London Section.

Meeting held at Burlington House on Monday, February 2nd, 1914.

PROF. W. R. HODGKINSON IN THE CHAIR.

OXYGEN AND METALLIC ANTIMONY IN CRUDE ANTIMONY.

BY W. R. SCHOELLER, PH.D.

IN a previous paper read before this Section (this J., 1913, 260) I have shown that the percentage of sulphur in crude antimony was much lower than that corresponding to the formula Sb_2S_3 , and that the result of the complete analysis of crude disclosed a more or less considerable deficiency; this was ascribed to the presence of oxygen, and the assumption supported by the observation that crude, unlike stibnite, was partly dissolved by cold solutions of sodium bitartrate. The present investigation was undertaken with a view to obtaining more convincing evidence of the presence of oxygen.

I. *Analysis of the material.*—The material experimented upon (Hu-nan crude) was crushed to pass a 90-mesh and analysed like the previous samples. The figures show a shortage of over 3 per cent., with low sulphur and unusually high antimony content:—

	per cent.	
Antimony	73.56	
Sulphur	22.45	As, Zn: traces.
Iron	0.70	Cu, Pb, Ag not determined.
Insoluble	0.05	
	96.76	

II. *Determination of oxygen.*—Oxygen was next tested for by fusing the material in a current of hydrogen sulphide. Hydrogen reduces both antimony oxide and sulphide to metal, whereas hydrogen sulphide acts only upon the oxide, thus:— $\text{Sb}_2\text{O}_3 + 3\text{H}_2\text{S} = \text{Sb}_2\text{S}_3 + 3\text{H}_2\text{O}$. Crude antimony containing oxide would thus increase in weight, and give off water.

The sample was dried for two hours at 107°C . and weighed out into a bulb tube connected at one end with three calcium chloride tubes for drying the hydrogen sulphide, and at the other with a condenser and a calcium chloride tube for collecting the water. After the air had been displaced from the apparatus the crude was gently heated, when water soon began to condense. The heat was increased until the mass had fused. It was then left to cool under hydrogen sulphide which was displaced by air before weighing. In this way 3.18 per cent. of oxygen was found, which accounts for the deficiency as $96.76 + 3.18 = 99.94$. The residue showed an increase in weight of 3.53 per cent. and was found to consist of nearly pure sulphide: antimony 71.13 per cent.; sulphur 27.56 per cent.; iron and insoluble 0.73 per cent.; total 99.42 per cent. The presence of oxygen in Chinese crude is thus placed beyond doubt.

III. *Action of bitartrate.*—The original crude and the product obtained by fusion under hydrogen sulphide were tested as to their behaviour towards cold sodium bitartrate solution of the same strength as the one previously used. After 20 hours' digestion the following quantities of antimony were dissolved:—Original crude, 8.72 per cent.; fused sulphide, 0.89 per cent. The result of the replacement of oxygen by sulphur is the comparative insolubility of the fusion product.

IV. *Antimonious oxide is present in crude.*—The amount of oxygen found, viz., 3.18 per cent., is equivalent to 15.90 per cent. of antimony in the form of trioxide. That the lowest oxide is present in crude was proved by the following three tests in which the total antimony and that existing as trioxide were estimated in aliquot portions of solution, the former by precipitation with hydrogen sulphide, solution of the sulphide in sulphuric acid and titration with permanganate, the latter by addition of sodium bicarbonate and titration with iodine.

1. It was shown above (III.) that cold bitartrate solution dissolved 8.72 per cent. of antimony. The estimation of the antimonious oxide in the same solution gave 8.35 per cent. of metal.

2. An attempt was made to extract the whole of the oxide by boiling 5 grms. of crude with 100 c.c. of 7 per cent. tartaric acid solution for 45 minutes. The determination of the total and trivalent antimony in the filtrate gave: Total antimony, 10.69 per cent.; antimony as Sb_2O_3 , 10.81 per cent. The residue from this extraction was not pure sulphide, as it assayed 72.40 per cent. of antimony.

3. The preceding test was carried out on 90-mesh material. A sample was now ground down to extreme fineness, and 1.25 gm. boiled with 100 c.c. of 10 per cent. tartaric acid for 45 minutes. The filtrate contained 13.29 per cent. of antimony, against 12.88 per cent. determined by iodine titration.

The last experiment shows that at least four-fifths of the total oxygen is present as trioxide; whether the remaining fifth exists partly as pentoxide could not be ascertained, as the test for pentoxide fails when sulphide is also present. I think, however, it is safe to assume that practically the whole of the oxygen is combined with antimony in the form of trioxide, because an excess of oxygen is necessary for the formation of the pentoxide. The experiments further show that part of the oxide is easily soluble in the cold, while a small proportion remains insoluble even on boiling and after most thorough crushing. As a possible explanation for this behaviour I would suggest that the bulk of the oxide is present in the free state, either dissolved in, or intermixed with, the sulphide, while the remainder has combined with the sulphide to form an oxysulphide. I shall have an opportunity later on of referring again to this matter. (VI.)

V.—*Presence of metallic antimony in crude.*—By recasting the complete analysis, the composition of the sample of crude is represented by the following figures:—

Analysis.	Calculated composition.	Calculated increase after fusion under H_2S .
	per cent.	per cent.
Insol.	0.05	Insol. 0.05
Fe	0.70	Fe ₂ 1.10
S	22.45	Sb_2S_3 .... 77.17
O	3.18	Sb_2S_3 .... 22.27
Sb	73.50	Excess Sb 2.54
Total ..	99.94	104.14

Apparently 2.54 per cent. of antimony remains uncombined. If these figures are correct, the metal should remain undissolved when crude is treated with hydrochloric acid. This was verified by experiment, by extracting powdered crude repeatedly with hot strong hydrochloric acid. The residue was washed with water and alcohol, and dried at low temperature; it showed the characteristic light-grey colour of powdered regulus, easily distinguishable from the bluish tinge of antimony sulphide: 0.5 gm. was assayed for antimony, giving 97.17 per cent. of metal: this is conclusive proof of the presence of regulus in crude antimony. The separation of the metal from the sulphide was also accomplished by caustic alkali which dissolves the latter, as well as the oxide. It is no doubt due to the presence of metallic antimony in the crude that its increase in weight in the oxygen determination is 0.61 per cent. lower than the calculated increase (see table): for, while antimony oxide is easily converted into sulphide when heated in a current of hydrogen sulphide, the metal itself combines less readily under the same conditions. This is also borne out by the low sulphur content (27.56) of the fused product and its slight solubility in bitartrate solution which is known to have a strong solvent action on regulus. (Cf. my previous paper, *loc. cit.*)

VI. *Glass of antimony*.—A fragment of black glassy crust, sometimes found on the surface of ingots of crude, was also examined. The glass is soft and heavy, and on crushing yields a powder the colour of which is more violet than that of ferric oxide. The quantity at my disposal was not sufficient for a thorough investigation, and its composition as far as ascertained is given by the following figures: Soluble antimony 73.28 per cent.; antimony tetroxide and insoluble 1.23 per cent.; sulphur 16.18 per cent.; oxygen 6.32 per cent.; iron 1.35 per cent.; total 98.36 per cent. Part of the soluble antimony was found to be present in the metallic state, remaining as a grey residue insoluble in hydrochloric acid but soluble in *aqua regia*; the amount of metal appeared to be at least as large as that observed in crude. The colourless residue from the *aqua regia* treatment consisted chiefly of antimony tetroxide. The determination of oxygen was carried out as described for crude, the substance showing an increase in weight of 6.70 per cent. after fusion.

Judging from the behaviour of crude towards bitartrate solution and the high oxygen content of glass of antimony, one would expect the latter to be strongly attacked by that solvent, but the reverse was found to be the case: after 18 hours' contact in the cold, the dissolved antimony amounted to no more than 1.31 per cent.; this was present as trioxide. The oxysulphide which is the chief constituent of glass of antimony is thus insoluble in bitartrate, and this may account for the incomplete extraction of the oxide from crude, by assuming that the latter contains a subordinate quantity of oxysulphide. (IV.) Other tests bearing on this point could not be carried out for want of material.

VII. *Conclusions*.—The results of the above experiments prove that Chinese crude antimony contains a considerable proportion of antimonious oxide together with a less important amount of metallic antimony. These facts are in contradiction with the generally accepted notion that crude antimony obtained by liquation is pure unaltered sulphide, as no mention is made in the standard books on metallurgy and chemistry of a possible contamination with oxide due to absorption of oxygen by the molten sulphide. No doubt in an inert atmosphere the latter melts without undergoing decomposition, and a liquation process in which air is excluded will yield a sulphide free from oxide, but this is difficult to attain in practice. For this reason liquation in vertical tubes should give a purer product than in reverberatory furnaces. In the type of furnace used in China, the molten sulphide discharges continuously into a cavity which is only separated from the outside air by a loosely fitting cover, where the material remains in the liquid state until ladled into moulds two hours after the beginning of the operation. During this time absorption of oxygen takes place, which sometimes leads to the formation of a film or crust of glass of antimony on the surface of the crude. The liquation residue (which was described in my previous paper) is of course subject to oxidation like the crude itself.

It seems strange that the absorption of oxygen by, and consequent oxidation of, fused antimony sulphide should not be mentioned in modern technical literature, all the more so because the effect of the fusion was known long before the establishment of chemistry as an exact science. The iatro-chemists, with whom antimony compounds were great favourites on account of their vigorous physiological action, were well acquainted with the fact that stibnite undergoes a change on being fused, though they were unable to assign a cause to it. They taught that the natural sulphide, "on account of the *Regulus* being corrected by the Sulphur, is not only safe, but in many cases a medicine of great service; that by simple fusion, it acquires a degree of malignity; . . . that equal parts of Antimony (i.e., stibnite) and Nitre, melted together, yield a virulent mass."* In other words, the emetic properties become more pronounced as the solubility increases with the progressive replacement of sulphur by oxygen. Decoctions of crude antimony appear to have

been used as diaphoretics,* and the following experimenter shows that it is actually attacked by water: 1 gm. of 90-mesh material was boiled with 100 c.c. of distilled water for five minutes. The acidified filtrate treated with hydrogen sulphide gave a stable fluorescent solution of colloidal antimony sulphide. This was coagulated by adding salt and passing more gas through the boiling solution: 1.66 per cent. of soluble antimony was found.

The simultaneous presence of sulphide, oxide, and metal in crude seems difficult to explain if we accept the statement, found in most books, that sulphide and oxide of antimony, unlike the corresponding lead or copper compounds, are incapable of reacting upon one another with formation of metal and sulphur dioxide, but fuse together to a glass of oxysulphide. The fact that metallic antimony occurs in crude makes it more than probable that the reaction $\text{Sb}_2\text{S}_3 + 2\text{Sb}_2\text{O}_3 = 6\text{Sb} + 3\text{SO}_2$ takes place, though to a very limited extent. I have found at least one statement, reproduced in Bloxam's Chemistry,† to the effect that the fusing together of oxide and sulphide results in the formation of metal, though the reaction is represented as taking place between sulphide and tetroxide. As regards the formation of glass of antimony, this does not, apparently, take place when the relative amount of oxide falls below a certain minimum: for the ratio of oxide to sulphide in the glass of antimony is very nearly 1:4, whereas in the case of the crude under examination it is almost exactly 1:4, and this material retains the crystalline structure and physical properties of antimony sulphide, while unlike glass of antimony it gives up most of its oxide content to bitartrate or tartaric acid solution.

Within a few years of opening up her mineral resources, China has become the foremost producer of antimony and especially of crude. The latter has been shown to be a more complex product than was generally supposed, and this knowledge may be of practical interest. Thus the purchase and sale of crude is not done on a certificate of assay, on the assumption that the article is pure sulphide containing 70–71 per cent. of antimony. Not only does this percentage vary within wider limits, but it may also be found desirable to ascertain the amount of metallic antimony and oxide in the material. In the preparation of antimonious chloride and other salts from crude the presence of metal is objectionable because it remains insoluble in hydrochloric acid, whereas it is rather advantageous in smelting for regulus by the precipitation method. Finally, the accidental formation of metallic antimony in the liquation process raises an interesting question, namely, whether it would be possible to convert the sulphide into metal by applying bossemeyerizing in the production of regulus from sulphide ores.

In conclusion I desire to thank Messrs. G. T. Holloway and Co., Ltd., for their courtesy in permitting the publication of this investigation which was carried out in their laboratory.

THE ESTIMATION OF ZINC IN COINAGE BRONZE BY VOLATILISATION.

BY T. K. ROSE, A.R.S.M., D.S.C.,
Chemist and Assayer of the Mint.

This is not a new method, but a very old one, the origin of which has been lost. A similar method for zinc ores is referred to by Percy‡ as having been used "formerly" and he states that the process is "still" (i.e., in 1861) "occasionally resorted to by some assayers." Percy gives the reasons for regarding the method as untrustworthy in the case of ores. The method was unknown to Agricola (1556), Ereker and Sir John Petty (1686), and is not mentioned in Thenard's Chemical Analysis, 1818, or in Vauquelin's Manuel de l'Essayeur, 1836. It is described by Makins,§ who says that "at the Mint, the bronze, mixed with exactly twice its weight of pure tin, is enclosed in a porous carbon pot, luted up in a crucible and strongly heated in an assay muffle for eight hours." According to tradition at the Mint the charge was embedded in

* The Chemical Works of Caspar Neumann, M.D. By William Lewis. London, 1759, p. 131.

* "La décoction de l'antimoine cru est sudorifique. Mais si l'on y mêle quelque drogue acide, elle sera vomitive." Dr. N. Lemery, Traité Universel des Drogues simples, Paris, 1698, p. 46.

† Chemistry, inorganic and organic. G. L. Bloxam, 10th edition, 1913, p. 470.

‡ Metallurgy: Fuel, Copper, Zinc, &c., 1861, p. 656.

§ Manual of Metallurgy, 2nd Edn., 1873, p. 524.