CCCXXXVIII.—*The Atomic Weight of Antimony from Different Sources.*

By Kolar Ramakrishnaiyer Krishnaswami.

Three determinations of the atomic weight of antimony have been made during the last seven years. Willard and McAlpine (*J. Amer. Chem. Soc.*, 1921, **43**, 797) obtained the value 121·773, Weatherill (*ibid.*, 1924, **46**, 2437) 121·748, and Hönigschmid, Linhard, and Zintl (*Z. anorg. Chem.*, 1924, **136**, 257) 121·76. These figures are in good agreement, but in each case the antimony used was obtained from Kahlbaum. Muzaffar (*J. Amer. Chem. Soc.*, 1923, **45**, 2009) has, however, published results for antimony from Brazil and other sources for which he obtained values varying from 121·444 to 122·374.

In order to see if similar variations were to be found with antimony from a different part of the world, determinations have been made with four ores of Indian and Burmese origin, whilst for comparison parallel determinations have been conducted with a sample of Kahlbaum's antimony. The results agree very closely with those of the three observers mentioned above, and the variation for different ores is within the limit of experimental error.

Experimental.

A few trials were made of Muzaffar's method, but in spite of its apparent simplicity certain disadvantages became evident in practice, and it was abandoned. These attempts will be referred to later. The method of Willard and McAlpine was then adopted in its entirety and found very satisfactory : Antimony tribromide is prepared in an atmosphere of nitrogen and distilled in a vacuum into a bulb which is sealed, weighed, and finally broken under a solution of tartaric acid; the quantity of bromine is then estimated by conversion into silver bromide, the amount of silver required being determined nephelometrically or weighed as bromide. Reference is only made to details in procedure when this differs in any way from that given by the above authors. The whole of the apparatus used in the course of the experiments was constructed from Pyrex or the very resistant T-glass of Greiner and Friedrichs.

Preparation of Materials.—The water, bromine, potassium bromide, sodium chloride, nitric acid, tartaric acid, and sodium and potassium cyanides required in this research were purified by the methods given by Willard and McAlpine. Silver was prepared from silver nitrate according to the procedure of Richards and Wells (*J. Amer. Chem. Soc.*, 1905, **27**, 459), but in most of the experiments Johnson and Matthey's " chemically pure " silver was used after being washed with absolute alcohol and ether and fused on a lime support, for the two samples were found to give almost identical results.

Hydrogen was generated by electrolysis of a 15% solution of sulphuric acid between platinum electrodes, and purified by passage over heated platinised asbestos and copper gauze, bubbling through a 20% solution of caustic potash containing some dissolved lead oxide, and drying by passage over phosphorus pentoxide (see Noyes, *Bull. Bureau Standards*, IV, 179).

Nitrogen was prepared in an all-glass apparatus by passing a mixture of air and ammonia over heated copper, and purified according to the method of Richards and Krepalka (*J. Amer. Chem. Soc.*, 1920, **42**, 2225).

Balance and Weighing.—A long-beam Oertling balance was employed. Successive weighings of the same object, which were made by substitution, agreed to 0·02 mg. The weights were carefully calibrated, and counterpoises were used whenever necessary. Calcium chloride was kept in the balance case and 50% humidity was assumed when calculating the vacuum correction.

Preparation of Antimony.—Five specimens of antimony were prepared from the following sources : (1) Kahlbaum's purest antimony trioxide, (2) stibnite from the Mysore State, (3) cervantite from the same area, (4) stibnite from the Amherst District in Burma, and (5) stibnite from the Southern Shan States.

The method of preparation of the metal was the same in all the cases. About 500 g. of the finely powdered material were digested with hot concentrated hydrochloric acid in successive portions until extraction was practically complete. The excess of acid was distilled off and the antimony trichloride distilled 4 or 5 times. It boiled regularly at 210—211°/680 mm., and was always obtained as a clear, pale yellow liquid solidifying to an ivory-white solid. The further steps were according to the method devised by Groschuff (*Z. anorg. Chem.*, 1918, **103**, 168) : The trichloride is treated with chlorine and hydrogen chloride to give chloroantimonic acid, $SbCl_5,HCl,\frac{1}{2}H_2O$; this is dissolved in a little water, and large dilution with water then precipitates antimonic acid, which is washed, evaporated to dryness with nitric acid to expel the last traces of chlorine, and ignited. The oxide thus obtained is reduced with sodium cyanide in a porcelain beaker in a muffle furnace at about 650°. The buttons of metal obtained are cleaned as recommended by Muzaffar, powdered in an agate mortar, dried in a current of hydrogen at 400°, and sealed in the containing tube.

Preparation of Antimony Bromide.—Antimony bromide was prepared exactly according to Willard and McAlpine's instructions, the only modification being the use of a mercury-vapour pump for the complete evacuation of the apparatus.

Purity of the Silver.—As a check on the purity of the silver, the ratio AgCl : Ag was determined by following exactly the procedure of Richards and Wells (*loc. cit.*). This work, and all subsequent operations in which silver salts were involved, was done in a special laboratory illuminated by ruby light. Table I shows the results of several determinations.

TABLE I.

Ratio AgCl : Ag.

Wt. of Ag, g.	Wt. of AgCl, g.	100 × AgCl/Ag.	Wt. of Ag, g.	Wt. of AgCl, g.	100 × AgCl/Ag.
7·49956	9·96437	132·866	7·57600	10·06474	132·850
7·41387	9·85066	132·867	7·74410	10·32871	132·862
7·59879	10·09663	132·870	7·48068	9·93930	132·866

The first two experiments were made with silver from silver nitrate, and the remainder with Johnson and Matthey's pure silver, which is evidently of a remarkable degree of purity for a commercial article. The mean value obtained by Richards and Wells was 132·864, and thus the agreement is as close as can be expected.

Weighing and Analysis of Antimony Bromide.—In this part of the work, also, the general method adopted was the one used both by Willard and McAlpine and by Hönigschmid. After being cleaned and dried as recommended by Baxter (*Proc. Amer. Acad. Arts Sci.*, 1924—25, **60**, 228), the bulb containing the antimony bromide was suspended from the balance by means of a platinum wire and weighed in air and under water. The platinum wire also was weighed in air and in water with the same portion of it immersed as when the bulb was weighed under water. The bulb was then broken with a Pyrex rod under a solution of tartaric acid (250 c.c. of 4—5% solution) in a thick-bottomed, tall beaker. Solution was complete in about 10 hours.

In Expts. Nos. 1—6, the solution was passed through a Gooch crucible to collect the glass. Subsequently, a silica crucible with a porous sintered bottom was used and proved much more satisfactory. In both cases, the glass was ignited to a dull red heat before weighing. Its density was determined and found to be 2·56 g. per c.c. (T-glass).

The analysis of the antimony bromide was effected by determination of the ratio $SbBr_3 : 3AgBr$, and in two cases of the ratio $SbBr_3 : 3Ag$ in addition. For the latter purpose a nephelometer of the Kober type with a Klett top-reader was used.

The gravimetric determination was at first (Expts. 1—6) carried out exactly in accordance with the description given by the authors already mentioned. A Gooch crucible was used, and the solution was refiltered through a small filter-paper to secure any particles of asbestos. As the volume of the solution was about 700 c.c., this was a tedious operation. A great improvement was effected by the use of a Jena-glass crucible with a sintered bottom. In these experiments, the silver bromide was dried for 14—18 hours at 180°, and the moisture content determined by fusing the bulk of the precipitate in a porcelain crucible. Subsequently, the drying was conducted at 300° for 12—18 hours, as recommended by Hönigschmid, and the loss on fusion of the bromide was then found to be negligible, so that it was not determined in every case. The bromide was, however, always fused and its appearance after fusion noted; it was found that when dark spots or a discoloration appeared (due to traces of silver nitrate) a low value for the atomic weight was usually obtained. Such experiments are distinguished by an asterisk in the following table, and are not included in calculating the means. In all other cases, the fused silver bromide was quite clear.

Table II gives the results of the determinations. For calculating the atomic weight, the values $Ag = 107·880$, $Br = 79·920$ have been adopted.

In Expts. 7 and 8, the ratio $SbBr_3 : 3Ag$ was determined by the nephelometer before filtering the silver bromide. The values 121·751 and 121·735 were found for the atomic weight, the agreement with the gravimetric value being fair. It was not, however, considered necessary to determine this ratio in every case, as it is sufficient for

Table II.

Expt. No.	Wt. of $SbBr_3$, g.	Wt. of AgBr, g.	$SbBr_3 : 3AgBr$.	Atomic weight of Sb.
		Kahlbaum's Antimony Trioxide.		
1	4·44079	6·92064	0·641664	121·753
2	3·15437	4·91639	0·641603	121·719 *
3	3·64246	5·67747	0·641566	121·701 *
4	3·97152	6·18954	0·641650	121·746
5	3·47255	5·41185	0·641654	121·750
6	3·80868	5·93549	0·641679	121·762
7	3·44766	5·37296	0·641669	121·756
8	4·12164	6·42335	0·641665	121·754
				Mean 121·754
		Mysore Stibnite.		
9	4·29146	6·68901	0·641569	121·700 *
10	4·03746	6·29236	0·641645	121·743 *
11	3·85444	6·00720	0·641637	121·738
12	4·25750	6·63517	0·641656	121·749
13	4·16876	6·49684	0·641659	121·751
14	3·40170	5·30160	0·641636	121·738
				Mean 121·744
		Mysore Cervantite.		
15	3·35625	5·23081	0·641631	121·735
16	3·98107	6·20437	0·641659	121·751
17	3·82381	5·95934	0·641650	121·746
				Mean 121·744
		Amherst Stibnite.		
18	4·61169	7·18715	0·641657	121·750
19	4·61851	7·19785	0·641651	121·746
20	4·11282	6·40990	0·641635	121·737
21	3·50233	5·45818	0·641666	121·755
22	3·98801	6·21524	0·641650	121·745
				Mean 121·747
		S. Shan States Stibnite.		
23	3·74847	5·84185	0·641658	121·750
24	4·94145	7·70114	0·641652	121·747
25	3·82442	5·96012	0·641668	121·756
				Mean 121·751

the present purpose to compare the relative values for the different samples of antimony, the absolute value of the atomic weight being of secondary importance.

The mean results show an extreme variation of 0·010 in the atomic weights; this is considerably less than the variation among individual experiments and may reasonably be ascribed to experimental error. The difference between these results and those of Muzaffar is considerable, this author having found a variation of 0·93 unit in the atomic weight of different samples of antimony. His individual results are not very concordant, the ratio $3Sb : KBrO_3$ ranging from 2·1802 to 2·1875 in the case of one sample, corresponding with 0·41 unit in the atomic weight, whilst the preliminary determination of the ratio $3As_4O_6 : 4KBrO_3$ gave results fluctuating over a range of 0·4%, showing that one of these materials was not very pure, or that the end-point of the reaction was not definite.

An attempt was made to investigate the bromate method as conducted by Muzaffar, but a difficulty was experienced in dissolving the pure antimony in concentrated sulphuric acid except by very prolonged boiling. On cooling, the mass became semi-solid, and although solution could be effected by the addition of a little water, too much water produced a precipitate and transference was troublesome. As Muzaffar gives no details of manipulation, it was considered preferable to make use of a method which had been fully described and experiments by the bromate method were not continued.

Summary.

The atomic weight of antimony has been determined in five samples, one from Kahlbaum and the others from India and Burma. Willard and McAlpine's method was used, and the results ranged from 121·744 to 121·754. These are in good agreement with the best previous determinations; there is no indication that the variation is due to a change in atomic weight, and in any case such variation does not exceed 0·01 unit for the samples examined.

In conclusion, I wish to express my gratitude to Professor H. E. Watson for his valuable suggestions during the course of this work, and to the Directors of Geology of the Governments of India and of Mysore for their kindness in supplying the necessary ores of antimony.

INDIAN INSTITUTE OF SCIENCE,
BANGALORE, INDIA.

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