[AMERICAN JOURNAL OF SCIENCE, VOL. 250, SEPTEMBER 1952, PP. 677-695]

DIFFERENTIAL THERMAL ANALYSIS OF CERTAIN IRON OXIDES AND OXIDE HYDRATES*

MOHAMED A. GHEITH

ABSTRACT. Amorphous hydrated ferric oxides formed both by direct neutralization of ferric ion solutions and the oxidation of ferrous salts were thermally analyzed. The curves for both compounds, when fresh, show loss of adsorbed water followed by direct crystallization to hematite. By aging, goethite crystallizes from both these brown and yellow gels respectively. Its presence is indicated on the thermal curves.

$MgFe_2O_4$ and gamma-Fe_2O_3 can be distinguished by differential thermal analysis. The method also provides an easy way of detecting gamma-Fe_2O_3 in its mixtures with hematite.

Synthetic magnetite shows two exothermic peaks indicating its oxidation first to gamma-Fe_2O_3 which in turn transforms to hematite. Natural magnetite is oxidized directly, although very slowly, to hematite. Its thermal curve is characterized by a single flat exothermic "plateau" which starts at about 635°C. and does not end even at 1100°C. If samples with a wide particle size range are used, the curve may be modified by a small exothermic peak at 380-395°C. due to the recrystallization of the finer particles.

INTRODUCTION

DIFFERENTIAL thermal analysis consists of simultaneously heating the sample to be analyzed, along with another sample of inert material which does not undergo any thermal reaction in the temperature range investigated. The differential thermal analysis apparatus used in this study is not different from others described in the literature except for the removable sample block, made of "inconel" metal, which was designed by Professor J. W. Gruner and photographed by Manly (1950). The rate of heating was kept constant, at 13.5°C. per minute, giving a straight line relation between time and temperature in the interval between 100° and 1100°C. The specimen, unless otherwise indicated, was ground to pass 150 mesh screen, and then packed in its proper place in the sample block. A correspondingly fine grained alundum powder was used as the inert material. Whenever the sample consisted of an artificial mixture of different compounds, these were ground together in an agate mortar, and thoroughly mixed by rolling on a sheet of paper prior to their analysis.

* This study constitutes part of a thesis submitted by the writer to the graduate faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree.

The substances used in this investigation include the following:

The brown gel.—$Fe_2O_3.nH_2O$, brown colloidal hydrated ferric oxide, prepared by the direct neutralization of a ferric salt solution with an alkali hydroxide.

The yellow gel.[1]—$Fe_2O_3.nH_2O$, yellow colloidal hydrated ferric oxide, prepared by the oxidation of freshly precipitated ferrous carbonate, usually with H_2O_2.

Natural magnetite.—Fe_3O_4, three samples of high purity from Mineville, New York, Kinney, Minnesota, and Kiruna, Sweden.

Synthetic magnetite.—Prepared by the reduction of various iron compounds as explained below.

Magnesium ferrite.—$MgFe_2O_4$, cubic ferromagnetic compound, similar in appearance and in x-ray powder pattern to gamma-Fe_2O_3 and might have been mistaken for it in the past.

Gamma ferric oxide.—Cubic ferromagnetic ferric oxide, prepared by the dehydration of synthetic lepidocrocite to constant weight in an open container at 280°C.

Synthetic lepidocrocite.—Gamma-$Fe_2O_3.H_2O$, obtained from the Minnesota Mining and Manufacturing Company (no. 2184), but not produced commercially. Its color corresponds to Ridgway's Ochraceous Orange, and it gives an excellent lepidocrocite x-ray pattern. Qualitative tests showed the presence of traces of ferrous iron which were quantitatively determined to be 0.15% FeO.

THERMAL BEHAVIOR OF THE BROWN AND YELLOW GELS

Through a combination of differential thermal analysis and x-ray powder photographs, several significant points were brought out which would have otherwise escaped notice. The changes that take place on aging[2] of either gel can be followed step by step by this method.

[1] Kulp and Trites (1951, p. 26) called this product also a brown gel. This is not the common practice.

[2] The process of aging includes the changes which take place spontaneously at room temperature, unless a different temperature is specified.

The Brown Gel

The first five curves (fig. 1) represent the thermal behavior of the brown gel at different stages of its aging process. Curves 1, 2 and 3 were made on the same sample, precipitated by adding excess 10N NH_4OH solution to a strong ferric chloride solution to pH 12. The dense precipitate was left overnight, then decanted and washed once with water. A sample was taken and used while slightly wet for the first determination (curve 1). The rest of the material was thoroughly washed with water and left wet at room temperature. The second determination was made on this wet material 3 days after its precipitation (curve 2). The third determination was made on the same material 46 days after its precipitation (curve 3).

Curve 1 shows a major endothermic reaction occupying the interval between 100°C. and 275°C. with the peak slightly below 200°C. This reaction is most probably due to the release of adsorbed water. It is followed almost immediately by a major exothermic reaction culminating in a sharp peak at 310°C. This reaction is caused by the crystallization of the amorphous anhydrous ferric oxide to hematite. Two x-ray powder photographs proved that the material was amorphous at 280°C., and consisted of hematite at 400°C.

Curve 2 shows an adsorbed water endothermic peak similar to curve 1. However, the exothermic peak due to the crystallization of amorphous Fe_2O_3 to alpha-Fe_2O_3 does not start until 400°C. It culminates in a peak, much broader than in curve 1, at 460°C. The composition of the material was proved by two x-ray powder photographs to be amorphous Fe_2O_3 and hematite at 300°C. and 550°C., respectively. This curve bears great resemblance to the one by Kulp and Trites (1951, fig. 9, curve 1, p. 42) made on material precipitated at pH 10, 25°C. and washed with dilute NH_4OH. Curiously enough, curve 1 (fig. 1) of the present study also shows a great similarity to Kulp and Trites' curve 2 (fig. 9, p. 42). The latter, however, was made on material precipitated at pH 5, 25°C. and thoroughly washed with water. In spite of the acidic solution and the thorough washing, the curve still presented a small endothermic kick around 400°C. indicative of ammonia, as was noticed by the authors. The important point is that Kulp and Trites obtained two curves on materials precipitated at two different pH values, while the author obtained two

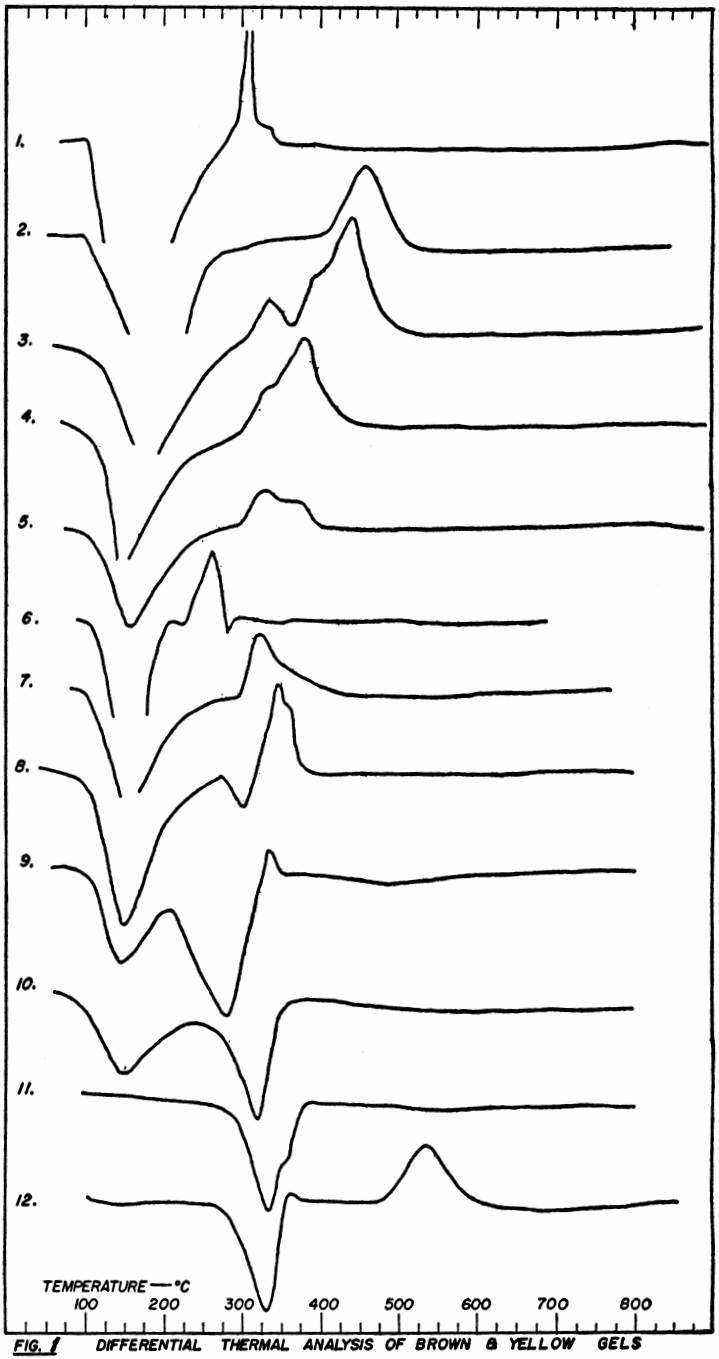

FIG. 1 DIFFERENTIAL THERMAL ANALYSIS OF BROWN & YELLOW GELS

curves similar to those of Kulp and Trites from the same sample before and after it was left to age at room temperature for 3 days. This fact suggests that the effect of the pH of the solution is possibly not as significant in the crystallization of goethite and hematite as has been assumed thus far.

Curve 3, unlike 1 and 2, was made with the sample uncovered, thus rendering the escape of water vapor much easier. An x-ray powder photograph taken of the sample just before the analysis showed a faint goethite pattern. The curve shows a strong endothermic reaction due to adsorbed water similar to those in curves 1 and 2. This is followed by a major exothermic reaction culminating in a peak at 440°C. and representing the crystallization of the amorphous Fe_2O_3 to hematite. This major exothermic peak is modified by an endothermic reaction due to the dehydration of the small amount of goethite present in this sample. The "endothermic" dent modifying the curve at about 365°C. represents the sum of the heat effects of the two simultaneous reactions: crystallization of the amorphous Fe_2O_3 and dehydration of goethite. X-ray powder photographs of this material heated to 290°C. and 500°C. showed faint goethite and good hematite patterns, respectively.

The small endothermic dent due to the dehydration of goethite does not show as well if the sample is covered, because the reaction and escape of water is spread over a longer period of time, thus giving a flattened dome which does not modify the exothermic peak as much. Curves 4 and 5 show the thermal record of two covered samples of aged brown gel. Curve 4 is that of an 18 months old brown gel which gave a fair goethite pattern before the analysis. The curve shows an adsorbed water, fairly strong endothermic peak at about 155°C. This is followed by the usual exothermic peak due to crystallization of the amorphous Fe_2O_3. This peak is but slightly modified by a steplike flattening around 330°C. due, it is believed, to the dehydration of the goethite which was present in the sample. This was proved by x-ray patterns of this material heated to 250°C. and 450°C. respectively.

Curve 5 represents the thermal behavior of a 28 months old brown gel. Its color was brownish red (more like hematite) but on x-raying it was found to show only goethite lines. Another x-ray photograph of this material heated to 250°C. showed no difference from the one at room temperature. The

curve shows an adsorbed water peak at 158°C. which is, however, much smaller in area and amplitude than in the previous cases. Loss of adsorbed water during aging is to be expected. The flattened dome or plateau occupying the interval between 300°C. and 385°C. represents the heat balance between the crystallization of amorphous Fe_2O_3 to hematite and the simultaneous dehydration of goethite, also to hematite. A significant point borne out by this analysis is the fact that even after 28 months of aging the material still retained a considerable amount of amorphous ferric oxide hydrate.

The Yellow Gel

The thermal behavior of the yellow gel is seen to be similar to that of the brown gel if one bears in mind the fact that its crystallization starts only a short period after its precipitation and usually proceeds at a faster rate. In the brown gel detectable crystallization never starts before several days and often a number of weeks after its precipitation, and proceeds very slowly. Another difference is that both the dehydration of goethite formed from the yellow gel and the crystallization of hematite from the amorphous material generally take place at a lower temperature than the corresponding reactions in the brown gel.

Curves 6, 7 and 8 were made on the same sample, formed by adding ammonium carbonate solution to a solution of ferrous chloride and oxidizing the precipitated ferrous carbonate with excess H_2O_2. The pH of the supernatant liquid was approximately 4.5. The dark yellow precipitate formed was left standing for one hour, decanted and washed once with water. A sample was taken and used while slightly wet for the first determination (curve 6) less than 2 hours after the precipitation of the gel. The rest of the material was thoroughly washed with water and left at room temperature. The second determination (curve 7) was made on slightly wet material 5 days after its precipitation. The third determination (curve 8), the only run in which the sample was not covered, was made on the same material 34 days later.

Curve 6 shows a major endothermic reaction covering the interval between 100°C. and 210°C. with the peak at approximately 185°C. This is followed by a rather sharp exothermic reaction culminating in a peak at 258°C. This reaction is

undoubtedly due to the crystallization of the amorphous material to hematite, a fact which was proved by two x-ray powder photographs of this material heated to 190°C. and 280°C., respectively. The small endothermic reaction following the major exothermic reaction is to be attributed to the presence of traces of an ammonium salt impurity. This is supported by the fact that the small endothermic reaction is absent from the following curves where the material was thoroughly washed before the analysis. An important point to be emphasized in connection with this curve is that the amorphous yellow ferric oxide hydrate goes directly to hematite with no indication of its crystallization to goethite as an intermediate step.

Curve 7 shows an endothermic reaction culminating in a peak at approximately 165°C., due to release of adsorbed water. The asymmetric exothermic peak covering the range between 297°C. and 415°C. with a peak temperature of 320°C. represents the net amount of heat produced when the crystallization of amorphous ferric oxide to hematite (exothermic) and the dehydration of goethite (endothermic) take place simultaneously. That a small amount of goethite was present in the sample was proved by an x-ray powder photograph of the yellow gel at room temperature which showed a very faint pattern of goethite.

Curve 8, made 34 days later and with the sample uncovered to facilitate the escape of water vapor, shows the usual adsorbed water endothermic reaction at 150°C. The dip in the curve, preceding the major exothermic peak, is to be attributed to the starting of the dehydration of goethite which was known to be present from a fairly good x-ray pattern taken at room temperature. The following exothermic reaction with the peak at 345°C. is of course due to the crystallization of the amorphous ferric oxide to hematite, while the dehydration of goethite is still proceeding. The small steplike flattening modifying the exothermic peak may also be due to the simultaneous dehydration of goethite.

It was noticed during the study of the colloidal ferric hydrates[3] that if $Na_2(CO_3)$ is used instead of $(NH_4)_2CO_3$ for precipitating the ferrous carbonate, a better crystallized goethite is obtained on oxidation and aging, provided other variables

[3]Gheith, M. A. (1951), Stability relations of ferric oxides and their hydrates; thesis submitted to University of Minnesota.

were kept constant.[4] The role played by sodium, however, is not satisfactorily understood. Curves 9 and 10 (fig. 1) represent the thermal behavior of yellow gel formed by adding a sodium carbonate solution to a ferrous chloride solution and oxidizing the precipitated ferrous carbonate with excess H_2O_2.

Curve 9, made with dry material, 9 days after its preparation shows a small endothermic peak at 145°C. representing the release of adsorbed water. This is followed by a major endothermic reaction with the peak temperature at 280°C. representing the dehydration of goethite. This reaction is probably interrupted or at least immediately followed by a rather small exothermic reaction with a peak at 330°C. due to the crystallization of the amorphous oxide to hematite. X-raying the starting material at room temperature gave a fairly good goethite pattern. The sample therefore must have consisted mainly of goethite and a small amount of amorphous hydrated ferric oxide.

Curve 10 represents a further stage in the aging of the yellow gel. The material, 23 months after its precipitation, consists only of goethite with some adsorbed water. The small adsorbed water peak lies at 150°C., while the goethite endothermic peak lies at 323°C.

Curve 11 shows the analysis of a 4½ year old sample which had been prepared by adding sodium carbonate solution to ferrous sulphate solution and oxidizing the product by blowing air through it for 2½ hours at 40°C. The yellow precipitate had given a good goethite x-ray pattern 2 days after its precipitation. The curve shows that this material represents the final stage in the aging process of the yellow gel. The only reaction present is the endothermic dehydration of goethite, culminating in a peak at 335°C.

Curve 12 represents the final stage of aging in another type of yellow gel, namely that precipitated under conditions favoring the crystallization of lepidocrocite rather than goethite. This particular sample had been prepared 4½ years earlier, by adding NaOH to a dilute $FeSO_4$ solution until pH 6, followed by blowing air through the solution for 2 hours. It had given a fairly good lepidocrocite x-ray pattern 2 days after its pre-

[4] Welo and Baudisch (1934) mention that a stabilizing effect of sodium was noticed by Hugget in connection with gamma-Fe_2O_3, formed by the oxidation of precipitated magnetite. Whenever NaOH was involved instead of NH_4OH during the preparation of gamma-Fe_2O_3, the product was stable at higher temperatures.

cipitation. Curve 12 shows the two familiar lepidocrocite reactions. An endothermic peak at 330°C. due to the dehydration of lepidocrocite to gamma-Fe_2O_3 is followed by an exothermic peak at 535°C., representing the phase transformation of gamma-Fe_2O_3 to alpha-Fe_2O_3. The curve shows only traces of adsorbed water.

Aging and Differential Thermal Analysis

Kulp and Trites (1951), noticing from the differential thermal analysis of a number of freshly prepared brown gels that they crystallize directly to hematite, concluded that in nature hematite is probably formed

> ". . . by the auto-dehydration of the hydrous ferric oxide gel which is a result of direct neutralization of a ferric ion solution. Goethite and lepidocrocite are not formed under these conditions but rather by the slow oxidation of certain ferrous compounds . . ."

The present study shows that on differential thermal analysis the fresh yellow gel, formed by the oxidation of certain ferrous compounds, behaves similarly to the fresh brown gel and crystallizes directly to hematite. Furthermore, the differential thermal analysis of aged gels indicates that in the laboratory goethite actually forms both from the direct neutralization of a ferric ion solution and the oxidation of certain ferrous compounds. There is no reason to believe that goethite does not form by the aging of the brown gel in nature.

The rather fast rate of heating generally used in differential thermal analysis in various laboratories (10 to 15°C./min.) seems to result in the dehydration of freshly prepared colloidal hydrated ferric oxide gels, whether yellow or brown, giving the amorphous anhydride Fe_2O_3, which crystallizes to hematite on further heating. Aging at room temperature, on the other hand, seems to fix part of the water present in the colloid more firmly to the solid framework, resulting in a definite hydrate of crystalline structure. Thus, this is another example following the hypothesis accepted by many chemists as to the effect of a spontaneous aging on some and probably all of the colloidal metal oxide hydrates.

THERMAL BEHAVIOR OF SYNTHETIC LEPIDOCROCITE AND GAMMA-FE_2O_3—HEMATITE MIXTURES

It was found that the thermal curve of synthetic lepidocrocite (curve 12, fig. 1, and curve 1, fig. 2) is identical with

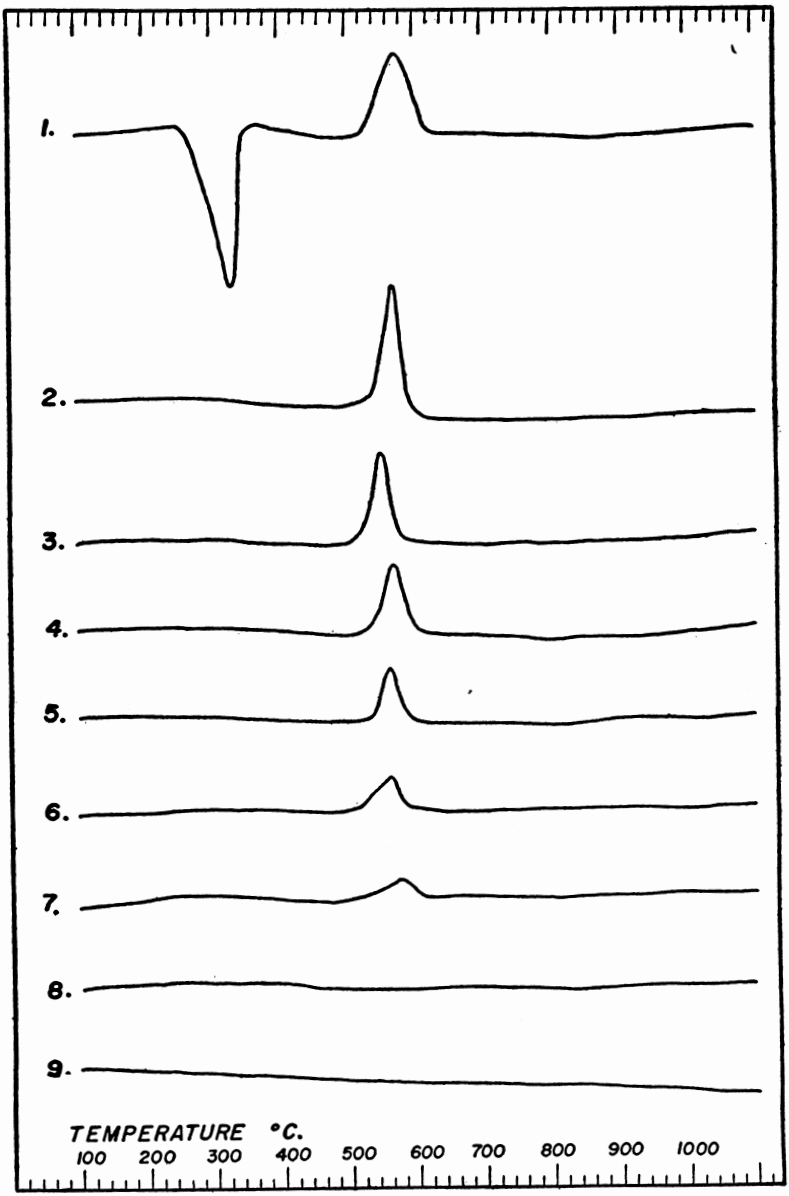

Fig. 2

1. Synthetic lepidocrocite
2. " " gamma Fe_2O_3
8. Hematite, Marquette Range, Mich.
9. Magnesium ferrite

3.	Hematite	20,	gamma—Fe_2O_3		80
4.	"	"	33.3	"	"	66.7
5.	"	"	50	"	"	50
6.	"	"	66.7	"	"	33.3
7.	"	"	83.3	"	"	16.7

those of natural lepidocrocite except for the decidedly lower temperature at which the endothermic peak occurs. This may be attributed to the small size of the particles.

Curve 1 (fig. 2) representing the purest sample of those analyzed shows an endothermic peak at about 320° C. due to the dehydration of lepidocrocite to gamma-Fe_2O_3. This is about 30° C. lower than the corresponding peak of natural lepidocrocite thermal curve obtained by Kulp and Trites (1951, p. 43). Curve 1 also shows an exothermic peak at 568°C. representing the transition from gamma-Fe_2O_3 to alpha-Fe_2O_3. This peak temperature is about 100°C. or more higher than that of the corresponding reaction in natural lepidocrocite. In fact, all of Kulp and Trites' curves (1951, fig. 3) of natural lepidocrocite present this exothermic peak at or below 450°C. It is believed that the higher the temperature at which gamma-Fe_2O_3 is formed by the dehydration of lepidocrocite, the lower is the temperature of its transformation to hematite. Curve 2 of gamma-Fe_2O_3 shows one exothermic peak at about 570°C. representing its transformation to hematite. The sharpness of the peaks is an indication of the uniform particle size distribution.

In nature one may encounter some "hematite" samples which adhere to a hand magnet. The reason for magnetism in such cases is usually the presence of a small amount of ferrous iron, either as a constituent of intergrown magnetite or as a constituent of a solid solution (Sosman and Posnjak, 1925, p. 329). In the laboratory, however, and probably under rare conditions in nature, magnetism may be due to two additional causes, namely the presence of a ferromagnetic ferrite of a divalent element, or the presence of gamma-Fe_2O_3 in the "magnetic hematite." In view of this fact magnesium ferrite ($MgFe_2O_4$) was analyzed. Its thermal curve (no. 9, fig. 2) shows no reaction in the temperature range investigated. Curves 3 to 7 (fig. 2) represent the thermal behavior of artificial mixtures of gamma-Fe_2O_3 and natural hematite in known proportions. Because hematite produces no distinctive thermal peaks (curve 8), it therefore acts as an inert impurity, reducing the height of the gamma-Fe_2O_3 peak.

The temperature of the gamma-Fe_2O_3 peak is affected by the presence of hematite in a rather peculiar fashion. A mixture

Fig. 2. Differential thermal analysis of lepidocrocite, gamma-Fe_2O_3-hematite mixtures and $MgFe_2O_4$.

with 20% hematite produces the peak at the lowest temperature (550°C.), whereas a mixture with 83.33% hematite produces it at the highest temperature (576°C.). There is no regular increase in the peak temperature, however, by increasing amounts of hematite.

THERMAL BEHAVIOR OF SYNTHETIC AND NATURAL MAGNETITES

The behavior of magnetite on heating has been a controversial subject. Whether natural magnetite is oxidized by heating to gamma-Fe_2O_3 or directly to hematite has been argued back and forth by Sosman and Posnjak (1925), Wagner (1927), Welo and Baudisch (1925, 1934), Twenhofel (1927), Gruner (1926, 1927, 1930), Thewlis (1931), Verwey (1935), Goldzstaub (1935), Starke (1939) and others. Part of the confusion, at least, resulted from the difference in behavior upon heating between natural magnetite with a unit cell containing:

$$8Fe^{+++} \quad 8Fe^{+++} \quad 8Fe^{++} \quad 32\ O^{--}$$

and precipitated magnetites which according to Starke (1939) may have a lower ferrous iron content, sometimes as low as to correspond to a unit cell containing:

$$8Fe^{+++} \quad 8Fe^{+++} \quad 5\tfrac{1}{3}Fe^{++} \quad 26\tfrac{2}{3}\ O^{--} \quad 5\tfrac{1}{3}\ OH^{-}$$

As most of the discussion of this problem was based mainly on theoretical structural evidence, the present study was therefore undertaken to determine experimentally the differences in behavior between natural and synthetic magnetite. The curves obtained show that differential thermal analysis is particularly adaptable for such a problem. Unless otherwise mentioned the samples were not covered, so as to facilitate the oxidation of the ferrous iron.

Synthetic Magnetite

Synthetic magnetite gives two distinct exothermic peaks. The first peak corresponds to the oxidation of magnetite to gamma-Fe_2O_3 whereas the second corresponds to the change of gamma-Fe_2O_3 to hematite. Curves 1, 2 and 3 (fig. 3) are typical of the thermal behavior of dry synthetic magnetite in the absence of all traces of water vapor. The temperature at the first exothermic peak is 375°C., 320°C., and 280°C., whereas the second peak lies at 590°C., 620°C., and 650°C. in those three curves respectively. Comparison of these three curves confirms the

writer's previously mentioned belief that the higher the temperature of formation of gamma-Fe_2O_3, the lower the temperature of its change to hematite. This statement seems to be true for gamma-Fe_2O_3 prepared by either of its two general methods of preparation: the dehydration of lepidocrocite and the oxidation of synthetic magnetite.

Curve 4 shows the effect of adsorbed water on the thermal behavior of synthetic magnetite. The sample was prepared by the reduction at 190°C. in a sealed tube of gamma-Fe_2O_3 by camphor which was not previously dried. Camphor was later dissolved in benzene and this was followed by a magnetic separation under water to eliminate the hematite formed. The magnetite was left to dry for 2 days at room temperature before it was thermally analyzed. The sample was covered during the analysis, rendering the removal of H_2O rather sluggish. The curve shows an endothermic adsorbed water peak at about 110°C. The temperatures of the two exothermic peaks of synthetic magnetite are lowered considerably. The catalytic effect of water vapor on the transformation of gamma-Fe_2O_3 to hematite is obviously indicated from the fact that although gamma-Fe_2O_3 formed around 210°C., it was transformed to hematite at the comparatively low temperature of 460°C., more than 130°C. lower than when moisture is completely absent.

Natural Magnetite

Curves 5, 6, 7, 8, 9 and 10 (fig. 3) are typical of pure natural magnetite. The main and striking feature of the curve is the extremely flat exothermic "peak" denoting the oxidation of the ferrous iron. The reaction starts between 625°C. and 650°C., culminates roughly at 1000°C. and does not end even at 1100°C. X-ray powder diagrams of the products of differential thermal analyses showed the presence of both magnetite and hematite. The color of the products was reddish black, and the presence of magnetite was further confirmed by quantitative oxidimetric determination of the ferrous iron content. From 3.26 to 4.12% FeO was found to remain in the material after it was heated to about 1100°C. This means that 10.52 to 13.29% of the original magnetite had not yet been oxidized. All this points to the stability and difficulty of oxidation of Fe_3O_4 magnetite in nature in the absence of water vapor and/or catalysts.[5]

[5] Gruner (1930) noticed that magnetite starts to oxidize to hematite in the presence of steam at 258°C. The reaction is catalyzed by traces of HCl.

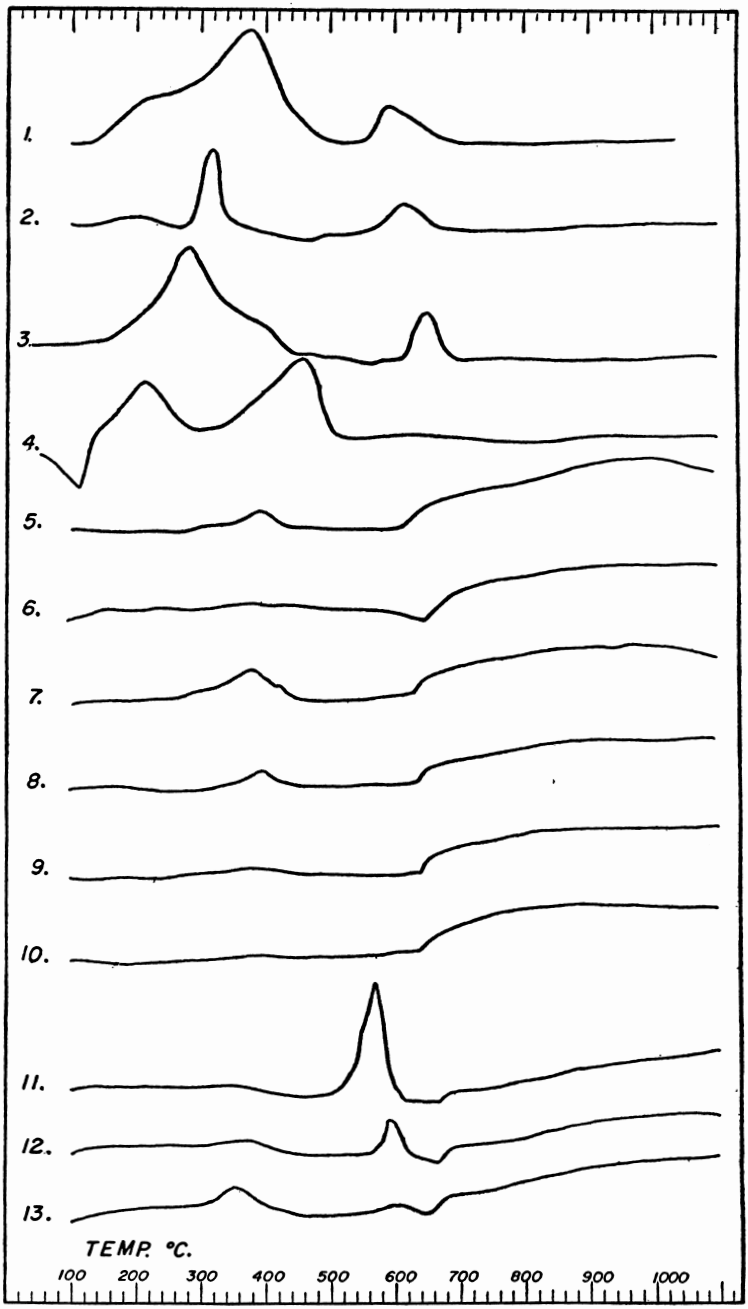

FIG. 3 DIFFERENTIAL THERMAL ANALYSIS OF MAGNETITES.

The second feature of the thermal curve of natural magnetite is the small exothermic peak whose temperature ranges from 380°C. to 395°C. This peak, which shows better on curves 5, 7 and 8 (fig. 3) is rather problematic. It cannot be attributed to an impurity inasmuch as the possibility of the presence of the same type of impurity in magnetites from such varied localities and with different geneses is rather meager. Besides a careful magnetic separation under water under the binocular microscope was carried out before the samples were thermally analyzed. The possibility of the presence of some maghemite as an oxidation product in the original magnetite is negligible as the small exothermic peak occurs at a temperature much lower than that of the phase transformation of gamma-Fe_2O_3 to hematite in the absence of water vapor. Microscopic examination of the samples indicated the absence of oxidation products. Furthermore, artificial mixtures of natural magnetite and synthetic gamma-Fe_2O_3 in various ratios were thermally analyzed and the results are shown in curves 11, 12 and 13 (fig. 3). The effect of "dilution" is indicated by the lower amplitudes of

---

Fig. 3. Differential thermal analysis of magnetites.
(Samples 1 to 7 were X-rayed prior to their analysis.)

1. Synthetic magnetite: formed by the reduction of artificial goethite with a large amount of oxalic acid at dull red heat in open tube.
2. Synthetic magnetite: formed by the reduction of hematite with a large amount of oxalic acid at dull red heat in open tube.
3. Synthetic magnetite: formed by the reduction of gamma-Fe_2O_3 with dried ethyl acetate at 190°C. in sealed tube.
4. Synthetic magnetite: formed by the reduction of gamma-Fe_2O_3 with camphor at 190°C. in sealed tube.
5. Natural magnetite crystals: Kinney, Minnesota; pure, with only 0.05% excess of Fe_2O_3; finely powdered to pass 150 mesh screen.
6. Natural magnetite: Mineville, New York; portion of a single coarse crystal. University of Minnesota No. B380; size: —35 + 60 mesh.
7. Natural magnetite: Kiruna, Sweden; very finely crystalline, powdered to pass 150 mesh screen.
8. Natural magnetite: the same as used in curve 7; powdered to pass 60 mesh screen.
9. Natural magnetite: the same as used in curve 7; size: —60 + 100 mesh.
10. Natural magnetite: the same as used in curve 7; size: —20 + 35 mesh.
11. Artificial mixture of natural magnetite (Kiruna) and gamma-Fe_2O_3 (from dehydration of lepidocrocite at 280°C. for 4 days) 1:1; size: —150 mesh.
12. Mixture of the same materials as in curve 11, but the ratio is 5:1; size: —150 mesh.
13. Mixture of the same materials as in curve 11, but the ratio is 15:1; size: —150 mesh.

the peaks. Examination of these three curves shows that a calibration curve can be drawn by plotting the area under the peak of the gamma-Fe_2O_3 to hematite phase transformation against the concentration of either gamma-Fe_2O_3 or magnetite. Therefore, whenever the claim is made that a crystal of magnetite was partly oxidized to maghemite, a differential thermal analysis curve might be of great use in settling the question by correctly identifying the products.

A third possibility is the oxidation of the magnetite to gamma-Fe_2O_3. This possibility is immediately eliminated after seeing the thermal behavior of the material at higher temperatures and noting that the final product still contains magnetite. Microscopic examination of the magnetite samples before and after this reaction of the first peak took place showed no difference except for the very slightly more blue color of the sample.

The only explanation that might account for this small exothermic peak is the recrystallization of the extremely fine magnetite particles present in the sample. Recrystallization in a monomineralic system reduces the total amount of free energy in the system which thus attains increased physical stability. Such a process will result in an exothermic peak, the area of which is proportional to the amount of energy released. The extent to which such recrystallization progresses is governed by the main forces which promote the recrystallization. In the present case those forces are the range in grain size within the sample and the mobility of the substance in the intergranular film (a function of temperature).

The fact that such a recrystallization occurs in magnetite and not in most other minerals might be at least partially explained by the high "force of crystallization" of magnetite, or to use Eskola's terminology, its high "form energy." In his crystalloblastic series Becke, arranging metamorphic minerals in order of decreasing "force of crystallization," places magnetite almost at the top of the list, preceded only by sphene and rutile.[6]

The next logical step to determine whether this small exothermic peak was due to recrystallization of the fine particles or not, was to thermally analyze magnetite samples with carefully controlled particle sizes and mixtures thereof. The results of such investigation are shown in figure 3, curves 6, 8, 9, and

[6] For further discussion of the "force of crystallization" see Turner, 1948, pp. 154-158.

10. It is seen that the height of this exothermic peak decreases with decreasing amounts of fine particles in the sample until it almost completely disappears when comparatively coarse material of a narrow particle size range is used (curves 6 and 10).

In this connection it is significant to mention two general observations made by workers in the field of differential thermal analysis. The first is by Spiel et al. (1945), concerning the effect of particle size on the thermal analysis curves of kaolinite. They found that the areas of the peaks (except for the adsorbed water peak) decreased appreciably with decreasing particle size (except for the interval between 5 to 20 and 1 to 5 micron fractions). The second observation is by Kerr et al. (1949), to the effect that a narrow range of particle size results in a much sharper peak than does a wide range. As the preceding one, this observation was made in connection with the clay minerals. In the present investigation it is seen that the small exothermic peak of magnetite behaves diametrically opposite to the above two observations: the finer the particle size the larger the area of the peak; and the narrower the particle size range the flatter and less sharp is the peak (curves 6, 7, 8, 9, and 10, fig. 3). This indicates that we are dealing here with a different type of reaction than those investigated by Spiel and by Kerr. This negative approach also favors the idea of explaining this small exothermic peak by the recrystallization of the fine particles.

To recapitulate, differential thermal analysis shows experimentally that when natural magnetite (Fe_3O_4) is heated it is oxidized directly to hematite. Gamma-Fe_2O_3 does not form as an intermediate step, in contradistinction to the oxidation of most synthetic magnetites. This is in harmony with theoretical evidence presented by Gruner (1927), Verwey (1935) and others, based mainly on the crystal structure of both magnetite and gamma-Fe_2O_3. The oxidation of magnetite in dry air is a rather difficult and extremely slow process which starts to proceed at a noticeable rate only above 620°C. Fine grained magnetite may undergo slight recrystallization to form coarser grains before this temperature is reached.

ACKNOWLEDGMENTS

The writer wishes to thank Professor J. W. Gruner for supervising this research throughout its stages, and for his

critical reading of the manuscript. Professor G. M. Schwartz supplied the writer with a number of magnetite samples; Mr. L. Gardiner's help with the technical problems is sincerely appreciated.

The writer's study at the University of Minnesota was made possible through financial aid by the Wakfia Fahmia, administered by the Egyptian Government, and is hereby gratefully acknowledged.

References

Benard, J., and Chaudron, G., 1937. Preparation de ferrites par substitutions des ions ferreux dans la magnetite: Acad. Sci. Paris Comptes rendus, vol. 204, pp. 766-768.

Gilbert, G., 1927. Changes in the oxidation of iron in magnetite (discussion): Econ. Geology, vol. 22, pp. 308-310.

Goldzstaub, M. S., 1931. Deshydratation des hydrates ferriques naturels: Acad. Sci. Paris Comptes rendus, pp. 193 and 533.

———, 1935. Etudes de quelques derives de l'oxyde ferrique (FeO.OH, FeO_2Na, FeOCl); determination de leurs structures: Soc. franç. minéralogie Bull., vol. 58, pp. 6-76.

Goranson, R. W., 1940. "Flow" in stressed solids; an interpretation: Geol. Soc. America Bull., vol. 51, pp. 1023-1034.

Grim, R. E., and Rowland, R. A., 1942. Differential thermal analyses of clay minerals and other hydrous materials: Am. Mineralogist, vol. 27, pp. 756-761, 801-818.

Gruner, J. W., 1926. Magnetite-martite-hematite: Econ. Geology, vol. 21, pp. 375-393.

———, 1927. Changes in the oxidation of iron in magnetite (discussion): Econ. Geology, vol. 22, pp. 744-749.

———, 1930. Hydrothermal oxidation and leaching experiments, their bearing on the origin of Lake Superior hematite-limonite ores: Econ. Geology, vol. 25, pp. 697-719, 837-867.

Kerr, F., Kulp, J. L., and Hamilton, P. K., 1949. Differential thermal analyses of reference clay mineral specimens: Am. Petroleum Inst., Project 49, Clay Mineral Standards, Prelim. Rept. 3.

Kulp, J. L., and Trites, A. F., 1951. Differential thermal analysis of natural hydrous ferric oxides: Am. Mineralogist, vol. 36, pp. 23-44.

Manly, R. L., Jr., 1950. The differential thermal analysis of certain phosphates: Am. Mineralogist, vol. 35, pp. 108-115.

Smith, F. G., and Kidd, D. J., 1949. Hematite-goethite relations in neutral and alkaline solutions under pressure: Am. Mineralogist, vol. 34, pp. 403-412.

Sosman, R. B., and Posnjak, E., 1925. Ferromagnetic ferric oxide, artificial and natural: Washington Acad. Sci. Jour., vol. 15, pp. 329-342.

Speil, S., Berkelhamer, L. H., Pask, J., and Davies, B., 1945. Differential thermal analysis: U. S. Bur. Mines, Tech. Paper 664.

Starke, K., 1939. Zur Struktur künstlicher Magnetite: Zeitschr. physikal. Chemie, vol. B42, pp. 159-172.

Thewlis, J., 1931. The structure of ferromagnetic ferric oxide: Philos. Mag., vol. 12, pp. 1089-1106. Chem. Abst., 1932, p. 1170.

Turner, F. J., 1948. Mineralogical and structural evolution of the metamorphic rocks: Geol. Soc. America Mem. 30.

Twenhofel, L. H., 1927. Changes in the oxidation of iron in magnetite: Econ. Geology, vol. 22, pp. 180-188.

Van der Marel, H. W., 1951. Gamma ferric oxide in sediments: Jour. Sedimentary Petrology, vol. 21, pp. 12-21.

Verwey, E. J. W., 1935. The crystal structure of gamma-Fe_2O_3 and gamma-Al_2O_3: Zeitschr. Kristallographie, vol. 91, pp. 65-69.

Wagner, P. A., 1927. Changes in the oxidation of iron in magnetite (discussion): Econ. Geology, vol. 22, pp. 845-846.

Welo, L. A., and Baudisch, O., 1925. The two stage transformation of magnetite into hematite: Philos. Mag., vol. 50, pp. 399-408.

———, ———, 1934. Active iron II: Relationships among the oxide hydrates and oxides of iron and some of their properties: Chem. Rev., vol. 15, pp. 45-97.

Geology Department
University of Minnesota
Minneapolis, Minnesota