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THE ATOMIC WEIGHT OF ANTIMONY FROM DIFFERENT SOURCES. I. PRELIMINARY

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Ever since the discovery of isotopes, investigation of samples of an element from different sources has become important. Values for the density, the melting point and the atomic weight may show slight variations among different samples. The differences are accounted for on the isotopic theory, and whenever observed indicate the presence of isotopes in an element.

A review of the earlier work on the atomic weight of antimony suggested that its equivalent weight might be different in samples prepared from ores from different parts of the earth. With this idea in mind the present work was undertaken with stibnites from Hungary, Bolivia, Borneo and Peru. The results indicate a striking variation in the value of the atomic weight, but since this seems to be the second case of its kind (that of lead being the first), the figures need a confirmation by the study of the element from other sources and by more work on the methods of the purification of the element. This is, therefore, a preliminary notice of the phenomenon.

Preparation of Materials

Ammonium Bromide was prepared according to the method suggested by A. Scott.[1]

Silver.—Through the kindness of Mr. C. T. Heycock, a sample of silver was used that had been purified and employed by him in his work on the atomic weight of rubidium, and also by A. Scott[1] in his work on the ratio of ammonium bromide to silver.

Arsenious Oxide, a chemically pure grade, was sublimed 6 times at 90° in a long, evacuated hard-glass tube which was sealed under reduced pressure and warmed before sealing to fill it with the vapor of the substance. The oxide was weighed into the titration bottles immediately after its preparation.

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[1] Scott, *J. Chem. Soc.*, **103**, 849 (1913).

Potassium Bromate, a chemically pure grade purchased from a commercial source, was found to contain 0.02% of hygroscopic moisture when it was dried in a vacuum desiccator over fused calcium chloride. *Accessory Reagents* used in the analytical work, or incidental to the purification of materials, were purified and always tested to assure their freedom from interfering impurities. Distilled water was specially prepared and was free from ammonia.

Preparation of Pure Antimony

Stibnites from Peru, Bolivia, Borneo and Hungary were obtained. Each ore was separately digested in concd. hydrochloric acid and from the extract antimony trichloride was obtained by fractional distillation at 220° followed by 5 redistillations. The chloride was next transformed into chloro-antimonic acid ($SbCl_5.HCl.4^1/_2H_2O$) by the method of W. Schmid.[2] $SbCl_3 + Cl_2 + 4^1/_2H_2O \longrightarrow SbCl_5.HCl.4^1/_2H_2O$. The fourth crop of the crystals of this salt was broken up in a large amount of distilled water and the solution boiled to complete the hydrolysis. Antimonic acid thus precipitated was washed and evaporated to dryness with nitric acid to expel the last traces of the chloride. The antimony oxide thus formed was reduced with potassium cyanide in silica crucibles and the metal cast in plaster moulds free from iron. The buttons of antimony obtained were scrubbed with clean sand and from them a 1mm. layer was filed off all around. They were then washed thoroughly and etched in dil. sulfuric acid, washed again in distilled water and melted in silica crucibles under borax. The metal was kept at its melting point for a long time and slowly cooled. It was again superficially cleaned as described above, and powdered in an agate mortar.

The powdered metal was melted in a current of pure dry hydrogen over a lime support as employed by T. W. Richards in his purification of silver.[3] Bright buttons of antimony thus obtained were etched, dried and powdered in an agate mortar. The powdered metal was heated in a current of pure dry hydrogen to dry it and to reduce the traces of oxide that may have been formed during powdering. This treatment was given just before the metal was weighed for the determination of the density or the atomic weight.

All of the 4 samples of antimony were prepared and purified under identical conditions to assure their superficial uniformity. The method as outlined above was suggested by E. Groschuff[4] after a rigorous investigation and comparison of all the methods so far known for obtaining pure antimony, and was adopted by H. H. Willard and McAlpine[5] in the preparation of antimony for determination of its atomic weight.

Balance and Weighings.—Weighings were made on a balance sensitive to 0.05 mg., using standardized weights and the method of substitution.

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[2] Schmid, *Z. anorg. Chem.*, **44**, 37 (1905).

[3] Richards, THIS JOURNAL, **27**, 459 (1905).

[4] Groschuff, *Z. anorg. Chem.*, **193**, 164 (1918).

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

Ratio of Potassium Bromate to Arsenious Oxide

Method.—Arsenious acid was transferred directly from the balance pan into stoppered bottles. After a few cubic centimeters of sodium hydroxide solution had been added, the bottles were warmed on a water-bath to effect solution, and when they had cooled 100 cc. of moderately strong hydrochloric acid was poured into each. Titration with potassium bromate solution was carried out in exactly the same manner as described later for antimony.

On standardization, 1.000 g. of potassium bromate in solution was found to be equivalent to 0.0034487 g. of arsenious oxide. The ratio $3As_4O_6:4KBrO_3$ was found to be: (1) 1.78154, (2) 1.77983, (3) 1.77870, (4) 1.77455, (5) 1.77805, (6) 1.77901, (7) 1.77875; av., 1.778633. The calculated molecular weight of potassium bromate is 167.02; that determined from the above ratio is 166.92, with 0.02% moisture and 0.04% experimental error.

Ratio of Ammonium Bromide to Silver

This was determined in a Stas box by the method of A. Scott.[1] Ammonium bromide solution was standardized against silver. 1.000 g. was found to be equivalent to 0.00108015 g. of silver or 0.00098082 g. of silver bromide. One g. of silver nitrate solution was equivalent to 0.99335 g. of ammonium bromide solution. Solid ammonium bromide was compared to pure silver and the ratio $NH_4Br:Ag$ was found to be (1) 0.90770, (2) 0.90734, (3) 0.90788; av., 0.90776. From this the atomic weight of silver is determined to be 107.91. This is affected by 0.03% experimental error.

Ratio of Silver to Potassium Bromate

A weighed quantity of potassium bromate was transferred to a stoppered bottle, dissolved in distilled water and reduced to potassium bromide with a slight excess of sulfur dioxide solution. The bottle was then warmed and a few drops of fuming nitric acid were added to oxidize sulfite to sulfate. In a separate bottle the requisite quantity of silver was dissolved in nitric acid according to the method of Stas. Both the bottles were taken into a dark room, and the silver solution after dilution was transferred completely into the bromide solution bottle. The titration was completed in the Stas box in the same manner as described for the ratio of ammonium bromide to silver. The ratio $KBrO_3:Ag$ was found to be (1) 1.54923, (2) 1.54875, (3) 1.54900, (4) 1.54900, (5) 1.54892; av., 1.54924 (reduced to a vacuum). The molecular weight of potassium bromate, from the ratio, is found to be 167.13, from which 0.02% moisture and 0.045% experimental error are to be deducted.

Ratio of Antimony to Potassium Bromate

Antimony was dried in a current of hydrogen immediately before use. It was weighed by transfer from a weighing bottle into a clean, conical flask. The metal was dissolved in concd. sulfuric acid and the cooled solution was transferred completely to a stoppered bottle containing 100 cc. of distilled water and 20 cc. of hydrochloric acid. A quantity of potassium bromate, approximately but slightly less than equivalent, was weighed, dissolved in hot distilled water and the solution poured into the bottle that contained antimony solution, in small quantities at a time. The reaction is represented by the equation $3SbCl_3 + KBrO_3 + 6HCl \longrightarrow 3SbCl_5 + KBr + 3H_2O$. Since the quantity of potassium bromate added is less than the equivalent amount, an excess of antimony trichloride is left in the above process. This was titrated with 0.01 *N* potassium bromate solution, using methyl orange as the indicator. The bromate solution was standardized against the sample of antimony under consideration. As the ratio of the metal to bromate is different with different samples of antimony, the standardization of the solution was repeated before each new sample of the metal was analyzed. The solution was drawn from a weight pipet and the strength expressed as grams of antimony equivalent to 1.000 g. of solution. The amount of antimony that reacted with the solution was deducted from the total antimony taken, and thus only that quantity of the metal was considered that had reacted with the solid bromate. All of the samples of antimony were titrated under precisely the same conditions; therefore, there could be no error of experiment that could modify the relative differences of the element from different sources. The ratio of the different samples of antimony to potassium bromate, $3Sb:KBrO_3$, was found to be as follows.

TABLE I

RATIO OF THE VARIOUS SAMPLES OF ANTIMONY TO POTASSIUM BROMATE

Samples from			
Hungary	Borneo	Peru	Bolivia
2.17590	2.1828	2.1857	2.2001
2.17593	2.1830	2.1863	2.2001
2.17590	2.1802	2.1869	2.1970
2.17589	2.1875	2.1865	2.1986
2.17594	2.1857	2.1863	2.1998
2.17595	2.1846	2.1859	2.1975
2.17593	2.1811	2.1860	2.1986
	After repurification of the same sample		2.1990
			2.1982
			2.1979
			2.1985
Atomic Weights			
121.144	121.563	121.720	122.374

In conclusion the author wishes to express his thanks to Mr. C. T. Heycock for his keen interest in the problem.

Summary

Antimony metal has been prepared from stibnites from Hungary, Borneo, Peru and Bolivia, and compared with potassium bromate by

solution in sulfuric acid, addition of solid potassium bromate and completion of the titration with 0.01 *N* potassium bromate solution. The purity of potassium bromate was established by comparison with silver and arsenious acid. The atomic weights of antimony thus obtained are as follows: stibnite from Hungary, 121.14; from Borneo, 121.56; from Peru, 121.72; from Bolivia, 122.37.

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[Contribution from the Laboratory of Grinnell College]

ELECTROMETRIC TITRATION OF IODATE, BROMATE, CHLORATE, FERRICYANIDE WITH TITANOUS SULFATE

By W. S. Hendrixson

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In a recent paper from this Laboratory[1] it was stated that work was in progress on the titration of oxidizing substances with titanous ion.

In the work described in the present paper the same general methods and the same apparatus as mentioned in the former paper were used. The stirrer was provided with a mercury seal and all titrations were carried out in an atmosphere of carbon dioxide. All solutions affected by light were kept in bottles coated with a black enamel paint, provided with siphons and never unstoppered. Titanium solutions were standardized with permanganate and dichromate. The latter and the solutions of pure potassium iodate, bromate and chlorate were made up by weight and the contents of calibrated flasks at 20°.

Titration of Iodate with Titanous Ion

A 0.05 *N* solution of iodate was made up by weight and also standardized with pure iodide and thiosulfate. The volume of the solution at the end of the titrations was about 300 cc. and its acidity was between *N* and 2 *N* with sulfuric acid. Hydrochloric acid was unsatisfactory. A sharp drop of about 0.3 volt occurred when the iodate was all decomposed, as shown in Fig. 1. The iodine set free reacted slowly on further addition of titanium and an excess was required to drive the reaction to completion. Possibly the sharp rise in voltage at first shows the effect of hypo-iodous acid, the first fall the decomposition of all the iodate, and the final fall the completed reduction of the iodine. The

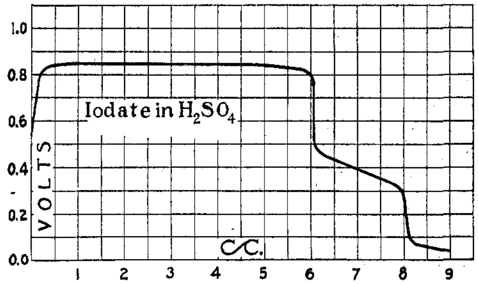

Fig. 1

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[1] Hendrixson and Verbeck, This Journal, **44**, 2382 (1922).