150. *The Reputed Arsenic Subsulphide.*

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The reputed compound As_3S is shown not to exist.

Brunck (*Annalen*, 1905, **336**, 281) noted that an acidified arsenite solution treated with sodium hydrosulphite (dithionite) gave an amorphous brown precipitate of arsenic, the reaction also occurring, though more slowly, in neutral but not in alkaline solution.

Farmer and Firth (*J.*, 1926, 119; 1927, 2019) reported that the reaction product was arsenic subsulphide, As_3S, a compound which had been claimed to have been formed by an entirely different method by Scott (*J.*, 1900, 651). The existence of this compound appears not to have been generally accepted (cf. Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, London, 1929, Vol. IX, p. 265).

The present author, as a result of roughly quantitative work, agree with Farmer and Firth's reports that, in their reaction under acid conditions, arsenite gives a precipitate which is richer in arsenic than does arsenate, and that the arsenic content of the precipitates tends to decrease with rising temperature and increasing hydrosulphite concentration.

Detailed investigation showed that precipitates obtained by Farmer and Firth's or by Scott's method consisted of mixtures of elementary sulphur and arsenic (and traces of sulphides of arsenic), which can be separated by thorough extraction. The results claimed by these authors are ascribed to incomplete extraction. The compound As_3S does not exist.

Experimental.—Farmer and Firth's claims. Precipitates were prepared from sodium arsenite (10 g.), sodium dithionite (50 g.), water (250 ml.), and (i) 2 ml. or (ii) 5 ml. of 36% hydrochloric acid. Precipitates (iii) and (iv) were prepared from the same quantities of reagents but with sodium arsenate in place of sodium arsenite. In all cases reaction was allowed to occur at 30°. The amount of acid used caused no visible difference in the colour of the precipitates, but arsenate gave chocolate-brown and arsenite black products. The precipitates were washed with water, then with alcohol and ether, and placed in a vacuum-desiccator.

All gave a negligible amount of ash on ignition. Fusion with sodium carbonate, nitrate, and peroxide resulted in some loss of arsenic, so wet oxidation was used, with a double evaporation with nitric acid; the residue, dissolved in water, was made up to a known volume and aliquot parts were used for determination of sulphur (as barium sulphate) and arsenic (as magnesium pyroarsenate). The precipitates derived from arsenite dissolved in nitric acid rather violently, but those from arsenate much more quietly.

Ppt. no.	Original ppt.		After $(NH_4)_2CO_3$ extraction.				After CS_2 extraction.			
			1st.		2nd.		1st.		2nd.	
	As, %.	S, %.	As, %.	S, %.	As, %.	S, %.	As, %.	S, %.	As, %.	S, %.
i	92·8	7·2	96·3	3·7	96·8	3·2	98·7	1·2	99·4	0·5
ii	92·3	7·7	97·0	3·0	97·6	2·4	98·9	1·1	99·2	0·8
iii	80·9	19·1	89·8	11·5	89·8	10·2	97·1	2·8	99·0	0·9
iv	80·1	19·9	90·4	9·6	94·5	5·4	98·3	1·5	99·0	1·1

Further samples of the precipitates were extracted twice with (*a*) boiling ammonium carbonate solution or (*b*) carbon disulphide, the residues being analysed after each extraction, with the results shown in the table. It is clear from this that, although the composition varies according to the acidity and the salt used, there is no evidence that they are of the composition As_3S; thorough extraction with ammonium carbonate and carbon disulphide removes the impurities and leaves virtually pure arsenic.

Acidification of the ammonium carbonate extracts gave pure yellow precipitates, analyses of which, though varying slightly, agree fairly closely with those for As_2S_3. Evaporation of the carbon disulphide extracts yielded minute crystals which, on microscopical examination, appeared to be solely rhombic sulphur.

Scott's claims. Scott's preparation was repeated exactly, 200 g. of sodium arsenate, 3·5 l. of water, and 150 ml. of phosphorus trichloride being used. The precipitate was washed by decantation with water and alcohol, air-dried, and analysed. Four experiments yielded arsenic contents of 97·3, 96·4, 98·2, and 95·6%. The sulphur content was in all cases negligible. The precipitates were washed with dilute aqueous ammonia, then digested with concentrated ammonia solution and filtered. In no instance was a precipitate formed when the filtrates were kept, and saturation with hydrogen sulphide after acidification gave only minute amounts of bright yellow arsenic sulphide (As_2S_5; analysed). The black precipitates were suspended in concentrated ammonia solution which was then saturated with hydrogen sulphide and again filtered after 2 hours' digestion. The filtrates gave no precipitate on storage but yielded minute amounts of arsenic sulphide on acidification. At this stage the washed and alcohol-dried precipitates were again analysed, with the following results :

Ppt. no.	1	2	3	4
As, %	87·2	86·4	90·1	85·3
S, %	12·8	13·6	9·9	14·7

It will be seen that three of these four precipitates are very close to the composition As 87·7, S 12·3% calculated for As_3S.

The precipitates were next digested with hot ammonium carbonate solution for an hour, then with carbon disulphide in a Soxhlet apparatus, and the analyses repeated, with the following results :

Ppt. no.	1	2	3	4
As, %	88·4	87·9	90·8	88·1
S, %	11·6	12·1	9·1	11·9

After further extraction with carbon disulphide for 20 hours, the compositions were :

Ppt. no.	1	2	3	4
As, %	91·6	90·3	92·1	89·7
S, %	8·4	9·7	7·9	10·3

No further extractions were carried out, as it was apparent that very long solvent treatment would be necessary for complete removal of all the sulphur. It seems, however, that as in the case of Farmer and Firth's work, Scott's results can be attributed to insufficient solvent extraction, although the precipitates made by Scott's method are much more difficult to purify.

The filtrate from the black precipitates, when kept for a long time, continue to give precipitates of arsenic for several days, but after about the sixth day the precipitate was reddish and smelled strongly of phosphine or arsine. This is perhaps an adsorption phenomenon and is receiving further investigation.

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