CCLXI.—*The Reaction between Ferric Oxide and Hydrogen Sulphide at Temperatures between* 120° *and* 830°.

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THE most exhaustive study recorded hitherto of the reaction between ferric oxide and hydrogen sulphide is that of Pearson and Robinson (J., 1928, 814), in whose paper the relevant literature is discussed. Their work, restricted to the reaction at 100°, led them to conclude that the principal products were FeS, 9·76; Fe_2S_3, 69·4; and FeS_2, 7·83%, and they suggested that the primary product was ferric sulphide which, decomposing in part, gave equimolecular proportions of mono- and di-sulphide. The present investigation extends the inquiry and shows that the course of the reaction is profoundly modified at higher temperatures.

EXPERIMENTAL.

Ferric hydroxide, precipitated from ferric chloride in dilute hydrochloric acid by pure ammonium hydroxide, and washed first by decantation with 5% ammonium hydroxide until the supernatant liquid was free from chloride and subsequently in a Büchner funnel with distilled water, was drained and dried to constant weight at 50° (about 20 days) in a current of dry, carbon dioxide-free air. The material when sieved (150—200 mesh) was stored in stoppered bottles in a desiccator, but nevertheless absorbed moisture, and was therefore analysed frequently until it had attained constant composition (Found: Fe_2O_3, 87·00; H_2O, by diff., 13·00. Calc. for $3Fe_2O_3,4H_2O$: Fe_2O_3, 86·92; H_2O, 13·08%).

For the study of the reaction between 100° and 250°, hydrogen and hydrogen sulphide from two Kipp's generators were brought together, after thorough washing and drying, by means of a Y-piece carrying taps, and thence passed to a train of four tap-stoppered U-tubes. The first, third, and fourth of these were filled with alternate layers of glass-wool and phosphoric oxide, whilst the second acted as a reaction tube and held the ferric oxide, being maintained at the required temperature by immersion, for three-quarters of its height, in an oil-bath.

The experiments were carried out as follows: The four U-tubes were thoroughly swept out with hydrogen and then the second and third were weighed. The second was charged with approximately 1 g. of ferric oxide, rinsed with hydrogen, and again weighed. After reassembly, hydrogen was passed through the four tubes for ½ hour, and then the reaction tube was heated to the required temperature, and hydrogen sulphide passed at approximately one bubble a second for 3—5 hours (3 hours was subsequently proved to be adequate). Hydrogen then replaced the hydrogen sulphide for $\frac{1}{2}$ hour, during which heating of the reaction tube was discontinued to minimise possible reduction. The combined gain in weight of the second and third tubes gave the total weight of hydrogen sulphide absorbed.

For purposes of analysis, the contents of the reaction tube were wetted with 10% hydrochloric acid (air being strictly excluded meanwhile), washed into a beaker, and boiled with excess of the same acid until hydrogen sulphide ceased to be evolved. The operation was designed to dissolve ferrous sulphide, ferric sulphide, and unaltered ferric oxide, liberating sulphur equivalent to the ferric sulphide and leaving the disulphide untouched. The residue was extracted by washing with alcohol, ether, and finally with repeated small quantities of pure carbon disulphide, and the combined washings were evaporated for the estimation of soluble sulphur. This sulphur was regarded as a measure of the ferric sulphide in the preparation, a number of separate experiments having shown that, between 100° and 400°, only a trace of sulphur was extractable from it, before treatment with acid.

The residue, after removal of free sulphur, was ignited to ferric oxide and taken as a measure of the disulphide present; a number of complete analyses showed that it had the composition of iron disulphide, and it was also observed that, when left exposed to the air for some days, it swelled up considerably and then consisted of ferrous and ferric sulphates together with free sulphur.

The deductions for the analytical figures were based on the following considerations. The total combined sulphur was known from the weight of hydrogen sulphide absorbed, the sulphur in excess of that required for formation of ferric sulphide and disulphide existed as ferrous sulphide, and finally, the difference between the amount of iron in the three sulphides already found and the total iron, calculated from the weight of hydrated ferric oxide used, was a measure of the unaltered ferric oxide in the product.

For the reaction above 250°, the reaction tube was replaced by a clear silica vessel consisting of an elongated bulb, of approximately 20 c.c. capacity, blown upon the end of a tube 10 cm. long and 1·5 cm. in diameter. This tube was closed by a tap-stopper which either sealed the vessel or, when turned, admitted gas to the bottom of the bulb by way of an internal axial tube attached to the stopper. The bulb was enclosed in a small electric resistance furnace whose temperature, controlled by a rheostat, was measured by means of a thermocouple. The vessel was maintained in a horizontal position to prevent the return of moisture condensing around the stopper. At temperatures above 500°, considerable free sulphur was deposited in the cool portion of the vessel, and thus the gain in weight was without specific significance. Therefore, in the analysis of this product it was necessary to assume that the percentage of unaltered ferric oxide was the same as that found for lower temperatures—an assumption which was subsequently justified by another method of analysis. Apart from this the procedure was as before.

Discussion of Results.

Before discussing the results, it must be emphasised that individual experiments, particularly at lower temperatures, gave results so divergent that only the means of a number of analyses (as recorded in the table) had definite significance. Even so, these means are probably subject to an error of several units % in some cases. This inconsistency had two causes : (1) The reaction involved the conversion of one solid to another, with the consequent marked tendency for the product to coat the original material and prevent free access of the gas; and (2) it was highly exothermic, and the actual temperature of the materials was therefore higher, probably to a variable extent, than that of the oil-bath or furnace. Discrepancies from this cause would produce considerable variations in the product at 100—200° and at 500—600°, where its composition changes rapidly with temperature.

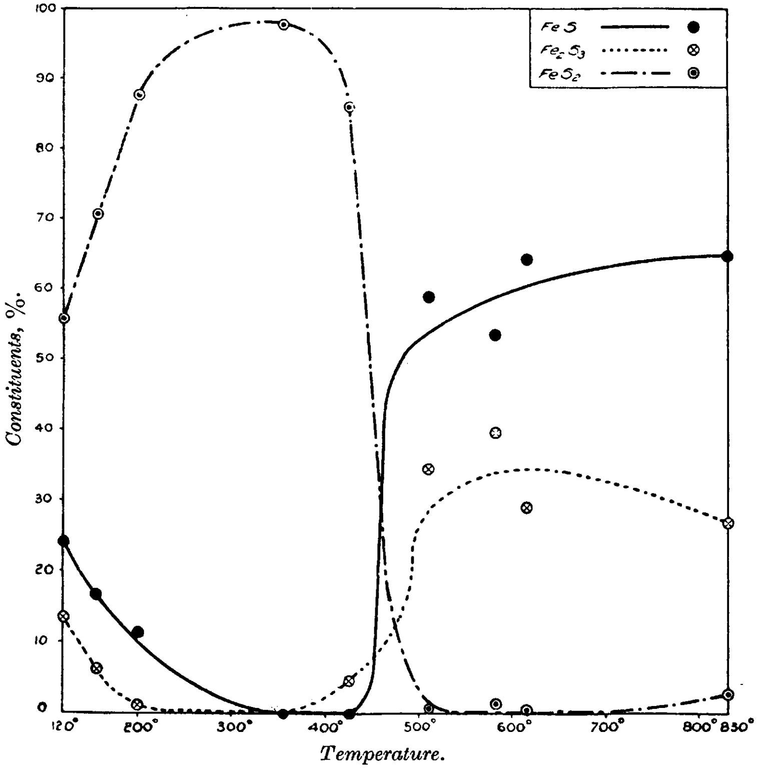
Mean Composition of Product of the Reaction between Ferric Oxide and Hydrogen Sulphide.

Temp.	Unaltered Fe_2O_3, %.	FeS, %.	Fe_2S_3, %.	FeS_2, %.
120°	6·74	24·00	13·47	55·79
155	6·54	16·59	6·23	70·64
200	0·00	11·23	1·10	87·67
355	2·49	0·00	0·00	97·51
425	9·43	0·00	4·73	85·84
510	6·05	58·79	34·26	0·90
582	5·98	53·26	39·57	1·19
616	6·10	64·09	28·98	0·83
830	6·08	64·58	26·84	2·50

A consideration of the results recorded in the table and plotted in Fig. 1 (in which, however, unchanged ferric oxide is not recorded) reveals that between 120° and 450° iron disulphide is the main product of the reaction, and that it becomes the only product in the region of 300°, being then a dark yellow powder of metallic appearance strongly resembling iron pyrites.

Between 400° and 500° the course of the reaction undergoes a profound change, for, whereas at 400° the product was almost entirely insoluble in 10% hydrochloric acid (*i.e.*, it consisted of disulphide), at about 500° it was almost completely soluble, and free sulphur appeared in the reaction vessel. The analysis of the product would appear to indicate that above 500° iron disulphide is replaced by a material which behaves like a mixture of ferrous and ferric sulphide. The formation of iron disulphide below 500° is most simply accounted for by the reduction of hydrogen sulphide thus: $Fe_2O_3 + 4H_2S \longrightarrow 2FeS_2 + 3H_2O + H_2$; this assumption

FIG. 1.



throws into error the method of calculating the total sulphur in the product (and thence the ferrous sulphide and unaltered ferric oxide), but not sufficiently to obscure the general trend of the reaction. The almost entire absence of free sulphur in the product formed at lower temperatures is noteworthy in view of the 2—3% of free sulphur invariably obtained by Pearson and Robinson at 100°. This is possibly due to the differences in drying the hydrated oxide; the material for the former work, having been dried at 100° and more completely dehydrated, may have retained more adsorbed oxygen. It is significant that the appearance of free sulphur in the reaction tube at 500° corresponds to the disappearance of iron disulphide.

Conclusion.—A consideration of the present work and of that of Pearson and Robinson (*loc. cit.*) indicates that the reaction between hydrogen sulphide and hydrated ferric oxide varies considerably with temperature. At and below 100°, the primary product appears to be ferric sulphide which partially decomposes to ferrous sulphide and iron disulphide, thus :

$$\text{(i) } Fe_2O_3 + 3H_2S \longrightarrow Fe_2S_3 + 3H_2O\,; \quad \text{(ii) } Fe_2S_3 \longrightarrow FeS + FeS_2.$$

Above 100°, these reactions give place more and more to the direct production of iron disulphide until, in the region of 300°, the only reaction concerned is

$$\text{(iii) } Fe_2O_3 + 4H_2S \longrightarrow 2FeS_2 + 3H_2O + H_2.$$

Between 400° and 500°, however, iron disulphide gives place to a product which is soluble in hydrochloric acid with liberation of sulphur. This material was regarded for purposes of calculation as a mixture of ferrous and ferric sulphides, although the reappearance of the latter as a product of the reaction is very improbable, and it is suggested that we have here some evidence of ferroso-ferric sulphide, Fe_3S_4.

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