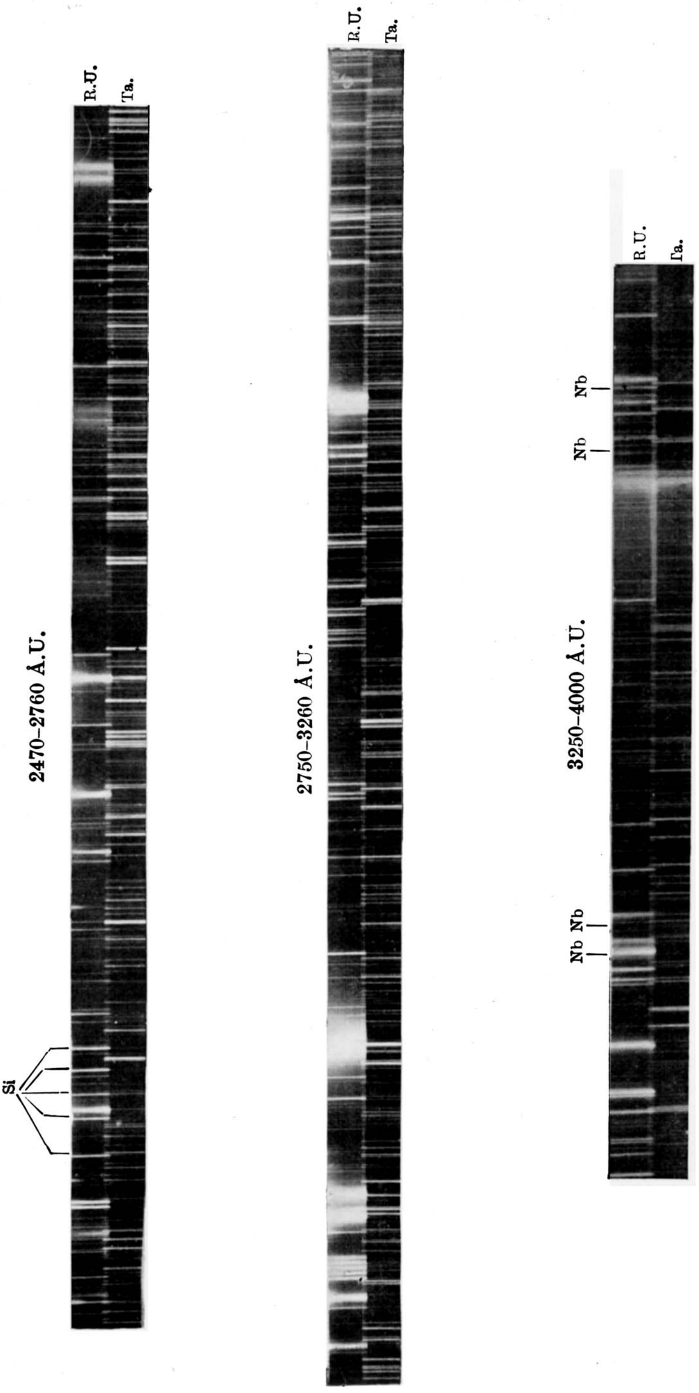
The bromide in the bulbs consisted of fine needles as well as some thin, lemon-yellow leaflets.

Preparation of Tantalum Pentachloride.—The chloride was prepared in an apparatus which was exactly like the foregoing except that it had no bubbler, the tube B being directly joined to the three-way tap by a tube having a constriction. The subsequent procedure was similar to that employed for the bromide, a slow stream of dry chlorine being passed over the powdered metal at 550—600°.

The chloride was perfectly snow-white during the earlier stages of the distillation, but later acquired a pale creamy colour, probably owing to prolonged heating.

Spectrographic Studies of the Purity of the Tantalum Preparations.—The instrument employed was a quartz Littrow spectrograph made by A. Hilger. The principle of the method consisted in the identification of the impurity lines in the spectrum of the tantalum compounds examined, by measurement as well as by superposition on the spectra of the probable impurities. The first step was the preparation of photographs of the ultra-violet and visible arc spectra of the tantalum compounds between copper poles, and also corresponding photographs of the copper arc. A series of photographs was prepared of the spectra of silica, iron, manganese, niobium, titanium, and molybdenum in the copper arc, each on a separate plate. The persistent lines of these elements were identified by measurement and suitably marked on the plates. By bringing each of these impurity spectra into juxtaposition with the tantalum spectrum, it was easy to note if any of the impurity lines were present in the latter, but as none of these could be traced it was decided to make an exhaustive examination for all the possible impurities by the R.U. (raies ultimes) powder method advocated by A. Hilger. Since the R.U. powder contains only small traces of nearly all the metals in a suitable diluent, its arc spectrum, although

FIG. 3.



[*To face p.* 1285.]

consisting of only a limited number of lines, includes all the strongest lines of all the elements in it. Therefore, by photographing the R.U. spectrum in juxtaposition with that of the specimen to be examined, it is a relatively simple matter to ascertain the impurities present; moreover, it is possible, within certain limits, to estimate quantitatively the impurities according to the order of sensitivity of the lines observed. An examination of the spectrum photographs (Fig. 3) will make this matter clear. Niobium, for instance, is present in the R.U. powder to the extent of about 0·05%, but it gives about 15 lines, some of which are marked on the plate. Since not even one of these can be traced in the tantalum spectrum, it is concluded that niobium is absent. Similarly with most of the other elements. The results, however, are not so definite in the case of silica. It will be seen from the plate that the group of lines marked Si (2506·9—2528·5 Å.U.), which are strong in the R.U., are present in the tantalum spectrum also, though with a smaller intensity. Since, however, this group of lines is present in the spectrum of the poles themselves and with an intensity approximately equal to that in the tantalum spectrum, it can be deduced that the tantalum is practically free from silica. The other metals regarding which there is similar uncertainty are calcium and magnesium. The quantity in which they are present must, however, be very small. Dr. J. W. Ryde and Mr. H. G. Jenkins, of the Research Laboratories of the General Electric Co., Ltd., who developed the R.U. method, kindly undertook a confirmatory examination of these specimens and reported that spectroscopically they were unable to find impurities. There is, however, the possibility that silica, calcium, and magnesium may be present to a total extent of about 0·05%.

Determination of the Ratios $TaBr_5 : 5Ag : 5AgBr$.—The bulb containing the bromide was cleaned and dried as usual (compare Baxter, *Proc. Amer. Acad. Arts Sci.*, 1924—25, **60**, 228), and its weight in air determined. It was then weighed in water by suspending it with a thin platinum wire, and from the observed loss of weight the vacuum correction was calculated in the usual manner. It was then placed on the bottom of a thick-walled conical Pyrex flask containing about 400 c.c. of a *ca.* 3% solution of ammonia, and broken by a blunt glass rod, which was quickly rinsed and removed. The flask was immediately stoppered, left for about 2 hours, and then rotated so as to disturb the flocculent precipitate which had settled, this operation being repeated 4 or 5 times at intervals of about an hour. After standing over-night, the clear supernatant liquid was poured through a Jena-glass Gooch crucible having a sintered-glass filter, and the filtrate caught directly in a large conical precipitation flask, made of Pyrex glass and kept inside an evacuated bell-jar. The material remaining in the original flask, *viz.*, the precipitate of tantalic acid and the glass fragments of the bulb, was washed by decantation 10—12 times with 70—80 c.c. portions of a hot (60°) 1% aqueous solution of ammonium nitrate, as recommended by Biltz and Voigt (*Z. anorg. Chem.*, 1922, **120**, 171), with the modification that it contained nearly 2% of free nitric acid in addition. The clear wash-liquids were passed through the Gooch crucible in each case, and the filtrates added to the first filtrate, which thus increased to about 1200 c.c. and was preserved for halogen estimation. The washing process was effective because the tantalic acid settled easily in the wash-liquid and so facilitated the decantation. It is shown later (p. 1291) that the washed residue was halogen-free and that practically none of it (either tantalic acid or glass) was transferred from the flask during washing.

To dissolve out the tantalic acid in order that the glass pieces might be weighed, the residue in the flask was digested on a boiling water-bath for about 2 hours with some 50 c.c. of a saturated solution of oxalic acid. The liquid in the flask was then diluted with about 300 c.c. of water, whereupon the solution became quite clear and was free from any particles of tantalic acid. The glass fragments appeared quite clean and transparent. The clear liquid was poured through a weighed silica Gooch crucible with a sintered-silica filter. The glass pieces were washed by decantation 10—12 times with 50 c.c. portions of warm water, then transferred with a jet of water to the crucible, dried, and weighed. (The washings from the above operations were discarded.) The glass pieces were dried slowly by being kept at 90—110° for about 2 hours and then at 400—420° for about 8 hours; and their weight was corrected to vacuum and subtracted from the corrected weight of the bromide bulb in order to obtain the weight of the bromide originally in the bulb. This was, however, corrected for a small error (0·03 mg.) which appeared to be incidental to the collection and weighing of the glass fragments (see p. 1291).

The estimation of halogen in the bromide solution, which contained only nitric acid and ammonium bromide and nitrate, was carried out according to the Harvard methods as developed by Hönigschmid. The standard solutions of silver nitrate and potassium bromide required to make up for the deficiency of either silver or bromide ions in the analytical solution, and for the generation of opalescence in the test mixtures, were all made up with the concentrations recommended by the author mentioned above. On the assumption that Ta = 181·37, which was calculated from the mean of two gravimetric determinations of the ratio $TaBr_5 : 5AgBr$, a quantity of silver was weighed out which was insufficient by about

0·1—0·2 mg. to precipitate quantitatively the bromide ion in the analytical solution. The silver was dissolved in about 50 c.c. of nitric acid (*d* 1·20) in a conical Pyrex flask having a four-bulbed tube ground into its neck. After being gently boiled for a few minutes, the solution was diluted to about 0·1*N* and then transferred quantitatively to the flask containing the bromide solution, which was then stoppered, and shaken at frequent intervals. After standing for about 48 hours, the precipitate was found to have settled completely, leaving the supernatant liquid perfectly clear. Two 25-c.c. portions of the clear liquid were withdrawn and tested for excess of bromide or silver by addition of 1 c.c. of silver solution (1 in 1000) to one and 1 c.c. of an equivalent bromide solution to the other. The test solutions were allowed to stand for 4 hours with frequent stirring with glass rods, and then examined in a nephelometer of the Kober type with a Klett top-reader. According as the tests indicated excess of bromide or silver, standard solution of silver (0·1 in 1000) or equivalent bromide solution was added to the analytical solution until a nephelometric test indicated that the two ions were in exact equivalence as revealed by the equality of the intensity of opalescence developed when equal portions of the solution were treated with equivalent quantities of either silver or bromide test solution. After the end-point had been reached, excess of one of the standard solutions was added, and the end-point again obtained by back-titration in the nephelometer. The quantity of silver (in the standard solution) introduced in order to reach the point of equivalence was added to the weight of silver originally added in bulk to the analytical solution, and the ratio $TaBr_5 : 5Ag$ calculated. The results of the determinations are given in Table I (*a*).

After completion of the nephelometric titration, 25 c.c. of *N*/10-silver nitrate solution were added to the contents of the flask in order to precipitate all the dissolved silver bromide. The flask was stoppered and occasionally shaken during the next 24 hours, and the precipitate then allowed to settle. The clear liquid was poured through a weighed Jena-glass Gooch crucible with a sintered-glass filter. The silver bromide in the flask was washed ten times by decantation with about 60 c.c. portions of 0·5% nitric acid, transferred to the crucible, dried for about 18 hours at 300—320°, and weighed. Most of the silver bromide was transferred to a porcelain crucible and fused in an electric furnace maintained at 500—520°; it was then seen to be transparent and free from dark patches —a clear indication of its purity. In two experiments in which the silver bromide was weighed both before and after fusion, the loss (due to expulsion of the last traces of moisture) was not more than 0·02 mg. Since this result is in agreement with the long experience of Hönigschmid that silver bromide dried at 300° does not retain an appreciable amount of moisture, no attempts were made to determine the loss on fusion in every experiment. Confirmatory evidence regarding the purity of the silver bromide precipitate was obtained from determinations of the ratio AgBr : AgCl (see p. 1292).

The weight of the silver bromide obtained by weighing the dried precipitate was corrected for the quantity which escaped weighing owing to solution in the nitric acid washings, and also for the small amount which was retained by the walls of the precipitation flask. The estimation of these two sources of error was carried out jointly as recommended by Hönigschmid (*Z. anorg. Chem.*, 1924, **136**, 278; *Annalen*, 1923, **433**, 201), *i.e.*, by dissolving out the traces of the silver bromide in the precipitation flask by the addition of ammonia, adding this solution to the nitric acid washings * of the silver bromide, diluting the combined solution to a known volume, and comparing it nephelometrically with solutions containing known amounts of silver bromide. The quantity of silver bromide so estimated was added to the weight of the precipitate, and the ratio $TaBr_5$: 5AgBr calculated. Table I (*b*) gives the results of the determinations.

Determination of the Ratios $TaCl_5$: 5Ag : 5AgCl.—The sealed bulbs containing the chloride were weighed in air and in water, and then broken under a solution of ammonia. The subsequent procedure was exactly as in the case of the bromide, except that sodium chloride was substituted for potassium bromide in the solutions employed during the nephelometric determinations. The silver chloride precipitate was dried at 300—320° for about 18 hours before weighing. It always fused to a transparent, light amber-coloured mass, free from any dark patches : this was considered to be a definite indication of its purity. The results of the various determinations are given in Table II, all the weights being reduced to vacuum. The atomic weights of silver, bromine, and chlorine were assumed to be as on p. 1282.

The individual values for the atomic weight given in Table I(*a*) show an extreme variation of 0·03 unit (1·7 parts per 10,000). Their mean variation is 0·008 unit (0·5 part per 10,000) from the mean value 181·36, the probable error of which is found to be ± 0·003 unit.

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* These washings were collected separately from the mother-liquor from which the precipitation was made. The mother-liquor was discarded, as the quantity of silver bromide in it must have been negligible owing to the excess of silver nitrate present.

TABLE I.

		(a) Ratio $TaBr_5$: 5Ag.			(b) Ratio $TaBr_5$:5AgBr.		
No.	$TaBr_5$, g.	Ag, g.	$TaBr_5$:5Ag.	Ta =	AgBr, g.	$TaBr_5$:5AgBr.	Ta =
1	3·07127	—	—	—	4·96415	0·61869	181·36
2	3·72095	—	—	—	6·01413	0·61870	181·37
3	3·81890	3·54594	1·07698	181·34	6·17267	0·61868	181·35
4	3·59654	3·33939	1·07700	181·36	5·81303	0·61870	181·37
5	2·69071	2·49831	1·07701	181·37	4·34926	0·61866	181·33
6	2·61163	2·42488	1·07702	181·37	4·22133	0·61868	181·35
7	3·92094	3·64064	1·07699	181·35	6·33750	0·61869	181·36
8	2·04583	1·89956	1·07700	181·36	3·30681	0·61867	181·34
(a) Total	18·68455	17·34872	1·07700	181·36	—	—	—
(b) „	25·47677	—	—	—	41·17888	0·61868	181·35

The corresponding variations in Table I (b) are 0·04 and 0·011 unit respectively, giving a mean of 181·35 with a probable error of 0·004.

TABLE II.

		(a) Ratio $TaCl_5$: 5Ag.			(b) Ratio $TaCl_5$:5AgCl.		
No.	$TaCl_5$, g.	Ag, g.	$TaCl_5$:5Ag.	Ta =	AgCl, g.	$TaCl_5$:5AgCl.	Ta =
1	3·15350	4·74301	0·66488	181·35	6·30152	0·50044	181·37
2	2·96215	4·45549	0·66483	181·33	5·91874	0·50047	181·40
3	4·08061	6·13756	0·66486	181·34	8·15438	0·50042	181·36
4	3·21073	4·82972	0·66479	181·30	6·41613	0·50042	181·36
5	3·49922	5·26278	0·66490	181·36	6·99201	0·50046	181·39
Total	16·90621	25·42856	0·66485	181·34	33·78278	0·50044	181·37

The individual values for the atomic weight given in Table II(a) show an extreme variation of 0·06 unit (3·3 parts per 10,000). Their mean variation is 0·019 unit (1·0 part per 10,000) from the mean value 181·34, the probable error of which is found to be ± 0·007 unit.

The corresponding data for Table II (b) are 0·04 and 0·015 unit, the mean atomic weight being 181·37 ± 0·004.

Summary of Results.—The mean values obtained from the four series of determinations are collected in the following table, from which it will be seen that the most probable value for the atomic weight of tantalum is 181·36.

Ratio.	No. of expts.	Mean value for at. wt. of Ta.	Probable error.
$TaBr_5$: 5Ag	6	181·36	±0·003
$TaBr_5$: 5AgBr	8	181·35	0·004
$TaCl_5$: 5Ag.....................	5	181·34	0·007
$TaCl_5$: 5AgCl	5	181·37	0·004
	General mean	181·357	0·0002

Investigation of Some Possible Sources of Error.

Sears (*loc. cit.*) found that, although tantalum pentachloride exists as a stable compound in an atmosphere of dry nitrogen and does not occlude chlorine, it is unsuitable for use in work where a high degree of accuracy in its analysis is desired. This conclusion was based on the following observations : (*a*) Broken glass cannot be filtered off from the hydrolysed tantalum chloride because of the insoluble tantalic acid formed; (*b*) tantalum pentachloride cannot be weighed accurately in a vessel with a ground joint owing to hydrolysis caused by moist air diffusing in through the joint; (*c*) volatility of glass during fusion prevents an accurate estimate of the weight of tantalum pentachloride contained in a sealed glass tube of known weight; (*d*) when tantalum chloride is sealed in a glass bulb, some of it gets melted into the glass at the point of sealing.

The present work seems to be free from any of the above-mentioned sources of complication. The first did not arise because the tantalic acid could be completely dissolved out and so permitted the determination of the weight of the glass pieces. The second and third sources of error were avoided in the method employed for determining the weight of the sample : volatility of glass during fusion is a negligible factor, for Briscoe and Little (J., 1914, **105**, 1315) and Weatherill (*J. Amer. Chem. Soc.*, 1924, **46**, 2437) experienced no difficulty from that source. The last objection seems to be due to the tantalum pentoxide formed by hydrolysis of the chloride owing to the presence of moisture in the system. The tantalum chloride and also the tantalum bromide bulbs prepared in the earlier experiments had the appearance of frosted glass close to the point of sealing. The bulbs prepared in the later experiments and used for analysis were, however, free from this defect.

As spectrographic investigation afforded definite evidence that the tantalum halides prepared for analysis were almost entirely free from foreign metals, and as contamination from oxygenated compounds was obviated by carrying out the preparation and weighing in the absence of oxygen, air, and moisture, little uncertainty could be entertained regarding their purity. The method of analysis, however, involved several steps which demanded scrutiny.

A study was made of the process employed for washing the tantalic acid and glass fragments in order to extract all the halide present. As in every experiment the clear liquid was filtered through a Gooch crucible, it was easy to test whether any solid material was conveyed to it, by weighing the crucible before and after the filtration. Three experiments were performed with two different crucibles and the observed variations in weight were + 0·02, 0·00, and + 0·03 mg., respectively, giving an average increase in weight of 0·02 mg. If this increase is due solely to tantalic acid, it is of no significance, since the crucibles employed for this process were never used for the collection of either glass fragments or silver bromide precipitate; if it is due entirely to fine particles of glass, this would be a source of error, for this amount of glass would escape weighing and the apparent weight of the tantalum halide would be too high to this extent. Since, however, 0·02 mg. is within the limit of error of the determinations, the precise cause is immaterial.

The next point tested was whether any portion of the glass fragments was lost owing to solution, either colloidal or otherwise, in the wash-liquid. Bulbs similar to those employed for collecting the tantalum halides were fused on to a vacuum line and then sealed after evacuation. They were weighed in air and in water so as to obtain their weight in vacuum. They were then broken under a solution of 3% ammonia contained in a conical Pyrex-glass flask, and subjected to exactly the same treatment as the glass fragments in the actual determinations, *viz.*, washing with ammonium nitrate, decantation of the clear liquid, digestion with hot saturated solution of oxalic acid, and washing with water. They were then collected in a weighed Gooch crucible, dried as usual, and weighed. This weight was reduced to vacuum and compared with the weight of the bulb as determined at the beginning of the experiments; the results were as follows:

Bulb, g.	1·81427	1·70330	1·74959	1·68884
Glass pieces, g.	1·81425	1·70325	1·74958	1·68880
Difference, mg.	0·02	0·05	0·01	0·04

They indicate a definite average loss of 0·03 mg. This quantity was therefore added to the weight of glass as actually determined.

The next point to be tested was whether the process of washing removed the bromide quantitatively and left the residue of tantalic acid and glass fragments bromide-free. Although aqueous extracts of the residue failed to give any test for halogen, it was feared that adsorption of bromide ions might have proceeded in such a way as to escape detection in this manner. The material was therefore heated with sulphuric acid and tested for formation of hydrogen bromide. This was done by introducing the tantalic acid (and glass pieces) into a bulb (50 c.c.) through a side tube with a ground joint to accommodate a separating funnel. The condensing tube, which was fused to the bulb, was bent at right angles. With the end of the condensing tube dipping in 25 c.c. of 0·1*N*-silver nitrate solution, 10—15 c.c. of sulphuric acid (*d* 1·84) were introduced into the bulb through the separating funnel, the tap of which was afterwards closed. The bulb was then heated in a bath at 120—125°. The silver nitrate solution remained clear without developing any opalescence. The distilling bulb was then allowed to cool, 0·05 mg.

of ammonium bromide (0·5 c.c. of 0·1 in 1000 solution) introduced into it, and the bulb reheated. The silver nitrate solution became strongly opalescent in less than 5 minutes. As the above test is very delicate, and as three lots of washed tantalic acid did not respond to it, it was concluded that the extraction of the halide was quite satisfactory.

The purity of the silver bromide precipitate was indicated by its appearance on fusion as already stated, and was confirmed by its conversion into silver chloride as follows. A portion of the dried silver bromide was transferred to a weighed porcelain crucible and fused in an electric furnace. The weight of the fused silver bromide was ascertained by reweighing the crucible. The crucible was then suitably supported in the centre of the furnace, which was maintained at about 500° while a stream of chlorine passed through it. After 5—6 hours, the chlorine supply was replaced by argon for about 2 hours in order to expel all the free chlorine. The crucible was then taken out of the furnace, cooled, and weighed. The results of three such experiments were :

AgBr, g.	4·16021	6·30116	5·99453
AgCl, g.	3·17510	4·80924	4·57492
AgBr/AgCl	1·31026	1·31022	1·31030

The mean of the three determinations (AgBr/AgCl = 1·31026) is in tolerable agreement with the value obtained by Baxter (*Proc. Amer. Acad. Arts Sci.*, 1905, **41**, 82; 1906, **42**, 201), *viz.*, 1·31017, thereby showing that the silver bromide formed in these experiments was adequately pure.

Summary.

Pure tantalum, prepared by a modified Berzelius–Rose method, was employed for the preparation of its bromide and chloride by direct union with the elements in an inert atmosphere. The halides were purified by distillation and sublimation in a vacuum, and collected in sampling bulbs for analysis. Spectrographic examination gave satisfactory evidence regarding their purity. They were analysed both nephelometrically and gravimetrically by the Harvard method as developed by Hönigschmid. Twenty-four closely-agreeing results pointed to the value 181·36 for the atomic weight of tantalum.

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