with silver, 118.698. The percentage of tin in stannic chloride found by us is 45.562, while Briscoe found 54.439% of chlorine. The sum is 100.001%, a highly satisfactory and convincing outcome. The more recent experiments of Brauner and Krepelka also are in entire accord with the above result.

It is a great pleasure to express our gratitude to the Carnegie Institution of Washington and to the Elizabeth Thompson Science Fund for very generous assistance in providing indispensable apparatus.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF BOHEMIAN CHARLES UNIVERSITY OF PRAGUE.]

A REVISION OF THE ATOMIC WEIGHT OF TIN.[1] I.

BY BOHUSLAV BRAUNER AND HENRY KREPELKA.

Received February 13, 1920.

In his critical discussion on atomic weight determinations,[2] Brauner has given the following summary of all the earlier atomic weight determinations of tin:

	Ratio.	At. wt.
Gay-Lussac. 1811......	$Sn : SnO_2$	117.65
Berzelius. 1812..........	$Sn : SnO_2$	117.65–118.08
Mulder. 1849............	$Sn : SnO_2$	117.00–116.30
Vlaanderen. 1858........	$Sn : SnO_2$	118.16
Dumas. 1859............	*a.* $Sn : SnO_2$	118.06
	b. $SnCl_4 : 4\ Ag$	117.98
V. d. Plaats. 1885........	*a.* $Sn : SnO_2$ (oxidation)	118.09
	b. $SnO_2 : Sn$ (reduction)	118.07
Bongartz and Classen. 1888	*a.* $Sn : SnO_2$	119.34
	b. $(NH_4)_2SnCl_6 : Sn$	119.09*
	c. $K_2SnCl_6 : Sn$	119.07*
	d. $SnBr_4$: Sn	118.97*
	e. $Sn(SnS_2) : BaSO_4$	119.05*
	The Mean of starred values......	119.05

While our work was being carried on, Briscoe[3] and Baxter and Starkweather[4] published the values 118.69 ($SnCl_4 : 4Ag$) and 118.703 ($Sn : 4Cl$), respectively. On account of the embargo placed by Austria on English publications during the war the present authors were entirely ignorant of both above-mentioned researches until some time after the armistice was signed.

Until the year 1888 the atomic weight of tin had been taken as 118;

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[1] Presented to the Bohemian Academy of Sciences, Prague, 1917.

[2] Abegg's "Handbuch der anorg. Chemie," Group 4, 529.

[3] *J. Chem. Soc.*, **107**, 76 (1915).

[4] *Proc. Nat. Acad. Sci.*, **2**, 718 (1916).

later as 119. Brauner points out that the earlier value (118) is necessarily too low, as in converting tin into the dioxide the weight of the latter is increased by the weight of occluded products of decomposition of nitric acid. On the other hand, Brauner regards the value, 119, as too high, since Bongartz and Classen worked with or finally used electrolyt tin; obtained in this way, tin cannot be entirely pure (*i. e.*, 100%) and its occluded impurities would cause a proportionate increase in atomic weight. The error in the accepted atomic weight was 0.35, indicating that tin such as they used contains approximately 0.3% of occluded matter. The same opinion is held by Cohen, the prominent Dutch expert on tin.

The work described in this paper, stimulated by the above considerations, included an examination of the respective worths of methods hitherto used in determining the atomic weight of tin, an examination of the purity of electrolytic tin, and finally a revision of the atomic weight, correcting the high value in the International Table.

A. Oxidation of Tin by Nitric Acid.

The material with which we started was tin foil, containing, according to Mylius' analysis, only 0.004% of foreign matter. This tin foil was oxidized by dil. nitric acid in a platinum crucible. The metastannic acid thus formed was heated in an electric furnace to 900°, but it was found not to give constant weight even after 3 or 4 heatings. Possibly the adsorption of air on the large surface of stannic oxide increased the total weight.

0.2239 g. of stannic oxide differed in single weighings by from 0.00005 to 0.00015 g. The orientation values obtained in this way did not differ much from older determinations,[1] although the metallic material we used was far purer than that used by the earlier investigators. The mean of 3 determinations gave 118.02 for the atomic weight.

B. Removal of Occluded Products.

In order to set free the occluded gaseous products of nitric acid and to prevent adsorption we heated stannic oxide obtained on oxidation, with remelted potassium sulfate. Thus 3 syntheses were made, whose mean gave, as expected, a higher value, 118.66.

	SnO_2 given by 1 g. of Sn.	At. wt.
Mean of results *A*	1.27121	118.02
Mean of results *B*	1.26960	118.66
Difference	—0.00161	+ 0.64

This difference denotes mainly the quantity of adsorbed air and liberated gaseous products which had been occluded.

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[1] Berzelius, 118.08; Dumas, 118.06.

C. Electrolysis of Diammonium Stannic Chloride.

For the preparation of pure substance Classen's methods[1] were used. The electrolytic process, however, was modified: the cathodes used consisted of tin only, prepared from pure tin. By this arrangement the overvoltage of hydrogen evolution was considerably increased (amounting to 0.5 volt for normal solutions of tin, according to Caspari); moreover, use of tin cathodes made it possible to remelt the electrolytically deposited tin, together with the cathode. A weighed quantity of ammonium chlorostannate ($(NH_4)_2SnCl_6$) was dissolved in a solution of ammonium hydrogen oxalate, saturated in the cold. The electrolyte was kept above 20°, the transition point of gray tin. The compact tin-coating, consisting of well-defined silvery crystals, was weighed, together with the cathode after a thorough washing in water and drying at 120°, and placed in a porcelain boat, the cathodes having the form of the boat, and remelted in a current of hydrogen. Subsequently it was oxidized at a temperature above the melting point of tin and again reduced by hydrogen.

Hydrogen, evolved in Kipp's apparatus by means of redistilled sulfuric acid acting on pure zinc free from arsenic, was passed through a system of washing flasks, containing 20% sodium hydroxide solution, 15% silver nitrate solution and distilled water, then over red-hot copper-wire gauze, and into the reducing tube of combustion glass, at the end of which the gas was ignited. Single connections in the system were made by means of ground glass joints. Oxygen from a gasholder was washed with water and led into the oxidizing tube. Thus the following 5 electrolyses were made:

TABLE I.—TIN FROM THE ELECTROLYSIS OF DIAMMONIUM STANNIC CHLORIDE.

$(NH_4)_2SnCl_6$. G.	Density of current.		Sn before melting. G.	Sn after melting. G.	Δ.	Sn.
0.66721	0.1 A	0.2–0.5	0.21589	0.21598	+0.00009	119.11
0.94915	0.2A	0.6A	0.30723	0.30717	—0.00006	119.06
1.19720	0.1A	0.5A	0.38753	0.38732	—0.00021	119.00
1.93170	0.15A	0.45A	0.62475	0.62456	—0.00019	118.89
4.21585	0.2A	0.3–0.5A	1.36463	1.36451	—0.00012	119.08
					Mean =	119.03

In all these cases a compact coating of silvery tin crystals was deposited. After the first remelting in hydrogen a silvery grain was obtained, on the surface of which carbon was distinctly visible, identified afterwards by dissolving the tin in hydrochloric acid. Besides this, the bottom of the boat was covered with a dark gray incrustation (unaffected by hydrochloric acid) which, during the following oxidation, disappeared and after reduction reappeared. In all these cases quantitative reduction was found to be impossible; it could not be effected even at higher temperatures; there

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[1] Classen and Bongartz, *Ber.*, 21, 2900 (1888).

always remained a tiny spot of oxide floating on the molten silvery surface.

Parallel experiments made with the pure tin used in A showed that these phenomena, observed during oxidation and reduction, are due to the impurities in electrolytic tin and are not caused by the hydrogen or oxygen used.

Omitting the first electrolysis, where the produced tin showed, after remelting, a small inexplicable increase, we got from the other 4 a mean value for the impurity of the electrolytic tin, of 0.00021 g. per g. of tin, which would have the effect of increasing the atomic weight by +0.08.

D. Synthesis of Tin Tetrabromide.

The next step in the revision of the atomic weight was the synthesis of tin tetrabromide from pure tin and bromine prepared by Brauner's method, described later.

The first experiment, involving the synthesis and weighing of the stannic bromide, when the excess of bromine had been distilled off, gave a negative result, owing to the volatility of stannic bromide.

The second experiment was carried out in a Landolt tube, excess of bromine being determined by titration, with 0.05 *N* sodium thiosulfate solution. A piece of tin foil was placed in one arm of the Landolt tube; in the other was placed a glass bulb containing a weighed quantity of bromine, which had been introduced into the bulb under a bell-jar by repeated alternate evacuation and introduction of pure dry air. However, this experiment also gave negative results, because of difficulties caused by the titration of the excess of bromine.

E. Analysis of the Tetrabromide.

Preliminary Determination of the Atomic Weight.

The best and most reliable method for atomic weight determinations has always proved to be the analysis of compounds with halogens, as elaborated by Richards and his co-workers. Dumas had used tin tetrachloride for atomic weight determinations, but his method did not prevent hydrolysis from taking place during the titration of the silver excess with sodium chloride solution and neglected thus an occlusion of silver nitrate by liberated stannic acid. Moreover, the value obtained was unfavorably affected by the use of impure silver and by the mixing of highly concentrated solutions.

In the case of tin, the chloride or bromide alone is to be considered. The chloride perhaps would be more suitable, since it can be obtained very pure, because it can be distilled without decomposition, and is less easily hydrolyzed than the bromide. On the other hand, the preparation of bromide is simpler (pure dry bromine being easily obtainable), the tetrabromide shows less tendency to form the oxy-salt, and the formation of dibromide does not take place. The bromide is far more stable at higher temperatures, and as it solidifies below 30°, it can be handled as a crystalline mass. For these reasons the bromide was chosen for this work.

Preparation of Pure Substances.

Tin.—Pure tin was rolled out into thin foil which was then cleaned with sea-sand, washed in pure benzene, in alcohol, and finally in distilled water, and dried at 145°.

Bromine was prepared by Brauner's method, namely by liberating bromine from pure potassium bromide by means of chromic acid and collecting under water. The bromine thus obtained was shaken with water, purified from chlorine and iodine by rectification over a mixture of water, potassium bromide and zinc oxide, and dried by shaking with calcium bromide and calcium oxide, the last traces of water being removed by phosphorus pentoxide. The dry bromine was then redistilled in a glass apparatus, connections having been made with air-tight joints.

Tin Tetrabromide.—The preparation of this substance was accomplished in a suitably adjusted Lorenz's[1] apparatus. The whole apparatus was of glass, single parts being sealed together or connected by air-tight ground joints.

The single parts, as well as the whole apparatus, were thoroughly steamed out in a room perfectly free from hydrogen chloride. Then through the whole apparatus there was passed dry air supplied by a water pump and purified by washing first with alkaline permanganate solution, passing over conc. sulfuric acid, then through 2 tubes filled with melted potassium hydroxide and finally through 2 tubes containing phosphorus pentoxide and glass beads.

Pieces of the purified tin foil were then placed into the chief reaction bottle R and the whole system finally dried by repeated evacuation over tubes with phosphorus pentoxide and calcium bromide. Bromine from Bottle A distilled into Bottle B, which was provided with an air-tight tap[2] and ended in a capillary in the reaction Bottle R. In this way the flow of bromine was so regulated as to prevent an overheating of the reaction bottle as well as to keep the bottle free (as far as possible) from bromine vapors during the operation. During the reaction of bromine on tin Bottle R was kept shut off from the remaining parts by an air-tight glass Stopcock 2; while communication with outside air was made through a drying tube system, similar to that of Bottle D, containing Tube M, with calcium bromide and N, with calcium chloride. The reac-

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[1] *Z. anorg. Chem.*, 9, 365 (1895).

[2] The stopcocks were made with long necks and were ground very smooth. They were tested by being connected to a vacuum when it was found that no perceptible leakage occurred during an hour and a half. No lubricant was used.

tion started violently, sparks being formed at the points of contact of bromine with tin, but became moderate as more tetrabromide was formed and the addition of bromine suitably regulated. The dripping of bromine was stopped so as to leave some tin uncombined. stopcock connecting with Bottle A and Vessel B and Stopcock 2 were closed. The reaction bottle, containing tin tetrabromide, thus isolated, was warmed. During the warming the slight brownish bromine coloration disappeared and the liquid tetrabromide, colorless and refracting like carbon disulfide, was distilled through Stopcock 2 into the fraction Bottle C, which was provided with a narrow tube sealed in the neck for thermometer. Then after Stopcock 2 had been closed the distilled portion was again divided into 3 parts. The first part boiling at 200.5–201°, distilled over into the Bottle D (the communication with the bell-jar was cut off by means of Stopcock 3), through the stopcock 4. The middle fraction, with a constant boiling point of 201°, was distilled through Stopcock 3 into a glass beaker placed under the bell. In this beaker were suspended small resistance-glass bulbs, each of which had been weighed and marked. The connection with the glass-bell was made by means of a fine ground stopper to which was sealed a narrow tube extending to the bottom of the glass beaker.

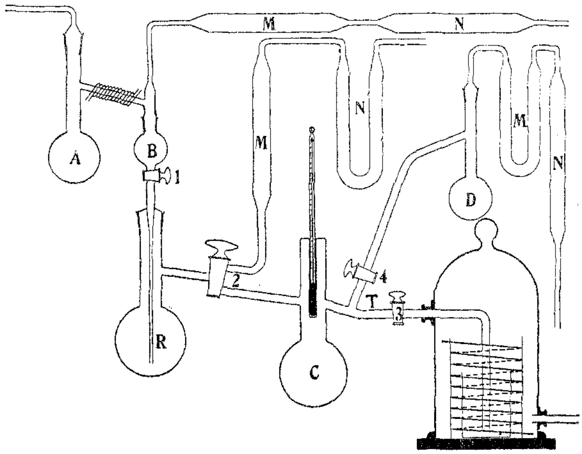

Fig. 1.

In order to keep the tetrabromide liquid, the temperature inside the bell was maintained at 45° by means of an electric oven to which the electric current was conducted through Tubes M and N, terminating in airtight joints.

The bulbs were filled by repeated evacuation and slow admittance of dry pure air (Fig. 2), whereupon the electric current was cut off and the tetrabromide allowed to solidify on cooling. Then the tube T was

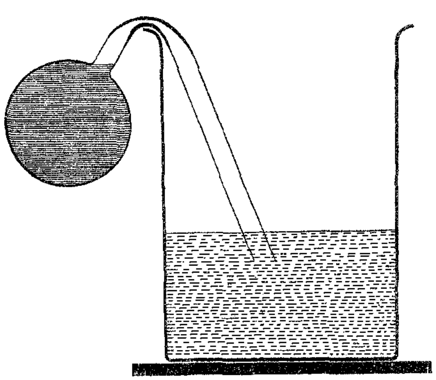
Fig. 2.

cut, the contents of the bell taken out, and every bulb quickly sealed. During this operation the column of solid tin tetrabromide in the necks prevented the air from coming into contact with the inside of the bulbs (Fig. 3). The single bulbs and the corresponding necks were then washed with nitric acid and distilled water and finally dried in desiccators over phosphorus pentoxide.

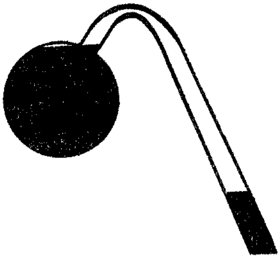
Fig. 3.

Water.—To the distilled water for ordinary laboratory use alkaline permanganate solution was added and left to stand in sunlight for 2 or 3 months. Then it was distilled through a silica condenser and the middle portion redistilled through a platinum condenser. The middle portion of this distillate was kept in resistance-glass bottles.

Nitric Acid was distilled twice and the middle fraction of the second distillation used.

Tartaric Acid was "purissimum pro analysi" purchased in the open market. Water, nitric acid, tartaric acid were all examined nephelometrically.

Silver.—Material was used which was prepared according to Stas by the reduction of silver chloride with glucose.

All these operations were performed in a room free from hydrogen chloride and hydrogen sulfide.

Weighing was done on a balance made by Nemetz-Vienna of which the sensitivity was adjusted so that the addition of one milligram to a 10-g. load changed the zero position by 10 scale divisions. All weighings were corrected for vacuum, the specific gravity of brass taken as 8.33 that of tin tetrabromide as 3.349, and that of silver as 10.49.

Analysis of Tin Tetrabromide. Series A.

The ratio $SnBr_4 : 4Ag$ was determined, the atomic weight of tin being thus directly compared with the fundamental atomic weights of silver and bromine. The weight of tetrabromide was found by weighing the empty bulbs and adding the pieces of glass sealed off. An amount of silver calculated according to the weight of tetrabromide, was weighed and dissolved in a 500 cc. flask provided with a column of bulbs to catch possible spatterings. For the solution of silver 10% nitric acid was used in small excess. All of the silver dissolved overnight without warming; after this the nitrous acid and oxides of nitrogen were expelled by heating and the solution was then diluted through the column of bulbs so as to be less than 0.1 *N*.

The bulb containing tetrabromide was introduced into a calibrated glass cylinder with a finely ground stopper, then broken under water which contained nitric acid and tartaric acid, and the solution diluted.

Only through this introduction of tartaric acid was it found possible to solve the problem of the revision of the atomic weight of tin. Tartaric acid, even in greatly diluted solutions, keeps tin in solution, probably as a complex stannyl-tartrate ion, which is not precipitated by silver, so that no silver stannate can be formed. The advantage of similar complex compounds has been used in the determinations of the atomic weights of antimony by Cooke and tellurium by Brauner.

Solutions were mixed in a dark room in yellow light. After all of the silver nitrate solution had been poured slowly and with continuous agitation into the cylinder containing the bromide, the cylinder was closed by a glass stopper, put into a cardboard box and strongly shaken, first by hand, then about 4 hours on a shaking machine. After standing overnight the precipitated silver bromide had settled in a fine compact form. Since the solutions were very dilute before mixing, all occlusion was precluded. At the end of 36 hours, when the supernatant liquor was clear, the solution was tested nephelometrically, according to the method elaborated by T. W. Richards:

Analysis No. 1 (trial analysis), 2.11620 g. of $SnBr_4$ was dissolved in water containing 25 cc. of distilled nitric acid and 3 g. of tartaric acid. This solution was then diluted to 280 cm. For the preparation in this first trial analysis a quantity of silver nitrate recrystallized several times in the dark was used, corresponding to Sn = 118.80, *i. e.*, $AgNO_3$ = 3.28050 g. or reduced to vacuum = 3.28093 g. The volume of the silver nitrate solution was 150 cm.; the total volume was 440 cm. The analysis was then carried out according to the above-mentioned method used at Harvard University.

In a similar manner 3 other analyses were made, for which silver was weighed directly. The following results were obtained:

TABLE II.—ANALYSES OF TIN TETRABROMIDE.

No. of analysis.	$SnBr_4$. G.	Vacuum cor. G.	Silver. G.	$SnBr_4$:4Ag.	Atomic weight.
1.......	2.11620	2.11664	2.08430	1.01551	118.55
2........	1.11940	1.11964	1.10206	1.01595	118.73
3.......	1.97386	1.97428	1.94359	1.01579	118.67
4.......	2.35420	2.35469	2.31788	1.01588	118.71

Mean of analyses Nr 2, 3, 4 = 118.70 (Ag = 107.88, Br = 79.916).

Discussion.

The low value of the trial analysis (with weighing of silver nitrate) would be expected, since the error due to the use of crystals of silver nitrate not 100% pure lowers the result. The mean of the 3 other analyses is 118.70. Stoichiometrically it is of interest that the ratio $SnBr_4 : 4Ag = 1.01587 : 1$ is nearly ideal. In these analyses Stas' silver and the sample of tin tetrabromide denoted as A were used. Since the silver, remelted in air, always contains some absorbed oxygen, the true value must be somewhat higher than that found (118.70); however, the error affects only the second decimal.

A final determination will be carried out later with new tin tetrabromide, using silver prepared expressly by Richards' method.

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[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF BOHEMIAN CHARLES UNIVERSITY OF PRAGUE.]

A REVISION OF THE ATOMIC WEIGHT OF TIN.[1] II.

BY HENRY KREPELKA.

Received February 13, 1920.

We have determined in a new and more careful series of trials, the ratio $SnBr_4 : 4Ag$ by analysis of newly prepared tetrabromide of tin.

The materials for this purpose were prepared with great care and cleanliness, and chief attention was paid to removing all traces of moisture from the bromine used for the synthesis of the tetrabromide and to keeping the latter in an absolutely dry state. Individual analyses were carried out in the same way as before,[2] although one profited, of course, by the experience gained in the earlier work. The details follow:

Preparation of New Materials.[3]

Bromine.—Ordinary bromine was shaken in portions in a separatory funnel containing distilled water, every portion being thus treated 3 times. This bromine was then redistilled from a saturated solution of potassium bromide. The distillate was allowed to drip into a solution of potassium oxalate prepared by neutralizing pure oxalic acid with pure potassium carbonate. The potassium bromide thus obtained was recrystallized 3 times, and its solution was evaporated with a small quantity of potassium dichromate and twice distilled sulfuric acid. The bromine thus set free removed all iodine that may have been present. This evaporation was repeated 3 times. In order to remove organic matter the dry bromide was melted in small quantities in a platinum crucible. From this remelted bromide, bromine was set free by means of an amount of potassium dichromate and sulfuric acid, such as to leave undecomposed bromide in the distilling flask. The bromine was then redistilled and from a portion of this distillate was prepared the calcium bromide used to dry the remaining part of the bromine, which was then further dried by shaking it with phosphorus pentoxide (twice sublimed in a stream of oxygen), and was afterwards distilled directly into the apparatus in which the synthesis of tetrabromide took place.

Tetrabromide of tin was prepared in the modified Lorenz apparatus. During the preparation the communication with the outside air was ef-

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[1] Presented to the Bohemian Academy of Sciences, Prague, 1919.

[2] B. Brauner and H. Krepelka, THIS JOURNAL (preceding paper).

[3] The remaining reagents not mentioned here were prepared in the same way as stated in the preliminary work.