CXII.—*The Reaction between Monohydrated Ferric Oxide and Hydrogen Sulphide at* 100°.

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THERE exists a considerable literature on the production of ferric sulphide by wet methods and on the use of oxides of iron and other metals for purifying coal gas, but little work has been done on the simple reaction concerned. As it has nowhere been summarised, the following brief résumé is given.

The earlier workers found that the product of the reaction of

hydrogen sulphide on hydrated ferric oxide contained more sulphur than does ferric sulphide (Deiche, *J. Gasbel.*, 1868, 106; Cox, *ibid.*, 1869, 584; Brescius, *ibid.*, 1869, 62), its exact nature being uncertain; Wright (J., 1883, **43**, 156) regarded it as a mixture of ferrous and ferric sulphides with free sulphur; Gedel (*J. Gasbel.*, 1905, **48**, 400, 432) reported that in alkaline conditions it was wholly ferric sulphide, whilst in acid conditions it was a mixture of the mono- and di-sulphides with free sulphur; and Allen, Crenshaw, Johnston, and Larsen (*Z. angew. Chem.*, 1912, **76**, 215) found it to be a mixture of ferrous sulphide and sulphur, the former being completely soluble in cold dilute hydrochloric acid after the sulphur had been extracted with ammonium polysulphide. Using a suspension of ferric hydroxide in water and excluding air, Mecklenburg and Rodt (*Z. anorg. Chem.*, 1918, **102**, 130) identified the dried product as ferric sulphide, which was pyrophoric if suddenly exposed to air but could be stabilised by treatment with carbon dioxide and then gained weight slowly in air, rather by absorption of moisture than by oxidation. After this treatment the material yielded a considerable amount of sulphur on extraction with carbon disulphide, and 31% of the residue was insoluble in dilute hydrochloric acid, whereas the original product contained but 2% of extractable sulphur and was wholly decomposed by acid, yielding $2FeCl_2 + 2H_2S + S$. Most of these workers agree in finding about 2% of free sulphur in the product.

The reactivity of ferric hydroxide towards hydrogen sulphide varies with the temperature (between 100° and 800°) at which the hydroxide has been dried (Weyman, *J. Soc. Chem. Ind.*, 1918, **37**, 333T), and this variation has been explained in terms of the difference in molecular state (Nicolardot, *Ann. Chim. Phys.*, 1905, **6**, 334).

An attempt has been made (Rodt, *Z. angew. Chem.*, 1916, **92**, 422) to explain these varying results by (i) the ready conversion of moist ferric sulphide to oxide and free sulphur by air; (ii) the change of ferric sulphide into a mixture of ferrous sulphide and iron disulphide on standing; (iii) the possible formation of water-soluble colloidal sulphur when ferric sulphide is dissolved in dilute hydrochloric acid, which would cause it to be mistaken for the ferrous salt. It seems probable, however, that differences arise chiefly because the course of the reaction actually varies in different experiments, and the few analyses recorded have been insufficient to exhibit the variation fully or to establish an average course for the reaction.

The most serious attempt to investigate the reaction appears to be that of Wright (*loc. cit.*), who prepared pure monohydrated ferric

oxide, treated it at laboratory temperature with pure hydrogen sulphide, and dried the product in hydrogen at 100°.   In nine runs the increase in weight on sulphidation was estimated, and the water produced was collected and weighed.   In four of these cases the dry solid residue was also analysed : it was black, intensely pyrophoric, soluble in hot aqueous potassium cyanide, and completely decomposed by aqueous cupric sulphate or silver nitrate solutions (compare Robinson, Sayce and Stevenson, preceding paper).   Wright's data for the " sulphide "/hydroxide ratio and the percentage conversion to " sulphide " calculated therefrom are given in Cols. 2 and 3 (a) of Table I, but these conversions are open to doubt, for those now calculated from the total increase in weight of the reaction tube and drying tube [Col. 3 (b)] are much smaller and more variable.

TABLE I.

		% Oxide converted, as calculated from		
Run.	"Sulphide". Hydroxide	(a) ratio.	(b) total increase.	% S in "sulphide."
6	1·167	100·4	77·5	—
2	1·163	100·0	92·5	43·78
3	1·158	99·6	86·5	40·05
1	1·134	97·6	86·1	—

From the foregoing data and from determinations of free sulphur (in four cases) Wright concluded that there were two reactions, (A) $Fe_2O_3,H_2O \longrightarrow Fe_2S_3 + 4H_2O$, and (B) $Fe_2O_3,H_2O \longrightarrow 2FeS + S + 4H_2O$, the second applying to 17—30% of the hydrated oxide.

Evidently the subject needs further investigation, but the inquiry is complicated by the difficulty of carrying the reaction to completion, by the complex nature of the product, and by secondary reactions in, and possibly between, the substances primarily produced.   It seemed probable that the course of the reaction varies within certain limits, and that the best method of attack would be repeated sulphidation and analysis.

In this investigation ferric oxide of known hydration was treated with hydrogen sulphide at laboratory temperature or at 100° in about 50 distinct runs, the ratio " sulphide "/hydrated oxide being computed in each case.   Qualitative tests were made on the " sulphide " to determine its properties, but the main part of the work consisted in estimating, in the product produced at 100°, one or other of the following : (1) the total iron and sulphur, (ii) the sulphur soluble in carbon disulphide, (iii) the material insoluble in 10% hydrochloric acid, (iv) the material insoluble in boiling saturated aqueous potassium cyanide, (v) the sulphur liberated by 10% hydrochloric acid.   The results disclose an unexpected variation

in the course of the reaction, which may explain the discrepant results of earlier workers; nevertheless, the mean values derived from analytical data may serve to indicate the probable nature and extent of the fundamental reactions involved.

EXPERIMENTAL.

Materials and Apparatus.—The hydrated oxide was prepared by diluting a solution of basic ferric chloride, free from metallic impurities, in hydrochloric acid with distilled water so that the concentration of acid was about 10%, and adding this solution with stirring to cooled aqueous ammonia, free from carbonate and organic impurities. The precipitate was separated from the supernatant liquor, repeatedly washed by decantation with 5% aqueous ammonia, collected on a Buchner funnel, and washed several times with large quantities of distilled water. The drained hydroxide was then dried at 100° for 4—5 days. Two lots of material were prepared [Found : Fe_2O_3, (1) 88·41, (2) 89·17. Calc. for Fe_2O_3,H_2O : Fe_2O_3, 89·87%]. Neither preparation contained more than a trace of volatile material other than water. As such oxides are distinctly hygroscopic, they were preserved in stoppered bottles kept in a desiccator. Before bottling they were ground and sieved (150—200 mesh).

The hydrogen sulphide, prepared by the action of hydrochloric acid on ferrous sulphide, was washed with water in three Drechsel bottles, and dried by passage through a large, wide bottle, containing fused calcium chloride, and a tower filled with the same material. The hydrogen, prepared from arsenic-free zinc and hydrochloric acid, was washed with water in three Drechsel bottles, and dried by passage through a tower packed with calcium chloride and through about 3 feet of glass tubing containing a liberal supply of phosphorus pentoxide spread on glass wool.

The two gas trains, which were strictly air-tight, met in a Y-piece of glass, with taps on two of the limbs ; the gases passed *via* the third limb to the reaction tube, a U-tube with tap-stoppers, and thence through a length of glass tubing to a bubbler containing water, which marked their passage and prevented backward diffusion of air. The procedure consisted in washing out each train thoroughly with its respective gas, cleaning and drying the U-tube, slightly greasing its stoppers, sweeping it free from air with hydrogen and weighing it, charging the tube with oxide by means of a dry funnel which was not allowed to touch the tap-grease, and, finally, again sweeping with hydrogen and weighing. Hydrogen was then passed for upwards of 45 minutes to ensure the complete removal of the air admitted to the third limb of the Y-tube and the connecting tubes during the last operation. This was followed by the passage of

hydrogen sulphide, the reaction tube being kept in constant motion during the first $\frac{1}{2}$ hour, to minimise the caking of the material. From this point the procedure varied and is given below.

The Reaction at Laboratory Temperature, producing a Hydrated Sulphide.—During runs 5—8 (Table II) the reaction tube was suspended in a beaker of water at laboratory temperature, and the product dried by passing hydrogen for the time stated. As the calculated ratio $Fe_2S_3/Fe_2O_3,H_2O$ is 1·170, the ratios observed, which were substantially unchanged by the passage of dry hydrogen over a long period, suggest that a hydrated sulphide was produced; this idea is supported by the fact that water was at once evolved when the temperature was raised to 100°. The data for the ratio of " sulphide " to water liberated are too variable to show the formula of the hydrate, and it is not known in what proportion the various sulphides are present, or how much, if any, of the liberated water is derived from unconverted oxide which has suffered further hydration by the moisture produced in the reaction. (This matter is receiving further attention, and an attempt is being made to isolate the hydrate.) Runs 9—15 indicated that the degree of conversion may be very variable, and this was borne out by runs 16—22 (not shown), where the product produced in precisely the same way was far from uniform in each case, and gave values for sulphur varying from 43% (almost Fe_2S_3) to 20% in different runs. It is believed that this was due principally to protective caking of the product by the water produced, and that under these conditions a material of uniform composition could not be attained. The authors are unable to account for the serious discrepancy between these results and those of Wright (*loc. cit.*), and of Weyman (*loc. cit.*), who reports a conversion into material of the composition of ferric sulphide.

TABLE II.

Run.	Oxide (g.).	H₂S (hours).	H₂ (hours).	"Sulphide" / Oxide	H₂ at 100° (hours).	"Sulphide" / Oxide
5	2·3260	22	4	1·247		
6	2·3437	17	34	1·235		
7	5·1543	17	17	1·242		
8	2·4509	17	12	1·253		
9	1·7499	72	6	1·352	4·0	1·165
10	1·2900	17	8	1·280	2·3	1·160
11	2·4066	17	8	1·300	3·0	1·091
12	1·9096	17	4	1·216	3·0	1·102
13	3·0327	20	19	1·417	2·5	1·124
14	1·6252	17	0	1·217	3·0	1·072
15	1·0704	17	3	1·215	3·0	1·068

The Reaction at 100°.—In the following runs the reaction was carried out at 100° by immersing the U-tube in boiling water. After the tube had been charged and the air removed as described

above, hydrogen sulphide was passed for 3 hours, followed by dry hydrogen for 30 minutes. The product, although not actually pyrophoric, usually became hot on exposure to air and increased in weight sufficiently to vitiate analysis. Dry air was therefore passed over it for 30 minutes in order to stabilise the weight, and the tube was then filled with hydrogen and reweighed. Thus the amount of the unoxidised "sulphide" could be computed. The sulphide was analysed for iron by weighing the ferric oxide left on ignition to constant weight, and for sulphur by oxidation to sulphate and weighing as barium sulphate. Oxidation was effected by both a dry and a wet method : (1) About 0·35 g. of sulphide was intimately mixed with fusion mixture and potassium nitrate in a platinum crucible, covered with a further quantity of these materials, 3 g. in all of each being used, and the upper edge of the crucible was gently heated until reaction began ; when reaction had apparently ceased, the temperature was raised sufficiently to keep the mixture molten for about 15 minutes. (2) In the wet method fuming nitric acid and bromine were used. The results by the two methods were in excellent agreement. The dry method was tested on pyrites and on laboratory monosulphide; with the former it gave excellent results, but for the latter it was practically useless. In all cases blanks were carried through on the materials used.

TABLE III.

Run.	Oxide (g.).	"Sulphide" / Oxide.	Fe in sulphide, %.	S in sulphide, % (found, and mean).	Fe + S, %.
23	1·1819	1·167	53·98	42·74, 42·91; 42·83	96·81
24	1·0553	1·151	54·95	40·72, 39·96; 40·34	95·29
25	1·3369	1·171	53·78	43·51, 43·35; 43·43	97·21
26	1·3297	1·167	53·32	42·10, 41·51; 41·81	95·13
27	1·2958	1·177	53·06	43·75, 42·25; 43·00	96·06
29	1·1539	1·173	53·96	42·53, 39·29; 40·91	94·87
30	0·9349	(1·213)	52·06	43·40, 43·40; 43·40	95·46
31	0·5224	(1·191)	52·78	43·16, 43·06; 43·11	95·89
32	0·7654	1·163	52·64	41·20, 42·12; 41·66	94·30
	Mean	1·167 *	53·39	42·28	95·67

$O + H_2O$ (by diff.) = 4·33

* Nos. 30 and 31 are omitted because of a short drying period.

Table III shows that the ratio "sulphide"/oxide is much more constant than that found previously, and, though variations of about 3% may be found in one sample of sulphide, its composition is much more uniform. The total sulphur and iron are 3—5% below 100% : this is probably due to incomplete conversion and to the retention of some water by the material. It is, however, clear that the procedure employed above gives a readily reproducible product of reasonably uniform composition.

Sulphur Soluble in Carbon Disulphide.—After the ratio "sulphide"/

oxide had been determined, the U-tube was again attached to the train and, with hydrogen passing, the stop-cock farthest from the source of hydrogen was taken out and the tap-grease removed from the mouth of the tube with a cloth moistened with ether.   A cork carrying a tap-funnel was now fitted to the tube, and 20 c.c. of carbon disulphide (thrice-distilled material, without objectionable odour, and leaving no residue on evaporation) were run in and allowed to stand thus, with frequent shaking, for 1 hour.   The solution was carefully decanted through an ashless filter-paper, and the residue was similarly treated with two further lots of solvent.   A positive pressure, or a stream, of hydrogen, according to circum-stances, prevented ingress of air during the whole operation.   The extracted residue is pyrophoric when dry.   The combined filtrates were evaporated to dryness and the sulphur estimated by weighing, or by conversion to barium sulphate, or both.   Table IV gives the results, and shows that sulphur was produced in each run, and as this might have been due to atmospheric oxygen retained by the hydrated oxide, in runs 52 and 53 the hydrogen used to displace the

TABLE IV.

Run.	Oxide (g.).	"Sulphide". $\dfrac{\text{"Sulphide"}}{\text{Oxide}}$	S sol. in CS_2 in "sulphide," %.
33	0·7806	1·200	1·93
34	0·7912	1·159	2·52
35	0·6633	1·167	2·41
36	0·8991	1·174	2·53
37	1·3796	1·168	1·96
52	0·4532	1·150	3·17
53	0·2895	1·140	2·55
		Mean	2·44%

air was passed for 3 hours, instead of the usual 45 minutes, in order to reduce the residual oxygen to a minimum, but this did not diminish the yield of sulphur.

Material Insoluble in 10% *Hydrochloric Acid (Iron Disulphide).*— The acid, about 20 c.c., was added exactly as described for carbon disulphide.   The tube, with both stop-cocks removed, was then immersed above the acid level in a beaker of boiling water and gently shaken until gas ceased to be evolved.   The residue was completely transferred to a filter-paper, well washed with warm 10% hydro-chloric acid, and finally ignited to ferric oxide.   Analysis of this residue in a number of cases (after its extraction with carbon disulph-ide, see below) showed it to be entirely due to the iron disulphide present in the product, and results calculated on this assumption are given in Table V; the values vary considerably, but they tend to be about 7%.

TABLE V.

Run.	Oxide (g.).	"Sulphide" / Oxide	Fe_2O_3.	FeS_2, calc. from Fe_2O_3 (as % of "sulphide" in each case).	S liberated.
38	0·2716	1·172	4·52	6·80	
39	0·4135	1·165	4·32	6·49	
41	0·1777	1·165	9·33	14·03	
42	0·2512	1·166	4·71	7·07	
49	0·3397	1·153	2·86	4·30	13·46
50	0·7405	1·151	8·64	12·99	12·49
51	0·7657	1·180	3·19	4·79	13·20
52	0·4532	1·150	4·95	7·44	
53	0·2895	1·140	4·37	6·57	13·40
		Mean	5·21	7·83	13·14

Material Insoluble in Concentrated Potassium Cyanide Solution (Iron Disulphide and Unchanged Hydrated Oxide).—Saturated potassium cyanide solution was added to the "sulphide" by the same means and with the same precautions as above. The tube was well shaken, its contents were transferred to a beaker containing a further 200 c.c. of solution, and the liquid was gently boiled for 6 hours. It was then diluted, and the residue collected on a filter-paper, well washed, and ignited to ferric oxide. No definite inform-ation was found in the literature as to the solubility of the various sulphides in potassium cyanide solutions, but a reinvestigation showed that whilst ferrous and ferric sulphides dissolved, iron disulphide was apparently insoluble under the conditions of the experiment. Thus it is assumed that the residue contained only the unaltered hydrated oxide and the disulphide previously shown to be present.

TABLE VI.

Run.	Oxide (g.).	"Sulphide" / Oxide	Fe_2O_3 as % of "sulphide."
44	0·2510	1·171	6·84
45	0·7283	1·144	9·87
46	0·2830	1·168	18·19
47	0·6942	1·169	8·78
48	1·0920	1·121	9·15
54	0·2904	1·127	19·44
55	0·1967	1·168	11·24
		Mean	11·93

Table VI gives the weight of the ferric oxide (expressed as a per-centage of the "sulphide") resulting from the ignition of the residue, and it is obvious that the mean value is about twice the mean value of the same oxide in Table V, the difference of 6·72% Fe_2O_3 being ascribed to 7·48% of unaltered Fe_2O_3,H_2O. Again, the products of various runs differ considerably, probably because of variation in the proportion of disulphide rather than in the un-attacked hydrated oxide.

E E 2

Sulphur Liberated on Dissolution of "Sulphide" in Hydrochloric Acid.—It has already been pointed out that there was no evident liberation of sulphur when the products were treated with 10% hydrochloric acid, but the black residue was more bulky than would be anticipated from the comparatively small amounts of oxide left after ignition.   When washed with pure alcohol and ether, to remove water, and then extracted with pure carbon disulphide, it yielded sulphur, which was estimated by weighing and by conversion into barium sulphate.   The results are given in the last column of Table V, and it is evident that they include in each case the " free " sulphur mentioned in Table IV.   They appear to be remarkably concordant when compared with the figures for disulphide plus unchanged material; it is indeed possible that the variation which does exist is brought about by variation in " free " sulphur present before the addition of hydrochloric acid.   When this " free " sulphur is deducted the mean sulphur liberated becomes 10·70%, and from this one may calculate the percentage of ferric sulphide to be 69·40% on the assumption that it yields $2FeCl_2 + 2H_2S + S$ on treatment with hydrochloric acid.

Discussion of Results.

The black product of this reaction tends to oxidise when exposed to air, but is not pyrophoric until it has been extracted with carbon disulphide, indicating that the particles are coated with a film of free sulphur which, by preventing actual contact with air, gives the material an apparent stability.   The ratio " sulphide "/oxide corresponds very closely with that required for a complete conversion into ferric sulphide (see Table III, where the oxide was fresh, the later discrepancies being due to the further hydration of the oxide); the material is partly soluble in dilute hydrochloric acid with the evolution of hydrogen sulphide, whilst the black residue contains sulphur extractable with carbon disulphide, although the supernatant liquid is free from the opalescence usually associated with the liberation of that element.   There is evidence of considerable variation in the course of the reaction, but its general nature may be deduced from the mean values shown above as set out in Table VII.   The ferrous sulphide is calculated by assuming that the additional 3·56% sulphur required by the complete analysis of the material (see Table III; 53·39% of Fe requires 45·84% S, as compared with 42·28%) existed as this compound, and the moisture is obtained by deducting 2·78 (= $3O + H_2O$ in 7·48% Fe_2O_3,H_2O, see p. 821) from 4·33 ($O + H_2O$ in Table III).   It will be seen that all but 1·5% is accounted for, the discrepancy being thrown entirely on the iron by the method of calculation.

TABLE VII.

	%.	% S.	% Fe.
Free sulphur	2·44	2·44	—
Iron disulphide	7·83	4·18	3·65
Ferric sulphide	69·40	32·10	37·30
Ferrous sulphide	9·76	3·56	6·20
Fe_2O_3,H_2O unaltered	7·48	—	4·70
Moisture	1·55	—	—
Totals	98·46	42·28	51·85

Free sulphur is invariably found in this reaction under either dry or moist conditions; this has been ascribed by Wright (*loc. cit.*) to his reaction (B), and by Mecklenburg and Rodt (*loc. cit.*) to oxidation of hydrogen sulphide by residual adsorbed air. The evidence brought forward here supports the latter contention, for if Wright's reaction takes place, 13·38% ferrous sulphide would be required for the free sulphur alone, and none would be left to balance the disulphide which is most probably produced by the decomposition of ferric sulphide: $Fe_2S_3 \longrightarrow FeS_2 + FeS$. The 7·83% disulphide requires 5·74% ferrous sulphide for equimolecular proportions, and thus the total ferrous sulphide required would be of the order of 19·12%. The conclusions are that (1) the free sulphur is due to oxygen adsorbed on the surface of the oxide, which appears to be unreduced by long washing with hydrogen, (2) the primary reaction leads to the production of ferric sulphide, and (3) some ferric sulphide decomposes with the formation of equimolecular proportions of disulphide and monosulphide. The discrepancy in the ratio of disulphide to monosulphide is probably due to the slight solubility in acid of the former when in a finely divided condition.

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