

205. *The Interconversion of Iron Oxides and Sulphides.*

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The primary reaction product of hydrogen sulphide with any form of ferric oxide is hydrated ferric sulphide. The rate of penetration through the layer of sulphide formed generally controls the rate of change. Decomposition of the ferric sulphide takes place in the presence of excess of hydrogen sulphide at temperatures above 20° , but only slowly under alkaline conditions. The product is a mixture of FeS_2 and a highly magnetic sulphide Fe_3S_2 .

The oxidation of $\text{Fe}_2\text{S}_3, \text{H}_2\text{O}$ is slower than the reaction of hydrogen sulphide with ferric oxide; it is greatly influenced by temperature, by moisture conditions, and by the pore structure of the hydrated sulphide. Oxidation of the magnetic sulphide takes place much more slowly, and oxidation of FeS_2 only occurs at much higher temperatures.

The product of oxidation of moist $\text{Fe}_2\text{S}_3, \text{Fe}_3\text{S}_2$, or precipitated ferrous sulphide at temperatures below 50° is $\alpha\text{-Fe}_2\text{O}_3, \text{H}_2\text{O}$. In aqueous suspension, both ferric and ferrous sulphides give $\gamma\text{-Fe}_2\text{O}_3, \text{H}_2\text{O}$. At high temperatures, all the sulphides give a mixture of ferric sulphate with an oxide which is mainly $\gamma\text{-Fe}_2\text{O}_3$.

For the removal of hydrogen sulphide from fuel gases, it has been customary to use iron oxide. The iron sulphide first formed is readily oxidised to iron oxide, so the overall effect is that of oxidation of hydrogen sulphide with deposition of sulphur.

The nature of the sulphides formed has been studied by Gedel (*J. Gasbeleucht.*, 1905, 48, 428), Rodt (*Z. angew. Chem.*, 1916, 29, 42), Rodt and Mecklenburg (*Z. anorg. Chem.*, 1918, 102, 130), and Pearson and Robinson (J., 1928, 814), whose work was confined to the use of amorphous hydrated ferric oxide. The rate of sorption of hydrogen sulphide by various forms of iron oxide has been studied by Brückner (*Brennstoff-Chem.*, 1936, 17, 21; *Gas u. Wasserf.*, 1938, 81, 822), but his description of the samples employed cannot be correlated with modern nomenclature. The same comment applies to results obtained by McLeish (*Gas J.*, 1944, 243, 50, 85).

In the present investigation, the sorption of hydrogen sulphide by the following iron oxides was studied: (1) α -Fe₂O₃; (2) α -Fe₂O₃·H₂O; (3) β -Fe₂O₃·H₂O; (4) γ -Fe₂O₃; (5) γ -Fe₂O₃·H₂O; (6) δ -Fe₂O₃·H₂O; (7) amorphous hydrate. The preparation of these materials and kinetic studies of their reaction are described. Identification of the resulting sulphides, and their oxidation and decomposition, are then recorded.

EXPERIMENTAL.

Preparation of the Iron Oxides.—(1) α -Ferric oxide was obtained by dehydration of its monohydrate at 300°. (2) This monohydrate was prepared by atmospheric oxidation of ferrous carbonate, precipitated by sodium or ammonium carbonate from solutions of ferrous sulphate or ferrous chloride, and washed free from soluble salts. (3) β -Ferric oxide monohydrate was prepared by hydrolysis of dilute ferric chloride solution (Weiser and Milligan, *J. Amer. Chem. Soc.*, 1935, 57, 238); this material always contained chlorine. (4) γ -Ferric oxide was made either by atmospheric oxidation of freshly precipitated Fe₃O₄ at 110° (Baudisch, *Phil. Mag.*, 1925, 50, 399) or by dehydration of its monohydrate at 250° (Baudisch and Albrecht, *J. Amer. Chem. Soc.*, 1932, 54, 943). (5) This monohydrate was obtained by atmospheric oxidation of ferrous pyridyl chloride solution (Baudisch and Albrecht, *loc. cit.*). (6) δ -Ferric oxide monohydrate was prepared by oxidation of freshly precipitated ferrous hydroxide by hydrogen peroxide in the presence of very concentrated alkali (Glemser and Gwinner, *Z. anorg. Chem.*, 1939, 240, 161; Chevallier, *Compt. rend.*, 1927, 184, 674; Quartaroli, *Gazzetta*, 1933, 64, 279). (7) Amorphous hydrated ferric oxide, precipitated from a ferric salt solution by alkali hydroxide or ammonia, was washed free from soluble salts (Böhm, *Z. anorg. Chem.*, 1925, 149, 203).

These oxides were prepared as coarse powders containing 10–12% of free water; a grade passing an 18-mesh and retained on a 60-mesh sieve was used to make tablets, and "fines," passing a 200-mesh, were taken for extrusion of rods. The tablets were $\frac{3}{8}$ in. in diameter and $\frac{3}{16}$ in. in maximum thickness, with convex ends, produced in a tablet machine at a setting which gave reasonable strength for each raw material. Rods of $\frac{1}{8}$ in. diameter were either built up from a large number of tablets with flat ends, or obtained by extrusion of a thick paste from a die with $\frac{1}{8}$ in. orifice. The pH of these oxides was usually adjusted to >8.5 by suitable addition of sodium carbonate; under acid conditions some preliminary experiments showed that conversion into sulphide was incomplete, and the need for alkaline conditions for industrial purposes has long been appreciated. For this reason, no satisfactory results could be obtained with β -Fe₂O₃·H₂O, which only appears to exist at a low pH.

Identification of the Oxides.—Two methods have proved suitable for identification of iron oxides, particularly when applied simultaneously to a given sample. These are: (a) solubility in acids, (b) magnetic measurements.

(a) **Solubility in acid.** 5 c.c. of concentrated hydrochloric acid were mixed with 45 c.c. of water to give an acid of about 4% content; 1 g. of the finely powdered oxide was added and shaken in a closed flask for 15 minutes by hand. The remaining solid was then separated by filtration, the liquid treated with zinc amalgam with thorough shaking, and then titrated with N/10-potassium dichromate solution. The proportion of the total iron dissolved in each case is here given as a percentage: α -Fe₂O₃, 25.8; α -Fe₂O₃·H₂O, 12.7; γ -Fe₂O₃, 6.8; γ -Fe₂O₃·H₂O, 0.5; δ -Fe₂O₃·H₂O, 7.9; amorphous Fe₂O₃·H₂O, 93.5. Among the hydrated forms, the rate of solution of the amorphous oxide is outstanding, whereas the anhydrous α -dissolves much more rapidly than the ferromagnetic γ -oxide.

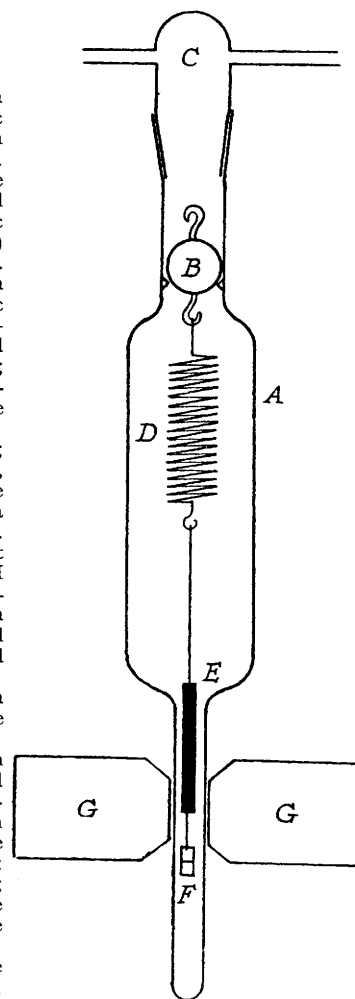
(b) **Magnetic properties.** The measurement of magnetic susceptibility by the Gouy balance, or of magnetisation, provides a ready method of identification, particularly in conjunction with changes on heating. Of the hydrated oxides, only the δ - is ferromagnetic, and it loses this property on heating, slowly at 100° and rapidly at 150°. Only the γ -hydrate becomes ferromagnetic on heating at 250°, but prolonged treatment at this temperature leads to conversion into the paramagnetic α -Fe₂O₃. The ferromagnetic γ -Fe₂O₃ also changes completely into α -Fe₂O₃ on prolonged heating above 250°. Dehydration of the α - and the β -hydrate or of the amorphous hydrate, results in practically no change in susceptibility. Positive identification of the β -hydrate alone requires X-ray data.

An electromagnet was made for use in these experiments, which would provide a variable field up to 2000 gauss, with pole pieces tapered to 1 in. diameter and with $\frac{1}{2}$ in. gap.

The Rate of Sorption of Hydrogen Sulphide.—The apparatus used in measuring the rate of reaction of hydrogen sulphide with the iron oxide rod or tablet, shown in Fig. 1, is a modification of the McBain-Bakr sorption balance (*J. Amer. Chem. Soc.*, 1926, 48, 690). The iron oxide rod or tablet *E* was suspended from a quartz spring *D* in a cage of glass or of fine nickel-chrome wire, and the extension of the spring was observed against a scale placed behind it by means of a reading telescope. The specimen and spring were handled by means of hooks on the glass bulb *B*.

The vessel *A* was closed by a ground-glass cone *C* carrying a manometer and a connection for exhaustion or admission of gas from a burette. At the start of each run, the system was exhausted down to the aqueous vapour pressure in equilibrium with the iron oxide specimen, and a measured quantity of hydrogen sulphide was admitted until the pressure

FIG. 1.



rose to about 3–6 cm. The rate of sorption of hydrogen sulphide was then observed by frequent readings on the manometer, more gas being let in when the pressure dropped below 3 cm., and simultaneous changes in weight were recorded from the position of the spring. When it was intended to follow changes in the magnetic properties of the iron compounds, a rod of the material was used, 5 cm. long, and the lower limb of the sorption system was placed between the poles *GG* of the Gouy balance. The sighting wire *F* was carried by a suitable frame below the oxide rod.

In an experiment of this kind, little control is possible over the temperature of the solid, since the heat of reaction is appreciable and the conditions are unfavourable to its rapid dissipation. Observations on the weight of the tablet during its conversion into sulphide showed that the water content remained almost constant in the early stages of the reaction, so most of the water formed was evolved as vapour; the condensation of moisture on the walls of the vessel after $\frac{1}{2}$ –1 minute from the start also indicated that the atmosphere was saturated with water vapour almost throughout the conversion. In these circumstances, a heat effect of about 6 kg.-cals./g.-mol. of hydrogen sulphide absorbed would be expected, and the temperature of the tablet would be between 40° and 50° with the fastest rate of sorption, calculated on heat-transfer data.

In a reaction between a gas and a porous solid, the observed rate will depend on the actual rate at the internal surface and on the rate of penetration of the gas to the interior (Thiele, *Ind. Eng. Chem.*, 1939, **31**, 916). The conditions now chosen, where pure hydrogen sulphide is used at a low pressure, should decrease the extent to which the results are affected by penetration. When the gas–solid reaction proceeds unhindered by the slowness of penetration, the observed rate should be a function only of the pressure of hydrogen sulphide; if it is a first-order reaction, it should be directly proportional to this pressure, and a plot of the extent of reaction against the integrated product of pressure and time should be a straight line.

On the contrary, if the rate of penetration is the controlling factor, the observed rate should be inversely proportional to the extent to which the change has already proceeded, *i.e.*, to the thickness of the sulphide layer which has to be penetrated before unchanged oxide is reached. In these circumstances it may be shown that the extent of reaction is proportional to the square root of the integrated product of pressure and time.

FIG. 2.

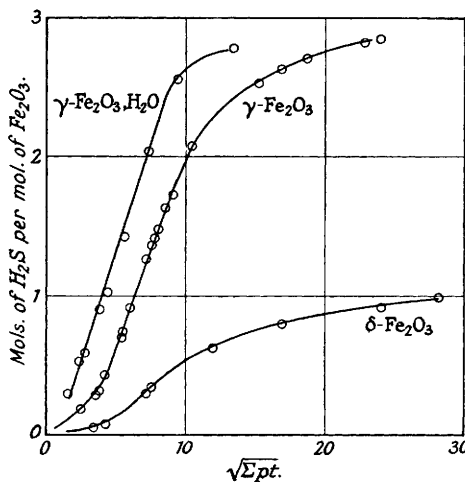
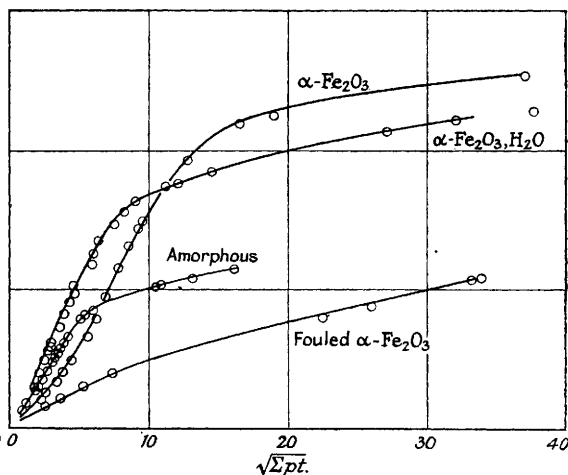


FIG. 3.



Examination of a tablet of α - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ which had taken up about half the total possible quantity of hydrogen sulphide showed that a core of unchanged oxide amounted to about one-third of the total volume; this indicated that the rate of penetration was likely to be the controlling factor with this material. The relation between porosity and rate of gas sorption was investigated with a series of tablets made at different pressures between 300 and 3750 atm., from one sample of α - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which showed that the rate of uptake was dependent on the rate of penetration and therefore on the porosity of the tablet. The least porous tablet still contained an unchanged core of oxide after it had ceased to react.

The differences among these specimens of α - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ are hardly less than those observed in the whole range of other forms of iron oxide. In Figs. 2 and 3 are shown results for the series, the number of hydrogen sulphide molecules taken up by each molecule of iron oxide being plotted against the square root of the integrated product of pressure and time. The properties of the specimens are given in the following table. Further results obtained with α - Fe_2O_3 which had been heated to 400°, 500°, and 650° showed progressive reduction in rate of reaction with hydrogen sulphide, and the rate of penetration with these materials no longer appeared to be the controlling factor. The specimen heated at 650° did not react at all until it had been in contact with the gas for more than 3 hours.

Porosity of iron oxides at 100°.

Sample.	Porosity, % by vol.	d_4^{20} .	Sample.	Porosity, % by vol.	d_4^{20} .
α - Fe_2O_3	76	5.13	γ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	87	3.90
α - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	71	3.82	δ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$	66	4.12
γ - Fe_2O_3	81	4.92	Amorphous monohydrate	55	3.76

The porosities were determined by measuring the weight of methylcyclohexane taken up by a tablet after exhaustion at 100°; the density is corrected for traces of water still remaining at this stage.

Discussion of Results.—All the curves of Figs. 2 and 3 except that for δ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ show well-defined periods over which the square root relation applies. The slope of this straight portion, which is a measure of the penetration rate, depends mainly on the porosity of the specimen. The anhydrous oxides both show portions,

in the early stages, where the slope increases, which indicates that the rate of reaction is initially of the same order as that of penetration; this is more strongly marked with the δ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, where retardation by alkali hydroxide is suspected. Amorphous oxide is distinguished by an early diminution in the rate of reaction, which may be attributed to progressive blocking of the pores due to changes in the volume of the gelatinous material.

A specimen of α - Fe_2O_3 , which had been converted fully into sulphide and then allowed to oxidise, gave the lowest curve on Fig. 3, thus illustrating the effect of reduction in porosity by the deposition of free sulphur.

Identification of Iron Sulphides.—Ferric sulphide has been identified as the product of the action of hydrogen sulphide on amorphous $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ by Gedel, Rodt, Pearson and Robinson (*loc. cit.*). Gedel stated that the product was $\text{FeS} + \text{FeS}_2$ under acid conditions, but Rodt considered that these sulphides were actually produced by rapid decomposition of Fe_2S_3 in the presence of excess of hydrogen sulphide and that this decomposition was inhibited by alkali. Quantitative results in confirmation of these were published by Pearson and Robinson; they extracted the sulphide produced by passing the gas over the oxide at 100° with carbon disulphide and then dissolved it in boiling dilute hydrochloric acid. FeS_2 remained unchanged, and the proportion of FeS to Fe_2S_3 was determined from a sulphur balance after allowance for unchanged oxide; 81% of the total sulphide formed was Fe_2S_3 .

In the present investigation, all the evidence points to the fact that Fe_2S_3 is formed when any ferric oxide or hydrate reacts with hydrogen sulphide. With amorphous $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, α - Fe_2O_3 , α - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and γ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ the change of the Fe_2S_3 into ferrous sulphide and FeS_2 has been observed by analytical and magnetic measurements. With the γ - Fe_2O_3 similar changes may be assumed to occur but cannot be followed with the Gouy balance; with δ - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ the presence of a large amount of caustic alkali prevented the decomposition of Fe_2S_3 .

Decomposition and Magnetic Properties of Iron Sulphide.—Juza, Biltz, and Meisel (*Z. anorg. Chem.*, 1932, 205, 273) determined the magnetic susceptibility of iron sulphides in the range FeS to FeS_2 . These two definite compounds were only slightly paramagnetic but the solid solution of sulphur in FeS (pyrrhotite) was ferromagnetic with a maximum susceptibility at the composition $\text{FeS}_{1.118}$, which they considered to be Fe_8S_9 . These authors found no evidence of the existence of Fe_2S_3 under their conditions. By the use of the Gouy balance it has now been found that Fe_2S_3 has no ferromagnetic properties, and accordingly little change in magnetic susceptibility could be observed when hydrogen sulphide acted on the paramagnetic forms of ferric oxide. If, however, the resulting sulphide was allowed to remain in an atmosphere of the gas, the susceptibility sometimes increased markedly after several hours. The change did not occur if the temperature was below 20° or if no free hydrogen sulphide was present. If the pH was above 8.0 the conversion was not observed below 90° . After 50 hrs. at 25° and pH 7.0, the apparent susceptibility at 850 gauss field strength was about 8800; further investigation showed that the product exhibited hysteresis to a marked degree, and susceptibility data therefore have little significance unless the precise conditions are known.

At 40° , the change was complete in 3–4 hours, 42% of the iron being present as FeS_2 ; from a sulphur balance, the remainder had the composition $\text{FeS}_{1.125}$ (Fe_8S_9). As this substance is certainly the magnetic component, its specific magnetisation can be calculated to be 16.9; this is considerably greater than the figure given by Ziegler (Thesis, Zurich, 1915; *Int. Crit. Tables*, Vol. 6, p. 413) for mineral pyrrhotite in the maximum axial direction for an oriented crystal. In the present investigation, the arrangement of the crystals must have been random and the maximum value might have been nearly $\sqrt{3}$ as great.

Rate of Oxidation of Iron Sulphides.—The vessel A (Fig. 1) containing the tablet or rod of sulphide was evacuated to remove residual hydrogen sulphide but not sufficiently to cause dehydration. Oxygen was then admitted to a pressure of about 4 cm., the reaction being followed by pressure change, and by weight observations in order to determine the state of hydration. The reaction is much more exothermic than that between iron oxides and hydrogen sulphide and accurate control of the temperature is therefore not possible. Rapid loss of water always occurred and, unless great care was taken during the admission of oxygen, dehydration continued until the normal oxidation reaction leading to α - $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ could no longer proceed. Oxidation then either ceased or continued pyrophorically with formation of sulphate.

In Fig. 4 is shown, plotted against the integrated product of time and pressure, the number of atoms of oxygen taken up by one molecule of $\text{Fe}_2\text{S}_3 \cdot \text{H}_2\text{O}$ obtained by starting with five forms of iron oxide and converting them fully into ferric sulphide. The sulphide prepared from amorphous hydrated ferric oxide, and all the mixtures of Fe_8S_9 with FeS_2 , oxidised so slowly that the rate cannot be shown on this diagram.

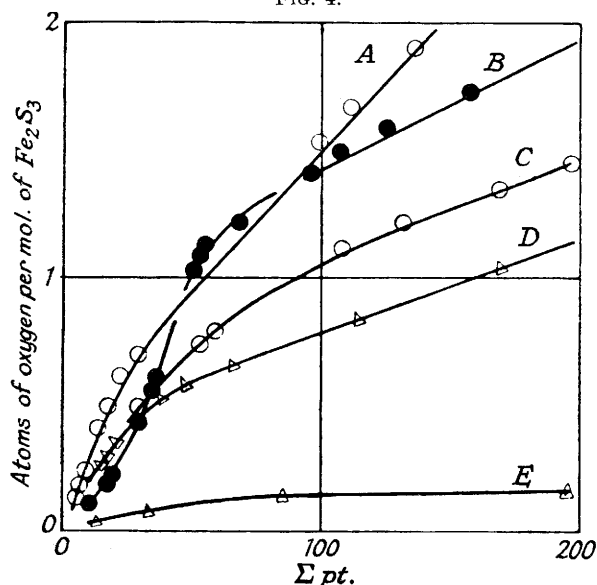
Owing to the lack of control of temperature and moisture content the results can be considered only qualitatively. The initial steep part of each curve represents the rate of oxygen absorption in the presence of excess moisture. At the points of flexion, the water content had been reduced in each case to approximately 1 mol., per mol. of Fe_2S_3 , and thenceforth remained almost constant. The order of increasing rate of oxidation, as deduced from the slopes of the curves, is also the order of increasing porosity of the original oxides, so the differences in oxidation rate may be attributed to the greater extent of the reacting surfaces in the more porous materials. All the observed rates are slower than the rate of penetration of oxygen into the solid, as deduced from data already given for hydrogen sulphide, and it has also been observed that in all instances the exterior of a tablet did not become fully converted into oxide any more quickly than did the interior.

Measurement of the rate of oxygen absorption, with better control of temperature and moisture content, can be carried out by determining the oxygen content of a stream of gas before and after passage through a layer of iron sulphide. Preliminary experiments along these lines confirm the important effect of moisture

content and indicate a rate of oxidation at least as great as that represented by the steepest portion of the curves in Fig. 4.

Oxidation Products of Iron Sulphides.—Veil (*Compt. rend.*, 1928, 186, 753) showed that wet oxidation of ferrous sulphide gave an iron oxide hydrate of which the magnetic susceptibility increased on dehydration, so it was presumably the $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$, and Böhm (*Z. Krist.*, 1928, 68, 567) found that ferric sulphide also produced $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ when oxidised by air. Investigation of the product obtained by slow oxidation with oxygen of iron sulphide resulting from the action of hydrogen sulphide on tablets of all the individual ferric oxides showed only very small changes in magnetic properties on heating, corresponding to the presence of a negligible amount of $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$. Further experiments involving measurement of the rate of solution in dilute hydrochloric acid showed that the bulk of the material was $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ and not the amorphous form. Repetition of Veil's experiments confirmed that the product of oxidation of ferrous sulphide in aqueous suspension gave $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$. The same product was also obtained when ferric sulphide was oxidised in aqueous suspension whether it had been prepared by wet precipitation from a ferric salt solution or by the action of hydrogen sulphide on a ferric oxide. When precipitated ferrous sulphide was dried by evaporation under reduced

FIG. 4.



A, $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$; B, $\gamma\text{-Fe}_2\text{O}_3$; C, $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$;
D, $\alpha\text{-Fe}_2\text{O}_3$; E, $\delta\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$.

pressure and then exposed to moist air, it oxidised very slowly but eventually gave $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ containing a little $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$. The magnetic sulphide $\text{FeS}_{1.125}$ behaved in the same way.

It appears from these results that the oxidation in aqueous suspension is fundamentally different from that of the moist solid, and it probably takes place in solution; this may explain the observation by Glud and Reise (*Gas u. Wasserf.*, 1929, 72, 1251) that the rate of oxidation of suspended ferrous and ferric sulphides is affected by the concentration of alkali in the liquid. All other known methods of preparing $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ involve oxidation of ferrous iron in solution.

The Existence and Behaviour of $\text{Fe}_2\text{S}_3\cdot\text{H}_2\text{O}$.—As the interaction of hydrogen sulphide and iron oxide produces water, the sulphide obtained in this way always contains water; since the product of the low-temperature oxidation of moist ferric sulphide was always $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$, it is evident that this water is essential in the oxidation. It is also known that the anhydrous ferric sulphide is stable in air, unless suddenly exposed, whereupon the heat of adsorption may be sufficient to initiate pyrophoric combustion. It was, therefore, interesting to determine whether a definite hydrate of the sulphide can exist, or whether the water was simply adsorbed. $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ was treated with hydrogen sulphide until fully saturated; the reaction vessel was

then exhausted, the equilibrium vapour pressure being measured at intervals and the weight of the specimen recorded.

A study of the relation between the water content of the sulphide and the pressure at 20° indicated that about 1 mol. of water is held at a very low vapour pressure, and suggested the existence of an unstable monohydrate. This water is driven off on heating, slowly at 60°, quickly at 90°, under reduced pressure. On readmission of water, approximately 1 mol. is again taken up at a very low vapour pressure, but much less is taken up at higher vapour pressures owing to physical shrinkage on the first drying. Oxidation of the rehydrated sulphide specimen takes place at a rate comparable with that for the original undried material. The sulphide is thus different from an anhydrous ferric oxide which does not revert to the hydrate in contact with water.

Changes in Volume and Pore Structure.—As already mentioned, shrinkage of the porous tablet of $\text{Fe}_2\text{S}_3\cdot\text{H}_2\text{O}$ took place on drying; this amounted to about 5% in linear dimensions. The further conversion into $\text{Fe}_2\text{S}_3 + \text{FeS}_2$ led to an overall contraction of about 13%. Similar changes have been observed on drying the amorphous hydrated oxide, and it is probable that the $\text{Fe}_2\text{S}_3\cdot\text{H}_2\text{O}$ is present as a gel.

The density of pure ferric sulphide has not been recorded; measurements have now been made with specimens prepared from ferric oxide by reaction with hydrogen sulphide, which gave a mean value of 3.25 for the anhydrous form, and about 2.7 for the monohydrate. The latter value shows that considerable expansion must occur when the hydrated sulphide is formed from an oxide. Since no equivalent change in the overall dimensions of the tablet was observed, although a slight expansion occurred with the amorphous oxide only, it follows that closing of the pores must take place. This explains the fact that a core of unchanged oxide can indefinitely survive treatment with hydrogen sulphide when the initial porosity is below a given value. It also explains the highly unreactive character of the sulphide towards oxygen when it has been formed from the amorphous oxide or from other oxides of low initial porosity.