CXI.—*An Examination of a Method of Estimating Iron and Sulphur in Sulphides of Iron.*

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IT has been stated that neutral aqueous copper sulphate solution dissolves the whole of the iron from iron sulphides (Wright, J., 1883, **43**, 162), and an analytical procedure based upon this statement has been described (Weyman, *Gas J.*, 1920, 310) whereby the unweighed iron sulphide is treated with warm aqueous copper sulphate, iron is determined in the filtrate, and sulphur is estimated indirectly in the residue by dissolving it in nitric acid and precipitating copper electrolytically. As such a method appeared to be of value in connexion with another research (see following paper), it was re-examined because there appeared to be two possible sources of error: (1) it is always difficult to secure complete conversion of one solid into another by the above means, and (2) it is not impossible that free hydrogen sulphide might exist in presence of copper sulphate.

Moist ferrous sulphide, prepared by precipitating slightly acid aqueous ferrous sulphate with a freshly made solution of ammonium monosulphide, and giving on analysis a ratio Fe : S = 55·8 : 32·1, was treated in a series of experiments with 30 c.c. of cold 10% aqueous copper sulphate solution with or without the addition of sulphuric acid. The mixture was heated slowly to 100° in a water-bath and digested at that temperature for 2 hours. The residual solid was then filtered off and washed, and its copper was determined electrolytically and iron gravimetrically, with the results shown in the table.

No.	H_2SO_4 (g. per 100 c.c. of soln.).	FeS taken, g.	% Total S converted into CuS.	% Total S unconverted into CuS.	% Total S unaccounted for (by diff.).
1	0	0·1370	86·96	16·87	− 3·83
2	0	0·1406	80·63	19·96	− 0·59
3	0·92	0·1875	73·41	4·64	21·95
4	0·92	0·1298	69·53	7·12	23·35
5	1·84	0·0825	84·37	4·53	11·10
6	1·84	0·2132	69·36	7·07	23·57
7	3·68	0·2320	69·63	8·73	21·64
8	3·68	0·2623	65·67	3·02	31·31

It will be seen that up to 85% of the sulphur present forms cupric sulphide, but that the conversion is greatly retarded by acid even at relatively low concentrations. The sulphur unaccounted for is small at low acid concentrations (and even negative in the absence of acid, probably owing to the formation of insoluble basic copper salts), but increases with increasing acid concentration to about 10—30%. Addition of ammonia to the acid filtrate produced a considerable black precipitate, whence it appears that the missing sulphur was probably present in solution as hydrogen sulphide through displacement to the left of the equilibrium : $H_2S + CuSO_4 \rightleftharpoons CuS + H_2SO_4$. The evolution of hydrogen sulphide was not detected during the course of any of these experiments.

A further series of experiments on fused ferrous sulphide, in the form of a fine powder passing a 200-mesh sieve, showed that in the absence of free acid there was very little reaction between the sulphide and the copper sulphate solution, and that with varying concentrations of acid results both low in sulphur and discordant amongst themselves were obtained.

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