696. *The Preparation of Active Solids by Thermal Decomposition. Part IX.* The Calcination of Hydrous Ferric Oxide and of Lepidocrocite.*

By J. F. Goodman and S. J. Gregg.

Calcination studies have been made of three materials, a precipitated ferric oxide gel slightly contaminated with chloride ions, one grossly contaminated with sulphate ions (probably as basic sulphate), and lepidocrocite (γ-FeO·OH): separate samples of each have been heated for five hours at a succession of fixed temperatures between 25° and 1100°, and a number of properties of the product have been examined, including the surface area by sorption of nitrogen, the density by immersion in water or in carbon tetrachloride, the lump volume by immersion in mercury, *X*-ray diffraction, and electron micrograph. The original material was also submitted to thermogravimetric analysis and to extensometric examination, both with a steadily rising temperature.

Results show that the first gel, a hydrous oxide, does not become activated when it loses water as the temperature of calcination is raised, but progressively diminishes in specific surface; lepidocrocite does show an increase in specific surface when it decomposes but the increase is small probably because the change in lattice is slight; the decomposition probably involves merely a shrinkage in thickness but not in diameter of plate-like particles. The sulphated gel increases in pore volume but not in surface when the sulphur trioxide is expelled at 700°, indicating that the SO_3 vacancies migrate to the surface of the micelles and coalesce there. All three substances, as well as the pure ferric oxide gel of Part II,[1] show an enhanced rate of sintering when a temperature at or near the Tammann temperature is reached.

In Part II [1] the effect of calcination on a hydrous ferric oxide (say batch A) was studied. From the results it seemed that the region around and above the Tammann temperature was of particular interest and should repay detailed examination. (The Tammann temperature is one-half of the melting temperature expressed in °K. Fe_2O_3 melts, with some

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* Part VIII, *J.*, 1956, 1506.

[1] Gregg and Hill, *J.*, 1953, 3945.

decomposition to Fe_3O_4, at 1730° K; its true melting point probably lies somewhat above this temperature and below that of Fe_3O_4, *viz.*, 1870° K. The Tammann temperature of Fe_2O_3 probably lies therefore between 600° and 660° C.) It happened that two other batches which had been prepared at about the same time as batch A were available, one (say batch B) containing slightly more chloride impurity than A, and the other (C) grossly contaminated with sulphate ions; these offered the further opportunity to study the effect of ionic contamination on the sintering behaviour of an active oxide, thereby representing an extension of the work of Parts VI and VII.[2,3] Further, in order to compare the behaviour of the hydrous oxides with that of a corresponding substance containing combined " water," lepidocrocite (γ-FeO·OH) was included in the study.

The procedure was much the same as in previous Parts, *viz.*, to prepare a " calcination series " from each batch by heating separate portions of it for 5 hours at different fixed temperatures within the range 25—1100°, and then to examine certain properties of the cooled product. In addition, separate portions of the starting material of each batch were subjected to thermogravimetric analysis on the thermal balance, and to extensometric examination, both with temperature rising at a constant rate.

EXPERIMENTAL

Materials.—The preparation of batch A is described in detail in Part II,[1] whence it will be seen that the precipitate, prepared from the chloride, has been formed in extremely dilute solution and washed many times. Batch B represents an earlier stage in the washing of batch A, and it had a chloride content of 0·15%, as compared with the 0·04% found for A (of Gregg and Hill,[1] *viz.*, 0·015—0·03%).

Batch C had been prepared [4] by precipitating saturated ferric ammonium sulphate solution with 11·2% potassium hydroxide solution in slight excess. The gel was washed by decantation till the supernatant solution failed to give any reaction for sulphate ions; it was then filtered at the pump, air-dried after being squeezed through a grease gun, and broken into lumps. It contained some 15% of sulphate ions, probably as a basic sulphate.

Batch D, lepidocrocite, was prepared by Baudisch and Hartung's method.[5] Ferrous chloride was first converted into the more stable tetrapyridineferrous chloride, which was then dissolved to a concentration of 20 g. per l. in 10 l. of distilled water. Oxygen was bubbled through the solution rapidly for 15 min. and more slowly for an additional 30 min., lepidocrocite then being slowly precipitated. It was filtered at the pump, washed several times on the filter, and transferred to a 1 l. beaker, which was then filled with distilled water. Excessive peptisation ensued, and so the mixture was left for two weeks, some recoagulation occurring; the supernatant liquid then gave no reaction for chloride ions, so the precipitate was filtered off at the pump and dried at 25°. This batch, unlike the other three, was in the form of a fine powder.

Procedure.—The thermogravimetric analysis was carried out in air, on the thermal balance,[6] the rate of rise of temperature being 200° per hr. For the extensometric examination the same rate of rise was usually employed, the accompanying change in length (and therefore in volume) of a compact of the original material being followed. The extensometer (Fig. 1*b*), of simple design, had been constructed by R. C. Asher.[7] The compact was placed at *S*, and the change in length was measured by observing through a cathetometer the difference in height between the indicator rod *I* and the reference rod *F*. The compact was made by adding a little distilled water to the crushed material and compressing it with a standard force (usually 4000 lb.) in a die with a ramrod (3/8" in diameter). The compact being assumed to shrink isotropically, its volume v_E at any temperature T is calculated from its length l_T as $v_E = (\pi/4)(d/l)^2 l_T^3$, where d and l are respectively the diameter and length of the compact at the end of the experiment.

For the preparation of a member of the calcination series at a temperature T_c, say, about 10 g. of the starting material were placed in the furnace of a thermal balance, heated to T_c during a definite period ($\frac{1}{2}$ hr.), and kept at T_c for 5 hr. It was then removed from the furnace and separate portions of it were used for (*a*) volumetric sorption [15] of nitrogen at $-185°$ for

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[2] Gregg and Packer, *J.*, 1955, 51.

[3] Gregg and Wheatley, *J.*, 1955, 3804.

[4] Hill, Ph.D. Thesis, London University, 1950.

[5] Baudisch and Hartung, " Inorganic Syntheses," 1939, **1**, 184.

[6] Gregg and Winsor, *Analyst*, 1954, **70**, 336.

[7] Asher, Ph.D. Thesis, London, 1955.

calculation of the specific surface, (*b*) determination of the density by immersion [9] in water or in carbon tetrachloride, (*c*) measurement of the lump volume by immersion in mercury, (*d*) gravimetric determination [8] of the sorption isotherm of water, methanol, or carbon tetrachloride, (*e*) *X*-ray analysis, and (*f*) electron-microscopic examination (batch D only). The volatile matter content was obtained from a separate sample of the starting material by repeating the preparation procedure at T_c then raising the temperature to 1000° in the thermal balance.

For determination of lump volume, about 1 g. of solid was weighed into the bulb *A* (Fig. 1*a*), which was attached to the tap unit *B*, and the whole container *D* was weighed before and after out-gassing at 100°. Freshly distilled mercury was then admitted through *C* and *B* till the level was above *B*, and after an hour (to allow penetration under 1 atm. pressure) *B* was closed, the excess of mercury removed, and *D* again weighed. The lump volume v_L (*i.e.*, the volume of the space per g. of Fe_2O_3, not penetrated by the mercury) is then given by $v_L = (1 + w)(v_B - W_2/\rho_T)W_1$, where v_B is the volume of the container *E* (*i.e.*, to tap *B*), W_1 the weight of outgassed solid, W_2 the weight of mercury in *E*, ρ_T the density of mercury at the temperature of experiment, and *w* the content of volatile matter per g. of Fe_2O_3. In order that the mercury shall surround the grains of solid completely they must not be finer [10] than 70 μ; the gel lumps of batches A, B, and C were well above this size, but no measurements were made on batch D because the particles were much too fine.

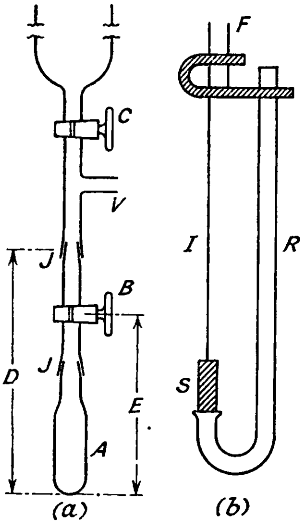

FIG. 1. (*a*) *Determination of lump volume.* *A*, sample bulb; *B*, *C*, taps; *J*, *J*, B-10 joints; *V*, to tap and high vacuum. (For *D* and *E* see text.)

(*b*) *Extensometer.* *F*, reference rod; *I*, indicator rod; *R*, supporting rod; *S*, compact. (*F*, *I*, nichrome; *R*, " Brightray S " alloy.)

The lump volume thus measured is then the volume of the solid plus the volume of all the pores below 50,000 Å in radius, because mercury cannot enter any finer pores when the pressure across the meniscus is 1 atm.

The *X*-ray examination of batches B and C was kindly arranged for by Mr. J. T. Richmond (of Laporte Titanium Ltd.) and of batch D by Mr. J. H. Harwood (of Peter Spence and Co.), the electron micrographs being kindly taken by Miss D. L. Tilleard with a magnification of 5000 diameters.

The specific surface (*S*) is usually expressed as the number of square m. per g. of the outgassed sample, and this is a suitable measure of the absorbing power for practical purposes. Two other measures of the surface area are of value, however, in discussing the opposing processes of the loss of surface by sintering and the development of new surface in an active solid produced by calcination of a parent solid with evolution of a gaseous product; these are S', the area per g. of non-volatile material, and S'', the area per cm.^{3} of the outgassed sample. The first, given simply by $S' = S(1 + w)$, shows by its variation along the calcination series the way in which one and the same sample of gel (having an Fe_2O_3 content of 1 g.) would change in area when heated for 5 hr. at each temperature, if the effect of all previous heating could be ignored.

[8] Gregg, *J.*, 1955, 1438.
[9] Cf. Culbertson and Dunbar, *J. Amer. Chem. Soc.*, 1937, **59**, 306.
[10] Shapiro and Kolthoff, *J. Phys. Colloid Chem.*, 1948, **52**, 1020.

The second, given by $S'' = S\rho$, is merely the ratio of the surface to the true volume of the material. (Here ρ is the true density, *i.e.*, nearly the density by immersion in water or carbon tetrachloride.)

RESULTS AND DISCUSSION

According to the views expressed in Part I,[11] a hydrous oxide should not develop an increased surface (*i.e.*, become " activated ") on being heated but should show a continuous loss of surface—through sintering—as the temperature progressively rises; but with a hydrate or hydroxide which undergoes a change of lattice structure when the volatile product is driven off by heat, an activation is expected to result from this change—if it is drastic enough—followed as the temperature increases by a sintering of the same kind as for the hydrous oxide; a maximum in the curve of specific surface plotted against temperature of calcination would thus be produced. The results of the present work substantially confirm these views, and they indicate that the decomposition of lepidocrocite is a special case in that, although a lattice change occurs, it is too slight to necessitate recrystallisation, so that the increase in specific surface is small. They also indicate that upwards from some temperature near the Tammann point, the movement of ions through the bulk of material plays a rapidly increasing part in the mechanism of sintering.

Batch D.—It will be convenient first to discuss the results for batch D (lepidocrocite). In the curve for thermogravimetric analysis (T.G.A.) (Fig. 2), the composition at the inflection *F*, near 250°, is close to that required by the formula $FeO{\cdot}OH$; the fall between *E* and *F* (cf. the first peak in the derived curve, II) corresponds to the loss of absorbed water, and the further fall between *F* and *G* (cf. second peak in I) to the chemical decomposition. The T.G.A. curve is in broad agreement with the curve for volatile-matter content (Fig. 3), though as each point now corresponds to the static conditions of a fixed, in contrast to the dynamic conditions of a rising, temperature the fall naturally occurs at a somewhat lower temperature. The reality of the decomposition is confirmed by the *X*-ray photographs for the samples of the calcination series (Plate 1) : the original material and the sample corresponding to 150° both show the pattern of lepidocrocite, that for 200° is very indistinct but gives faint indication of α-Fe_2O_3, whereas for all higher temperatures the pattern is exclusively that of α-Fe_2O_3.

At first sight the chemical decomposition might, as already indicated, be expected to lead to a marked increase in surface. In actual fact, however, the rise in S (Fig. 4) and in S'' was relatively small, and, most strikingly, the surface S' per gram of Fe_2O_3 scarcely changed at all; the actual ratios were $S_2/S_1 = 1{\cdot}115$, $S_2''/S_1'' = 1{\cdot}425$, and $S_2'/S_1' = 1{\cdot}01$ (suffix 2 refers to 250° and suffix 1 to 150°). These results are readily explained if the crystallites of lepidocrocite are plates (*i.e.*, with negligible area of side faces) which on decomposition merely shrink in a direction perpendicular, but not parallel, to the plane of such plates; for then $S_2'/S_1' = 1{\cdot}0$ and (on insertion of the appropriate values of ρ and w in the conversion formulæ for S'' and S—see p. 3614) $S_2/S_1 = 1{\cdot}105$ and $S_2''/S_1'' = 1{\cdot}415$, close to the experimental values. Any model in which approximately isodimensional particles shrink equally in all directions would give ratios divergent from the experimental data; cubic crystallites, for example, give $S_2'/S_1' = 0{\cdot}80$, $S_2/S_1 = 0{\cdot}87$, and $S_2''/S_1'' = 1{\cdot}12$; to keep S' constant it would be necessary for exactly the correct proportion of particles to split up in such a manner as to give an additional 25% of area as compared with non-splitting (*e.g.*, by 75% of the cubes splitting parallel to one face). The plate model does not involve an arbitrary occurrence of this kind and would seem more plausible inasmuch as the lattice of lepidocrocite is layer-like. The electron micrographs too are not incompatible with the model : the finest spots could be individual plate-like particles, and the larger ones aggregates of these particles (Plate 2). To account for the experimental value of S'' the thickness of the plates would have to be $\tau = 2/(300 \times 10^4)$ cm., *i.e.*, *ca.* 67 Å for the 25° sample, with a diameter at least tenfold greater if they are to act as plates. The finest particles in the photographs are of the correct order of size to represent side or end faces of such plates.

A simple shrinkage of the kind envisaged could only occur if the difference in the lattices of the parent substances and of the final product is small enough; and since in both lattices

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[11] Gregg, *J.*, 1953, 3940.

the ferric ions are in octahedral co-ordination [13] with the oxygen ions, the elimination of water between the hydroxyl groups of neighbouring layers of lepidocrocite need not destroy the arrangement.

FIG. 2.

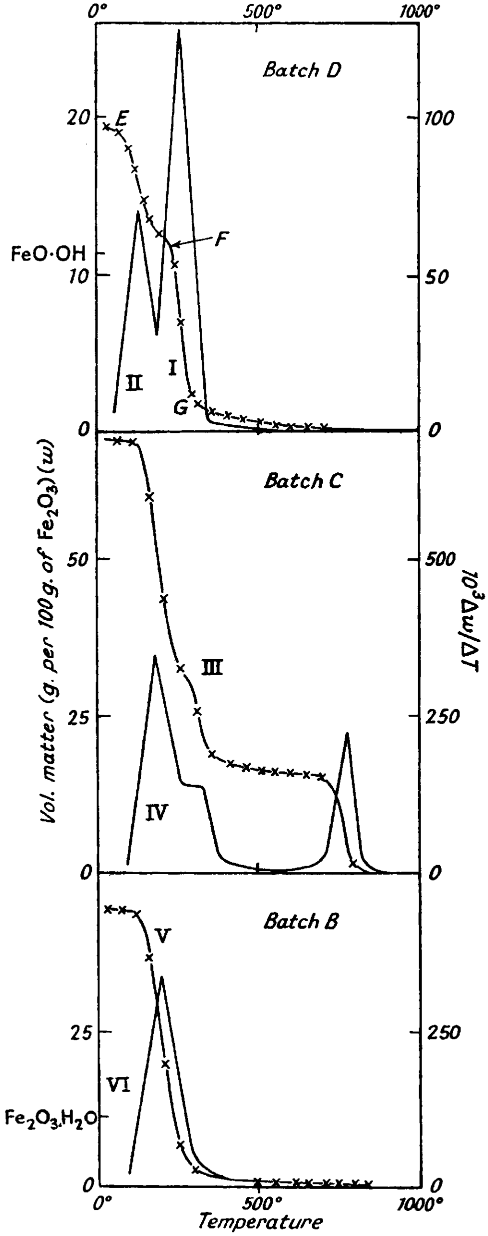
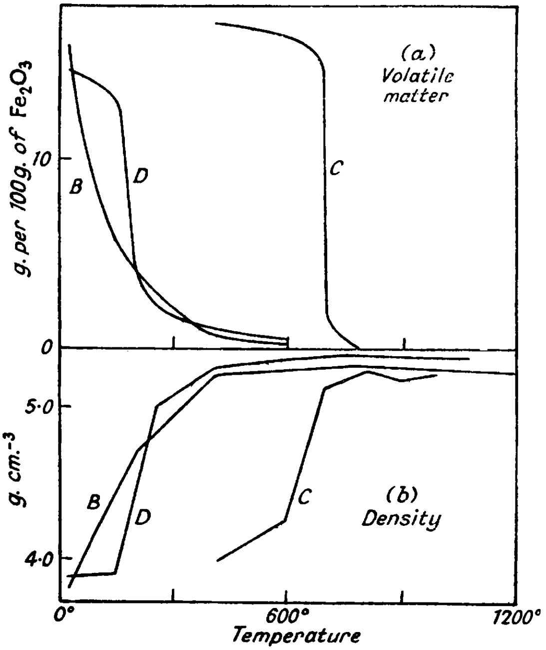


FIG. 2. *Thermogravimetric analysis.*
Curves I, III, V, plot of content of volatile matter (w) per 100 g. of Fe_2O_3 against temperature of calcination T.
Curves II, IV, VI, plot of $\Delta w/\Delta T$ against T.

FIG. 3. (*a*) *Plot of volatile-matter content against temperature of calcination.*
(*b*) *Plot of density against temperature of calcination.*
(The batch is marked on each curve. In Fig. 3*b* the density was by immersion in water for B and C, and in carbon tetrachloride for D.)

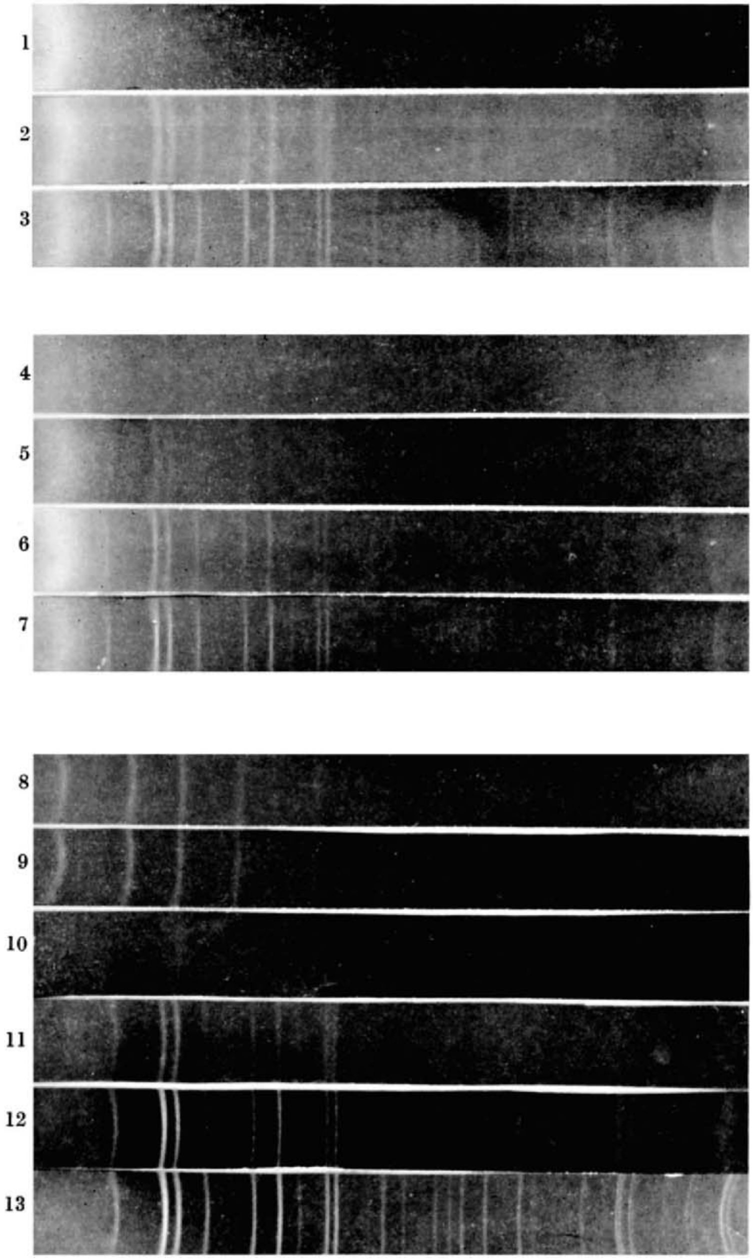
FIG. 3.



As the calcination temperature progressively rises above 250° the surface diminishes in the manner usual for many active solids, indicating some kind of sintering process. As is seen from the plot of log S'' against the temperature of calcination (Fig. 5), the rate of fall becomes much greater above 600°, and reference to the electron micrographs indicates a reason: between 600° and 800° the proportion of medium-sized and large particles grows at the expense of the very small ones, and in the 1000° and 1100° samples the effect is much

PLATE 1.

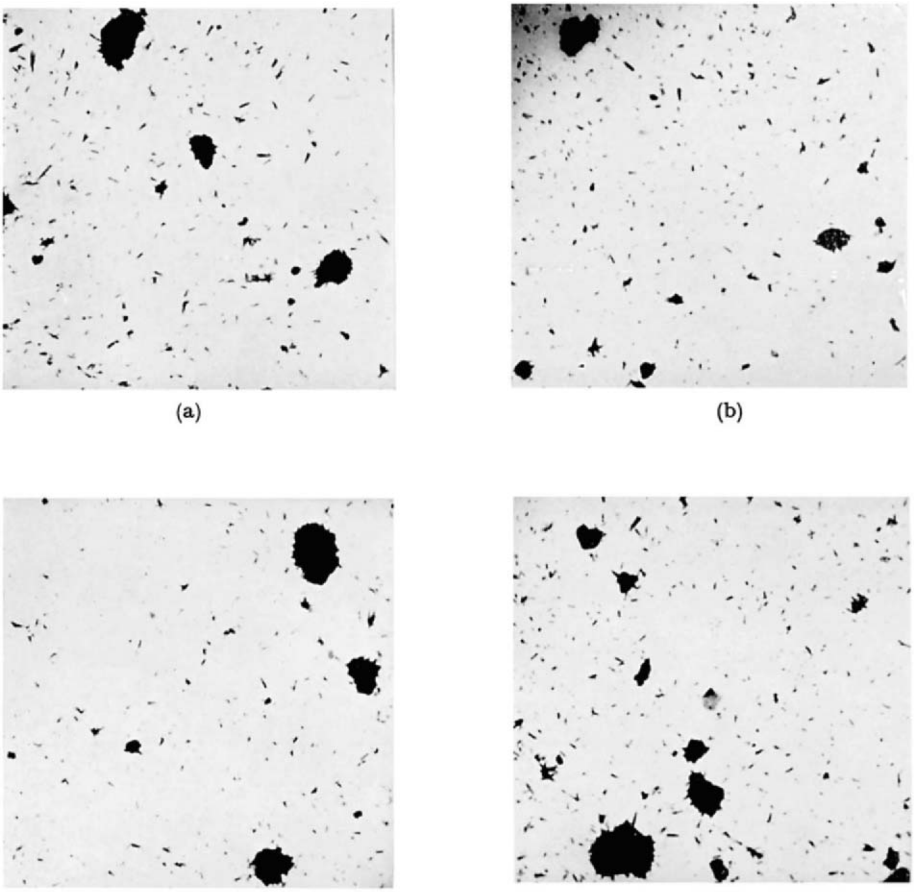
X-*Ray diagrams for batches B, C, and D heated for* 5 *hours at the temperature stated.*



Batch B: (1) original material, (2) 600°, (3) 1000°.
Batch C: (4) original material, (5) 600°; (6) 700°; (7) 900°.
Batch D: (8) original material, (9) 150°, (10) 200°, (11) 250°, (12) 400°, (13) 1000°.

PLATE 2.

Electron micrographs of batch D (lepidocrocite) after calcining at various temperatures for 5 hours.

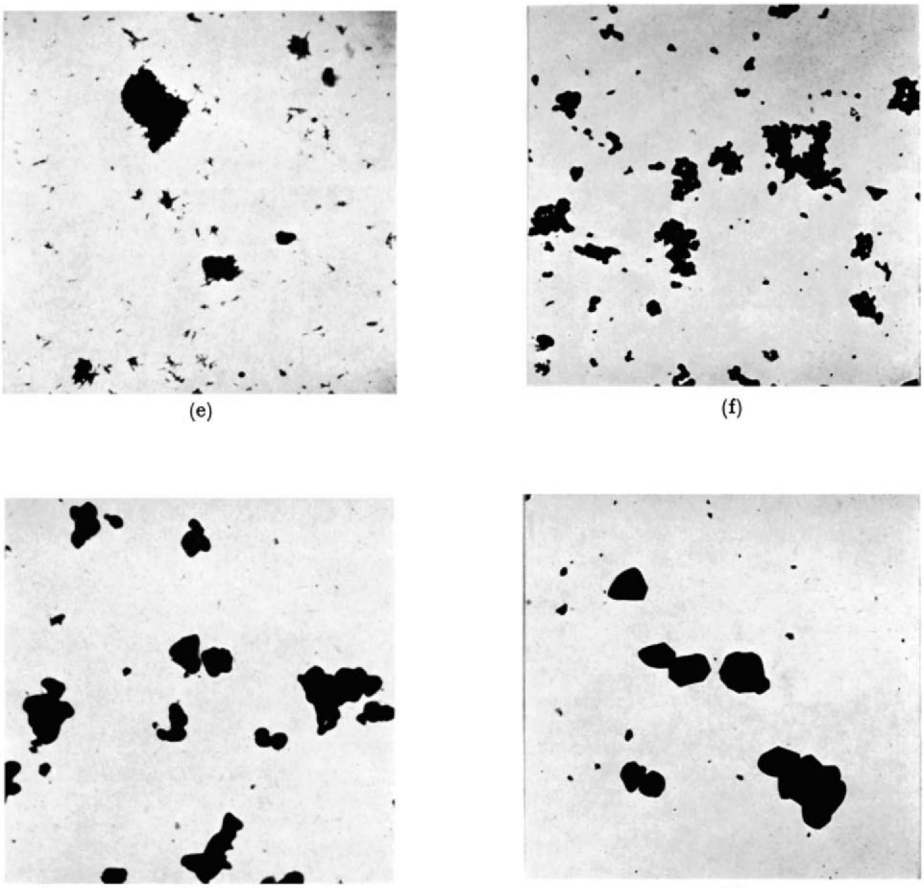


(a) (b)

(c) (d)

Calcination temperatures : (a) original material, (b) 150°, (c) 250°, (d) 400°.
2·5 cm. = 10μ

Plate 2 (*contd.*).



(e) (f) (g) (h)

Calcination temperatures : (e) 600°, (f) 800°, (g) 1000°, (h) 1100°.

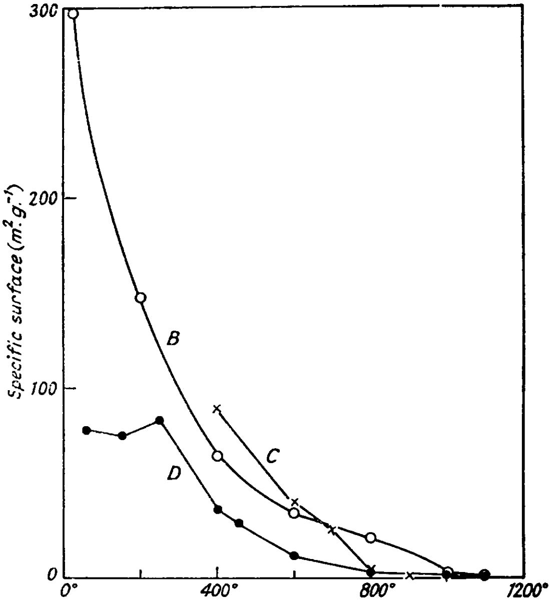
2·5 cm. = 10μ

(By courtesy of Miss D. L. Tilleard and Paint Research Station.)

accentuated. The rapid reduction in surface setting in above 600° is therefore attributable to an actual union of the individual grains—a process which is able to occur because the Tammann temperature is now probably exceeded so that migration of ions between contiguous particles can occur.

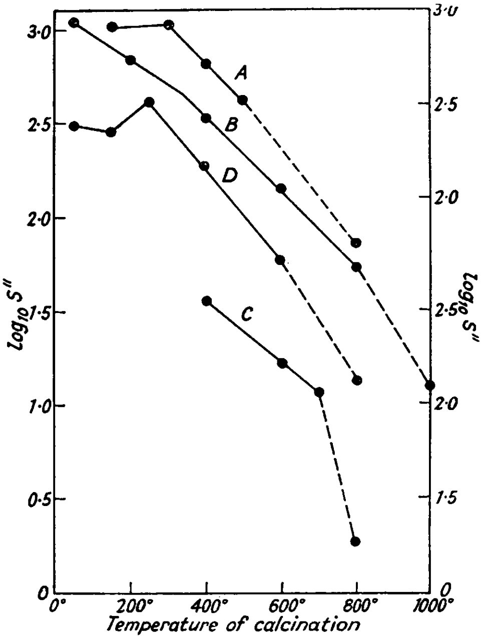
The disappearance of surface *below* 600° (Figs. 4 and 5) must be caused by the progressive annihilation of the internal rather than the external surface, *i.e.*, it arises from the closing of fine pores and channels within the grains. Reference to the adsorption isotherms [12] (not shown) bears this out: those of water show a hysteresis loop for temperatures up to 400° but not for 600°, and those of carbon tetrachloride a loop for 250° but not for 400°; thus any pores wide enough to accommodate carbon tetrachloride molecules have disappeared by 250° and any wide enough for water molecules by 400°. The *mechanism* of this low-temperature loss of surface will be considered later.

FIG. 4. *Plot of specific surface (by sorption of nitrogen at* —183°) *against temperature of calcination.*



(The batch is marked on each curve.)

FIG. 5. *Plot of* $\log_{10} S''$ *against temperature of calcination.*



(S'' is the surface area per cm.^{3} of sample.)

(The batch is marked on each curve.)

Curves *B* and *D*, left-hand scale.

Curves *A* and *C*, right-hand upper and lower scales respectively.

Batch C.—The main point of interest in the results for batch C relates to the loss of sulphate ions (mainly as sulphur trioxide) at high temperature. The T.G.A. derived curve (Fig. 2, Batch C) shows two main peaks, at *ca.* 200° and 800° respectively, with a subsidiary one at 350°; the first is clearly due to loss of adsorbed water, and the second of sulphur oxides, the third being unexplained but possibly due to loss of water of hydration from the basic sulphate. The curve of volatile-matter content against temperature (Fig. 3*a*) which corresponds to static conditions shows that the loss is almost complete at 700°, a temperature lower, naturally, than for the dynamic conditions of Fig. 2C. Correspondingly the density has risen, by 700°, to a value near that of α-Fe_2O_3.

Now, it is very curious that this quite drastic occurrence—the loss of nearly 15% by weight of volatile material—should produce scarcely any effect on either the lump volume

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[12] Goodman, Ph.D. Thesis, London University, 1955, pp. 63 *et seq.*

[13] Wells, "Structural Inorganic Chemistry," Oxford Univ. Press, 1950, 413, 423.

(Fig. 7*a*) or the surface area (the point for 700° in Fig. 5 lies quite well on the same straight line as those for 400° and 600°, and only for 800° is an acceleration of sintering apparent); yet the pore volume (Fig. 7*b*) increases markedly, by an amount, in fact, which is equivalent to the volume the volatile product would occupy in the form of solid sulphur trioxide with its normal density. (Increase in pore volume, 0·084 cm.^{3}; volume of lost SO_3 calc. as solid, 0·081 cm.^{3}; both per g. of Fe_2O_3.)

It is thus clear that the holes left by the expelled sulphur trioxide cannot remain in the interior, but must move to the exterior, of the micelles, and there merge with the intermicellar pores, thus contributing to the measured pore volume without adding to the specific surface. The constancy of the lump volume is accounted for if a framework structure is postulated, for this could remain intact despite changes *within* its constituent units (the micelles) provided the main intermicellar bridges were unaffected.

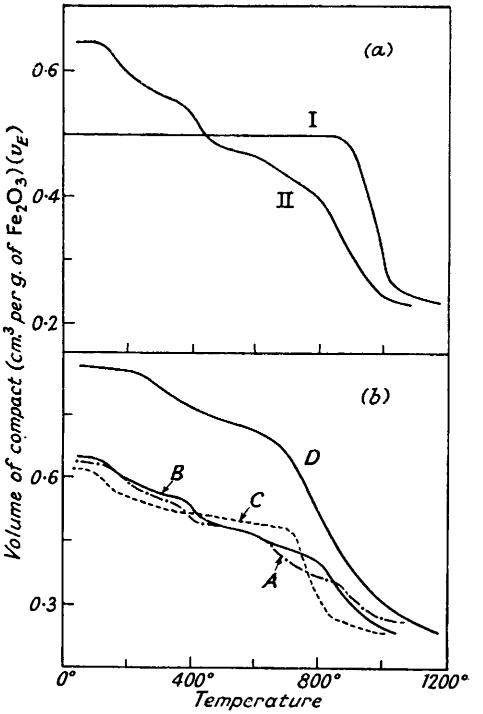

FIG. 6. *Extensometric examination. Plot of v_E against temperature of calcination.*

(*a*) I, the compact had been heated previously to 950°, then cooled before the run was commenced.

II, the compact was raised by 200° per hour without pre-treatment.

(*b*) Curves for batches A, B, C, D (as marked on the curve) with temperature rising by 200° per hour.

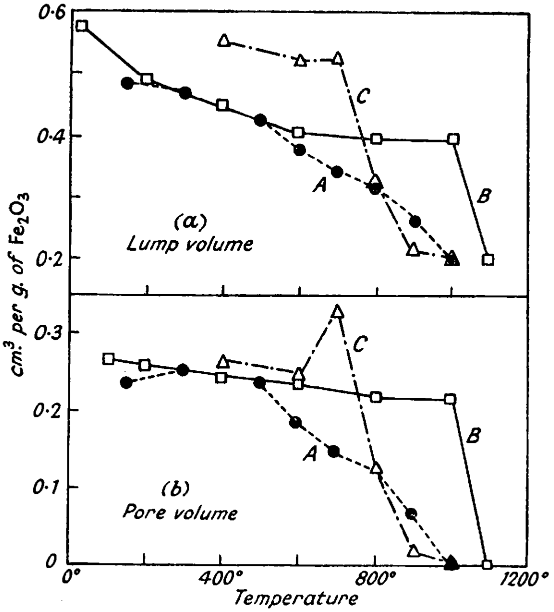

FIG. 7. (*a*) *Plot of lump volume (by immersion in mercury) against temperature of calcination.*

(*b*) *Plot of pore volume (calculated from lump volume and density in water or CCl_4) against temperature of calcination.*

(The batch is marked on each curve.)

Incidentally, it is probably no accident that the loss of sulphur oxides first occurred at a temperature (700°) near the Tammann temperature of Fe_2O_3 (and presumably near that of the basic sulphate also); for in a basic sulphate the sulphate ions comprise only a portion of the anions and so could not occupy adjacent positions in the lattice. They could therefore not escape to the exterior by a place-exchange mechanism, but would have to wait until the remaining ions of the lattice became mobile. A mobility of this kind is also indicated by the coalescence of the sulphur trioxide vacancies already referred to.

By 800° there are signs of a general collapse of the framework: the surface area decreases more rapidly (Figs. 4 and 5), the lump volume falls sharply (Fig. 7*a*), and the compact in the extensometer shows a marked contraction (Fig. 6). That the collapse did not occur at 700° when the sulphur trioxide was expelled is somewhat surprising; and a possible explanation is that the large shrinkage which occurs in each micelle when the gas is expelled (cf. Fig. 3*b*) breaks many of the subsidiary junctions of the framework and weakens others so that the area over which intermicellar migration can occur is greatly reduced. It may also be significant that the content of sulphur trioxide still retained at 700° is sufficient to cover an area equal to that of the whole surface of the sample (if each SO_3 molecule covers 24 Å^2 the area of all the SO_3 molecules is 24·0 m.^{2}, cf. area of sample 22·9 m.^{2}, per g. of Fe_2O_3); its presence on the micellar surfaces could hinder the migration of ferric and oxygen ions, until it is driven off at 800° upwards.

The reduction in surface (Figs. 4 and 5) which accompanies an increase in temperature of calcination in the range below 700° still needs to be accounted for; it requires that a portion of the micelles shall be held within the framework by relatively weak bridges so that as temperature rises they can progressively " shake down " : the contiguous surfaces of neighbouring micelles join up and the common surface is annihilated without a disruption of the structure as a whole. The mechanism of such union is probably adhesion promoted by deformation [14] of the participant micelles under the influence of surface forces at and near the areas of contact. Such a suggestion is supported by the fact that the rate of decrease of surface with increasing temperature, measured by the slope of the line for C in Fig. 5, is so small—a mere 0·0016 degree^{-1}, corresponding to a reduction in surface of 0·3% for each degree rise in temperature (for a fixed period of heating of 5 hr.). The rate-controlling process must accordingly be one having very low energy of activation, if indeed it is an activated process at all. The magnitude of the temperature coefficient is perhaps more suggestive of rigidity or viscosity than of, *e.g.*, surface diffusion.

Batch B.—The T.G.A. curves for batch B are, as expected, consistent with the progressive loss of water from a hydrous oxide, with no chemical decomposition (Fig. 2; *B*). Correspondingly, there is no maximum in the curve of specific surface against temperature (Fig. 4) and the only effect of increased temperature is to enhance the degree of sintering, and not to produce an activation. It is of interest, however, that the original material on progressive outgassing at room temperature does show a slight increase in surface as the water content diminishes :

Time of outgassing at 22° (hr.)	1·5	5	20
Volatile matter (g. per g. of Fe_2O_3)	0·182	0·156	0·140
Surface S' (m.^{2} per g. of Fe_2O_3)	337	343	367

The most likely explanation is that adsorbed water present in very narrow spaces between neighbouring micelles is being progressively removed, so that the walls of the spaces are added to the measured surfaces.

The actual course of the reduction in surface area with increase in temperature broadly resembles that for batches C and D, and also for batch A : [1] following the gradual fall in the low-temperature range, there is a much sharper fall at the high-temperature end (Fig. 5) denoting a collapse of the gel framework; but with batch B this sets in near and possibly above 800°, in contrast to batch C (700—800°), batch A (500—800°), and also to batch D where the coalescence of grains commences at 600—800°. Each of these ranges includes or is near to the Tammann temperature, but it would seem that second-order effects may supervene to cause a variation in the actual temperature of collapse or of coalescence according to the mode of preparation of the material.

The lump volume is especially interesting in this connection (Fig. 7*a*, curve *B*), indicating as it does a persistence of the framework structure to a temperature (1000°) some 300° above the Tammann temperature, and then a rapid collapse so that at 1100° the lump volume only slightly exceeds the true volume itself. That the relatively rapid heating during the preparation of the sample is an important factor is apparent from a comparison of the results of two experiments (curves I and II of Fig. 6*a*) with the extensometer. For curve I the compact was prepared at 25° in the usual manner but was then raised to 950°

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[14] Bangham, *Trans. Soc. Glass Tech.*, 1947, **31**, 264.

[15] Gregg and Stephens, *J.*, 1953, 3951.

during ½ hr. in the thermal balance, and maintained at 950° for 5 hr., exactly as in preparing a sample of the calcination series; after cooling to 25° it was examined extensometrically with a temperature rising at 100° per hr. For curve II, the compact, prepared at 25°, was merely placed in the extensometer and raised by 200° per hr. in the usual way. The delayed collapse in I is quite clear. It seems that the rapid pre-heating with its corresponding rapid shrinkage (cf. the large increase in density, Fig. 3*b*) leads to a complete rupture of the weaker bridges of the framework and a partial rupture of many of the others; thus, though the framework still persists the transfer of ions across the bridges is slowed down.

The difference between the lump volume curves for batch B and batch A is remarkable in view of their very small difference in chloride content (A 0·04, B 0·15%). Yet when one recalls the extreme sensitivity of the properties of the electrical double layer to the concentration of the counter-ions in solution, it becomes clear that very small changes in such concentrations could profoundly affect the intermicellar forces and thus the structure of the gel when the sol particles join up.

Chemisorbed Water.—Attention has been drawn in earlier Parts [1,2] to the fact that in the preparation of active solids a small content of volatile matter persists until very high temperatures are reached; *e.g.*, with batch B 0·3% was still present at 600°. "Water" held at such high temperatures must be chemically sorbed, and since its quantity is of the order required to form a monolayer it probably exists as hydroxyl groups on the surface of the micelles. The values of the fraction θ of the surface thus covered are given in the Table for batches B and D, calculated on the assumption that a molecule of chemisorbed water occupies 15 Å^2. (For temperatures up to 200° the area 10 Å^2 is used, corresponding to physical adsorption.) The values in excess of unity for batch D at the high temperatures could imply that a proportion of the hydroxyl groups are located on the surface of cracks too narrow to admit nitrogen, though if this were so the inaccessible area would have to be almost as large as the measured area itself.

Temp. of calcination	Batch B		Batch D		Temp. of calcination	Batch B		Batch D	
	S'	θ	S'	θ		S'	θ	S'	θ
25°	343	1·6	89·2	1·2	400°	64·2	0·5	35·5	1·7
150	—	—	83·6	0·7	450°	—	—	24·0	1·8
200	153	0·9	—	—	600	33·7	0·5	11·2	2·2
250	—	—	84·3	1·4	800	10·2	0·3	—	—

S' = surface area per g. of Fe_2O_3.
θ = fraction of surface covered with chemisorbed water.

If the "chemisorption" hypothesis is correct it means that the anion part of the surface is heterogeneous—part O^{2-} and part OH^-—from 200° or so up to 600° and probably beyond.

Conclusion.—The results of this study confirm the conclusion of Part II that the loss of water from a hydrous gel on calcination does not bring about an activation but only results in progressive deactivation. With the hydroxide lepidocrocite the thermal decomposition results merely in a shrinkage in thickness of the plate-like particles with comparatively small change in lattice structure; the corresponding activation is accordingly very slight. In the sulphate gel the expulsion of the sulphur trioxide again produces no activation, for the SO_3 vacancies merely migrate to the surface of the micelles and coalesce there, producing no increase in specific surface. In the two gels the framework is remarkably persistent and only breaks down at temperatures above (for one gel well above) the Tammann temperature; and only above this temperature do the discrete grains of lepidocrocite begin to coalesce.

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