ACTIVE IRON. II

Relationships Among the Oxide Hydrates and Oxides of Iron and Some of Their Properties

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I. INTRODUCTION

A study of the extensive literature (2, 32) on synthetic oxide hydrates and oxides of iron, both ferrous and ferric, suggests a simple way of classifying them and of exhibiting the relationships among the various members. This is to express their generic relations to the iron compounds from which they were formed and to specify the chemical operations that were used.

The experimenters in the field of our survey started with either a ferrous salt, a mixture of ferrous and ferric salts, or a ferric salt, and carried out at least one of the following operations: (1) Precipitation with an alkali. In the case of the ferrous hydrates and oxides, this precipitation was carried out under oxygen-free conditions. (2) Oxidation with either molecular oxygen or with some oxidizing agent containing oxygen. (3) Dissociation. (4) Hydrolysis. (5) Heating. (6) Aging. By aging is meant the changes that take place spontaneously. Unless otherwise specified the temperatures at which aging occurs are those of the room. The distinction between heating and aging is generally arbitrary, since they differ only as to rate. The justification for considering aging as a chemical operation is the fact that the paths and the rates can, in general, be modified by changing the chemical environment.

The general scheme of classification that has been indicated has led us to construct the diagram of figure 1. We shall let this diagram serve as an outline throughout our discussion of the synthetic hydrates and oxides. Necessarily, the physical and chemical properties must be considered member by member. It is hoped that frequent reference to the diagram will maintain a certain coherence among the various parts of this review.

It was not deemed advisable to complicate the diagram by indicating special methods of preparation which do not fit readily into the general scheme. None of these appears to affect the indicated relationships. To

indicate, for example, that the ferric oxides may be reduced to Fe_3O_4 or FeO would not add to the value of the diagram as a generic scheme. If pertinent to the main discussion, special methods will be described during the discussion of the member that is concerned.

It must not be assumed that we regard this diagram as a permanent representation of the relationships between the hydrates and oxides of iron, and that the only future changes will be to add new members or new series. In our view, the existence of some members and the paths of some changes are doubtful. The diagram is intended only to summarize prevailing opinions among the more active workers in this field. We believe that a
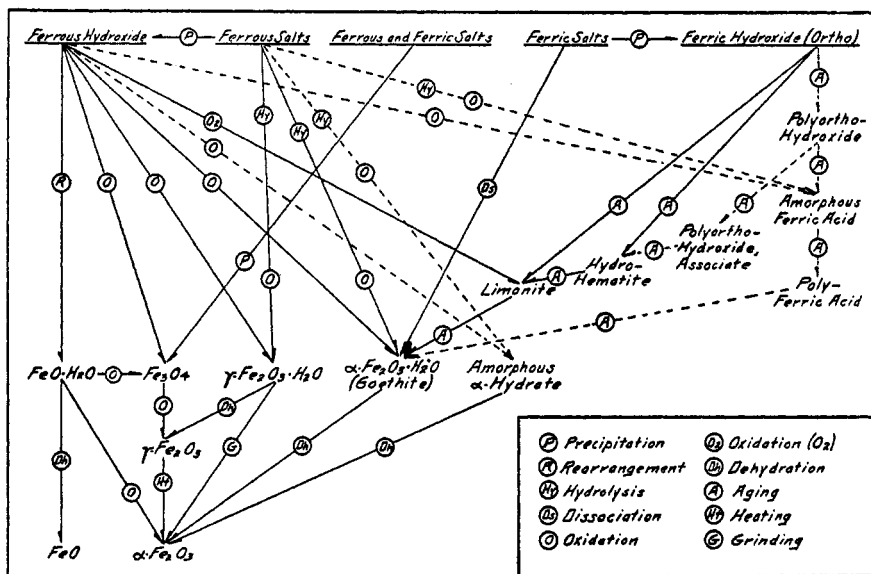

FIG. 1. RELATIONSHIPS AMONG THE OXIDE HYDRATES AND OXIDES OF IRON

review does not serve its full purpose if it records only positive and well-established knowledge. A review should, rather, emphasize the existence of uncertainties. It should present a field as a growing and developing one and should allow free presentation of the newer results obtained by newer methods. New results must be tested and weighed by numerous workers before final acceptance. Time and further studies, alone, will bring truth.

Finally, it will be apparent that this review will reflect, to a considerable extent, our own particular interests. For this we offer no apologies. Lack of space compels limitation. We shall not describe all properties nor list all physical and chemical constants. We shall limit ourselves to significant

phenomena that occur in the paths of change as they may be followed by the dehydration isobars, the x-ray spectra, the magnetic properties, the specific heats, the silver analysis, and the catalytic and chemical activities. We consider that these are, precisely, the experimental methods and data that have led to the progress of recent years. And it is with the more recent results that this review will be mainly concerned.

II. FERROUS HYDROXIDE, OR FERROUS OXIDE MONOHYDRATE

The snow-white flocculent substance which is precipitated when an alkali is added to a solution of a ferrous salt is perhaps the least known and understood of the hydrates of iron. Indeed, few chemists have ever
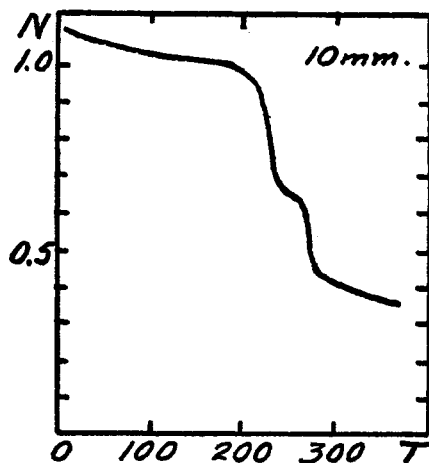

FIG. 2. DEHYDRATION ISOBAR FOR FeO·H₂O
(Hüttig and Möldner)

seen it in its snow-white state because of its sensitiveness to minute traces of oxygen. It is necessary to boil both the salt and alkali solutions previous to mixing in order to eliminate dissolved oxygen, and the apparatus (15) should be arranged in such a way that all operations and subsequent observations may be made in the presence of some oxygen-free neutral gas such as nitrogen or hydrogen. Another effective way of obtaining oxygen-free conditions is to boil the solutions separately while they are covered with a thick layer of vaseline or castor oil and then to pour the contents of one vessel, both solution and covering material, into the other. Ferrous hydroxide is usually obtained with a green color which turns black or red according to the amount of oxygen that is admitted. The difficulty of insuring strictly oxygen-free conditions has discouraged chemists from a

study of its properties. They have been interested, rather, in its strong reducing properties, and in the higher oxides that are so easily formed.

The first definite information as to chemical structure was obtained by Hüttig and Möldner (49), who proved the existence of the monohydrate, $FeO \cdot H_2O$, by means of the dehydration isobar shown in figure 2. They recognized and discussed the irregularity in the range 0.65 to 0.40 H_2O, but its presence does not vitiate the main conclusion as to the existence of the monohydrate.

Hüttig and Möldner did not analyze the x-ray spectra of the monohydrate in detail, but were satisfied with the conclusion that they differed from the spectra of FeO, Fe_3O_4, α- or γ-$Fe_2O_3 \cdot H_2O$, and α- or γ-Fe_2O_3. They were probably identical with the spectra of Natta and Cassaza (71), from which it was determined that ferrous oxide hydrate is rhombohedral with $a = 3.24$, $c = 4.47$, and $c/a = 1.38$.

Ferrous oxide hydrate is known to be paramagnetic. Quartaroli's (76) experimental methods hardly excluded oxygen and the formation of higher oxides, especially magnetite, so that one must favor his smallest susceptibility value, $\chi = +20 \times 10^{-6}$.

Hüttig and Möldner observed that small amounts of hydrogen were formed when they dehydrated ferrous oxide hydrate. They assumed that in addition to the main reaction

$$FeO \cdot H_2O \rightarrow FeO + H_2O$$

there was another

$$3FeO \cdot H_2O \rightarrow Fe_3O_4 + 2H_2O + H_2$$
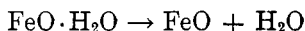
The black dehydration product that they describe was, therefore, ferrous oxide with an admixture of magnetite, Fe_3O_4. This is in accord with the result of Chaudron and Forestier (22) that ferrous oxide is not stable below 570°C. There should also be some free iron because of the reaction

$$4FeO \rightleftarrows Fe_3O_4 + Fe$$

Using a thermodynamic argument, Hüttig and Möldner make it appear probable that ferrous oxide hydrate is not stable at ordinary temperatures and that some slow change does occur. Whether it is this change beyond ferrous oxide hydrate or whether it is a previous change implied in a rearrangement like

$$Fe(OH)_2 \rightarrow FeO \cdot H_2O$$
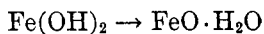
is not known, but Baudisch and Welo (17) have shown that a spontaneous change does take place. They found that a hydrate that had been aged

for four days in a neutral solution, in the absence of air, yielded α-ferric oxide when oxygen was admitted, together with a small amount of γ-ferric oxide, as indicated by a weak ferromagnetism. This is entirely opposite to what is observed when oxidation is carried out shortly after precipitation. On oxidation freshly precipitated ferrous oxide hydrate yields Fe_3O_4 in alkaline solution, α-$Fe_2O_3 \cdot H_2O$ in acid or neutral solution and, in certain circumstances, γ-$Fe_2O_3 \cdot H_2O$. This experiment has significance in connection with the difference between fresh and aged ferrous oxide hydrate as a reducing agent in the reduction of alkali nitrates (7, 13, 14, 15).

It is only in the presence of molecular oxygen (air) that freshly precipitated ferrous hydroxide can reduce alkali nitrates to nitrites or oxidize oxidizable substances that may be present, such as lactic acid to pyruvic acid or uracil to isobarbituric acid. In the absence of oxygen, either with or without nitrate, the hydroxide remains snow-white even when left to stand for years, showing that it does not dissociate water into hydrogen and oxygen. However, after long standing or aging under anaerobic conditions, ferrous hydroxide is unable either to reduce nitrates or to oxidize lactic acid and uracil. But it remains autoxidizable and may be completely oxidized to ferric hydroxide.

This peculiar behavior of ferrous hydroxide raises three questions: (1) What happens to ferrous hydroxide when it ages in the absence of air? (2) Why is oxygen necessary in order that ferrous hydroxide may reduce nitrates? More specifically, why is oxygen necessary for the production of activated hydrogen? (3) Whence comes the activated oxygen which is able to oxidize lactic acid to pyruvic acid or uracil to isobarbituric acid?

The fact that oxidation of aged ferrous hydroxide yields an oxide and neither of the hydrates points to the conclusion that the aging under anaerobic conditions involves the formation of a compound with water bound in another way.

Answers to the second and third questions are suggested by the work of Goldberg (33), who found that ferrous hydroxide dissociates water to liberate hydrogen and oxygen when the temperature is 200°C. or more. It is known that even at room temperature, in the presence of oxygen, ferrous hydroxide can reduce nitrates or oxidize certain organic compounds. Hence it appears that if oxygen is present, water is dissociated by ferrous hydroxide even at room temperature, according to the scheme: $H_2O \rightarrow H + OH$ (H_2O_2).

Since the aged ferrous hydroxide can bring about neither oxidation nor reduction, and since the outstanding difference between the aged and the fresh ferrous hydroxide is the absence or presence of this water of hydration, it follows that the water which is dissociated into activated hydrogen and oxygen is this labile water. It is neither the adsorbed nor the solvent

water. Ferrous hydroxide which has been aged for a sufficient length of time and has no labile water left has, therefore, lost the power to reduce nitrates or to oxidize uracil and lactic acid.

III. THE FORMATION OF MAGNETITE, Fe_3O_4

In order to obtain the partly oxidized magnetite and not the fully oxidized $Fe(OH)_3$ on oxidation of $Fe(OH)_2$ (we retain the conventional notation), the rate of oxygen supply must be low and the liquid medium must be alkaline. The latter condition was emphasized by Miyamoto (69) when he found that high hydroxyl-ion concentration retarded oxidation, which is apparently in contradiction with the well-known fact that ferrous hydroxide is a stronger reducing agent in an alkaline medium. Krause (53) and Deiss and Schickorr (26) have given the explanation and resolved the contradiction.

They regard the full oxidation of ferrous hydroxide to ferric hydroxide as the primary process. According to Krause the isoelectric point of ferric hydroxide, when formed by oxidation of ferrous hydroxide, is at pH = 5.2. It finds itself in an alkaline medium and immediately assumes an acid character. It then combines with the still unoxidized, strongly basic ferrous hydroxide, of isoelectric point pH > 11.5, to form ferrous ferrite according to the reaction:

$$Fe(OH)_2^+ + 2Fe(OH)_3^- \rightarrow FeO \cdot Fe_2O_3 + 4H_2O$$
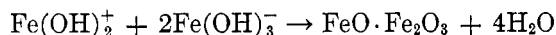
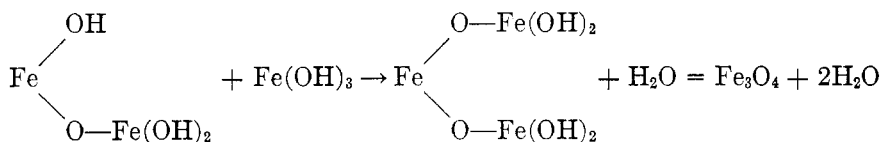Ferrous ferrite does not oxidize further under these conditions.

When the rate of oxygen supply is low enough there is sufficient time for reaction between ferrous and ferric hydroxides to form ferrous ferrite. At boiling temperature, particularly, the formation of ferrous ferrite is favored because the rate of combination is increased and at the same time the supply of oxygen is diminished. On the other hand, when the supply of oxygen is plentiful, and especially at low temperatures when the rate of oxidation is high as compared with the rate of combination of ferrous hydroxide and ferric hydroxide, we will have nearly complete oxidation to ferric hydroxide. This view of the matter explains very well the fact that a favored way of preparing magnetite from ferrous hydroxide is to work at boiling temperatures. And it explains the interesting fact that a piece of iron kept at the bottom of a vessel of water becomes covered with a black rust, while one suspended just beneath the surface acquires a reddish brown coating.

While the explanation that has been given suffices to account for the formation of magnetite instead of ferric hydroxide, it does not account for the green intermediate product that is always observed. Deiss and Schickorr noticed that the green substance is formed after a momentary appearance

of the red ferric hydroxide and assumed that the green compound is also a combination of ferric hydroxide with unoxidized ferrous hydroxide. A possible combination is:

$$Fe(OH)_2 + Fe(OH)_3 \rightarrow Fe\underset{O-Fe(OH)_2}{\overset{OH}{\Big<}} + H_2O = 2FeO \cdot Fe_2O_3 + 5H_2O$$
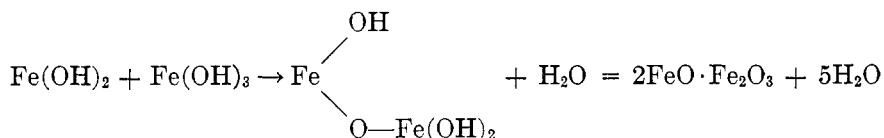
The formation of magnetite would then involve the combination of this green substance with newly formed ferric hydroxide, according to the scheme

$$Fe\underset{O-Fe(OH)_2}{\overset{OH}{\Big<}} + Fe(OH)_3 \rightarrow Fe\underset{O-Fe(OH)_2}{\overset{O-Fe(OH)_2}{\Big<}} + H_2O = Fe_3O_4 + 2H_2O$$

Whether this path or the more direct one is followed, the primary process is the oxidation of ferrous hydroxide to ferric hydroxide, followed by reaction between these two kinds of hydroxides. The effect of varying the rate of oxidation would be the same. Deiss and Schickorr were unable, because of experimental difficulties, to secure analytical proof that the green compound had the composition $2FeO \cdot Fe_2O_3$.

Essentially the same principle of the reaction between ferrous hydroxide and ferric hydroxide is involved in the preparation of magnetite by precipitation of an equimolar solution of ferrous and ferric salts with an alkali (61, 104). Ferric hydroxide is already present so that no oxidation is necessary. While the crystal structures and the magnetic properties of magnetite obtained in this way correspond to those of magnetite obtained by slow oxidation of ferrous hydroxide, there are marked differences in detail which follow from the altered conditions of precipitation.

These differences arise from the different solubilities of ferrous hydroxide and ferric hydroxide and from the fact that when ferrous hydroxide is oxidized there are two opportunities for the crystallization process to operate, whereas in the simultaneous precipitation of ferrous hydroxide and ferric hydroxide the crystallization process operates only once and then under very unfavorable conditions.

Ferrous hydroxide is not extremely insoluble. The accumulation velocity (the Häufungsgeschwindigkeit of Haber (36)) is also not extremely high so that there is time for the formation of good crystals of considerable size; that is, the rate of crystallization (Ordnungsgeschwindigkeit) is not exceeded by the accumulation rate. The oxidation which follows involves

recrystallization and is slow, so that the crystals of this magnetite are large and well developed, as shown by the sharpness of the x-ray lines, and are free from strain, since the magnetic properties do not alter greatly on annealing.

Ferric hydroxide, on the contrary, is extremely insoluble in water, and the rate of accumulation is high, since it is proportional to the density excess over the solubility. It exceeds the rate of crystallization and the crystals, if any, are imperfect. Also, according to the precipitation laws they should be small. The x-ray lines of this magnetite, formed by simultaneous precipitation of ferrous hydroxide and ferric hydroxide, are diffuse, showing that the crystals are either of small size, or imperfect, or both. The magnetic properties alter greatly on annealing.
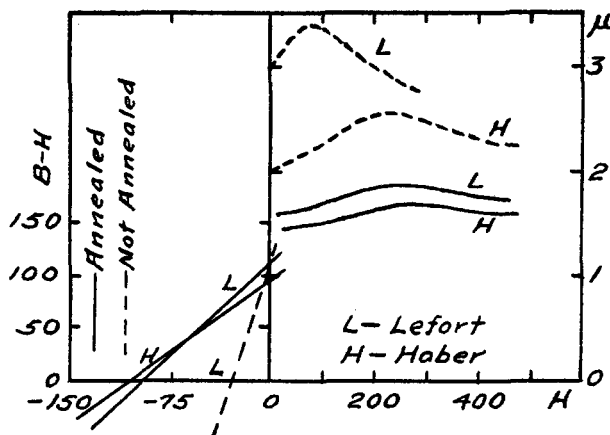

FIG. 3. EFFECT OF ANNEALING AT 1000°C. ON PERMEABILITIES AND COERCIVITIES OF MAGNETITES

Figure 3 shows the permeability curves and portions of the hysteresis loops for two magnetites studied by Welo and Baudisch (104). The intersections of the hysteresis loops with the axes give the remanences and the coercive forces. "Lefort's" refers to the magnetite obtained by simultaneous precipitation of ferrous hydroxide and ferric hydroxide. "Haber's" refers to the magnetite formed by oxidation of ferrous hydroxide precipitated with ammonia in the presence of potassium nitrate at boiling temperatures. Haber's undergoes very little change on annealing at 1000°C., from which it is inferred that the crystals were initially well formed. Lefort's is markedly changed on annealing, and its magnetic properties approach those of Haber's. Lefort's was certainly imperfectly crystallized. Results since obtained, which will be considered later, make it probable that smallness of crystal size also plays a part.

The special place which Lefort's magnetite occupies as the most suitable material for the preparation of "active iron oxide" is due to its small crystals and to their poor quality as brought about by the precipitation conditions. Also, the unlike chemical characteristics of ferric hydroxide obtained by oxidizing ferrous hydroxide, and of ferric hydroxide obtained directly by precipitation from a ferric salt solution may persist in the magnetites formed from them. To this possibility, serious consideration has not yet been given. Krause and Pilawski (58) assign different structural formulas for these hydrates (the meta- and ortho-hydroxides considered in the last section of this review) on the basis of their silver analysis. It is known that the isoelectric point of the former is at pH = 5.2 and of the latter at pH = 7.7 (53).

Magnetite has been prepared by oxidizing ferrous hydroxide with nitric oxide (104). A magnetite that is free of impurities other than 0.001 per cent of carbon, and which has the very rare property of having exactly the theoretical percentage of ferrous oxide, 31 per cent, has been obtained by burning iron carbonyl in a controlled air supply (68). The group of French workers (3, 22, 30, 43) who have devoted themselves to thermo-magnetic analyses have made their magnetites by reducing α-ferric oxide with hydrogen in the presence of water vapor at temperatures of 300 to 600°C. Another way to reduce ferric oxides to magnetite is to leave them for a short time in molten sodium acetate (105). To describe, or even mention, all methods of preparing magnetite would lead us too far afield.

The various formulations of precipitated magnetite found in the literature, such as $2FeO \cdot 3Fe_2O_3$, $4FeO \cdot Fe_2O_3$, etc., are improbable. The possibility of forming mixtures of $Fe_3O_4 = FeO \cdot Fe_2O_3$ with $FeO \cdot H_2O$ and ferromagnetic ferric oxide is inherent in the precipitation and oxidation method. X-ray analyses have always given the same set of lines regardless of the procedure in preparation (104). The x-ray lines yield the same spacings of the lattice planes as are found in natural magnetite and in magnetite derived by dry reduction of ferric oxide. An underoxidized magnetite studied by Hüttig and Möldner (49) showed lines of ferrous oxide hydrate. Lefort's magnetite is generally overoxidized, but the excess ferric oxide is ferromagnetic ferric oxide which, as will be seen, has the same x-ray spectrum as magnetite except for slight differences in relative intensities.

The x-ray analyses indicate, in addition, that there are no definite hydrates of magnetite. This conclusion is supported by the dehydration isobars obtained by Hüttig and Möldner (49), whose curves are shown in figure 4. Curve A is for a sample prepared by oxidizing ferrous hydroxide with oxygen (O_2). It was slightly underoxidized with Fe:O = 1:1.289, instead of Fe:O = 1:1.333 as in the theoretical ratio for Fe_3O_4. B is for a part of sample A which had been aged for 70 days in a sealed container at

room temperature. C is for a magnetite made by simultaneous precipitation of a mixture of ferrous and ferric chlorides giving $Fe:O = 1:1.335$. Curve D was obtained with an underoxidized product, $Fe:O = 1:1.196$. In curves A, B, and C there are no discontinuities and hence no indications of the existence of definite hydrates. A comparison of A and B shows the characteristic feature of the aging process in oxide hydrates containing water other than water of constitution. It is its loosening and gradual elimination. The discontinuity in curve D is due to the ferrous monohydrate whose dehydration isobar is shown in figure 2.

The crystal structures and magnetic properties of magnetite are so nearly like those of the ferromagnetic ferric oxide derived by oxidation of magnetite, hereafter called γ-oxide, that they will be considered together.
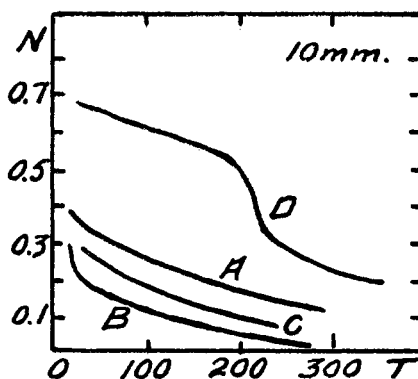

FIG. 4. DEHYDRATION ISOBARS FOR $Fe_3O_4 \cdot xH_2O$
(Hüttig and Möldner)

IV. γ-OXIDE

To describe the behavior of precipitated magnetite as it is oxidized at a low temperature, the magnetic and crystal structure transformations that occur at higher temperatures, and the crystal structure problem that arises, we shall quote in large part from our own paper (102).

"Generally speaking, the facts observed on heating the oxide in a stream of oxygen are as follows:—The color of the oxide changes suddenly from black to a dark red at about 220°C., the oxide remains magnetic, although the iron has been completely converted into the ferric form so that the composition has become Fe_2O_3. The ferricyanide test showed not a trace of Prussian blue, and hence no ferrous iron after oxidation for a sufficient time at 220°C. A solution of the oxide in hydrochloric acid titrated with potassium permanganate likewise yielded no iron in the divalent form. All of this shows that Fe_3O_4 may be completely oxidized to Fe_2O_3 at a temperature of 220°C. without loss of the magnetic properties.

"On further heating, the oxide, now Fe_2O_3, remains magnetic until a temperature of 550°C. is reached. At this temperature a non-reversible transformation takes place, for the oxide becomes permanently non-magnetic. This transformation is obviously a pure temperature effect, since the oxidation was already complete at the lower temperature of 220°C. But to test the point a sample which had first been oxidized at 220°C. was heated in an atmosphere of nitrogen carefully freed from oxygen. It again became non-magnetic. The necessary condition, however, for the loss of magnetism at 550°C. is that the Fe_3O_4 must first be oxidized to Fe_2O_3 at some lower temperature. If Fe_3O_4 is heated in nitrogen without a preliminary oxidation it is stable and retains its magnetic properties even if heated to 800°C. These
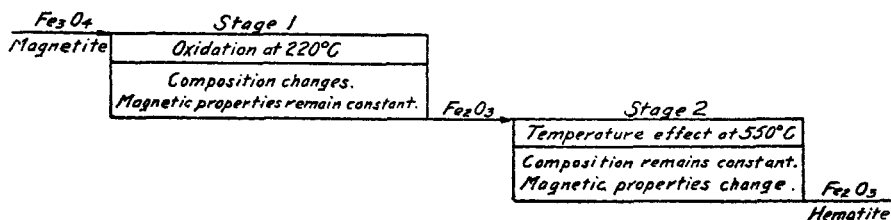

FIG. 5. TWO-STAGE TRANSFORMATION FROM MAGNETITE TO HEMATITE
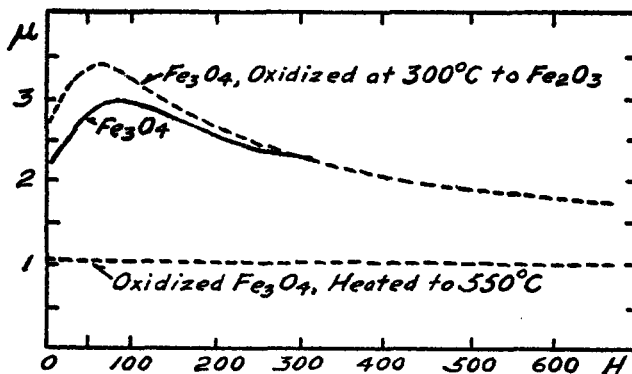

FIG. 6. PERMEABILITIES OF SYNTHETIC IRON OXIDES IN POWDERED FORMS
Densities of packing = 1.32 g. per cubic centimeter

observations are briefly summarized in the scheme shown in figure 1. (Figure 5 of this review.)

"It has been stated that the oxidation begins at 220°C. A more precise statement would be that the oxidation becomes sufficiently rapid at that temperature so that the change in color may be observed. It is recognized that oxidation may take place at a much lower temperature.

"The results of the magnetic measurements are shown in figure 2 (figure 6 of this review). Our qualitative observations are confirmed. The maximum permeability of the oxide after having passed the first stage of transformation is somewhat higher than that of the original Fe_3O_4, and there is shown a considerable shift of its position.

No reason is known for this. At higher fields the curves coincide, which accounts for our qualitative observation (made with high field intensities) that the magnetic properties remain unchanged on oxidation at a low temperature. After the second stage the permeability is seen to be nearly, but not quite, unity at all fields. The maximum residual permeability is 1.045, and is so small that the material would be considered non-magnetic towards rough qualitative tests.

"The crystal structures of magnetite and hematite are known to be different. Bragg (20) and Nishikawa (72) found for magnetite a diamond point structure and Davey (25) found that hematite is like corundum, which, in turn, resembles calcite. It was of interest to determine whether the change of one structure into the other takes place at stage I or at stage II. It seemed improbable that it changes at stage I on account of the constancy of the magnetic properties when the oxide passes through that stage. On the other hand, it was difficult to assume that it changes on stage II, for it would involve the assumption that Fe_2O_3 has allotropic forms, and can assume either the form for magnetite or the calcite structure usually obtained for hematite.

"Diffraction patterns of the original Fe_3O_4 and the resulting oxides after each stage of transformation were obtained. . . . . The original Fe_3O_4 and the Fe_2O_3 which had passed through stage I gave identical patterns, and the spacings were the same to within one-tenth of one per cent. The Fe_2O_3 which had been through stage II of the transformation, however, showed the pattern usually found for Fe_2O_3. The disappearance of the magnetic properties of the oxide is therefore associated with the change in structure taking place at stage II and is not connected with the change in composition. It is also evident that the atoms of iron and oxygen in Fe_2O_3 have two alternative arrangements in the crystal. If Fe_2O_3 is derived by oxidation of Fe_3O_4 at a low temperature, the Fe_3O_4 structure is retained, and only at a higher temperature of about 550°C. does this structure become unstable and change into the more stable one similar to calcite. The original Fe_3O_4, however, as has already been pointed out, remains stable up to temperatures of at least 800°C. if we prevent oxidation to Fe_2O_3.

"This result suggested the interesting problem of finding room for more oxygen in a crystal of Fe_3O_4 without a change in the arrangement of the atoms already in place. . . . .

"The unit cube contains eight molecules, so that Fe_3O_4 may be written $Fe_{24}O_{32}$. After oxidation to Fe_2O_3 the corresponding composition would be $Fe_{24}O_{36}$. We must find room for four additional oxygen atoms in the cube."

Miss Twenhofel (97) concluded that definite positions could not be assigned to the extra oxygen atoms, but Thewlis (93), after a thorough and critical study, has done this. He made photometric measurements on his x-ray films and found that the patterns of magnetite and of γ-ferric oxide, although very similar, are not identical. The reflections from the 400 and 440 planes are definitely more intense in γ-ferric oxide than in magnetite. His analysis involved the following special procedures in addition to those usually followed in crystal analysis.

(1) Determination of the space groups which can accommodate thirty-six oxygen atoms in the unit cube and at the same time allow twenty-four iron atoms to occupy the same positions as in magnetite. He found six such groups: O^6, T_d^2, T_d^1, T^4, T^2, and T^1.

(2) Decision as to the minimum permissible iron to oxygen and oxygen to oxygen distances. The smallest iron to oxygen distance in magnetite is the Fe^{++} to O distance of 1.88 A.U. (23) and the Fe^{++} and Fe^{+++} radii are, respectively, 0.78 A.U. and 0.63 A.U. (34). During oxidation Fe^{++} becomes Fe^{+++}, so that the least iron to oxygen distance in γ-ferric oxide can be shorter than in magnetite by 0.15 A.U. and becomes, say, 1.7 A.U. The same data yield 1.1 A.U. as the oxygen radius, so that the oxygen to oxygen distance may be taken to be 2.2 A.U.

(3) Two of Pauling's (73) coördination rules are applied in order to make a choice between two atomic arrangements which give the same calculated relative intensities and which agree with the intensities that are observed.

During the analysis, Thewlis kept in mind the possibility that the oxygen atoms already present in magnetite may have been rearranged while four more oxygen atoms were added during oxidation. He found no evidence of any such rearrangement.

The final result was that the structure of γ-ferric oxide is the same as that of magnetite with oxygen atoms added to the unit cell in the following positions:

0.125,	0.125,	0.125	0.625,	0.375,	0.875
0.875,	0.625,	0.375	0.375,	0.875,	0.625

The positions of the Fe^{++}, Fe^{+++}, and O^{--} ions for magnetite are completely listed in Thewlis' paper.

The cube edge is 8.40 A.U. long as in magnetite and the space group of γ-ferric oxide is O^6 or T^4. Thewlis remarks that another structure is possible belonging to space group O^7, since O^7 is enantiomorphous with O^6. Their structures are mirror images of each other and are indistinguishable by x-ray methods. The structure diagram for γ-ferric oxide is shown in figure 7.

Thewlis noted that some of the iron atoms have the unusual coördination number of five. Of this he has the following to say: —"A striking feature of the structure is that certain iron atoms (those occupying the Fe^{++} positions of Fe_3O_4) are placed between five oxygen atoms. An arrangement of this kind is most unusual and has to the author's knowledge only once previously been noted, namely, in the case of andalusite (92), where an aluminum atom was found to occur between five oxygen atoms. The structure may with regard to its coördination properties, be regarded as intermediate between Fe_3O_4 and α-Fe_2O_3. The fivefold oxygen groups of γ-Fe_2O_3 can be considered as intermediate between the fourfold groups of Fe_3O_4 and the sixfold groups of α-Fe_2O_3."

A brief résumé of the checkered history of γ-oxide may be of interest. Nearly a hundred years ago, 1838, von Kobell (100) recorded the fact that

the variety of goethite, now called lepidocrocite, becomes magnetic on heating, and in 1848 Plücker (74) noted the same behavior in an artificial ferric hydrate (10). These early observations had been entirely forgotten. The later work of Robbins (77), Malaguti (65) and Liversidge (62) was not generally accepted. This opinion of Dana (24), expressed in 1867, is typical of the skeptical attitude: —"Now, if a sesquioxyd occurs in *isometric* crystals as supposed to be true of Fe_2O_3 (but reasonably doubted) that sesquioxyd is not Fe_2O_3 but may be ....." The presence of ferrous iron was suspected. In 1909, Hilpert (42) proved that ferrous iron need not be present in a ferromagnetic iron oxide. In 1917, Sosman (89) wrote at length of the theoretical interest and importance of ferromagnetic ferric oxide, but it was not until 1925 that much attention was paid to this interesting substance.
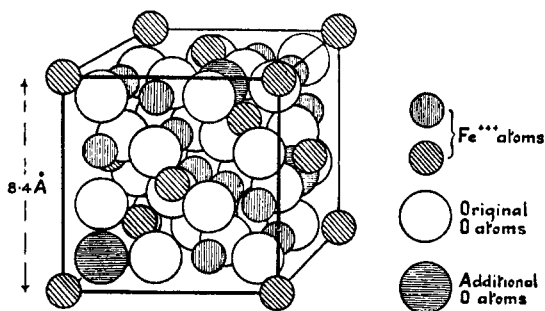

FIG. 7. UNIT CUBE OF γ-Fe_2O_3
(Thewlis)

In February, 1925, Welo and Baudisch (103) reported that they had found the x-ray diffraction patterns of oxidized magnetite and of the original magnetite to be identical and that ferromagnetism disappears during the transformation to the usual hematite structure that occurs at a higher temperature. In August of that year appeared their complete paper, a part of which has already been quoted in this review, and the paper of Sosman and Posnjak (90), who had obtained the same experimental results in 1922.

In this same paper Sosman and Posnjak announced that the dehydration of the mineral lepidocrocite, $Fe_2O_3 \cdot H_2O$, yields a ferromagnetic ferric oxide, while similar dehydration of goethite, which is also $Fe_2O_3 \cdot H_2O$, yields only paramagnetic ferric oxide. As has already been mentioned, this alternative path to γ-ferric oxide was known long ago and had long been forgotten. Instead of oxidizing magnetite we may obtain γ-ferric oxide by way of lepidocrocite or its artificial counterpart, γ-ferric oxide hydrate. It is this path, opened up by Sosman and Posnjak, that will now be considered.

V. CLASSIFICATION OF FERRIC OXIDE HYDRATES: THE YELLOW AND THE
RED SERIES

Synthetic γ-ferric oxide hydrate is an orange-yellow hydrate. This statement is much more than a description of its color. The statement identifies γ-ferric oxide hydrate as a member of one of the two great classes of ferric oxide hydrates now recognized, the yellow series and the red series.

TABLE 1

Comparison of the properties of yellow and red ferric oxide hydrates

	YELLOW FERRIC OXIDE HYDRATE	RED FERRIC OXIDE HYDRATE
General method of preparation..	Oxidation of $Fe(OH)_2$, $FeCO_3$, or $Fe_3O_4\cdot$ xH_2O with O_2, H_2O_2, $KClO_3$, KIO_3, etc., in presence of water	Precipitation from a ferric salt solution with an alkali
State of hydration.............	Monohydrate	No definite hydrate
Dehydration isobar (47, 86).....	Discontinuous	Continuous
Structure (19, 47, 86)...........	Orthorhombic, 2 modifications, α-$Fe_2O_3\cdot$ H_2O and γ-$Fe_2O_3\cdot H_2O$	Amorphous
Solubility in acids and ferric chloride solutions............	Slightly	Easily
Pyrophoricity..................	No	Yes
Isoelectric point (53)...........	pH = 5.2	pH = 7.7
Adsorption (37, 91, 101).........	Small	Large
Catalytic activity (decomposition of H_2O_2) (51).............	Low	High
Spontaneous change in catalytic activity (decomposition of H_2O_2) (51)..................	Slow	Rapid

They were named in 1879 by Tommasi (94, 96), who was apparently unaware that Muck (70), twelve years earlier, had also observed that two different methods of preparation led to hydrates of identical composition but with different sets of properties. The two general methods of preparation and comparisons of some of their properties are shown in table 1. In this

table, the properties for which no references are indicated are those noted and listed by Tommasi himself.

It will be noticed that the two different modes of preparation are closely analogous to the two ways of forming magnetite that we have already discussed. The reader is referred to that part of this review for a qualitative discussion as to why the yellow hydrates are crystalline substances of definite composition while the red hydrates are amorphous.

Of course the actual line of demarcation between yellow and red hydrates need not be as sharp as indicated in table 1. It is well-known that there is a continuous gradation in color. Sometimes crystal structure may not be detected in a yellow hydrate with x-rays, and red hydrates may contain difficultly soluble yellow hydrates. In all such border-line cases it is found that the fundamental distinction between the two modes of preparation, slow reactions for yellow hydrates and extremely rapid precipitation for the red, has not been maintained. Another reason for the overlapping of properties into the yellow that should be distinctive for the red is that red hydrates convert spontaneously (age) into crystalline α-ferric oxide hydrate. The several paths of aging are recorded in our diagram, figure 1, where the conventional name of ferric hydroxide is used, and will be considered in some detail later on.

The many special ways of preparing ferric hydrates, especially the yellow ones, will not be considered here, where we are more interested in systematic classification and general relationships. However, because α-ferric oxide hydrate occurs so rarely, α-ferric oxide hydrate being the usual product, and because the developments are so recent, we shall consider the chemical conditions necessary for its appearance.

VI. PREPARATION AND SOME PROPERTIES OF γ-FERRIC OXIDE HYDRATE

Böhm (19) seems to have been the first to recognize one way of preparing γ-ferric oxide hydrate. He mentions casually that the hydrate obtained by the action of oxygen on Fe_2S_3 (78) yields the lepidocrocite pattern. Next, Albrecht (4) showed that oxidation of a ferrous salt in dilute solution with an iodate in the presence of sodium thiosulfate (38) yields the γ-modification. Several newer methods have been described by Baudisch (11) and by Baudisch and Albrecht (12). The discussion in the latter paper as to the favorable conditions is as follows:—

"One of us has shown in earlier work (8, 14) that in catalytic oxidations with the aid of iron salts, the oxygen used for the oxidation becomes temporarily activated, becoming coördinatively linked in an intermediate iron complex. Such "active" iron complexes could be identified (9). This supposition contradicts two other theories. Manchot, as the leading representative of one, stipulates the formation of an intermediate iron peroxide, while Wieland, as the supporter of the other, sup-

poses the formation of intermediary hydrogen peroxide. An exact proof for the
existence of either the one or the other is lacking at the present time (2), while the
facts can be just as well explained by the aid of Baudisch's oxygen-complex theory,
with the further advantage that complexes of which oxygen is a member are known
with iron as well as with cobalt. If such a complex decomposes on further oxidation,
one should expect that ferric oxide hydrate of another structure would be formed
in this decomposition, as when, in the direct oxidation of a ferrous salt, the ferric salt
formed decomposes by hydrolysis into ferric oxide hydrate and acid.

"This theory explains the following experiment very well. If ferrous chloride
solution is oxidized at ordinary temperatures (about 18°), whether quickly or slowly,
only α-hydrate is formed. If, however, the oxidation is carried out *slowly* at a some-
what higher temperature (40–50°) while the solution is being stirred slowly (a satu-
rated solution diluted to one-half), a considerable percentage of γ-hydrate is formed.
At temperatures from 90–100° α-hydrate is obtained with slow as well as with rapid
oxidation. The self-complex formation of ferrous chloride solution at higher tem-
peratures has been shown as probable by other investigators (1), and Chandra (21)
has succeeded in isolating polynuclear ferrous–ferric complexes as their alkali salts
by the partial oxidation of ferrous salt solutions.

"An attempt was then made to obtain pure γ-oxide hydrate by oxidation following
the addition of suitable complex-forming compounds to ferrous salt solutions. It
has been shown that nitrogen-containing compounds are especially suitable, above
all pyridine. As can be seen from the experimental part, it was possible to obtain
pure γ-oxide hydrate by the addition of pyridine to ferrous chloride solutions. It
has been shown, moreover, that not only the addition of a suitable complex-forming
compound, but also the nature of the anions in the salt solution, is of importance
for the formation of γ-oxide hydrate, i.e., it was impossible to obtain γ-oxide hydrate
from ferrous sulfate or ferrous fluoride solutions. A γ-oxide formation from ferric
nitrate solutions was not expected and not found, as the oxidizing power of nitric
acid is too great for the formation of any kind of intermediate products with the
desired properties.

"In further preparations of γ-oxide hydrate, the addition of sodium azide to the
ferrous chloride solutions was found to be of great advantage. The question as to
whether this addition of sodium azide to the ferrous salt solutions forms a complex
cannot be definitely answered from our experimental material. The red color of the
solution points to the formation of an iron azide (63). In oxidations at a higher
temperature hydrazoic acid, which can be recognized by its odor, is given off abun-
dantly. It is interesting to note that the formation of γ-hydrate does not commence
until the solution is already partly oxidized, and the originally alkaline solution
(pH 8 to 10) has become weakly acid. The formation of γ-hydrate first starts from
a pH of 6.5 to *ca.* 2.0. It seems then that the formation of γ-hydrate is dependent
also on the hydrogen-ion concentration, for it is always found that γ-hydrate is
formed only in weakly acidic solutions (pH 2–6.5). This observation is in agreement
with that of Krause (58), who is of the opinion that his 'metaferric hydroxide' (eisen-
ige Säure) with the isoelectric point pH 5.2 is identical with the γ-hydrate."

We have only qualitative data as to the relative stability of α- and
γ-ferric oxide hydrate. Albrecht (4) states that γ-ferric oxide hydrate
dried for 72 hours at 100°C. had a water content of 6.7 per cent, which is
4.5 per cent less than the theoretical percentage, 11.2, in a monohydrate.
α-Ferric oxide hydrate remained constant in weight at 100°C. with 11.2 per

cent of water and first began to lose it at 150°C. γ-Ferric oxide hydrate is thus less stable than α-ferric oxide hydrate. In the corresponding minerals, lepidocrocite and goethite, it is also found that the γ-modification (lepidocrocite) is less stable than the α-form, but the dehydration temperatures are much higher than in the artificial hydrates. In lepidocrocite it is close to 240°C. and in goethite close to 275°C. It must be remembered, however, that the values obtained for dehydration temperatures are much affected by particle size and rate of temperature increase, so that these values are, very likely, too high.

An unpublished experiment of Baudisch shows that γ-ferric oxide hydrate is more easily dehydrated and reduced to form magnetite than is α-ferric oxide hydrate. The two hydrates were shaken for six to eight
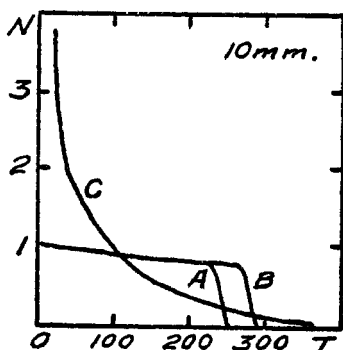

FIG. 8. DEHYDRATION ISOBARS FOR LEPIDOCROCITE, GOETHITE, AND COLLOIDAL FERRIC OXIDE HYDRATE
(Hüttig and Garside)

hours in glycol that was kept at 120–125°C. A black magnetite was formed from γ-ferric oxide hydrate. α-Ferric oxide hydrate did not become ferromagnetic and it retained its yellow-brown color, showing that it was not dehydrated either.

Dehydration curves for the natural minerals are shown in figure 8 (44, 47). Curve A is for lepidocrocite, γ-ferric oxide hydrate, and curve B is for goethite, α-ferric oxide hydrate. In this figure is shown also a curve, C, for an artificial red ferric hydrate for which no discontinuity was expected because no definite hydrates should be present. It is included in the figure to illustrate the fact that entirely different types of dehydration isobars are obtained from true hydrates of the red series. The adsorbed water obeys the laws of osmotic pressure (45, 85).

No such dehydration isobars have yet been taken for artificial γ-ferric oxide hydrate. The evidence for its existence is that it gives the same

x-ray spectrum as lepidocrocite and behaves the same way magnetically, in that it is converted to ferromagnetic γ-ferric oxide on dehydration at low temperatures. Goethite and artificial α-ferric oxide hydrate do not pass through the ferromagnetic γ-ferric oxide stage but convert directly to α-ferric oxide.

A proof that artificial γ-ferric oxide hydrate really has one molecule of water has been obtained by Welo and Baudisch (106). A sample made by the pyridine method which had been air-dried contained 16.3 per cent of water. On drying for five months over calcium chloride this was reduced to 15.6 per cent. When dehydrating at 180°C. the water content approached the constant value 4.4 per cent. The difference, 15.6 − 4.4 = 11.2 per cent, is the theoretical water content in a monohydrate of ferric oxide. The foregoing data, when viewed in the light of the general form of such dehydration curves as those of Posnjak and Merwin (75), show that the minimum dehydration temperature could not have been much less than the 180°C. that was used.

The crystallographic constants of γ-ferric oxide hydrate as determined by x-ray analysis are, according to Böhm (19): $a = 3.85$; $b = 12.5$; $c = 3.07$ A.U., giving $a:b:c = 0.308:1:0.246$; the density is 3.97 g. per cubic centimeter. The corresponding values for α-ferric oxide hydrate are: $a = 4.60$; $b = 10.01$; $c = 3.04$ A.U.; with $a:b:c = 0.459:1:0.303$. Its density is 4.195 g. per cubic centimeter. Virtually the same values were obtained by Goldsztaub (35).

The difficult task of establishing values for the magnetic susceptibilities of γ- and α-ferric oxide hydrate has been accomplished by Albrecht and Wedekind (4, 6). Both hydrates give $\chi = +42 \times 10^{-6}$ at room temperature. They conform to the Hausknecht (39) rule that the hydrates have higher susceptibilities than their anhydrides. In α-ferric oxide, $\chi = +19.7 \times 10^{-6}$, and it is independent of temperature (84). Both γ- and α-ferric oxide hydrate, on the contrary, obey the Curie-Weiss law of temperature variation (5).

γ-Ferric oxide from γ-ferric oxide hydrate by dehydration

Williams and Thewlis (107) studied the changes that occur in crystal structure when γ-ferric oxide hydrate is heated at a series of increasing temperatures. Their crystals had, initially, average linear dimensions of the order 10^{-5} cm. When crystals of γ-ferric oxide first appeared they were extremely minute with linear dimensions of the order 10^{-7} cm. A similar disintegration has been observed during dehydration of lepidocrocite by Goldsztaub (35). On heating at higher temperatures the crystals grew to final linear dimensions of the order 10^{-6} cm. At still higher temperatures, γ-ferric oxide transformed to α-ferric oxide, the crystals of which attained final dimensions of 10^{-4} cm.

The development of ferromagnetic γ-ferric oxide from the paramagnetic γ-ferric oxide hydrate as it is dehydrated has been studied in detail by Welo and Baudisch (106).   They dehydrated at 180°C. and measured the permeabilities, which are proportional to the volume susceptibilities, as functions of the field strengths, the remanences, and the coercive forces after various times of heating.   X-ray spectra were also taken at various times.   The permeabilities are shown in figure 9.   Two processes occur: gradual increase of permeability, owing to the formation of more and more ferromagnetic γ-ferric oxide; and magnetic hardening, as indicated by a shift of the permeability maxima to higher field strengths.   These two processes are definitely separated as to time of heating.   This is more
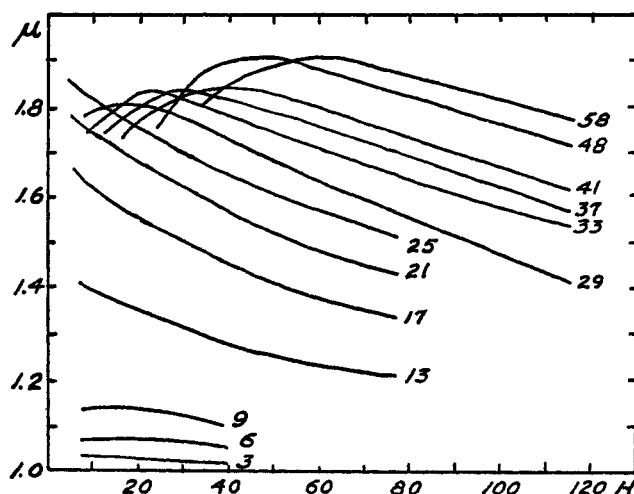

FIG. 9. DEVELOPMENT OF FERROMAGNETISM DURING DEHYDRATION OF γ-Fe$_2$O$_3$·H$_2$O

clearly demonstrated in figure 10, which shows the remanences and the coercive forces, which are measures of magnetic hardness, together with the maximum values of the volume susceptibilities as obtained from figure 9. $\left(\text{Susceptibility, } \kappa, \text{ and permeability, } \mu, \text{ are related by } \kappa = \dfrac{\mu - 1}{4\pi}.\right)$ The susceptibilities have reached practically their limiting values before either remanence or coercive force take on appreciable values.

Furthermore, the x-ray spectra showed no lines of γ-ferric oxide during the first 20 hours of heating.   Lines of γ-ferric oxide first appeared after about 25 hours of heating, when permeability was fully developed and when remanence and coercive force first became noticeable.

This is quite in agreement with the x-ray results of Williams and Thewlis. γ-Ferric oxide is present in increasing amounts from the start, but its

crystals are too small to be detected even by x-rays. And the observations suggest that in γ-ferric oxide (and in magnetite) there can be neither remanence nor coercive force until the crystals have attained a certain definite, although small, size which may be the magnetic domain (Barkhausen region) for this class of material. The permeability, however, is highest when the crystals are smaller than this critical size.
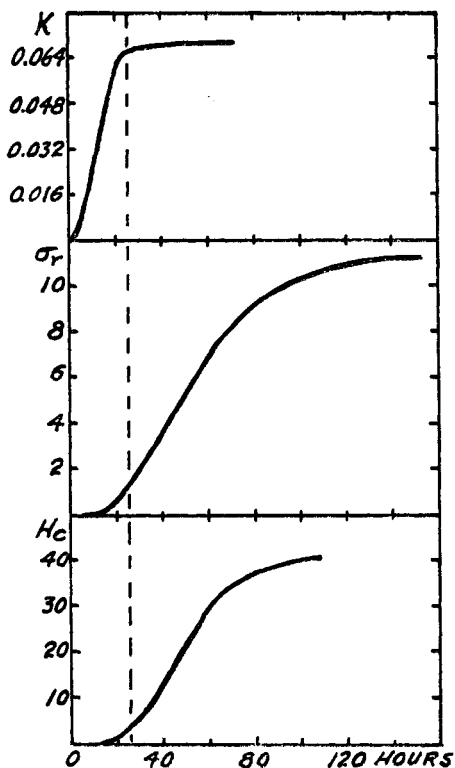

FIG. 10. VARIATION OF SUSCEPTIBILITY, REMANENCE, AND COERCIVE FORCE DURING DEHYDRATION OF γ-Fe$_2$O$_3$·H$_2$O

Essentially the same conclusion could be drawn from an experiment conducted in another way. The magnetic properties of a certain γ-ferric oxide were compared with the magnetic properties of the same oxide after it had been ground into much finer particles of colloidal dimensions. The colloids had been formed by grinding in a water solution of dextrin with either a ball mill or a colloid mill. Ferric chloride was present as a peptizing agent. The colloidal solution was then evaporated to dryness so that the oxide particles were embedded in and uniformly distributed

throughout a much larger quantity of dextrin. The ferric oxide content of the dry dextrin–oxide mixture was 6 per cent. The results of the comparison are shown in table 2 where the susceptibilities and the remanences are for unit mass of ferric oxide. Again it is seen that the susceptibilities are higher when the crystals or particles are small, and that the more finely divided material has the smaller remanence.

It has been suspected for some time (66) that ferromagnetism might be dependent on the state of division of the material within the range of extreme dispersion, and at the present time the problem of the nature, sizes, and properties of the "magnetic domains" is actively studied. Perhaps further study of the finely divided γ-ferric oxide, with linear dimensions of the order 10^{-7} cm., according to Williams and Thewlis, and even less, according to Welo and Baudisch, would yield important data bearing on this problem.

TABLE 2

Susceptibilities and remanences in γ-Fe$_2$O$_3$ and derived powders for colloids

SUBSTANCE	MAXIMUM SUSCEPTIBILITY χ	REMANENCE σ_r
		e.m.u.
γ-Ferric oxide	0.124	1.80
Same, from ball mill	0.215	0.635
Same, from colloid mill	0.207	1.025

We wish at this point to mention and to illustrate the behavior of colloidal γ-oxide solutions in magnetic fields. Without the magnetic field the usual form of the Brownian movement is observed. Figure 11 is an instantaneous microphotograph of such a solution. The average particle size was 0.1 micron. When the magnetic field is applied chains of particles are formed as shown in figure 12. The Brownian movement displays itself in a different way. The chain as a whole remains practically fixed, but the chains bend at various places from time to time and immediately straighten themselves again. It has also been observed that the length of a chain is a function of the strength of the field.

Before bringing together γ-ferric oxide, derived by way of γ-ferric oxide hydrate, and γ-ferric oxide, derived by low temperature oxidation of magnetite, for a joint discussion of their transformation to α-ferric oxide, we shall mention the fact that γ-ferric oxide hydrate does not necessarily transform to α-ferric oxide by way of γ-ferric oxide. It may transform directly to α-ferric oxide if dehydration is conducted in another way. This way is to grind it. Baudisch and Welo (18) put some γ-ferric oxide

hydrate in a ball mill which was operated for three weeks and observed a change in color from orange-yellow to brick-red. When heated at 180–200°C. this red product did not become ferromagnetic, showing that it was
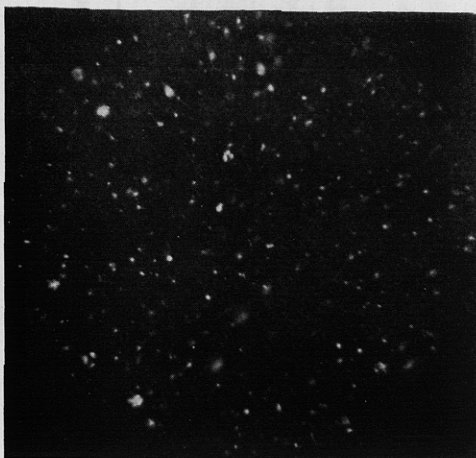

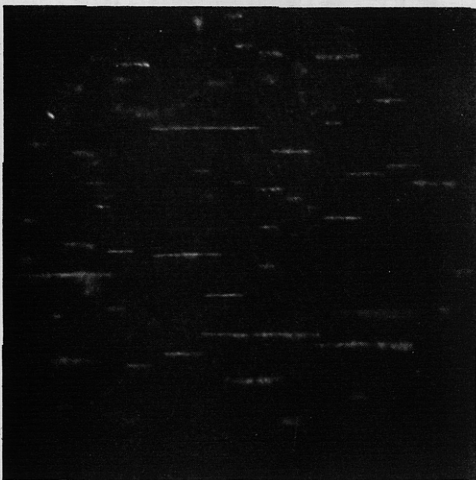FIG. 11. PHOTOMICROGRAPH OF γ-OXIDE COLLOIDAL SOLUTION WITHOUT MAGNETIC FIELD

FIG. 12. PHOTOMICROGRAPH OF γ-OXIDE COLLOIDAL SOLUTION IN A MAGNETIC FIELD

no longer γ-ferric oxide hydrate. It might have been either α-ferric oxide hydrate or α-ferric oxide. X-ray analysis proved it to be the latter. Ferromagnetism was not detected during the period of grinding so that conversion by way of γ-ferric oxide is excluded.

VII. THE TRANSFORMATION OF γ-Fe$_2$O$_3$ TO α-Fe$_2$O$_3$.

Figure 13 shows the typical magnetic behavior of ferromagnetic, cubic γ-ferric oxide as it transforms irreversibly to paramagnetic, rhombohedral α-ferric oxide when the temperature is raised, or if heated long enough at a sufficiently high temperature (106).

A definite temperature cannot be assigned because the transformation is monotropic and not enantiotropic. Nevertheless, the temperature necessary for a given rate of transformation varies so much from material to material that the cause of the variation assumes a certain interest.

The general experience is that pure materials transform more rapidly at a given temperature. The pure γ-ferric oxide used to obtain the data of figure 13 was studied in a separate experiment. At 250°C. its permeability fell at the average rate of 0.005 unit per hour during the first 72 hours. Even at 200°C. a definite decrease in permeability could be detected.
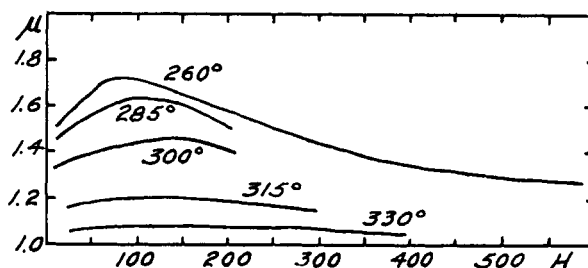

FIG. 13. DISAPPEARANCE OF FERROMAGNETISM ON HEATING γ-Fe$_2$O$_3$

Emmett and Love (28) found that 1.5 per cent of aluminum oxide (catalyst promoter) stabilizes the structure of γ-ferric oxide. The permeability of a certain γ-ferric oxide without aluminum oxide fell to unity in 3 hours when heated at 450°C. With aluminum oxide in addition the permeability was still 1.10 after heating 18 hours at the same temperature. A γ-ferric oxide from magnetite that had been precipitated with sodium hydroxide instead of ammonia was still more stable. Heating for 18 hours at 550°C. reduced the permeability to only 1.2.

The same stabilizing effect whenever sodium hydroxide was involved during the preparation of γ-ferric oxide was observed by Huggett (43), and he showed by thermomagnetic analysis that small amounts of sodium ferrite, Na$_2$O·Fe$_2$O$_3$, were present. Still another factor which determines the stability was noted by him. The magnetite which he used for the preparation of γ-ferric oxide by low temperature oxidation, was formed by the reduction of α-ferric oxide with hydrogen in the presence of water vapor. When the reducing temperature was low, for instance, 300°C., the

γ-ferric oxide subsequently formed by oxidation was much more stable than when the reducing temperature had been high, 500 or 600°C.

These facts in regard to the stability of γ-ferric oxide are neatly combined with a demonstration that the transformation, γ-ferric oxide to α-ferric oxide, is exothermal in Huggett's thermal analysis curves which are reproduced in figure 14. A silica tube containing γ-ferric oxide was placed in a furnace and a thermocouple inserted in the oxide. Beside this tube was placed another containing chromic oxide, also with a thermocouple. The thermocouples were oppositely connected to a galvanometer. When the transformation occurred, the temperature of γ-ferric oxide increased, and the galvanometer registered the peaks shown in figure 14. In all three cases, A, B, and C, γ-ferric oxide was formed by oxidizing magnetite at 250°C. In case A, magnetite was formed by reduction of α-ferric oxide
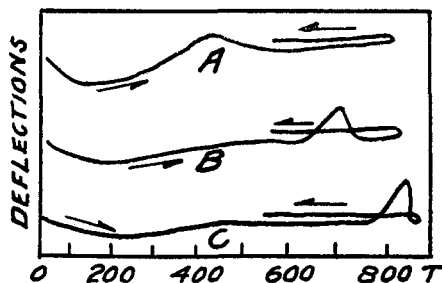

FIG. 14. THERMAL ANALYSES OF γ-Fe₂O₃
(Huggett)

at 500°C. and in case B at 300°C. In both these cases, A and B, α-ferric oxide had been formed by precipitating ferric nitrate with ammonia and calcining at 750°C. In case C, the original precipitation had been carried out with sodium hydroxide instead of ammonia. The temperature of reduction, α-ferric oxide to magnetite, was 500°C. as in case A. Huggett also observed that the stability of γ-ferric oxide is influenced by the purity of the ferric nitrate used as starting material in its preparation.

We may note that when the transformation temperature is above the Curie point, the temperature of reversible transformation, it can be directly determined only by a thermal analysis such as in figure 14. For γ-ferric oxide the Curie point is 620°C. Figure 15 illustrates this. The ordinates are proportional to the magnetizations. A and C refer to the same oxides as in figure 14. Oxide A transforms to paramagnetic α-ferric oxide before the Curie point is reached and is never ferromagnetic when the temperature falls from slightly above 620°C. Oxide C transforms beyond the Curie

point of 620°C. If the transformation temperature has not been reached
the magnetization begins to rise as the oxide passes 620°C. on cooling.

It should be noted that in Huggett's curves the magnetizations were
observed at varying temperatures. Elsewhere in this review, unless other-
wise mentioned, the magnetic properties are described as they appear at
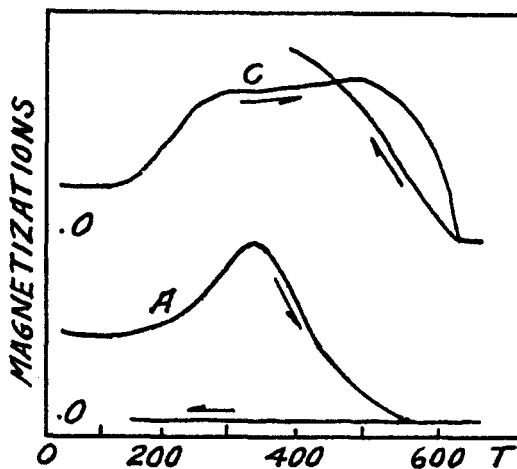room temperature and any reference to temperature means that the

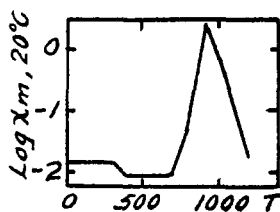FIG. 15. THERMOMAGNETIC ANALYSES OF γ-Fe$_2$O$_3$

(Huggett)

FIG. 16. EFFECT OF PREVIOUS HEATING ON THE MAGNETIC SUSCEPTIBILITY OF
NONTRONITE

(Geilmann, Klemm, and Meisel)

magnetic properties were measured *after* heating to the temperature that is
indicated.

An analogous and still firmer stabilization in ferromagnetic ferric oxide
has been reported by Geilmann, Klemm, and Meisel (31). The natural
ferric silicate nontronite, [Fe$_2$O$_3$·3SiO$_2$·H$_2$O] 4H$_2$O, was heated at various
temperatures and measured magnetically after cooling to 20°C., with re-
sults shown in figure 16. The first susceptibility change corresponds to the

elimination of water of constitution. After heating at 900°C. the susceptibility is one hundred times its original value. The x-ray analysis indicated the presence of several intermediate phases at higher temperatures, one of which was probably γ-ferric oxide. At such temperatures as shown, γ-ferric oxide could not exist alone. The lines of α-ferric oxide first appeared when the temperature had exceeded 1000°C.

Sachse and Haase (81) found γ-ferric oxide to become less magnetic when left to stand at room temperature. During four years the susceptibility fell from $\chi = 0.250$ to $\chi = 0.116$. γ-Ferric oxide aged for this length of time shows an enormously increased rate of transformation at a higher temperature as compared with the fresh substance. Their half-value times, that is, the times of heating necessary to reduce the susceptibilities by one-half, are given in figure 17 for fresh and aged samples as functions of the
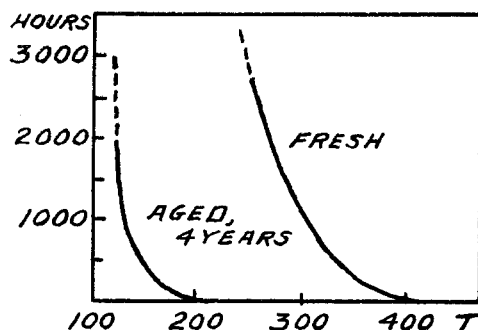

FIG. 17. HALF-VALUE TIMES FOR THE TRANSFORMATIONS OF FRESH AND AGED γ-Fe₂O₃ TO α-Fe₂O₃
(Sachse and Haase)

temperature. In neither the fresh nor the aged substance did they observe true exponential relations between the susceptibilities and the time of heating at a given temperature. The aged material shows an induction period which is entirely missing in the fresh. Figure 18 shows type forms of curves for fresh and aged γ-ferric oxide.

It was mentioned during the discussion of Huggett's work that the stability of γ-ferric oxide made by oxidizing magnetite depends on the temperature at which the magnetite was formed by reduction of α-ferric oxide. A similar result was obtained by Luyken and Bierbrauer (64) who experimented with the conversion of low grade limonite ores into γ-ferric oxide as a preliminary step to ore concentration with the magnet. They found that when the reduction of limonite had been carried out at 500°C. less current was required for the operation of the magnetic separator than when the reduction had been carried out at 700°C. They attribute this

difference to the fact that, in the former case, less γ-ferric oxide was transformed to non-magnetic α-ferric oxide during the subsequent oxidation of the magnetite.

Luyken and Bierbrauer concluded from their experiments that, since a ferromagnetic ferric oxide could be formed from limonite only by way of a preliminary reduction to magnetite, there was no advantage, in this respect, over leaving the ore at the magnetite stage. However, they cite two advantages in reoxidizing magnetite to γ-ferric oxide. The danger is avoided of carrying the reduction too far so as to form weakly magnetic products that do not go into the concentrate and there is, in many cases, a distinct gain in efficiency.

These authors also mention the precautions that are sometimes taken in ore concentration plants employing magnetic separation, to prevent oxida-
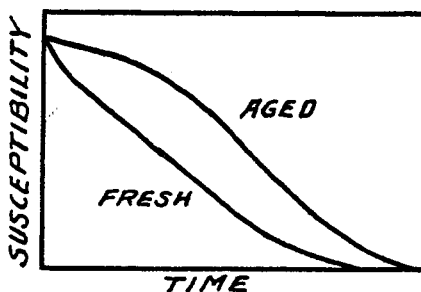

FIG. 18. TYPICAL SUSCEPTIBILITY–TIME RELATIONS FOR THE TRANSFORMATIONS OF FRESH AND AGED γ-Fe$_2$O$_3$ TO α-Fe$_2$O$_3$

(Sachse and Haase)

tion of the ore while it is cooling off after reduction. These precautions are taken on the supposition that the ore becomes non-magnetic on oxidation. It is pointed out that the ferromagnetic ferric oxide is formed and that the precautions are quite unnecessary.

VIII. VARIOUS FACTS ABOUT Fe$_3$O$_4$ AND γ-Fe$_2$O$_3$

Variability in magnetic properties (104, 105)

Examples have already been given of variable magnetic properties in magnetite prepared in different ways (figure 3). Further examples are given in figure 19. Figure 20 shows correspondingly large variations in γ-ferric oxide. Remanence data for both magnetite and γ-ferric oxide are given in table 3.

The magnetites and γ-ferric oxides used to obtain the curves of figures 19 and 20 and the data of table 3 were prepared as follows:

Magnetites.—(1) By precipitation of an equimolar mixture of $Fe(SO_4)_2$ and $Fe_2(SO_4)_2$ with sodium hydroxide. The product was not pure.

(2) By burning iron carbonyl in a limited supply of air. This magnetite was pure and the Fe:O ratio was the theoretical ratio in magnetite.
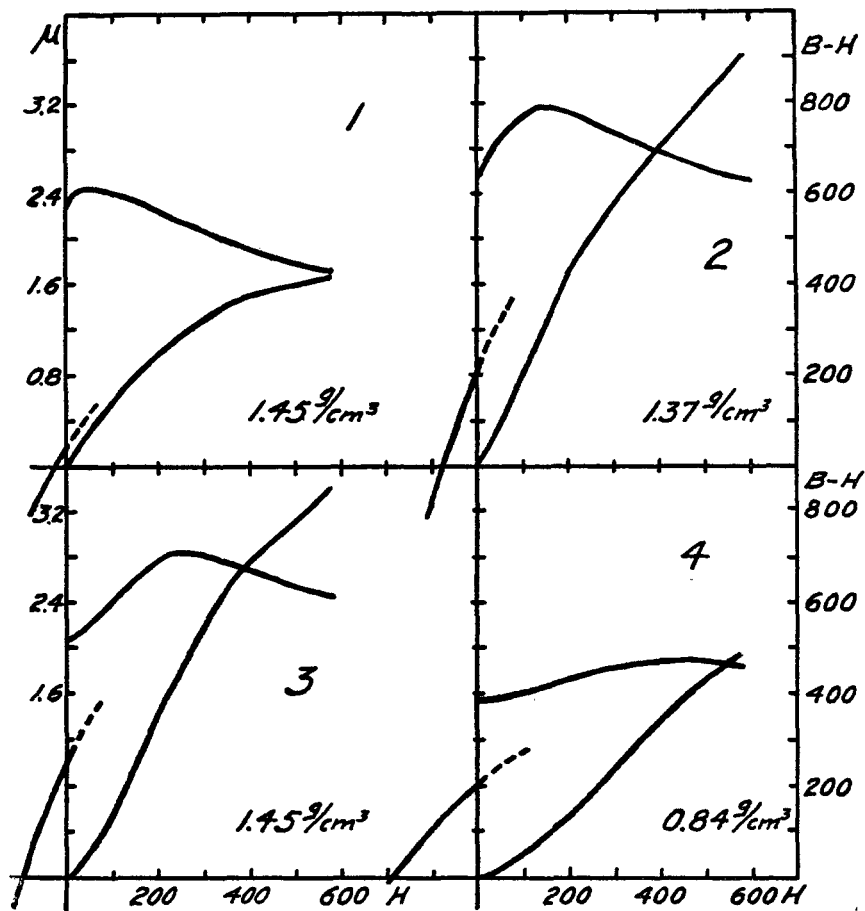

FIG. 19. MAGNETIC PROPERTIES OF MAGNETITES

(3) Magnetite No. 1 was oxidized to γ-ferric oxide in oxygen at 200°C. and then reduced in molten sodium acetate at 320°C. for 10 minutes. The product was not pure.

(4) α-Ferric oxide was made by burning iron carbonyl in a plentiful supply of air and then reduced as in No. 3. The only impurity was carbon from the sodium acetate.

γ-Ferric Oxides.—(5) Magnetite No. 1 was heated in oxygen at 200°C. The product was not pure.

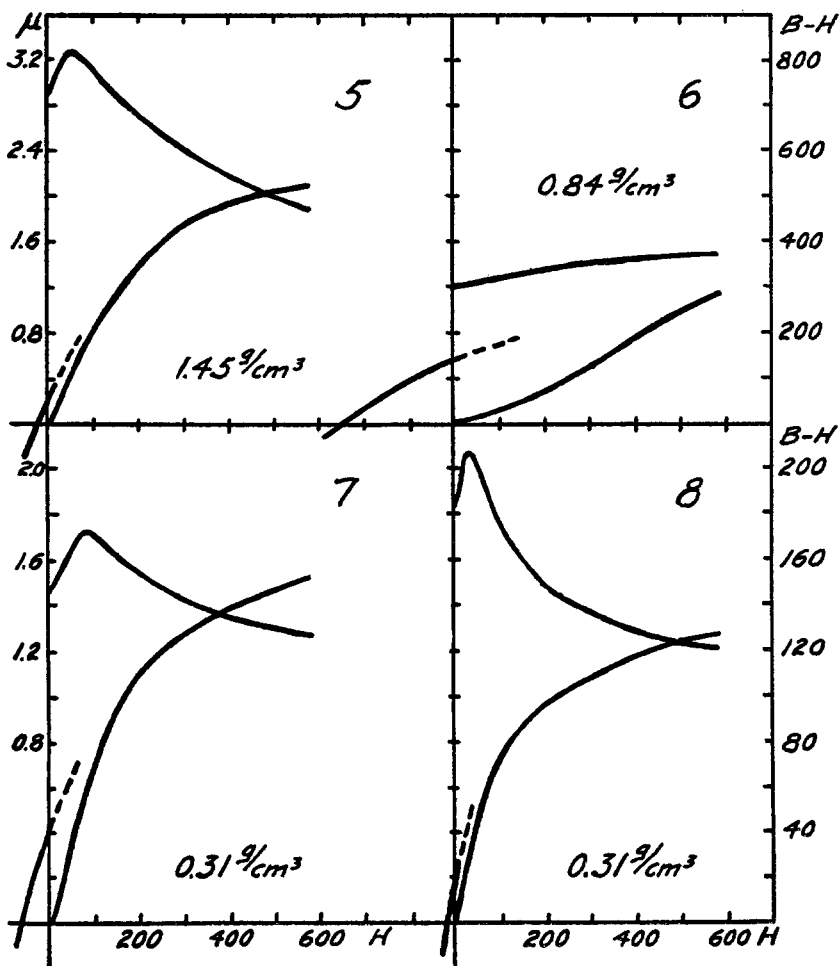(6) Magnetite No. 4 was reoxidized in molten potassium nitrate at 360°C. for ten minutes.

FIG. 20. MAGNETIC PROPERTIES OF FERROMAGNETIC FERRIC OXIDES

(7) By dehydration of γ-ferric oxide hydrate prepared by passing oxygen through a mixture of ferrous chloride and pyridine. The product was very pure.

(8) Same as No. 7 except that ferrous iodide was used instead of ferrous chloride.

From these data and others of the same character Welo and Baudisch (105) have concluded that: (1) There are no major differences in the magnetic properties of magnetite and γ-ferric oxide. A minor difference that always appears, a slightly higher maximum permeability and a shift, to the left, of the permeability maximum in γ-ferric oxide as compared with magnetite, is shown in figure 6. (2) The effect of impurities is a minor one. (3) The magnetic properties are largely determined by crystalline condition, either as to the sizes of the crystals or their perfection, or both. These conditions, in turn, are determined by the method of preparation and subsequent history as to temperature.

TABLE 3

Remanences in Fe_3O_4 and γ-Fe_2O_3

REFERENCE NUMBER*	CLASS OF MATERIAL	DENSITY OF PACKING	REMANENCE σ_r
		g. per cc.	*e.m.u.*
1	Fe_3O_4	1.51	1.97
2	Fe_3O_4	2.24	15.8
3	Fe_3O_4	1.58	16.2
4	Fe_3O_4	1.15	17.0
5	Fe_2O_3	1.69	1.80
6	Fe_2O_3	1.57	15.5
7	Fe_2O_3	—	—
8	Fe_2O_3	0.69	7.37

* The reference numbers are those of figures 17 and 18.

Trace of magnetite in γ-ferric oxide

With his thermomagnetic analysis, Huggett (43) found minute traces of magnetite in all of his samples of γ-ferric oxide, although, in agreement with all observers, he found no ferrous iron with the most sensitive chemical tests. This detection depends on the fact that there is a discontinuity in the thermomagnetic curve at 570°C., the Curie point of magnetite. A typical case is shown in figure 21. The discontinuity at 675°C. is characteristic of α-ferric oxide. Huggett considers the magnetite to be in solution in γ-ferric oxide and remarks that its presence cannot be detected until after the transformation to α-ferric oxide. The small discontinuity is not visible when superposed on a thermomagnetic curve for γ-ferric oxide, which must be taken at low sensitivity. It would be interesting to see if magnetite is present in γ-ferric oxide made by dehydration of γ-ferric oxide hydrate. Huggett's samples were made by oxidizing magnetite.

Fe_3O_4, γ-Fe_2O_3, *and the Heisenberg theory of ferromagnetism*

According to the Heisenberg theory (41) a condition necessary for the appearance of ferromagnetism in a crystal is that each atom must have at least eight nearest neighbors. Sachse (80) applied this test to magnetite, γ-ferric oxide, and α-ferric oxide, and found that the condition is satisfied by magnetite and γ-ferric oxide, but is not satisfied by α-ferric oxide. The same result was obtained by Thewlis (93).

Photoelectric effect in γ-ferric oxide

Schwarz (83) has found the photoelectric current from γ-ferric oxide made by oxidizing Lefort's magnetite to be larger than from α-ferric oxide and from iron powder. He employed the full radiation from the quartz
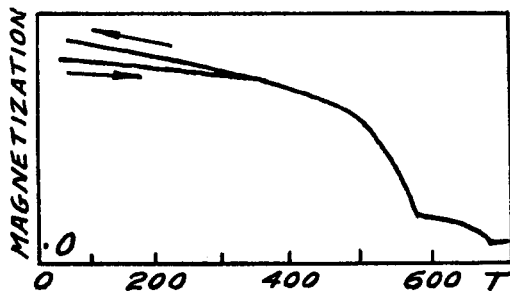

FIG. 21. THERMOMAGNETIC ANALYSIS SHOWING PRESENCE OF Fe_3O_4 IN γ-Fe_2O_3
(Huggett)

mercury arc and observed the following relative values for the photoelectric currents: pure γ-ferric oxide, 6.5; technical γ-ferric oxide, 4.3; α-ferric oxide made by burning iron carbonyl, 2.5; iron powder formed by dissociating iron carbonyl, 1.6; and ferrum reductum, 1.0.

Technical γ-ferric oxide or "Siderac"

A γ-ferric oxide is manufactured and marketed by the Auer Gesellschaft under the name of "Siderac." It is a Lefort magnetite (61, 104) which has been oxidized at about 200°C. until free of ferrous iron.

IX. COLLOIDAL OXIDE HYDRATES

The classical experiments of van Bemmelen (98, 99) have firmly established the fact that there need be no definite stoichiometric proportions between the anhydride and water in colloidal oxide hydrates of multivalent metals, and the capillary theory of Zsigmondy (112) has provided a satisfac-

tory theoretical interpretation. The question as to the chemical constitu-
tion of the capillary system's solid framework was, however, left open.
It could be either the anhydride or one of several stoichiometric hydrates.
The view that the framework is anhydrous is supported by the fact that all
of the water in many colloidal oxide hydrates can be reversibly replaced by
organic liquids such as alcohol or benzene. In many other colloidal oxide
hydrates, however, not all of the water may be so replaced. Several
moles of water may remain. There is also the difficulty that many natural
minerals corresponding to the colloids whose water is entirely replaceable
by organic liquids often appear as definite stoichiometric hydrates.

Foote and Saxton (29) attempted to distinguish water that might be
stoichiometrically bound in the framework from all of the other water by
measuring the expansion of the colloid on freezing. It was assumed that
the water of constitution would take no part in the expansion and that all
of the other water would expand as if it were free. It was found, indeed,
that the total expansion was less than that corresponding to an equal
amount of free water, but that the calculated quantity of combined water
did not, in general, correspond to any definite hydrate.

The problem of the chemical nature of the capillary framework assumed
a practical as well as theoretical importance when Willstätter and his
students (108, 109, 110, 111) began to use colloidal oxide hydrates of
aluminum and tin for the selective adsorption and isolation of enzymes.
The selectivity depended on the method of preparation and on the age,
and it was considered that the selectivity indicated the existence of a
number of hydrates in the framework, each having definite adsorptive
properties. The well-known method of acetone drying was then developed
in an effort to displace the water of adsorption and the water in the capil-
laries and thus to identify the various stoichiometric hydrates. In this
Willstätter was no more successful than Foote and Saxton. In general,
stoichiometric relations were not obtained. For example, the percentages
of water that remained in a series of ferric hydrogels after acetone drying
were 29, 30, 32, and 28 per cent instead of the 33.7 per cent required in a
ferric hydrate of the type $Fe(OH)_3$.

Willstätter proposed a new theory. It was assumed that well-defined
hydrates are present in the fresh colloids but that they are unstable and
changeable, especially in the presence of the capillary water. They
either react with each other in the sense of salt formation or else they
undergo inter- and intra-molecular dehydration so as to form a complex of
various hydrates. Neither the paths of spontaneous dehydration nor the
final stages are unique, so that the final product is a very complicated
mixture. In such a mixture, stoichiometric relations cannot be observed.
The dehydration isobars would closely approach continuous curves. The

chemical changes that occur with time, and especially the changes in adsorptive power towards enzymes, were referred to by Willstätter as being in agreement with the view that numerous new hydrates are formed on aging.

Simon (85) has pointed out that all of these phenomena are equally well explained by the older views as to what occurs when a substance ages and mentions, particularly, the process of aggregation. However, Simon's principal argument against Willstätter's view is that it is possible, by "starke Eingriffe," to form definite hydrates from colloids, which will have crystalline structure and which will give discontinuous dehydration isobars. According to the Willstätter theory we should have, instead,
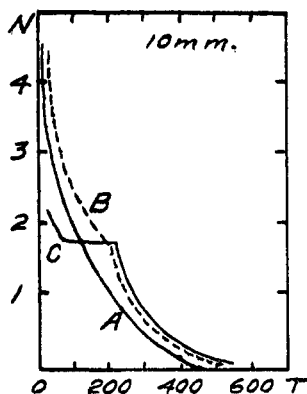

FIG. 22. DEHYDRATION ISOBARS FOR ANTIMONY PENTOXIDE HYDRATE
(Simon and Thaler)

strong dehydration and should obtain a complicated mixture which would give a continuous curve of dehydration.

This point Simon illustrated by his own and Thaler's (87) work on colloidal antimony pentoxide hydrate. Their dehydration isobars are shown in figure 22. Curve A is for a colloid that had aged for a few months. Another portion of the same sample was studied after aging for about a year and gave curve B. There is observed not only a firmer binding of the water but also an indication of a hydrate with 1.66 moles of water per mole of antimony pentoxide. Further aging for another year brought about little change, so another sample was prepared in the same way and heated with water in a sealed tube for several days at 300°C. This material gave curve C and confirms the supposition that aging of a colloid consists, in part, of the fixing of the water to form a definite hydrate. In this case the hydrate is $3Sb_2O_5 \cdot 5H_2O$. Similar results as to the firmer fixation of water

have been obtained by Simon and Schmidt (86) in their study of colloidal ferric hydroxide, with the important additional result that this fixation of water is accompanied by crystallization to such an extent that it can easily be detected by x-ray methods.

We may sum up the immediately preceding discussion as follows: That in some and most probably in all of the colloidal metal oxide hydrates, the solid framework of the capillary system consists of the anhydride, and there is no evidence that it ever consists of a definite stoichiometric hydrate; and that the result of spontaneous aging is to fix a part of the water more firmly and to form definite hydrates of crystalline structure.

X. THE AGING PATHS FROM COLLOIDAL FERRIC OXIDE HYDRATES

Because of the relative free energies in amorphous and crystalline systems it is self-evident that the direction of aging must always be from and never towards the colloidal state and we need only to consider the various paths, the intermediate phases that may appear, and the final stage that is reached.   We shall consider, first, the views to which Hüttig and Zörner (52) and others of the Hüttig school have been led.

A slow elimination of water to form hydrohematite is one of the possible paths, since many ferric oxide hydrate colloids that had been aged for a period of years showed all of its characteristics.   Hüttig and Zörner cite Ruff's (79) observations on a 6-year old hydrate and describe their own comparative studies on a fresh hydrate, a hydrate that had been prepared in the same way twenty-nine years earlier, and a natural hydrohematite. The dehydration isobars are shown in figure 23 where curve A is for the fresh colloid, curve B is for the 29-year old hydrate, and curve C is for the natural mineral.   There is a general similarity in isobars B and C, although the amount of combined water in the aged artificial hydrate is somewhat higher than in the natural.   On comparing curves A and B we see that the aging consists, not in a general loosening of all of the water but, rather, in nearly complete elimination of water above 0.8 mole and an even firmer binding of this remainder, since curve B lies above curve A at the higher temperatures of dehydration.   Both the 29-year old artificial hydrate and the natural hydrohematite gave the x-ray spectrum of α-ferric oxide with no determinable departures from the lattice dimensions of true α-ferric oxide.   According to Kurnakow and Rode (60) the combination with water is zeolithic in character, and they regard the water as being in solution in hematite.   The water content in hydrohematite is variable and it seems, from the results of both Kurnakow and Rode and Hüttig and Zörner, that the upper limit is at about 0.8 mole per mole of ferric oxide.

Very interesting subsidiary evidence that hydrohematite is one of the intermediate steps in the aging of colloidal ferric hydroxide is found in the magnetic studies of Hüttig and Kittel (48). They consider $\chi = +116 \times 10^{-6}$ to be the most probable susceptibility value for fresh colloidal ferric hydroxide, and show that it is paramagnetic. Their criterion for paramagnetism is that the susceptibility value shall be independent of the field strength. If the susceptibility decreases with increase of the field, the substance is considered to be ferromagnetic. They then proceeded to show that colloidal ferric hydroxide, on aging, not only assumed higher susceptibilities but that the values became more and more dependent on the field strengths that were used during the measurements. Hydrohematite,
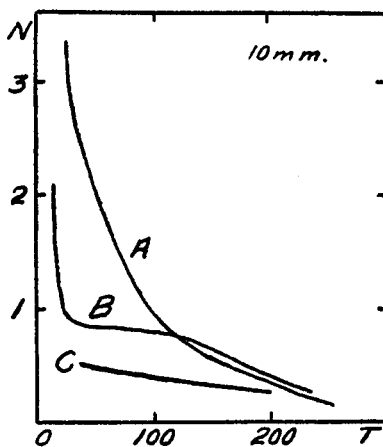

FIG. 23. DEHYDRATION ISOBARS FOR FRESH AND AGED COLLOIDAL FERRIC OXIDE HYDRATES AND OF HYDROHEMATITE

(Hüttig and Zörner)

therefore, should be ferromagnetic in the sense of the foregoing definition. They found this to be true of both the natural hydrohematite and of the 29-year old artificial hydrate. The susceptibility values for the natural hydrohematite were 207, 144, and 117×10^{-6}, respectively, for magnetizing currents of 0.5, 1.0, and 1.5 amperes. For the 29-year old hydrate the susceptibilities were 114 and 98×10^{-6} for magnetizing currents of 0.5 and 1.0 amperes, respectively. Both are therefore ferromagnetic. The smaller susceptibilities for the aged artificial hydrate are probably due to partial conversion to limonite or to goethite. Both of these are paramagnetic with much lower susceptibilities which fall within the range 31 to 44×10^{-6} according to Hüttig and Kittel.
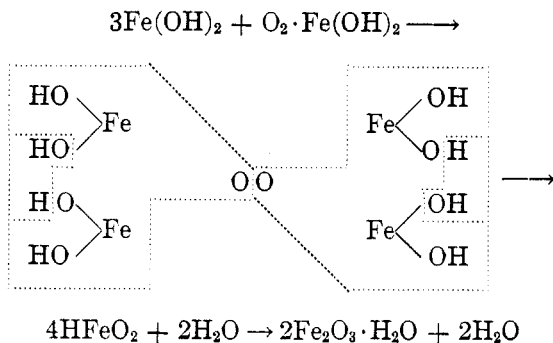
When beginning the discussion of hydrohematite as a product of the aging of colloidal ferric hydroxide it was stated that it was formed by the elimination of water down to about 0.8 mole. Actually the mechanism is not so direct. Otherwise we would not find hydrohematite with less than 0.8 mole of water and it would be difficult to understand how hydrohematite can change to limonite and eventually to goethite, α-$Fe_2O_3 \cdot H_2O$. The probable true mechanism was first described by Ruff (79). He considered that the primary step in the aging process, under ordinary conditions of temperature and pressure, is the elimination of all of the water to form the anhydride, but that this anhydride, in the course of time, dissolves water (zeolithic binding). The amount of zeolithic water may exceed 1 mole. Whenever zeolithic water exceeds or is not too much below 1 mole, recrystallization takes place and we have a gradual conversion to α-$Fe_2O_3 \cdot H_2O$. Limonite is thus an intermediate step in the aging path from hydrohematite to goethite. Hüttig and Zörner (52) consider this to be the only possible path and that hydrohematite cannot convert directly to α-$Fe_2O_3 \cdot H_2O$.

The chief experimental basis for the belief that colloidal ferric hydroxide ages to limonite (goethite crystal structure with zeolithic water) is an old observation of Schiff (82), who found that he could not reduce the water content of a 15-year old hydrate below 11 per cent by heating in air at 100°C. Eleven per cent of water corresponds very closely to 1 mole of water per mole of ferric oxide. The other evidence, which we owe to Doelter (27), is that colloidal ferric oxide hydrate, like many other colloids, was partly crystallized after having been shaken in water; in this particular case, for 88 days. It should be noted, however, that Doelter's colloid was made by oxidation of ferrous hydroxide, so that his results might not be valid for a colloid made by precipitation from a ferric salt.

Hüttig and Zörner (52) note that limonite is also obtained by the oxidation of ferrous hydroxide, but in a pure or unmixed form only when molecular oxygen is used as the oxidizing agent. Other oxidizing agents such as hydrogen peroxide, in which the ultimate oxidizing medium is atomic oxygen, lead at the most to only a partial formation of limonite. They also note that this oxidation to limonite proceeds best with fresh, highly dispersed, ferrous hydroxide. In their explanation they assign an orienting as well as an oxidizing rôle to the oxygen molecule. It is assumed that the primary process is the formation of a peroxide

$$Fe(OH)_2 + O_2 \rightarrow O_2 \cdot Fe(OH)_2$$
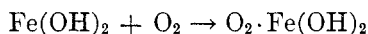
and that this peroxide combines with three unoxidized ferrous hydroxide groups according to the scheme:

$$3Fe(OH)_2 + O_2 \cdot Fe(OH)_2 \longrightarrow$$

$$
\begin{array}{ccc}
HO \\ \!\!>Fe \\ HO \\
H O \\ \!\!>Fe \\ HO \\
& O\,O & \\
& & Fe<{OH \atop O\,H} \\
& & Fe<{OH \atop OH}
\end{array} \longrightarrow
$$

$$4HFeO_2 + 2H_2O \rightarrow 2Fe_2O_3 \cdot H_2O + 2H_2O$$

The structure represented by the second stage of this scheme is regarded as a sort of seed or nucleus which initiates crystallization to goethite, α-$Fe_2O_3 \cdot H_2O$.

We cannot, as we have seen, distinguish limonite from goethite by magnetic measurements. They can be distinguished by their x-ray spectra and the dehydration isobars. While the positions of the lines in the limonite x-ray spectrum are the same as those of goethite, α-$Fe_2O_3 \cdot H_2O$, they are, regardless of source or age, more diffuse and less intense. This is attributed by Hüttig and Zörner to high dispersion and incomplete ordering as long as zeolithic water is present. This excess water must be eliminated before true goethite crystals can be formed. Typical isobars for limonite are shown in figure 24 along with one for goethite. Curve A is for a natural mineral of the limonite class and curve B is for a natural goethite. Limonite does not dissociate into two phases until the composition of goethite is reached with 1 mole of water. Between 1 mole of water and about 0.4 mole the two phases are α-ferric oxide hydrate and hydrohematite. When the water content is less than 0.4 mole, there are also two phases, hydrohematite and hematite itself. Hüttig and Zörner note that in the range of the two phases, α-ferric oxide hydrate and hydrohematite, the dissociation pressure of 10 mm. was reached at very close to 177°C. in all of the limonites that were studied. They consider that the conditions of thermodynamic equilibrium were more nearly fulfilled at this pressure in the limonites than in goethite. When fully developed crystals are present, as in goethite, dissociation is retarded until a higher temperature is reached. The corresponding temperature for the dissociation of α-ferric oxide hydrate to hydrohematite is about 100°C. higher in goethite.

In figure 24, curve C is for a fresh hydrate made by the oxidation of ferrous hydroxide according to a procedure followed by Tommasi (95), and curve D is for a hydrate prepared in the same way twenty-nine years earlier. They are of particular interest. We may recall that since these

two hydrates were formed by the oxidation of ferrous hydroxide, they belong to the yellow series, whereas hydrates precipitated from ferric salts are classed as of the red series. We have seen, while comparing the isobars A and B in figure 23, that a red hydrate changes greatly during twenty-nine years. The yellow hydrate, on the other hand, has scarcely changed at all during the same time. It was crystalline and the free energy content was near the minimum from the start. We may infer that it would require an extremely long time, under ordinary temperature and pressure conditions, for the limonites, or rather, yellow hydrates, to assume the final stable state of goethite. It should hardly be necessary to state that while we have been discussing limonite as one member of the aging path from colloidal ferric hydroxide, we have at the same time been considering the conversion of a hydrate of the red series to one of the yellow.
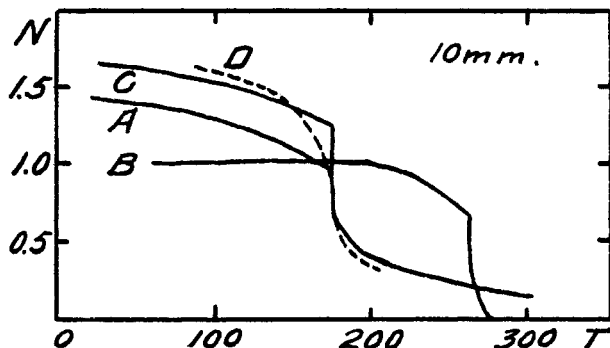

FIG. 24. DEHYDRATION ISOBARS FOR LIMONITE, GOETHITE, AND FRESH AND AGED YELLOW FERRIC OXIDE HYDRATES
(Hüttig and Zörner)

XI. THE SPECIFIC HEATS AND THEIR CHANGES

The specific heats of colloidal ferric oxide hydrates with various amounts of water have been measured by Hüttig and Garside (47). The range of water content covered was from 0.14 to 3.8 moles per mole of ferric oxide. To obtain material with so little water as 0.14 mole, drying at as high a temperature as 200°C. was resorted to. Even after heating to this temperature, the material remained colloidal in the sense that no crystallization had occurred. It was much more readily soluble in hydrochloric acid than crystalline ferric oxide and remained pyrophoric. When they tried to reduce the water content still further, crystallization set in and the material became unsuitable for their purpose, which was to measure the specific heats and to study the chemical and catalytic activities of colloidal (uncrystallized) ferric oxide hydrates with various amounts of water.

The specific heats were measured within two or three days after preparation, so that the data are considered to be for fresh and not for aged material. They are plotted as functions of the water content in figure 25. N is the number of moles of water per mole of ferric oxide. For $0.2 < N < 1.0$ the relation is linear. At $N = 1$, the specific heat, Cp, appears to be a mean value between the specific heat of goethite, $Cp = 0.2040$, and the calculated value of 0.2458 for an equimolar mixture of ferric oxide and water. These two values are indicated by (g) and (e) in the figure. A discontinuity appears at $N = 1$. Beyond $N = 1$ the curve is steeper as if a part of the water were free. However, the water is not present as an independent phase, since the course of the curve beyond $N = 1$ is not linear. For $N < 0.2$ the curve departs from linearity and for
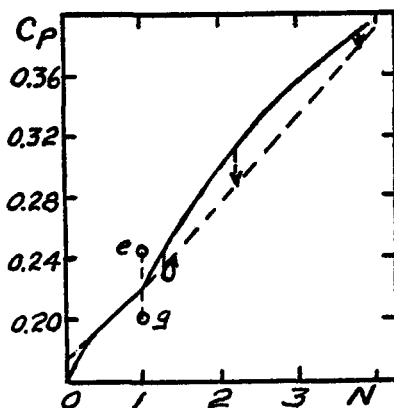

FIG. 25. SPECIFIC HEATS OF COLLOIDAL FERRIC OXIDE HYDRATES
(Hüttig and Garside)

$N = 0$, $Cp = 0.1608$, the specific heat of hematite, α-ferric oxide. Extrapolation of the linear part of the curve to $N = 0$ yields $Cp = 0.175$, which Hüttig and Garside consider to be the specific heat that would be found for ferric oxide if it were possible to completely dehydrate colloidal ferric oxide hydrate without crystallization and without destroying its chemical and catalytic activity.

The vertical arrows of the figure indicate the directions and the magnitudes of the changes in specific heat as the hydrates are allowed to age under ordinary conditions of temperature and pressure. The specific heat of the hydrate with $N = 3.8$ fell from 0.382 to 0.370 in 80 days. For the hydrate with $N = 2.1$, the change was from 0.302 to 0.284 in 78 days. In the hydrate with $N = 1.2$, the specific heat decreased from 0.240 to 0.233 during the first 14 days and then increased to the original value during

the following 36 days.   A similar but very slight fall and rise was observed in the hydrate with $N = 0.25$.

Hüttig and Garside consider a decrease in specific heat to be an indication that the path of aging is towards goethite, α-ferric oxide hydrate, with firmer finding of the water.   An increase in specific heat would then indicate that water is being set free with the formation of crystalline α-ferric oxide.   They note that the former occurs in hydrates rich in water and that the latter is more likely to happen when there is not enough water present to form a monohydrate.

XII. THE ACTIVITIES OF FERRIC OXIDE HYDRATES AND THEIR CHANGES

The hydrates that were used for specific heat measurements were also used in the study of catalytic and chemical activities.   We shall consider, first, these activities as functions of the water contents.   As a measure of
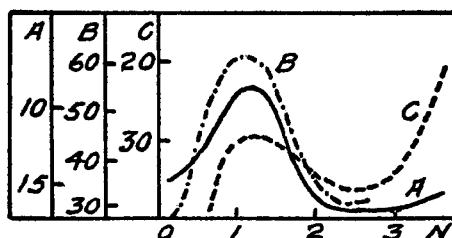

FIG. 26. EFFECT OF WATER CONTENT ON ACTIVITIES OF COLLOIDAL FERRIC
OXIDE HYDRATES
(Hüttig and Garside)

catalytic activity, Hüttig and Garside (47) chose the rate of decomposition of hydrogen peroxide.   The time necessary for the evolution of 100 cc. of oxygen with 0.2 g. of ferric oxide was measured, the strength of the hydrogen peroxide solution being 5 cc. of 30 per cent hydrogen peroxide in 50 cc. of water.   Chemical reactivity was tested by measuring the volume of hydrogen sulfide that combined with 0.2 g. of ferric oxide in a given time. Finally, the rate of solution in hydrochloric acid was determined by measuring the time required for completely dissolving 0.2 g. of ferric oxide when shaken in 1000 cc. of a half-normal solution.   All of these measurements were made within three days from the time the hydrates were prepared, so that the data pertain to "fresh" material.

It is necessary to explain the three scales of ordinates that are used in figure 26 which exhibits the parallelism between catalytic activity and chemical reactivity, and their striking changes with variation in water content.   When the catalytic activity is high, less time is required for the

evolution of a given volume of oxygen from hydrogen peroxide. In the figure, therefore, the ordinate scale designated by A reads downward. The unit of time is the minute. The scale of ordinates, B, measures the volume of hydrogen sulfide that combined with ferric oxide. Evidently the scale reads upward in the usual manner. Hüttig and Garside do not state the time adopted as a standard for this reaction. Again, on scale C, on which is represented the rate of solution in hydrochloric acid, we must read downward. The unit is the minute. The letters A, B, and C for the curves, correspond, of course, to those for the ordinates. On the abscissa the unit is the moles of water per mole of ferric oxide.

In regard to the data of figure 26 we shall content ourselves, as did Hüttig and Garside, with a résumé of the facts. In relatively fresh colloidal ferric hydrates, the changes in catalytic activity, chemical reactivity, and rate of solution, in relation to the water contents of the hydrates, run closely parallel. The hydrates with little water have low activities. The activities increase with increase in water content and reach a maximum at about $N = 1$. Beyond $N = 1$ the activities decrease to a minimum between $N = 2$ and $N = 3$. Beyond $N = 3$ the activity increases again. One would expect to find, in hydrates very rich in water, activities greater than any that were observed in these experiments.

Remarkable to-and-fro changes in the same activities were found in aging ferric oxide hydrates. Hydrates with water contents of 0.73, 1.23, and 3.72 moles were set aside to age, and from time to time portions were examined as to activity as described in the preceding paragraphs. From the data, the activities of a hydrate with a given water content could be plotted as functions of the time of aging. It was found that the oscillatory changes were most marked in the hydrate with the least water. Only the results for $N = 0.73$ will be shown here (figure 27). The letters A, B, and C have the same significance as in figure 26, but the abscissa measures the time of aging in days.

The interpretation to be given such striking periodic changes in activity is as yet rather vague. This is not surprising, since we are still too much accustomed to the view that the activity function in an aging system is always a continuously decreasing one. The qualitative theory advanced by Hüttig and his associates (46, 47, 50, 51, 52) will be briefly outlined. They consider that a system, already crystalline, is most active when it, or some part of it, is undergoing a change to another crystalline form. They cite as an example the observation of Hedvall and Sjöman (40) that ferric oxide reacts with quartz only at the temperatures of 575 and 950°C. which are, respectively, the temperatures of the transformations β-SiO_2 to α-SiO_2 and α-SiO_2 to cristobalite. Now the change in structure generally involves the existence of a highly disperse intermediate phase, so that the total

surface may be very large. Also, the intermediate phase may not be truly crystalline. It may consist of a loose, unordered aggregate in the sense of the Smekal (88) theory of the structure of catalysts. In either case, a change in structure would lead to higher catalytic activity, and it remains to account for the periodic changes in structure in aging ferric oxide hydrate.

As we have seen (figure 1), colloidal ferric oxide hydrate ages along two different paths at first. One is to goethite by way of limonite and the other is to hydrohematite. Actually, both paths are followed by separate portions of the material. According to Hüttig, the part that ages to hydrohematite cannot reach the most stable form, goethite, unless the path is changed to limonite. It is assumed that this change in path can occur spontaneously, and it is at this time of change that we find the high cata-
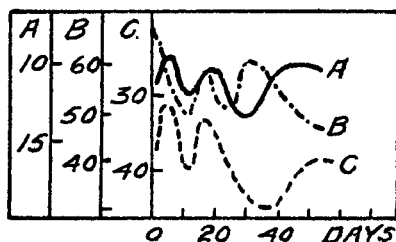

Fig. 27. Variation with Age of the Activities of Colloidal Ferric Oxide Hydrate

(Hüttig and Garside)

lytic activity. Of course only a small part of the material may change at a given time. Later on, another portion that has been following the path to hydrohematite may change to limonite and result in another period of high activity. Hüttig and Zörner (51) have observed as many as nine peaks in an activity curve within a period of 160 days.

A curious parallelism between catalytic activity and ferromagnetism has been noted several times. We have already mentioned the fact that hydrohematite has the characteristics of a ferromagnetic substance, while all the other members of the aging series from colloidal ferric oxide hydrate are paramagnetic. The greater catalytic activity of γ-ferric oxide, as compared with α-ferric oxide, has been observed by Baudisch and Welo (16). Merck and Wedekind (67) found that high catalytic activity and ferromagnetism often appeared simultaneously during the dehydration of cobalt oxide hydrates. It is not yet known whether or not the relation between catalytic activity and ferromagnetism is a causal one.

This parallelism can best be illustrated by the work of Hüttig, Radler,

and Kittel (50) on zinc–chromium spinel. A stoichiometric mixture of zinc oxide and chromic oxide was heated for 6 hours at each of a series of increasing temperatures. After each heating the material was examined as to the catalytic activity towards the dissociation of methanol, the magnetic susceptibility, and the packing volume. The variations in these properties are shown in figure 28. There seems to be no close correspondence between the various maxima and minima. However, it was pointed out by these investigators that the maxima occurred in the temperature range of previous heating, 300 to 500°C. After heating at these temperatures the x-ray spectra showed lines belonging to neither the mixture or
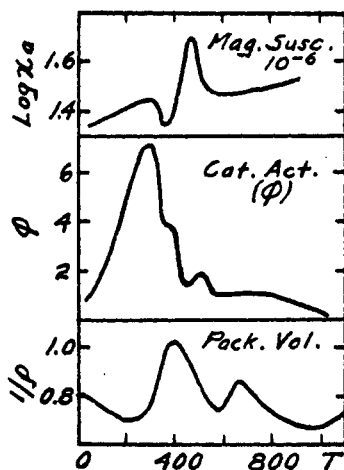

FIG. 28. VARIATIONS OF MAGNETIC SUSCEPTIBILITY, CATALYTIC ACTIVITY, AND PACKING VOLUME DURING THE FORMATION OF ZINC-CHROMIUM SPINEL
(Hüttig, Radler, and Kittel)

oxides nor the finished spinel. In other words, high activities and high susceptibilities are to be associated in some way with intermediate phases. That these phases are more highly dispersed is indicated by the higher values of the packing volumes.

Activities in yellow ferric oxide hydrates

The difference between red colloidal and yellow crystalline ferric oxide hydrate as a catalyst in the decomposition of hydrogen peroxide has been illustrated by Hüttig and Zörner (51). An 8-day old red hydrate, made by adding ammonium hydroxide to ferric chloride in the cold, yielded 6 cc. of oxygen per minute, while a hydrate that had been prepared in the same

way twenty-nine years earlier yielded only 0.11 cc. per minute under comparable conditions. A yellow hydrate, formed by adding sodium carbonate to ferrous sulfate in the presence of potassium chlorate, released 0.33 cc. of oxygen per minute when fresh. However, the activity of a yellow hydrate changes extremely slowly with time. One which had been prepared in the same way twenty-eight years earlier still yielded 0.25 cc. of oxygen per minute. As has been stated before, the yellow hydrates are crystalline from the beginning. Perhaps whatever change there was was due to small amounts of amorphous hydrates.

That the temperatures at which yellow hydrates are formed have some effect on the catalytic activity is illustrated by some unpublished measurements of Baudisch. The hydrates were prepared by the action of molecular oxygen on ferrous bicarbonate at temperatures of 0, 19.5, and 37°C. The
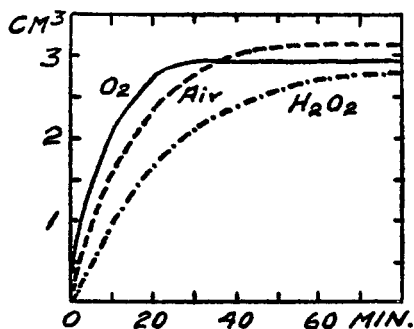

FIG. 29. CATALYTIC ACTIVITIES OF YELLOW FERRIC OXIDE HYDRATE

relative amounts of hydrogen peroxide dissociated under comparable experimental conditions were, respectively, 40.3, 38.8, and 28.0. When the temperature is low the rate of crystallization is slowed up. The crystals may be both smaller and less ordered than when the temperature is high.

Other unpublished work by Baudisch brings out the fact that the method of oxidation used in preparing yellow hydrates affects the activity. They were formed from ferrous bicarbonate solutions in three ways. In one, air was bubbled through the solution; in another, oxygen. In the third, hydrogen peroxide was added to the solution. The total volumes of oxygen that had been liberated from hydrogen peroxide were measured at various times as shown in figure 29. In each case the activity was small and the activities among the hydrates differed at the most by a ratio of about 2.

XIII. THE SILVER FERRITE ANALYSIS AND ITS APPLICATION TO THE STUDY
OF FERRIC OXIDE HYDRATES

Very interesting studies on the classification of ferric oxide hydrates and
the identification of the products of aging have been conducted by A.
Krause and his students during the past two years. Krause's points of
view and his methods of attack are closely analogous to those of the organic
chemist. Definite molecular structures are assigned to the freshly formed
hydrates and changes in them are considered on the bases of polymeriza-
tion, ring closure, aggregation, oxygen bridging, etc.

The underlying feature of this method of analysis is the synthesis of
silver ferrites and the difference that immediately appears between yellow
hydrates and red hydrates, or, as Krause terms them, respectively, meta-
hydroxides and ortho-hydroxides. Krause and Pilawski (58) found that
the composition of a silver ferrite formed from meta-hydroxide can be
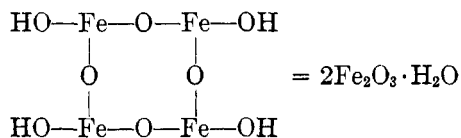represented by the proportion

$$Ag_2O:Fe_2O_3 = 1:1$$

In a silver ferrite formed from ortho-hydroxide, on the other hand, this pro-
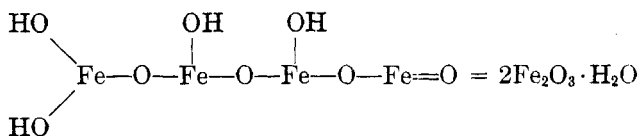portion proved to be

$$Ag_2O:Fe_2O_3 = 1:1.36$$
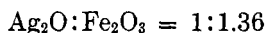
From considerations of a chemical nature, Krause and Pilawski conclude
that the true composition of a silver ferrite made from fresh ortho-hy-
droxide would be

$$Ag_2O:Fe_2O_3 = 1:1.33$$
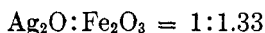
which suggests that meta- and ortho-hydroxides are four-membered
molecules. They assign to the meta-hydroxide a ring structure with
equivalent hydroxyl groups and in which each hydrogen is replaceable by
silver, thus:

$$
\begin{array}{cc}
HO-Fe-O-Fe-OH & \\
| \quad\quad | & \\
O \quad\quad O & = 2Fe_2O_3 \cdot H_2O \\
| \quad\quad | & \\
HO-Fe-O-Fe-OH &
\end{array}
$$

To the ortho-hydroxide is assigned a chain structure

$$
\begin{array}{l}
HO \quad\quad OH \quad OH \\
\quad\diagdown \quad\quad | \quad\quad | \\
\quad\quad Fe-O-Fe-O-Fe-O-Fe=O = 2Fe_2O_3 \cdot H_2O \\
\quad\diagup \\
HO
\end{array}
$$

in which only three OH groups are equivalent with replaceable hydrogens. The fourth OH group plays a different rôle, and it is this group which imparts to ortho-hydroxide its more basic character as compared to meta-hydroxide. We have already seen (53) that the isoelectric point of the former is at pH = 7.7, whereas that of the meta-hydroxide is at pH = 5.2.

The ring molecule which forms silver ferrite with $Ag_2O:Fe_2O_3 = 1:1$ is the γ-ferric oxide hydrate. By the silver analysis it is therefore possible to identify a γ-ferric oxide hydrate which is not sufficiently crystallized to show an x-ray spectrum. This has been done by Krause, Czapska, and Stock (55). α-Ferric oxide hydrate, either crystalline or amorphous, does not form ferrites with silver. The silver analysis thus provides an additional means of identifying the products of the oxidation of ferrous hydroxide. Professor Krause, in a private communication, informs us that amorphous (no x-ray lines) as well as crystalline γ- and α-ferric oxide hydrate have been obtained by this reaction. It is for this reason that the oxidation paths, ferrous hydroxide → amorphous ferric acid (amorphe eisenige Säure), and ferrous hydroxide → amorphous α-hydrate, have been added to the diagram of figure 1. It may be mentioned here that the aging paths and the numerous steps that have been disclosed by Krause and his associates are shown by broken lines in the figure. Paths which were already known are shown with unbroken lines.

As auxiliary aids in the analysis, Krause has used the fact that meta-hydroxide and other ring compounds dissolve extremely slowly in concentrated acetic acid and in 30 per cent nitric acid, while ortho-hydroxide and chain polymers dissolve very easily (53, 59). The fact that meta-hydroxide may be peptized in dilute solutions of either acids or alkalies, while the ortho-variety can be peptized only in acid solutions, is another way of distinguishing between them. Color changes also give valuable indications as to the nature of the changes taking place on aging.

We have seen that silver ferrites formed from meta-hydroxide have the composition

$$Ag_2O:Fe_2O_3 = 1:1$$

Consequently meta-hydroxide may be given the formula $(HFeO_2)_n$. The ferrite formed from ortho-hydroxide with

$$Ag_2O:Fe_2O_3 = 1:1.33$$
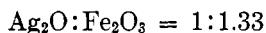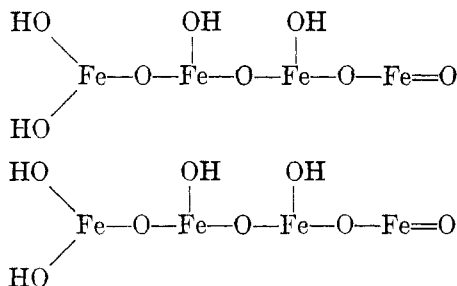
has for formula $Ag_3H(FeO_2)_4$.

XIV. AGING OF ORTHO-HYDROXIDE

The "activity" of ortho-hydroxide and its tendency to age is evident even in the moment of precipitation from a ferric salt with an alkali. Silver ferrites of the composition
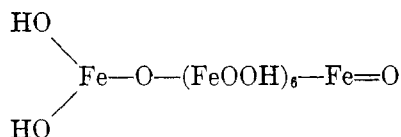
$$Ag_2O:Fe_2O_3 = 1:1.36$$
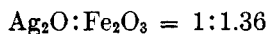
can only be obtained by precipitation in the presence of silver nitrate so that the silver reacts with ferric hydroxide in the nascent state. If silver nitrate is added immediately after precipitation some aging will already have occurred, as evidenced by $Ag_2O:Fe_2O_3$ ratios of more than 1:1.36. However, the rate of aging can be controlled by varying the hydroxide concentration. Aging of ortho-hydroxide is most rapid (59) when the alkalinity is between $N = 0.1$ and 0.05. With $N = 1$, the aging is much slower.

According to Krause and Ciokówna (54), the first step in the aging is the polymerization of the four iron atom chain molecules to form longer chains, and it is due to a loosening of the Fe$=$O double bond. For two ortho-hydroxide molecules this may be illustrated by the union of

$$
\begin{array}{c}
\text{HO} \\
\diagdown \\
\text{HO} \diagup \text{Fe—O—Fe—O—Fe—O—Fe} = \text{O} \\
\end{array}
\quad
\begin{array}{c}
\text{OH} \quad \text{OH}
\end{array}
$$

HO   OH   OH
   \\ | |
    Fe—O—Fe—O—Fe—O—Fe=O
   /
HO

HO   OH   OH
   \\ | |
    Fe—O—Fe—O—Fe—O—Fe=O
   /
HO

to form a molecule of eight iron atoms which may be abbreviated

HO
   \\
    Fe—O—(FeOOH)$_6$—Fe=O
   /
HO

Here, again, all but one hydrogen may be replaced by silver, but the ferrite would have the composition
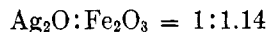
$$Ag_2O:Fe_2O_3 = 1:1.14$$

Evidently, as the degree of polymerization increases, the $Ag_2O:Fe_2O_3$ ratios of the silver ferrites that can be formed will approach asymptotically to unity. It was estimated that in solutions of normal alkalinity, the degree of polymerization might be as high as 40 or 50. Like the ortho-hydroxide, poly-ortho-hydroxide is soluble in concentrated acetic acid and in 30 per cent nitric acid. This conclusion regarding polymerization was drawn from experiments on rapid aging in boiling alkaline media. The same type of polymerization occurs on slow aging at room temperature (57).

Beyond poly-ortho-hydroxide, aging may follow either of two paths. We shall consider, first, the path to goethite which is followed when the hydroxide concentration is between 0.01 N and 3.5 N. Krause and his coworkers have identified two intermediate phases along this path, amorphous ferric acid and polyferric acid (polyeisenige Säure) (59). This path is characterized by decreasing affinity for silver and by the fact that the members are insoluble in concentrated acetic acid and 30 per cent nitric acid. This last property requires a ring instead of a chain structure, because this insolubility is also a property of meta-hydroxide. Hence, Krause and Ciokówna (54) consider that ring closure occurs in poly-ortho-hydroxide to form large ring molecules. All of the hydrogen atoms are replaceable by silver. The product of this ring closure is called amorphous ferric acid. Its chemical reactions are identical with those of meta-hydroxide, γ-ferric oxide hydrate, but they differ in two respects. Amorphous ferric acid ages in the direction of goethite, α-$Fe_2O_3 \cdot H_2O$, while γ-ferric oxide hydrate is stable. And it does not yield ferromagnetic γ-ferric oxide on dehydration. This circumstance requires an explanation and a defense of the classification given by the silver analysis. It has been given by Krause and Lewandowski (57).

According to Krause, Lakósciukówna, and Cichowski (56) the next step on the way to goethite is aggregation of the large ring molecules into a network of polyferric acid. Schematically this aggregation may be represented by:

$$
\begin{array}{c}
\text{HO—Fe—O—Fe—OH} \qquad \text{HO—Fe—O—Fe—OH} \\
| \qquad | \qquad\qquad\quad | \qquad | \\
\text{O} \qquad \text{O} \qquad + \qquad \text{O} \qquad \text{O} \qquad = \\
| \qquad | \qquad\qquad\quad | \qquad | \\
\text{HO—Fe—O—Fe—OH} \qquad \text{HO—Fe—O—Fe—OH}
\end{array}
$$

$$
\begin{array}{c}
\text{H}_2\text{O} \\
\text{HO—Fe—O—Fe—O—Fe—O—Fe—OH} \\
| \qquad | \qquad | \qquad | \\
\text{O} \qquad \text{O} \qquad \text{O} \qquad \text{O} \\
| \qquad | \qquad | \qquad | \\
\text{HO—Fe—O—Fe—O—Fe—O—Fe—OH} \\
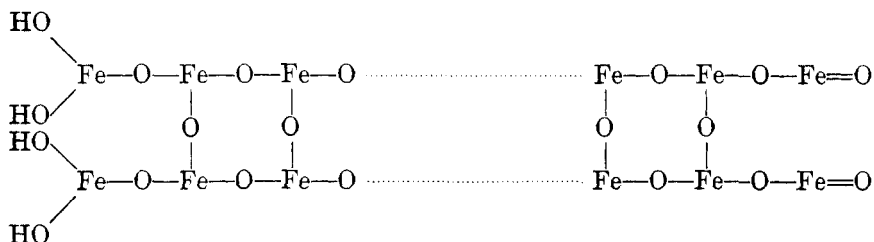\text{H}_2\text{O}
\end{array}
$$
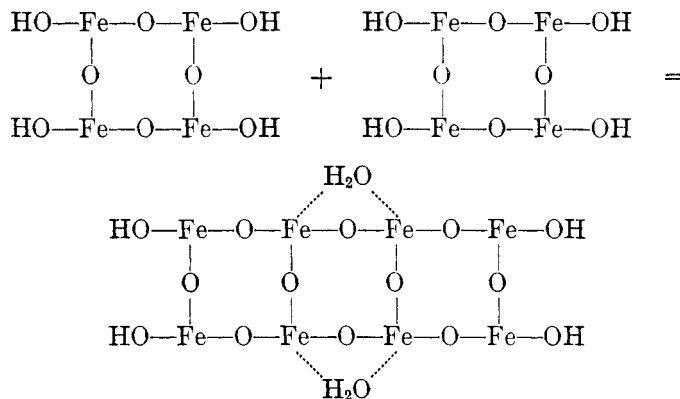
The amorphous ferric acid molecules are joined to each other by oxygen bridges, and the water becomes coördinatively bound. Obviously, as the network becomes large, all of the hydrogen appears in the water, so that polyferric acid, like goethite itself, does not form silver ferrite.

For a discussion of the complex mixtures that appear during the final

stage, crystallization to goethite, and of the difficulties in the way of separating them, the reader is referred to the original paper by Krause and Torno (59).

Under water or in a weakly alkaline medium, $N < 0.01$, aging from poly-ortho-hydroxide leads to hydrohematite. Along this path ring closure does not occur. The long chains of poly-ortho-hydroxide polymerize into a bundle of chains. Water is eliminated and the structure may be represented by:

$$\begin{array}{l}
HO \\
\quad \diagdown \\
\qquad Fe-O-Fe-O-Fe-O \cdots\cdots\cdots Fe-O-Fe-O-Fe=O \\
\quad \diagup \qquad\quad | \qquad | \qquad\qquad\qquad\qquad | \qquad | \\
HO \qquad\quad O \qquad O \qquad\qquad\qquad\qquad O \qquad O \\
HO \\
\quad \diagdown \qquad\; | \qquad | \qquad\qquad\qquad\qquad | \qquad | \\
\qquad Fe-O-Fe-O-Fe-O \cdots\cdots\cdots Fe-O-Fe-O-Fe=O \\
\quad \diagup \\
HO
\end{array}$$

It is called (59) poly-ortho-hydroxide-associate.

The final step along this path is crystallization of the aggregate of chain molecules to α-ferric oxide and the zeolithic binding of the water. Krause has not as yet considered further aging from hydrohematite. It will be recalled that, according to Hüttig, hydrohematite eventually ages to goethite by way of limonite, as indicated in the diagram of figure 1.

Krause, Lakósciukówna, and Cichowski (56) found that both paths, ring structure to goethite and chain structure to hydrohematite, are followed when aging beyond poly-ortho-hydroxide is carried out at higher temperatures up to 150°C.

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