807. *The Production of Active Solids by Thermal Decomposition. Part II.* Ferric Oxide.*

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Samples of pure ferric oxide gel have been calcined for 5 hours at a succession of fixed temperatures T_c between 50° and 800°, and the following properties of the product measured on cooling: (*a*) sorption of nitrogen and of oxygen at —183°; (*b*) sorption of carbon tetrachloride at 25°; (*c*) heat of immersion in carbon tetrachloride and in decalin; (*d*) apparent density in various liquids; (*e*) dissolution when immersed alternately in sodium dithionite (hyposulphite) and in hydrochloric acid; (*f*) rate of dissolution in hydrochloric acid; (*g*) *X*-ray powder photographs. The specific surface area S obtained from (*a*), (*b*), and (*c*) fell continuously from the lowest temperature investigated, so that—contrary to, *e.g.*, the production of magnesia from magnesium hydroxide—there is no maximum in the curve of S against temperature of calcination. This is probably because ferric oxide gel on being heated does not undergo a polymorphic change but merely loses its water continuously from an amorphous or slightly organised condition.

The data for apparent density reveal the presence of pores of micro- and molecular dimensions for all values of T_c up to 800°. The rate r of dissolution per unit area varies but little with T_c in the presence of the reducing agent; whereas in the absence of the reducing agent, the rate r, which likewise varies little with T_c from 150° to 500°, drops markedly for the 800° sample, probably because the lattice first becomes destrained in this sample.

As indicated in Part I*, many solids can be produced in an active condition as a result of the thermal decomposition of a parent substance from which a volatile product is released; and frequently there is an optimum temperature for the preparation of the active product with a given duration of heating, a maximum being obtained when, say, the specific surface of the product is plotted against temperature of calcination. Examples are magnesia from precipitated magnesium hydroxide, $Mg(OH)_2$, and alumina from precipitated gibbsite, $Al(OH)_3$, both of which have water contents corresponding to the stoicheiometric formula; and it was considered of interest to see whether precipitated ferric oxide gel, which has an indefinite water content, behaved similarly or differently on calcining. The results have shown that its behaviour is different, inasmuch as *no* maximum has been found in the curve of surface area against temperature of calcination.

EXPERIMENTAL

Materials.—Because of the known influence of foreign ions on the sintering of active oxides, the preparation of the starting material, ferric oxide gel, was such as to minimise its contamination by adsorption of foreign ions. It was arranged that streams of ferric chloride solution and of ammonia solution issuing from glass jets should meet just below the surface of 5 l. of water which was continuously stirred so as to ensure that the ionic concentration remained low throughout. 2 L. of N-ferric chloride in 0·2N-hydrochloric acid and 2·4 l. of N-ammonia were used, and the volume was then made up to 15 l. Next morning the supernatant liquid (about 10—12 l.) was siphoned off, an equal volume of water added, and the whole stirred. The sludge was washed three times in this way with water, and then twice with 0·025N-ammonia to prevent excessive peptisation. After being filtered off at the pump, the solid was washed on the filter with a volume of water equal to that of the sludge, and then sucked dry. The gel was then extruded through a Tecalemit grease gun (die 3·5 mm. in diameter) and was finally spread in shallow basins and allowed to dry in the air for 3—4 days. This gave a hard brittle product which was broken up and sieved, the −10 to 20 mesh portion being stored for use in this study; its content of chloride, estimated turbidometrically, was 0·015—0·03%.

Individual samples were activated in an electric furnace at 50°, 100°, 150°, 200°, 300°, 400°, 500°, 800°, and 1400°, severally, for a fixed period of 5 hr. [This time was chosen as a result of

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* Part I, preceding paper.

preliminary experiments in which samples were heated at 80°, 100°, and 120° in a thermal balance (cf. *Analyst*, 1945, **70**, 336), readings of weight being taken at frequent intervals; after 3 hr. the rate of loss of weight became very small.]

The nitrogen, oxygen, and carbon tetrachloride used as adsorbates were of the purity already described by Gregg and Sing (*J. Phys. Coll. Chem.*, 1951, **55**, 592, 597). The liquids used in the density determinations were as follows: water, distilled; decalin, shaken with concentrated sulphuric acid till no more tar was removed, then shaken with alkali, washed with water, dried ($CaCl_2$; P_2O_5), and distilled, the fraction of b. p. 182—185° being collected; it was a mixture of *cis-* (b. p. 178°) and *trans*-decalin (b. p. 192°); butyl phthalate was of technical grade and was stored over anhydrous sodium sulphate; carbon tetrachloride was sulphur-free and was boiled to expel air.

The following determinations were made on each sample.

Sorption Isotherms of Nitrogen and Oxygen.—The apparatus was that described by Gregg and Sing (*loc. cit.*, p. 592) and was based on a volumetric principle; the temperature of the liquid-oxygen bath, checked by an oxygen vapour-pressure thermometer, varied by not more than $\pm 0{\cdot}2°$. The oxygen and nitrogen were of commercial grade (British Oxygen Company). With both gases the measurements were carried up to a pressure of *ca.* 1 atm., representing a relative pressure p/p_s (p = pressure, p_s = saturated vapour pressure) of 0·25 for nitrogen and *ca.* 1·0 for oxygen. The samples were outgassed before each run for 1 hr. at 100°, except in the case of the " 50° " and " 100° " samples which were outgassed at 25° for 8 hours. In calculation of the results, allowance was made for the deviation of the two gases from the perfect-gas laws.

Sorption Isotherms of Carbon Tetrachloride.—These were determined with the aid of the electrical sorption balance (Gregg, *J.*, 1946, 561) as described by Gregg and Sing (*loc. cit.*, p., 597); the isotherms were not carried beyond a relative pressure of *ca.* 0·8, in order to avoid risk of attack by the vapour on the silicone grease used on the ground-glass joints of the balance " case."

The apparent density ρ was determined by a technique similar to that described by Culbertson and Dunbar (*J. Amer. Chem. Soc.*, 1937, **59**, 306; see Gregg and Sing, *J. Phys. Chem.*, 1952, **56**, 388); the sample (*ca.* 0·5 g.) was outgassed at 60° for 1 hr. A number of different liquids, having different molecular volumes V, were used in order to test for the presence of very fine pores: large molecules would either be excluded from such pores entirely, giving a low value of ρ, or would enter slowly giving a drift in density with time. The liquids were water (18), carbon tetrachloride (96·2), decalin (150), and butyl phthalate (266) (numbers in parentheses denote molar volumes in cm.^{3}).

Water Content.—Because of the hygroscopic nature of the ferric oxide, the water content corresponding to a given temperature of ignition, say T_c°, was determined in an indirect manner: a separate sample was prepared in the thermal balance exactly as were those actually used in the adsorption experiments (*i.e.*, by heating the hydrous gel at T_c° for 5 hr.) and the temperature was then raised to 1000° and the further loss in weight taken as the water content of the sample.

X-*Ray Diffraction.*—The powder photographs were taken and examined by Mr. Cundy in the laboratories of English Clays, Lovering, Pochin, Ltd., at St. Austell, and are reproduced in the Plate.

Heat of Immersion.—The calorimeter, specially designed for the measurement of the heat of immersion, will be described fully in a forthcoming paper. The sample of solid (0·4—2 g.) was outgassed at 100° for 1 hr. in a soda-glass bulb and sealed, before being placed in the calorimeter. Agreement between duplicate determinations was usually within 0·04 cal.

Dissolution in Sodium Dithionite Solution and in Hydrochloric Acid.—When ferric oxide is treated alternately with sodium dithionite and acid, the rate of dissolution is much greater than with acid alone, probably because of the reduction of the ferric ions in the surface (cf. Evans and Prior, *J.*, 1949, 3330). The details (cf. Galabutskaya and Gorova, see *Brit. Abs.*, 1935, 22) are as follows: about 0·3 g. of the oxide was weighed into a boiling-tube, 2 ml. of water were added, and the tube placed in boiling water for 2—3 min. 2 G. of sodium dithionite was dissolved in 50 ml. of water, and the whole immediately added to the sample. The mixture was stirred whilst the boiling-tube remained in water at 40—50° for 10 min., then set aside for 5 min., and the supernatant liquid decanted into beaker I. 50 Ml. of 0·05N-hydrochloric acid were added, and the whole was stirred for 3 min. and kept for 2 min. in water as before. The hydrochloric acid extract was decanted into beaker II. The extraction was then repeated with both reagents, and the residue washed twice with N-hydrochloric acid, the washings being added to beaker II. The beakers were placed on a boiling-water bath for 15 min. and then 40 ml. of 20-vol. hydrogen peroxide were added to beaker I and 15 ml. to beaker II. The mixtures were set aside until the liquid was clear, and then combined. The iron present was determined by precipitation with

N-ammonia, the precipitate being filtered off and ignited at 900°. The residue from the extraction was also treated in the same way.

Dissolution in Acid.—A sample of the solid (0·3—1·2 g.) was added to a bottle containing 200 ml. of 0·25N-hydrochloric acid in a thermostat at 25°, and the mixture was stirred continuously for the first two days and then set aside. Samples of the solution were withdrawn at intervals, and the ferric-ion concentration estimated by titrating the iodine liberated from acidified potassium iodide solution with sodium thiosulphate in the usual way. The quantity of acid present was never less than four times that required for complete dissolution.

RESULTS AND DISCUSSION

The isotherms of oxygen and of carbon tetrachloride are both of Type IV (B.E.T. classification, *J. Amer. Chem. Soc.*, 1940, **62**, 1723). The nitrogen isotherms resemble the lower parts of those of oxygen and of carbon tetrachloride and so are probably of Type IV also, though Type II is not absolutely excluded.

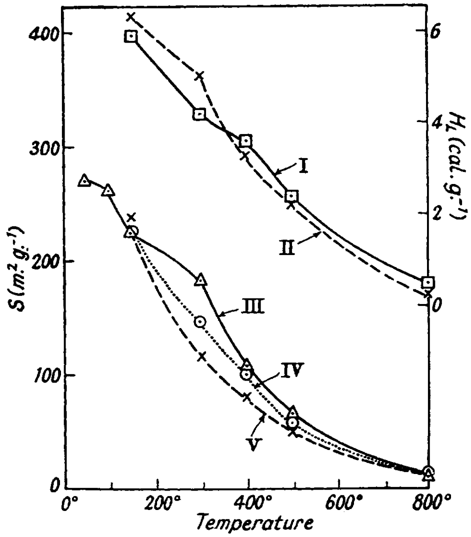


FIG. 1. *Specific surface S and heat of immersion H_L plotted against temperature of calcination.*

I, H_L in decalin; II, H_L in carbon tetrachloride; III, S by adsorption of nitrogen; IV, S by adsorption of oxygen; V, S by adsorption of carbon tetrachloride.

As is usual with Type IV isotherms, they are reversible outside the hysteresis loop. For points outside the loop equilibrium is reached in 10—15 min., but points on the loop require some 60 min., and the loop is reproducible, *i.e.*, in successive runs the points fall on the same curve within experimental limits.

The surface areas have been calculated from the isotherms by the B.E.T. procedure in the usual way (*ibid.*, 1938, **60**, 309): a plot of $p/v(p_s - p)$ against p/p_s gave good straight lines for all three adsorbates within the range to be expected, *viz.*, $0{\cdot}05 < p/p_s < 0{\cdot}30$ [v = amount adsorbed in c.c. (N.T.P.)]; and from the slope and intercept the monolayer capacity could be calculated, and the surface S obtained thence by assuming a value for the cross-sectional area A_m of the adsorbent molecules (oxygen, 14·6 Å^2; nitrogen, 15·4 Å^2; carbon tetrachloride, 30·0 Å^2). The three different measures of surface area are plotted against the temperature of calcination in Fig. 1; and, as will be seen, the values for a particular temperature differ according to the adsorbate used, to an extent usually much in excess of experimental error, the agreement between the "oxygen area" S_O and the "carbon tetrachloride area" S_C being much closer than that between the "nitrogen area" S_N and either of the other two. Moreover, a mere adjustment of the values of A_m for the three adsorbates could not bring the differing values of S for a given temperature into coincidence. Disagreement of this kind is not unusual (cf. Livingston, *J. Coll. Sci.*, 1949, **4**, 447) and there seems little doubt that, in general, the area deduced from the nitrogen isotherm is the most reliable.

The data for the heat of immersion H_L in carbon tetrachloride and in decalin are also plotted in Fig. 1; H_L should give a measure of the surface area of the solid (cf. Bangham and Razouk, *Proc. Roy. Soc.*, 1938, **166**, *A*, 572); in fact for an energetically uniform surface $H_L = hS$, where h is the heat of immersion per cm.^{2} of the material. Since, however, h would be expected to vary with the temperature of calcination, exact proportionality at all temperatures between H_L and S as measured by gas sorption is not likely, and the general similarity between the five curves of Fig. 1 must accordingly be regarded as satisfactory.

The feature of particular interest is that the curves of Fig. 1 do not show a peak, but fall continuously from the lowest experimental temperature (50°), in marked contrast to the curves for alumina and for magnesia already referred to. It thus seems that the activity of pure ferric oxide gel cannot be increased by thermal treatment, and that even the gentlest heating tends to sinter it and reduce its specific surface. If a product of high activity is required it must be precipitated as such in the first place and must be protected from heating thereafter.

The X-ray data indicate a reason for this difference in behaviour between ferric oxide gel and the other two systems : with gibbsite and with magnesium hydroxide the thermal decomposition involves the conversion of one definite lattice into another; but with ferric oxide gel the starting material is nearly amorphous (see Plate) with one or two very faint and broad lines corresponding to α-Fe_2O_3, and heating causes a sharpening of the lines and an increase in their number; but all the lines correspond to α-Fe_2O_3. [This sharpening is in accord both with the increase in micellar size demonstrated by the surface area data, and with a decrease in lattice strain which probably also occurs (see p. 3940).] The formation of a pseudo-lattice in the way discussed in Part I (*loc. cit.*) would therefore not occur, and there would be no reason for recrystallisation, with its attendant increase in specific area; and any thermal treatment subsequent to preparation would tend to cause sintering but not activation.

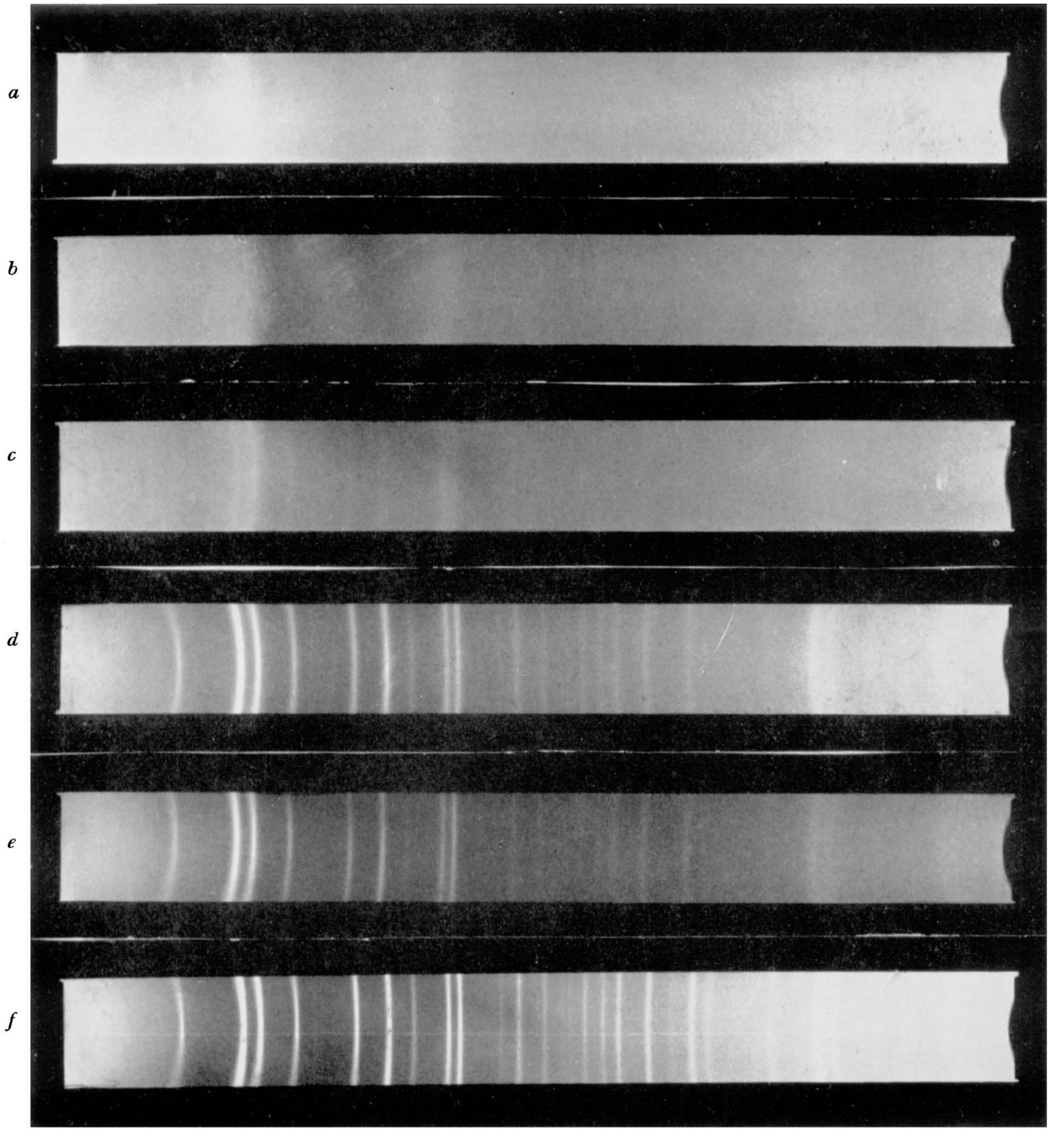
Evans and Prior (*J.*, 1949, 3330) found that even after 24 hr. at 300° their ferric oxide was almost completely amorphous : their starting material was, however, prepared by precipitation from a solution containing a high concentration of sulphate ions which, when adsorbed on the precipitate, are extremely difficult to remove by washing. If present in the solid they could affect the rate of crystallisation of the amorphous material.

T_c	50°	100°	150°	300°	400°	500°	800°
$v_L(O_2)$	—	—	0·210	0·257	0·234	0·248	0·136
$v_L(CCl_4)$	—	—	0·220	0·268	0·238	0·242	0·126
w	0·459	0·113	0·083	0·032	0·0167	0·0101	0·0011
S_N'	390	294	217	186	105	66	11
$10^3w/S_N'$	1·17	0·38	0·40	0·17	0·16	0·17	0·10
θ	5·9	1·9	1·9	0·85	0·80	0·75	0·50
r *	—	—	73	57	43	41	17
10^5r_a †	—	—	1·9	1·7	1·7	1·3	0·05
10^4r_a ‡	—	—	1·6	1·4	2·0	3·0	7·2

w, water content (g.) per g. of Fe_2O_3; S_N', surface area (m.^{2}) per g. of Fe_2O_3; θ, fraction of surface covered with OH; v_L, pore volume (= vol. in cm.^{3}, calc. as liquid) per g. of solid at apparent saturation. * % dissolved in HCl–$Na_2S_2O_4$ at 95° in 15 min. † Apparent rate of dissolution in HCl at 25° (g. of Fe m.$^{-2}$ min.$^{-1}$). ‡ Apparent rate of dissolution in HCl–$Na_2S_2O_4$ at 95° (in same units).

The isotherms of oxygen and of carbon tetrachloride obey Gurvitsch's rule fairly closely : the quantity of each adsorbed on a given sample at " apparent saturation," *i.e.*, along the horizontal branch, is nearly equal if calculated as volume v_L of liquid, the ordinary liquid density being assumed (cf. Table). This supports the customary view that the loop represents the filling of the pores with the adsorbate in a form similar to (though not necessarily identical with) the ordinary liquid. The value of v_L will accordingly be taken as equal to the total volume of pores per g. of material; and, adding to this the volume of the solid itself (calculated from the density in carbon tetrachloride, see p. 3946), one obtains the " lump volume " (Fig. 2, and Table).

Both the pore volume and the lump volume are seen to vary but little between 150° and 500°, and to fall markedly between 500° and 800°; the framework of the grains obviously begins to collapse at some temperature between 500° and 800° and it is perhaps significant that the Tammann temperature (*ca.* 650°) lies within this range.



X-Ray diffraction photographs of hydrated ferric oxide after calcining at a series of temperatures T_c.
(*a*) *Original material;* (*b*) $T_c = 150°$; (*c*) $T_c = 300°$; (*d*) $T_c = 400°$; (*e*) $T_c = 500°$;
(*f*) $T_c = 800°$.

The values for the apparent density ρ of the samples show a variation according to the nature of the penetrating liquid (Fig. 2*b*), a variation which for the most part is outside experimental error (0·5—1%). It will be noted that the values of ρ are always highest in water, which has the smallest molecules. One infers that the solid contains (presumably between the micelles) a significant volume made up of pores and crevices which are penetrated by molecules of water but not by those of the other liquids, and which therefore have a maximum width lying between the molecular diameter of the former (*ca.* 2·9 Å) and of the latter (*ca.* 5 Å). The values of ρ for the three remaining liquids do not lie in the same order for all temperatures and this suggests that the molecular shapes (which are very different for the three liquids) may also play a rôle, in relation to the shape of the pore cross-section; and a variation in the extent of compression of the liquid in the interfacial layer, according to the nature of the liquid, may also be involved (cf. Franklin, *Trans. Faraday Soc.*, 1949, **45**, 274).

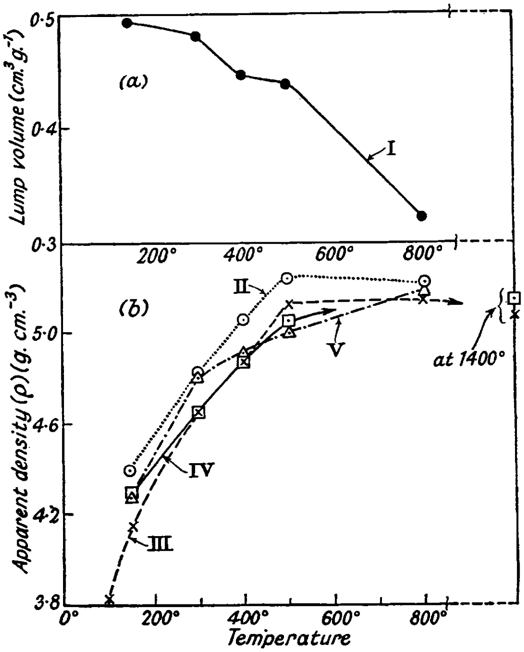


FIG. 2. (*a*) *Lump volume,* (*b*) *apparent density ρ, plotted against temperature of calcination.*

I, Lump volume; II, ρ in H_2O*; III, ρ in* CCl_4*; IV, ρ in decalin; V, ρ in butyl phthalate.*

The data for water content, *w*, are presented in the Table; from 300° upwards the ratio of water content to specific surface varies far less than does specific surface itself; *i.e.*, *w* is, very roughly, proportional to *S*. This suggests that the water is located in some form on the surface of the micelles, presumably as OH groups, for it is obvious that " water " which can withstand a temperature of 300° without expulsion is " structural " rather than molecular, *i.e.*, must be present as OH and not as H_2O. The conclusion is strengthened by the fact that the amount of the water is not far from that required for a completed monolayer, as may be seen by reference to the values of θ (= fraction of surface covered by OH) in the Table; θ has been calculated on the assumption that one molecule of structural water occupies the same area on the surface as do two OH groups, say 15 Å^2. In view of the uncertainties inseparable from the calculation—as to the *absolute* values of *S* and of the area occupied by OH ions, and as to the precise value of *w*—the proximity of the values of θ to unity from 300° upwards must be considered as strong evidence for the hypothesis. Actually, the water contents may be slightly low, for it is possible that the water is not *completely* expelled even at 800°; the effect of this would be to raise the 800° value of θ relative to the others and to bring them all nearer to unity.

A similar picture of the rôle of residual water in silica gel has been advanced by Shapiro and Weiss (*J. Phys. Coll. Chem.*, 1953, **57**, 219).

The higher values of θ at temperatures up to 150° denote the presence of water other than, and additional to, the chemisorbed hydroxyl groups. The fact that it is lost so much more readily points to a looser mode of binding, and it could, in principle, be present as (i) adsorbed water (molecules) external to the micelles, or (ii) absorbed water (molecules) within the micelles, or (iii) OH groups of an (extremely unstable) hydroxide such as $Fe(OH)_3$ or FeO·OH, with, of course, a highly distorted lattice. If all the water over and above that required by $\theta = 1$ were present as adsorbed molecules, one might perhaps expect the value of S to *increase* when it was driven off by raising the temperature, though in view of the extreme ease of sintering it could be argued that the tendency of S to increase is outweighed by the tendency to sinter. At present there is insufficient evidence to distinguish between possibilities (i), (ii), and (iii), which in any case are not mutually exclusive.

The rate of dissolution in acid falls with rising temperature of calcination, both in presence and in absence of the reducing agent. The experiments with the reducing agent present measured the percentage dissolved in a fixed time, and the results are given in the Table; with the pure acid, data were obtained for the amount dissolved at varying intervals and they are plotted in Fig. 3. As will be seen, the rate of dissolution falls with rising temperature of calcination in both sets of experiments, and particularly sharply from the 500° to the 800° sample in presence of the reducing agent (see Table). The fall is partly, but not entirely, accounted for by the reduction in specific surface: the change in the *nature* of the surface (and of the underlying bulk phase) also plays a part, as is seen from the approximate values of the apparent rates r_a of dissolution per unit area, given in the Table. To obtain r_a the average weight dissolved per minute was divided by the value of S_N for the sample, averaging over the first 50 min. for the experiments without reducing agent and over the whole period of the experiments (taken as 15 min.) for those with the reducing agent.

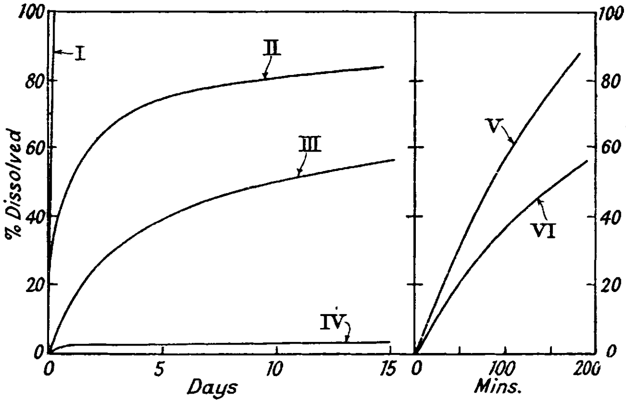


FIG. 3. *Dissolution in hydrochloric acid of ferric oxide calcined at various temperatures T_c.*

I, $T_c = 150°$ and 300°; II, $T_c = 400°$; III, $T_c = 500°$; IV, $T_c = 800°$; V, $T_c = 150°$; VI, $T_c = 300°$.

Considering first the results for dissolution in presence of the reducing agent, it will be noted that r_a does not vary greatly with the temperature of calcination—far less than does the area S. Now the values of r_a are not accurately proportional to the true rate r_t of dissolution per unit area, for the value of S must diminish as the solid dissolves, and this occurs to a different extent according to the initial activity of the sample. The correction cannot be assessed accurately without a knowledge of the shape of the micelles and of the relative rate of attack on its different faces, but its general sense is such as to raise r_t relatively for the more active samples; the variation in the initial r_t would accordingly be even less than that of r_a. Thus, if S were to vary with the $\frac{2}{3}$ power of the weight left behind (cubic or spherical micelles dissolving uniformly) the variation in the true rate of dissolution per unit area would be less than two-fold from 150° to 800°.

For dissolution in pure acid, the variation in r_a scarcely exceeds experimental error as T_c increases from 150° to 500°; but from 500° to 800° there is a sharp fall of some 30-fold, and because of the variation in S during a determination, already referred to, the difference in *true* rates between the 800° sample and the rest must be greater, perhaps 50-fold. Moreover, the difference cannot be confined to the surface layers, for the rate of dissolution was still high for the first four samples even when more than half their mass had dissolved.

The most probable explanation is that the lattices of the first four samples are considerably strained, whereas in the 800° sample the strain has largely disappeared. The rôle of surface defects in relation to dissolution of ferric oxide in acid has been thoroughly investigated by Evans and Prior (*J.*, 1949, 3330), who, however, confined their measurements to small percentages dissolved; in the present work the enhanced rate of dissolution was not restricted to the (originally) surface layers, and it would seem that the strain is not confined to defects (oxygen vacancies), for these, being formed by loss of oxygen by evaporation, would be unlikely to diffuse to the interior at temperatures below the Tammann temperature (*ca.* 650°). The *X*-ray evidence, though not inconsistent with this picture, does not lend unequivocal support to it; for the observed sharpening of the lines with increasing temperature would be expected in any case because of the increase in micellar size.

It is interesting that the 800° sample was the only one prepared at a temperature above the Tammann point, suggesting that the destraining of the lattice is, as would be expected, greatly facilitated by the bulk diffusion of the constituent ions.

The influence of lattice strain on the rate of dissolution in the presence of the reducing agent is small or negligible; in effect, the reducing agent is able to create its own defects by removal of oxygen at a rate which depends little, if at all, on the state of the lattice; and the effect of elevated temperature of calcination in diminishing the rate of dissolution per g. of solid is almost entirely explained in terms of the diminished specific area.

Our cordial thanks are offered to Mr. Cundy of English Clays, Lovering, Pochin Ltd., for taking the *X*-ray photographs; to Mr. K. H. Wheatley for making the measurements on the samples prepared at 50° and 100°; and to the Imperial Chemical Industries Research Fund for the loan of apparatus. One of us (K. J. H.) acknowledges receipt of a maintenance grant as a student-in-training fron the Department of Scientific and Industrial Research.

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