XXXIII.—CONTRIBUTIONS FROM THE LABORATORY OF
GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XVIII. *On the Sulphates of Antimony.*

By R. H. ADIE, B.A., Scholar of Trinity College.

1. THE compounds of antimonious oxide and sulphuric acid do not appear to have received a very complete investigation, judging by the published results. Hence I decided to examine these compounds, as I had previously done in the case of arsenious oxide and sulphuric acid (*Trans.*, **55**, 1889, 157).

2. In 1871, Schultz-Sellach (*Ber.*, **4**, 109) described the preparation of the compound $\text{Sb}_2\text{O}_3 \cdot 4\text{SO}_3$ from antimonious oxide and fuming sulphuric acid; his analysis gave Sb_2O_3 , 47·44 per cent., and SO_3 , 53·08 per cent. In a previous paper (*Ber.*, **4**, 13), he described the preparation of the normal sulphate $\text{Sb}_2(\text{SO}_4)_3$ by dissolving Sb_2O_3 in tolerably concentrated sulphuric acid. Basic sulphates have also been described, to which simple formulæ have been assigned, as $\text{Sb}_4\text{O}_5(\text{SO}_4)$, by Péligot.

3. As in the case of arsenious oxide, I started with fuming acid, then tried concentrated acid and sulphuric anhydride, and, finally, dilute acids and the action of solvents.

4. *Sulphuric Anhydride*.— Sb_2O_3 when dropped into liquid SO_3 , formed hard flakes, insoluble in excess of SO_3 , even when heated in a sealed tube at 180° . The flakes agglomerated on heating, and then the cake formed was freed from adhering SO_3 by tilting the tube and keeping the end containing the compound warm until the SO_3 solidified.

Specimens prepared as above by heating to different temperatures gave on analysis :—

	I. 120° .	II. 120° .	III. 160° .	IV. 180° .
SO_3	55.87	61.55	73.55	74.56
Calculated for				
$\text{Sb}_2\text{O}_3, 8\text{SO}_3$.	$\text{Sb}_2\text{O}_3, 9\text{SO}_3$.		$\text{Sb}_2\text{O}_3, 10\text{SO}_3$.	
68.98	71.45		73.52	

The results show that the formation of the compound of Sb_2O_3 with the highest proportion of SO_3 requires a temperature of about 160° . The compound formed at that temperature would seem to have the formula $\text{Sb}_2\text{O}_3, 9\text{SO}_3$, but as the corresponding arsenic compound can be freed completely from excess of SO_3 , and is probably $\text{As}_2\text{O}_3, 8\text{SO}_3$, it would perhaps be best to assume that the antimony compound possesses the same formula, viz., $\text{Sb}_2\text{O}_3, 8\text{SO}_3$. Considering the difference of density of Sb_2O_3 and of SO_3 , the adhering sulphuric anhydride would probably not exceed 2–3 per cent.

It is decomposed by water with formation of a basic salt.

5. *Fuming Sulphuric Acid*.—The acid used, as in the case of arsenic, contained about 88 per cent. of SO_3 , and was approximately $2\text{H}_2\text{SO}_4, \text{SO}_3$.

The oxide formed, as in § 4, a hard cake which is not readily soluble. Its solubility, though not so great as the corresponding arsenic sulphate, increased largely with rise in temperature. The product crystallised in fine needles, which, on recrystallisation, were practically pure $\text{Sb}_2\text{O}_3, 4\text{SO}_3$.

	1st crystallisation.	2nd crystallisation.	Calculated for $\text{Sb}_2\text{O}_3, 4\text{SO}_3$.
SO_3	50.93	53.70	52.63

The mother liquor only contained a small quantity of the sulphate. $\text{Sb}_2\text{O}_3, 4\text{SO}_3$ decomposes on exposure to the air and by the action of water.

6. *Concentrated Sulphuric Acid containing 98 per cent. H_2SO_4* .— Sb_2O_3 is very soluble in boiling sulphuric acid. On cooling, a large quantity of crystals separate out, which, on recrystallisation, are pure $\text{Sb}_2(\text{SO}_4)_3$.

	1st crystallisation.	2nd crystallisation.	Calculated for $\text{Sb}_2(\text{SO}_4)_3$.
SO_3	43·91	46·98	45·45

$\text{Sb}_2(\text{SO}_4)_3$ decomposes quickly on exposure to the air. The results of its decomposition by water, &c., are detailed in § 8.

7. *Dilute Sulphuric Acids*.—(i.) I have found the strength of acid limiting the formation and existence of $\text{Sb}_2(\text{SO}_4)_3$ in solution.

From $9\text{H}_2\text{SO}_4, 6\text{H}_2\text{O}$ the product contained 47·40 p. c. SO_3 .

„ $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ „ „ 50·65 „

These results show that the normal or trisulphate is formed from sulphuric acid of concentrations between the limits H_2SO_4 and $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ inclusive.

(ii.) From $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ a new compound was obtained, namely, the basic sulphate $\text{Sb}_2\text{O}_3, 2\text{SO}_3, \text{H}_2\text{O}$ or $\text{Sb}(\text{OH})\text{SO}_4$. It may be crystallised by slow cooling, and gave the following results:—

	I.	II.	III.	IV.	Calculated for $\text{Sb}_2\text{O}_3, 2\text{SO}_3, \text{H}_2\text{O}$.
Sb_2O_3 ..	—	—	—	62·16	61·7
SO_3 ...	35·75	35·54	34·64	—	34·3
H_2O ...	—	—	—	3·99	4·0

This sulphate gives off its water at 100° , but suffers no further decomposition until above 250° .

(iii.) From $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$, the compound separates out in small quantity as a fine powder, which it is difficult to free from adhering acid. At last I obtained one crystalline preparation by allowing the sulphate to remain in the mother liquor for about a month at 20° , (about) and the crystals thus obtained determined the deposition from the cooling solution of a crystalline sulphate, $\text{Sb}_2\text{O}_3, 2\text{SO}_3, 3\text{H}_2\text{O}$, or $\text{Sb}(\text{OH})\text{SO}_4, \text{H}_2\text{O}$.

Analyses:—

	I.	II.	III.	IV.	Calculated for.	
					$\text{Sb}_2\text{O}_3, 2\text{SO}_3, 3\text{Aq.}$	$\text{Sb}_2\text{O}_3, 2\text{SO}_3, 4\text{Aq.}$
Sb_2O_3 ..	—	54·15	55·35	—	57·37	55·39
SO_3 ...	31·88	30·68	—	—	31·87	30·69
H_2O ...	—	—	11·19	10·24	10·76	13·93

The crystals are scarcely decomposed by cold water, slowly by boiling water, and are not rapidly dissolved by boiling dilute hydrochloric acid. They are decomposed at 100° , at which temperature they lose all their water. The justification of the arrangement of my formula is found in the existence of the compound $\text{Sb}(\text{OH})\text{SO}_4$ in (ii).

Antimonious oxide is so little soluble in acids more dilute than $\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$ that I next proceeded to the investigation of—

8. *The Action of Solvents on Antimony Sulphate.*—Péligot states that by the decomposition of $\text{Sb}_2\text{O}_3, 4\text{SO}_3$ by cold water the basic salt $\text{Sb}_4\text{O}_5(\text{SO}_4)$ is formed. I repeated this to see whether he might have passed over any loosely combined water, using the trisulphate instead of the tetrasulphate.

Dry $\text{Sb}_2(\text{SO}_4)_3$ was decomposed and washed till the washings were free from sulphuric acid.

(i.) *By Water at 100°.*—The compound, that is, the basic sulphate obtained by this method, is approximately $7\text{Sb}_2\text{O}_3, 2\text{SO}_3, 3\text{Aq}$; this represents the limit of the decomposition of the sulphate by water.

Results of analysis :—

	I.	II.	III.	Calculated for $7\text{Sb}_2\text{O}_3, 2\text{SO}_3, 3\text{Aq}$.
SO_3	7.03	6.50	—	7.05
H_2O	5.16	4.57	33.59	4.73

I and II were dried by standing on a porous plate in air, I for five weeks, II for three days; III was pressed between porous plates till dry (see § 9).

(ii.) *By Cold Water.*—The basic salt, dried at 100°, is $2\text{Sb}_2\text{O}_3, \text{SO}_3$, as found by Péligot.

	I.	II.	III.	IV.	V.	VI.	Calculated for $2\text{Sb}_2\text{O}_3, \text{SO}_3$.
SO_3 ..	11.62	11.47	13.23	10.18	11.30	11.58	12.19

I to IV were decomposed by water at about 18°, V and VI by water at about 6°.

The water was estimated separately in preparations dried in various ways. In the following table the second column contains the results for the sulphate decomposed at 18°, and the third for that at 6°. In each case I, II, and II were allowed to stand in air on a porous plate in a fine state of division, I (at 18° only) for five weeks, and II and III for about three days; IV was dried by pressure between dry porous plates, and V by pressure between filter-papers.

Percentages of water only :—

	18°.	6°.	Calculated for.	
I	10.76	4.75	$2\text{Sb}_2\text{O}_3, \text{SO}_3, 2\text{Aq}$	5.20
II	7.31	5.58	„ 3Aq	7.30
III	10.48	7.21	„ 4Aq	9.88
IV	27.85	32.37	„ 5Aq	12.05
V	38.55	—	„ 10Aq	21.50
			„ 16Aq	30.51

(iii.) *By Absolute Alcohol* (18°).—The basic salt, when dried at 100° , only lost 2·2 per cent., and is $\text{Sb}_2\text{O}_3, 2\text{SO}_3$.

Analysis gave—

SO_3	35·11	Calculated for $\text{Sb}_2\text{O}_3, 2\text{SO}_3$.
		35·71

9. From these tables it is seen that the removal of the SO_3 -groups from the sulphate by means of water is accompanied by the substitution of a considerable amount of water therefor. When the product is dried rapidly by pressure between porous plates, the quantity of water retained, in all cases, is about 30 per cent., which corresponds roughly to $2\text{Sb}_2\text{O}_3, \text{SO}_3, 16\text{Aq.}$ This substance is rather akin to the cryohydrates than to the ordinary hydrates, since it parts with its attached water to the air at about 15 — 18° ; even after prolonged drying in air, the product of the action of cold water retains about 10 per cent. of water, and is thus approximately $2\text{Sb}_2\text{O}_3, \text{SO}_3, 4\text{Aq.}$, while that of the action of ice-cold and hot water respectively only retains about 5 per cent. of water in each case, and is thus approximately $2\text{Sb}_2\text{O}_3, \text{SO}_3, 2\text{Aq.}$

We seem to have here some evidence for the existence of complex hydrates, such as may be supposed to exist in solution.

10. I have here arranged the complete series of antimony sulphates now described in a column parallel with the arsenic sulphates prepared from the same acids.

SO_3 .	$\text{As}_2\text{O}_3, 8\text{SO}_3$.	$\text{Sb}_2\text{O}_3, 8\text{SO}_3$.
$2\text{H}_2\text{SO}_4, \text{SO}_3$.	$\text{As}_2\text{O}_3, 4\text{SO}_3$.	$\text{Sb}_2\text{O}_3, 4\text{SO}_3$.
H_2SO_4 .	$\text{As}_2\text{O}_3, 2\text{SO}_3$ }	$\text{Sb}_2\text{O}_3, 3\text{SO}_3$, or $\text{Sb}_2(\text{SO}_4)_3$.
$9\text{H}_2\text{SO}_4, 3\text{H}_2\text{O}$ to $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$.	$\text{As}_2\text{O}_3, \text{SO}_3$ }	
$\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$.	—	$\text{Sb}_2\text{O}_3, 2\text{SO}_3, \text{H}_2\text{O}$, or $\text{Sb}(\text{OH})\text{SO}_4$.
$\text{H}_2\text{SO}_4, 4\text{H}_2\text{O}$.	—	$\text{Sb}_2\text{O}_3, 2\text{SO}_3, 3\text{H}_2\text{O}$, or $\text{Sb}(\text{OH})\text{SO}_4, \text{H}_2\text{O}$.
Action on sulphate of—		
Alcohol.	—	$\text{Sb}_2\text{O}_3, 2\text{SO}_3$, or $\text{SbO}(\text{SO}_4)_2$.
Cold water.	As_2O_3 .	$2\text{Sb}_2\text{O}_3, \text{SO}_3, x\text{Aq.}$
Hot water.	—	$7\text{Sb}_2\text{O}_3, 2\text{SO}_3, y\text{Aq.}$

Where $x = 4$ to 16 and $y = 2$ to 16 .

On comparing the two series of compounds, it appears that:—

(i.) With H_2SO_4 and weaker acids, Sb_2O_3 forms a different order of sulphates from As_2O_3 , while it resembles it in forming acid sulphates when subjected to the action of stronger acids. The characteristic group salt $\text{Sb}_2(\text{SO}_4)_3$, which is formed by the former, is replaced by the basic $\text{As}_2\text{O}(\text{SO}_4)_2$ in the latter case. The limits of existence, both as regards dilution and temperature, are much narrower for the arsenic than for the antimony salt. The practically

complete formation of $\text{Sb}_2(\text{SO}_4)_3$ in one crystallisation also contrasts with the formation of $\text{As}_2\text{O}(\text{SO}_4)_2$ only by repeated crystallisation.

(ii.) Arsenious oxide does not form any basic sulphates containing water, whilst the oxide of the more metallic antimony does form hydrated sulphates in acids weaker than $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$. This acid is the limit of existence of $\text{Sb}_2(\text{SO}_4)_3$ in solution and of any arsenic sulphate whatever.

(iii.) In contrast to the case of the arsenic compounds, one cannot remove all the SO_3 from the antimony sulphates by water. The stability of the latter in dilute acids far exceeds that of the former.

In conclusion, I have great pleasure in thanking Mr. Pattison Muir for the use of his laboratory during this work, and for his kind attention and assistance during its progress.

I hope to be able to communicate the results of some work on the compounds of phosphorus and sulphur trioxide in a short time.