[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

THE ATOMIC WEIGHT OF ANTIMONY FROM DIFFERENT SOURCES

BY R. K. MCALPINE

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In 1923 Muzaffar[1] published a preliminary note under the above title in which he claimed that four samples of antimony, derived from stibnites from Hungary, Borneo, Peru and Bolivia, gave by titration against potassium bromate atomic weights as follows: 121.14, 121.56, 121.72 and 122.37. In 1927 Krishnaswami[2] reported the results of comparisons of Kahlbaum's antimony with the metal obtained from four ores of Indian and Burmese origin. "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." Instead, the metal was converted to bromide and comparisons made of the bromide with silver and with silver bromide, copying the procedure that had been employed in this Laboratory.[3] A sentence from the conclusion tells the story: "The results 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."

The present work was undertaken to review the work of Muzaffar using samples of antimony from the same sources and comparing them by density and by titration with potassium bromate. The materials used by Muzaffar had been exhausted, but through the kindness of Mr. C. T. Heycock under whose direction the work had been done it was possible to obtain some of the same ores from the supply house that had furnished the original materials. Since the extreme values were reported for the antimony obtained from Hungary and Bolivia, respectively, the ores from these countries were selected as sources of metal for detailed study.

Preparation of Materials

Antimony.—The metal was recovered by the same process that was used by the other workers. Following extraction with concentrated hydrochloric acid, the antimony was precipitated as oxychloride, dissolved in hydrochloric acid, oxidized with chlorine and several times recrystallized as metachloro-antimonic acid. This material was then hydrolyzed with water, the precipitate evaporated with nitric acid to remove chloride, ignited to oxide and reduced to metal by fusion with recrystallized potassium cyanide. The buttons thus obtained were cleaned mechanically and then alternately etched with nitric acid and fused in hydrogen until the latter process gave clear-surfaced globules which on solidifying formed crystalline masses with the highest luster on all surfaces.

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[1] Muzaffar, THIS JOURNAL, **45**, 2009 (1923).

[2] Krishnaswami, *J. Chem. Soc.*, 2534 (1927).

[3] Willard and McAlpine, THIS JOURNAL, **43**, 797 (1921).

Throughout all these operations all reagents were specially purified and all utensils scrupulously cleaned, employing the technique used in the previous work in this Laboratory.[3]

Potassium Bromate.—Some of Kahlbaum's special reagent was recrystallized several times from redistilled water, using centrifugal drainage of the crystals and conducting the operations in quartz and platinum ware. The material thus obtained was dried in a desiccator over potassium hydroxide sticks. Qualitative tests for halide and chlorate were negative. A portion of this material was further dried by heating for three hours at 130° for use as a standard. A very small amount of water was still present, probably several hundredths of one per cent. A small portion of the stock has been reserved for a moisture determination which it is hoped to carry out before long.

Experimental

The experimental work may be divided into two parts: I, the determination of the density of antimony from different sources and II, the determination of the ratio of antimony to potassium bromate.

I. The Density of Antimony from Different Sources.—According to the theory of isotopic mixtures, if the atomic weight of an element varies with different specimens, the density of these specimens should also vary, and in direct proportion to the atomic weight. Since the values in question differ by slightly more than 1% in their extremes, a determination of the density should give an immediate check on variations of that magnitude.

Experimentally the method finally employed for this determination consisted in weighing the buttons of antimony in air and then in water and calculating their volumes from the differences in weights and the density of the water at the temperature used. A small platinum wire basket was constructed to hold the antimony. This was then suspended from the hook on the balance and weighed carefully. Then it was immersed in water to a fine knot on the suspension wire and weighed again. Next, after the basket had been carefully dried, an antimony button was placed in it and the system weighed as before, first in air, then in water. From these weights and the density of the water at the temperature of the experiment the density of the metal was then calculated.

Preliminary experiments showed that the ordinary round buttons of antimony gave erratic results. It appeared as if spaces were formed inside the buttons when they solidified, causing the apparent density to vary and to be lower than the true density. This difficulty was overcome in the following manner. A 20-centimeter hard glass tube was heated in an oxy-gas flame until the closed end was perceptibly cone-shaped for a length of three or four centimeters. The test-tube was then cleaned thoroughly. Next, the antimony was placed in the tube and a clean two-holed rubber stopper inserted bearing an inlet and an outlet tube for hydrogen. The antimony was then fused in hydrogen and after removing the flame the tube was rotated in such a way as to cause the metal to solidify as a shell in the cone-shaped part of the test-tube. With this manipulation it was found possible to get reasonably concordant results on repeated fusions followed by density determinations. The specimens of antimony were therefore prepared in this way and the densities determined, using redistilled water that was freshly boiled and cooled. In each case, after immersion in water, the surface of the shell was searched carefully for air bubbles. Only occasionally was one found. In such a case it was effectively removed by careful manipulation with a fine glass rod. Boiling to displace air was considered of doubtful value, because of (*a*) the chance for action of boiling water on the antimony and (*b*) the decrease in density noted by Cohen[4] when antimony was maintained for some time at 102–105°. Since the average value obtained here is slightly higher than that of Cohen[4] and still higher than that recommended by "International Critical Tables" (Vol. I, p. 104), the error due to trapped air must be very small. The results are given in Table I.

TABLE I

THE DENSITY OF ANTIMONY FROM DIFFERENT SOURCES

Source of antimony	Wt. of Sb in air, g.	Wt. of Sb in water, g.	Temp. of water, °C.	Density of Sb
Kahlbaum's	15.3981	13.1024	22.3	6.694
Hungarian stibnite	14.9260	12.7342	22.3	6.703
Bolivian stibnite (a)	13.5033	11.4907	22.3	6.696
(b)	12.9599	11.0275	22.3	6.695

The inherent limitation of this method lies in the sluggish action of the balance when weighing in water. It was found possible, however, to determine the resting point of the balance to within one milligram; therefore the error in weighing, with two weighings in water involved, should not exceed two milligrams at the maximum. Since the weight of displaced water is approximately two grams, the density values should check within 0.1%.

The figures in Table I give no evidence of variation in the density of antimony from different sources. The variations from the average, +0.006 and −0.003, are within the limits of the method used. Even if the attempt were made to attach significance to these variations it would be noted that their indications are at variance with the work of Muzaffar, not only as regards magnitude, but also in direction. He reported 121.14 for the atomic weight of antimony from Hungary and 122.37 for that from Bolivia. On that basis the density of the antimony from Bolivia should be highest, Kahlbaum's antimony intermediate, corresponding to the atomic weight 121.77, and that from Hungary lowest.

II. The Ratio of Antimony to Potassium Bromate.—In analytical work the bromate method for antimony is recognized as one capable of distinct accuracy, but the size of the sample is commonly limited to two or three-tenths of a gram of metallic antimony. Since it was desirable to

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[4] Cohen and van den Bosch, *Z. physik. Chem.*, **89**, 757 (1915).

use larger samples to increase the accuracy of the determination, some preliminary experimentation was necessary to work out a satisfactory procedure. In these studies it was found that a sample as large as three grams could be converted to sulfate readily by digesting at near the boiling point with fifty milliliters of concentrated sulfuric acid. On cooling a considerable amount of antimony sulfate crystallized out, but this dissolved readily in dilute hydrochloric acid. The usual procedure recommends that the final solution contain approximately 20% by volume of concentrated hydrochloric acid, and be titrated with methyl orange as indicator at not less than 60°. With the large amount of sulfuric acid already present it was found that a lower concentration of hydrochloric acid gave better results, both in sharpness of end-point and in completeness of oxidation of the antimony by the bromate. It was also found that the reaction proceeds readily at room temperature, making it possible to add the bromate in solid form, swirl to dissolve the bromate, then heat to the proper temperature to obtain a sharp end-point and complete the titration. To avoid error in the transfer of the bromate it was found convenient to weigh the salt into a small shell vial, ten by thirty centimeters in size, and then drop vial and all into the solution, taking care to avoid spattering. This operation was carried out in a flask that could be stoppered until all of the bromine fumes were absorbed by the solution, thus avoiding error from loss of bromine. In the final determinations the following method was used.

A sample of 2 to 3 g. of antimony was weighed out, transferred to a half-liter glass-stoppered Erlenmeyer flask and treated with 50 ml. of concentrated sulfuric acid; the flask was covered with a watch glass and heat applied with a small flame until the metal was dissolved. This required one-half to three-quarters of an hour. As soon as the reaction was complete the flame was removed and when cool enough to permit it the flask was placed in running water for a few minutes. Then there was added 350 ml. of dilute hydrochloric acid containing 10% by volume of the concentrated acid, the cover glass and walls of the flask being rinsed with acid of the same strength. The solution was boiled for several minutes to remove sulfur dioxide, using a current of carbon dioxide to prevent access of oxygen from the air and continuing the process for two or three minutes after the odor had disappeared. The solution was then cooled in running water, with the atmosphere of carbon dioxide maintained, and when cold the glass stopper was inserted. Meanwhile an amount of potassium bromate was weighed out 3 to 5 mg. less than sufficient to oxidize the antimony. The stopper was then removed and the vial containing the bromate dropped in, the stopper reinserted and the solution swirled until the salt was completely dissolved and the solution again colorless. This required only two or three minutes. The cold solution was allowed to stand for about five minutes longer for complete absorption of any bromine fumes, then the stopper was removed, the solution heated to 60–70° under an atmosphere of carbon dioxide, three drops of methyl orange solution added and the titration completed with a standard solution of potassium bromate containing one milligram of the salt per milliliter. In some cases duplicate titrations were carried out by reducing with sulfur dioxide and repeating the above operations, starting with the removal of excess sulfur dioxide by boiling in a current of carbon dioxide. The blank to determine the correction to be applied for the end-point showed that one-tenth of a milligram of potassium bromate was sufficient to destroy the color of the indicator under the conditions used.

Table II gives the results of comparison of the different specimens of antimony with each other by titration with potassium bromate.

TABLE II

THE RATIO OF POTASSIUM BROMATE TO ANTIMONY FROM DIFFERENT SOURCES

Source	Sample, g.	Titrn.	$KBrO_3$ added solid g.	soln. ml.	total g.	Ratio $\frac{KBrO_3}{Sb}$	Ratio calcd.
Kahlbaum	2.3965	1st	1.0915	6.1	1.0976	0.4580	0.4571
(preliminary)		2nd	1.0928	3.4	1.0962	.4574	.4571
		3rd	1.0928	2.4	1.0952	.4570	.4571
Kahlbaum[a]	2.1560	1st	0.9829	4.5	0.9874	.4580	.4571
Hungary[a]	2.1234	1st	0.9679	5.1	0.9730	.4582	.4571
		2nd	0.9661	6.5	0.9726	.4580	.4571
	2.8452	1st[b]					
		2nd	1.2958	6.0	1.3018	.4575	.4571
Bolivia[a]	2.0906	1st	0.9526	4.3	0.9569	.4577	.4571
		2nd	0.9512	5.6	0.9568	.4577	.4571
	2.0695	1st	0.9434	4.4	0.9478	.4580	.4571

[a] Pieces of shell from density determination.

[b] In this determination, through error in calculation, an excess of potassium bromate was added as solid so the first titration was lost.

In examining the data in Table II two points are to be noted: first, that with repeated titrations the ratio of potassium bromate to antimony falls off slightly; second, that comparisons of the ratios for first titrations show a concordance indicating the essential identity of the different specimens of antimony. The average ratio for first titrations is 0.4580 and the maximum variation from this—0.0003—is shown between the two samples of antimony from Bolivia. This shows that the atomic weights of the different specimens of antimony studied are identical within 0.05 unit of each other in contrast to a difference of 1.23 reported.

Concerning the true ratio of potassium bromate to antimony, the value calculated from the accepted atomic weights is 0.4571. The average ratio for first titrations, 0.4580, is obviously too high because of the presence of a slight amount of moisture in the potassium bromate. It is doubtful, however, if the moisture alone would be sufficient to account for this difference. Further, the decrease in ratio with successive titrations suggests the possibility that the reaction of antimonous chloride with potassium bromate is not quite so simple as represented by the ordinary equation. This reaction is capable of experimental investigation, but since it does not affect materially the question of the atomic weights of antimony from different sources it has been set aside for the moment.

It is hardly worth while to speculate on the errors of Muzaffar's work. The paper as originally presented for publication contained density determinations indicating variations corresponding to the atomic weights reported. These were omitted in the published article, as well as several of the crudities noted in other parts of the work. In the paper as published the experimental details are lacking that should be considered if critical comment were to be made. The most charitable view, however, would be that he attempted the application of procedures to unknown material before he had tested them sufficiently to understand their behavior on known material, a not uncommon mistake in analytical work.

Summary

1. Muzaffar reported atomic weights of 121.14 and 122.37, respectively, for specimens of antimony derived from stibnites from Hungary and from Bolivia.
2. Specimens of metallic antimony have been prepared from stibnites from Hungary and Bolivia, the ores being obtained from the supply house that furnished the material for Muzaffar.
3. These specimens have been compared with each other and with Kahlbaum's antimony by density determinations and by titration with potassium bromate.
4. The densities of the three specimens lie within one-tenth of one per cent. of one another.
5. The ratios of potassium bromate to antimony lie within five-hundredths of one per cent. of each other,
6. There is no evidence of variation in the atomic weight of antimony from different sources.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF BRYN MAWR COLLEGE AND THE CHEMICAL LABORATORY OF THE UNITED GAS IMPROVEMENT COMPANY]

THE SHIFT IN THE 1.14μ ABSORPTION BAND OF SOME BENZENE DERIVATIVES

BY JAMES BARNES AND W. H. FULWEILER

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In an earlier paper[1] by the authors it was shown that the frequencies of the absorption bands (at approximately 0.87μ) of benzene and some of its derivatives are shifted progressively toward lower values as methyl and ethyl groups are added to the benzene ring. This note is to report that a similar effect has been observed in benzene, toluene, *p*-xylene and mesitylene in their next outstanding absorption band toward the infra-red, which has a wave length of approximately 1.14μ. The amount of the shift is the same within the limit of error as that observed in the 0.87μ band.

The apparatus used, namely, source of continuous radiation, six-foot

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[1] Barnes and Fulweiler, THIS JOURNAL, **49**, 2034 (1927).