

### 696. *The Passivity of Metals. Part X. The Mechanism of Direct Dissolution of Ferric Oxide.*

By M. J. PRYOR and U. R. EVANS.

$\alpha$ -Ferric oxide has been found to dissolve comparatively rapidly in hydrofluoric or concentrated hydrochloric acid, which readily form soluble complexes with ferric ions. In dilute solutions of hydrochloric, sulphuric, or perchloric acid, which do not easily form these complexes, the rate of dissolution falls off with time, and the resulting solutions contain ferrous iron. This may be attributed to preferential attack at surface defects involving oxygen deficiency and consequently the presence of ferrous ions in the oxide lattice. The fact that the dissolution is the same in dilute solutions of hydrochloric, sulphuric, and perchloric acid of equivalent concentrations, and is not influenced by additional chloride ions, suggests that the important step in the reaction is the combination of adsorbed hydrogen ions with oxygen ions belonging to the oxide lattice. The more rapid dissolution of hydrated oxides is considered to be due to the relative ease of breaking of the hydroxyl bonds believed to be present in these compounds.

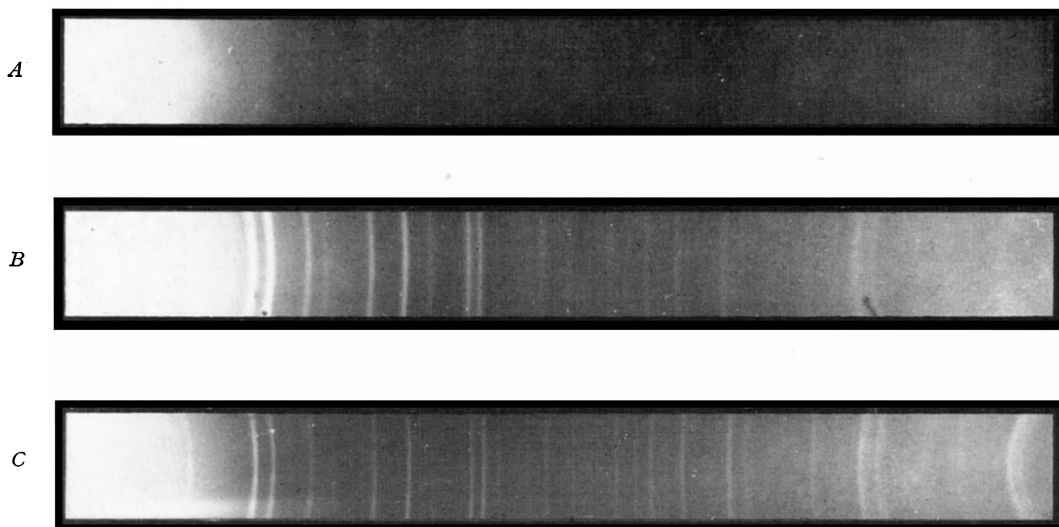
THE rate of dissolution of ferric oxide films is an important factor in determining the behaviour of iron towards acids. Early workers seem to have assumed that the rate of dissolution of all iron oxides was so great that passivity could not be attributed to the formation of oxide films (Senter, quoting Hittorf and others, *Trans. Faraday Soc.*, 1914, **9**, 204); W. J. Müller also expressed such views in his earlier papers (*Z. Elektrochem.*, 1928, **34**, 583; *Monatsh.*, 1929, **52**, 463, 474). Evans (*J.*, 1930, 478; *Nature*, 1930, **126**, 130), however, demonstrated that the rapid destruction of visible films on heat-tinted iron by acid was due to reductive dissolution, and not to direct dissolution, since the same films, once separated from the metal, could survive in the acid for weeks. The rapid reductive dissolution will be discussed in a later paper.

Griffith and Morcom (*J.*, 1945, 786) measured the "percentage solubility" of different oxides and hydrated oxides of iron, under conditions of manual agitation. Some of their results were confirmed by Mayne and Pryor (this vol., p. 1831) who found that precipitated, hydrated, oxides prepared from either ferrous or ferric salts with aqueous sodium hydroxide or ammonia were readily soluble in 0.1N-hydrochloric acid, even after ageing for one week. The precipitate formed by the action of ammonia on ferric salts was considered by Griffith and Morcom (*loc. cit.*) and by Böhm (*Z. anorg. Chem.*, 1925, **149**, 203) to be amorphous, but the electron-diffraction studies of Fordham and Tyson (*J.*, 1937, 483) showed well-defined rings characteristic of a face-centred cubic lattice with a side of 5.70 Å. Ignition of this material above 300° was stated by Griffith and Morcom to give  $\alpha$ -ferric oxide, and the view that this oxide is the stable phase at moderate temperatures, in air, is supported by others (Iimori, *Nature*, 1937, **140**, 278; Williams and Thewlis, *Trans. Faraday Soc.*, 1931, **27**, 767; Nelson, *J. Chem. Physics*, 1938, **6**, 606; Bernard and Coquelle, *Rev. Met.*, 1947, 113).

The present research aimed at establishing the mechanism of direct dissolution, with the use of samples of ferric oxide produced by ignition at different temperatures, in order to assist the understanding of reductive dissolution.

FIG. 1.

*X-Ray powder photographs of oxides ignited at different temperatures.*



Co-K $\alpha$  Camera 14, 9 cm.

$A = 300^\circ$ ,  $B = 385^\circ$ ,  $C = 1000^\circ$ .

## EXPERIMENTAL.

*Materials.*—The oxides under examination were prepared by precipitation from a boiling acidified solution of ferric ammonium sulphate (100 g. in 500 ml.) with aqueous ammonia. The precipitate was filtered under reduced pressure, through a Buchner funnel, and washed thoroughly with 5 l. of boiling distilled water. In order to displace adsorbed sulphate ions, the precipitate was then washed with 2 l. of a boiling, ammoniacal solution of ammonium acetate (100 g./l.), followed by a further 2 l. of boiling distilled water. The filtrate, which had been free from sulphate ions after the first washing, now contained much ammonium sulphate. Portions of the precipitate were dried, as far as possible, with filter-paper, and ignited in a platinum boat for 24 hours at different temperatures between 200° and 1000°. The temperature of the electric furnace used was controlled by means of a "Sunvic" thermo-electric regulator to within  $\pm 5^\circ$  of that required; each portion of oxide was finally ground, for 1 hour, in a mechanical mill to a particle size of approx. 300 mesh. Every sample of oxide was subsequently found to be free from acetate ions.

Three samples of oxide ignited at 300°, 385°, and 1000°, respectively, were examined by X-ray diffraction using the powder method; this investigation was kindly carried out by Dr. H. D. Megaw and Mr. A. R. Lang. The samples ignited at 385° and 1000° (Figs. 1B and 1C) gave patterns that were in excellent accord with those previously obtained for  $\alpha$ -ferric oxide (Index of X-ray Diffraction Constants, A.S.T.M., 1945). The oxide ignited at 300° (Fig. 1A) gave no well-defined lines and appeared to be amorphous.

FIG. 2.

Relation between temperature of ignition and percentage dissolution in 0.1N-hydrochloric acid at 25°.

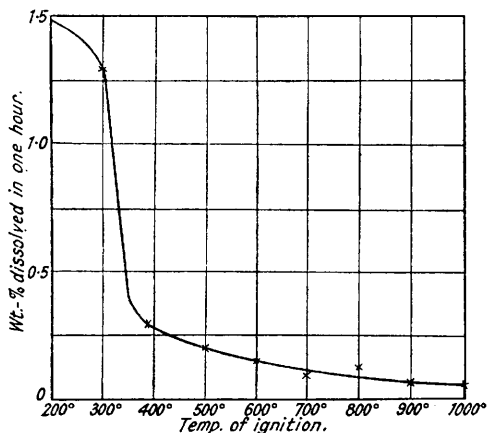
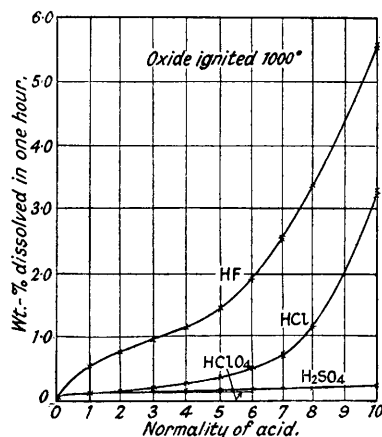


FIG. 3.

Relation between the normality of different acids and the percentage of the oxide, ignited at 1000°, dissolved in one hour at 25°.



Iron was determined colorimetrically by the thioglycolic acid method (Swank and Mellon, *Ind. Eng. Chem. Anal.*, 1938, 30, 7) in conjunction with the "Spekker" photoelectric absorptiometer.

*Experimental Method.*—Preliminary experiments showed that the percentage, by weight, of oxide dissolved in a given time was greatly influenced by temperature, and so the main experiments were carried out in vessels contained in an asbestos-lined box, placed in a thermostat controlled at  $25^\circ \pm 0.25^\circ$ . The experiments were carried out in square glass vessels measuring  $4 \times 4 \times 4$  cm., holding about 60 ml. of solution. The results were almost independent of the volume of acid, which was subsequently standardised at 50 ml., but were influenced by the original mass of oxide taken. A preliminary experiment indicated that, with 0.100–0.750 g. of oxide, the iron content of the solution was directly proportional to the original mass of oxide taken. With larger masses of powder the iron content of the solution was less than that predicted from the proportionality rule, probably owing to the oxide packing together. In the main experiments 0.250 g. of oxide was taken and the results expressed as the percentage by weight dissolved.

It was necessary for reproducibility to introduce the oxide into the solution in a standard manner. 50 ml. of the chosen solution were placed in a glass dish, and the oxide was dropped in by rotating a weighing tube gently, so that the powder sank to the bottom of the solution (dishes with flat bottoms were selected).

*Stagnant Conditions.*—0.250 g. of oxide, carefully weighed, was exposed to 50 ml. of acid for a chosen time; the solution was then filtered rapidly under reduced pressure, through 3 layers of Whatman No. 42 filter-paper in a Buchner funnel. A correction was applied for the time taken during filtration by roughly determining the rates of dissolution after different intervals of time. The percentage, by weight, of oxide dissolved was calculated from the iron content of the filtrate; all experiments were carried out in duplicate or triplicate.

The effect of temperature of ignition on the oxide dissolved in 1 hour by 0.1N-hydrochloric acid at 25° is shown in Fig. 2. The oxides ignited at 200° and 300° dissolved fairly rapidly, whilst those ignited at higher temperatures were much more resistant. The sample ignited at 1000° was the least soluble (0.05% dissolved in 1 hour) and was used in experiments designed to show the effect of hydrochloric acid

concentration. The results (Fig. 3) show a marked increase in dissolution between 7*N.* and 10*N.*, and an interesting rise between zero and 0.1*N.*, followed by a flattening between 0.1*N.* and *N.* This latter feature is also observed in the oxides ignited at 600° and 800° (Fig. 4), but not in the oxide ignited at 300° (Fig. 5).

FIG. 4.

Relation between the percentage dissolution in 1 hour of oxides ignited at 600°, 800°, and 1000°, and the concentration of hydrochloric acid.

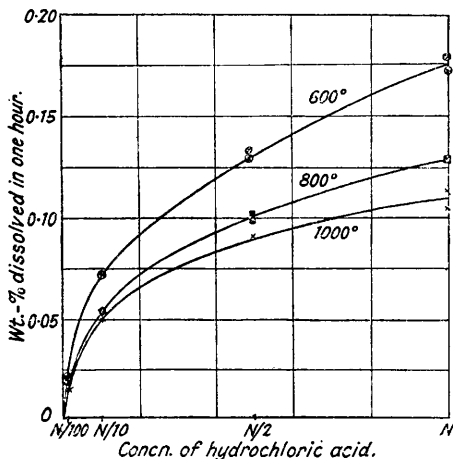


FIG. 6.

Relation between time and the percentage dissolution, in 0.1*N.*-hydrochloric acid at 25°, of the oxides ignited at 600°, 800°, and 1000°.

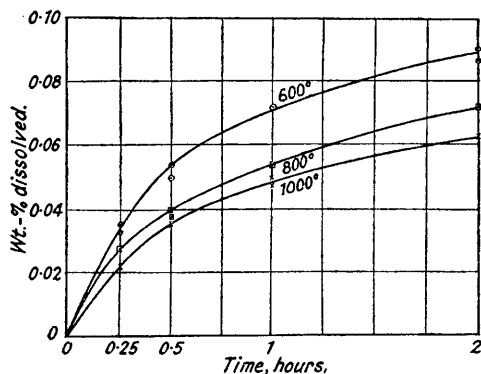


FIG. 5.

Relation between the percentage dissolution in 1 hour of the oxide ignited at 300° and the concentration of hydrochloric acid.

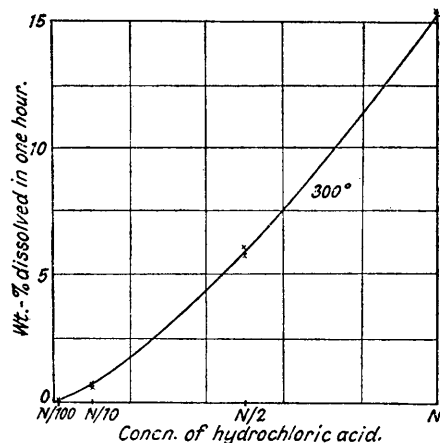
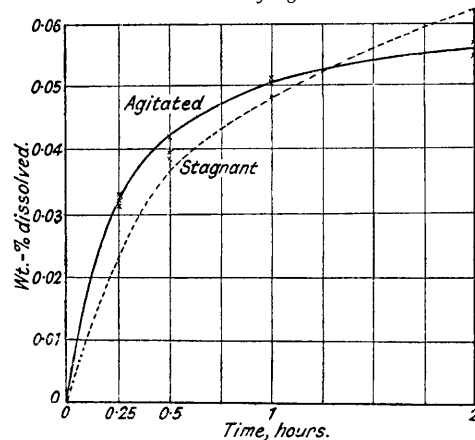


FIG. 7.

Relation between time and the percentage dissolution, in 0.1*N.*-hydrochloric acid at 25°, of the oxide ignited at 1000°, under both stagnant and mechanically agitated conditions.



The variation, with time, of the percentage of different oxides dissolved by 0.1*N.*-hydrochloric acid, at 25°, is shown in Fig. 6. The decrease in the rate of dissolution, with time, may be due to: (1) general exhaustion of oxide and acid, (2) local exhaustion of acid around the oxide particles, or (3) depletion of some preferentially-soluble constituent in the oxide. The effect of the first factor, calculated on the assumption that the rate of attack is proportional both to the bulk concentration of the acid and to the surface area of the oxide, is insufficient to reduce the rate of dissolution by even 1% whereas the decreases observed experimentally were of the order of 100%.

*Conditions of Agitation.*—To ascertain whether local exhaustion was the cause, experiments were carried out in which 0.250 g. of the oxide ignited at 1000° was shaken with 10 ml. of 0.1*N.*-hydrochloric acid in a sealed tube clamped horizontally on a mechanical shaker and mounted in the thermostat. The results (Fig. 7) show that the decrease in rate was slightly more marked than before. Although the volume of acid was less than in the stagnant solutions, the bulk concentration decreased by <1% in a 2-hours experiment, and so the results can safely be compared. If the exhausted-layer theory were correct violent agitation should permit dissolution at a more uniform rate.

*Presence of Ferrous Ions in the Filtrates.*—It would seem that the decrease of dissolution rate with

time must be attributed to the depletion of some preferentially-soluble constituent in the oxide. Pfeil (*J. Iron Steel Inst.*, 1929, **119**, 501) found that  $\alpha$ -ferric oxide contained more than the stoichiometric proportion of iron; evidently part of this excess must be in the ferrous condition, to maintain electrical neutrality. Consequently the filtrates from some of the experiments, the oxide ignited at 1000° and placed in 0.1N-hydrochloric acid, were tested qualitatively for ferrous ions, first with potassium ferricyanide and later with 2:2'-dipyridyl. No ferrous ions could be detected after 2-hour experiments, but special long-time experiments, in dishes covered with well-greased glass plates, gave positive results. The filtrate from a 2-days experiment was divided, one half being oxidised with hydrogen peroxide and subsequently boiled to decompose the excess thereof. Both solutions were diluted to 100 ml., and 1 ml. of ferricyanide solution (1 g./100 ml. of water) was added to each. A distinct bluish-green colour was obtained in the unoxidised solution, whereas the other remained practically colourless.

The 2:2'-dipyridyl test, which is more sensitive, detects 1 part in 1,660,000 parts according to Feigl ("Qualitative Analysis by Spot Tests," 1939, p. 96). Ferrous iron was found in the filtrate from a 24-hour experiment with 0.1N-hydrochloric acid, carried out under stagnant conditions, but not after shorter periods.

*Experiments with Different Solutions.*—Many of the previous experiments were repeated with solutions of sulphuric, perchloric, and hydrofluoric acid. The results (Fig. 3) show that solutions, up to 1N., of sulphuric and perchloric acid, dissolve the oxide ignited at 1000° at the same rate as solutions of hydrochloric acid of equivalent concentrations. Stronger solutions of sulphuric and perchloric acid, however, produced less attack on the oxide than did hydrochloric acid. Dilute solutions of sulphuric and perchloric acid also dissolved the oxides ignited at 600° and 800° at the same rate as equivalent concentrations of hydrochloric acid (Fig. 4). The experiments to determine the variation with time, of the percentage of different oxides dissolved by 0.1N-hydrochloric acid were repeated with 0.1N-sulphuric and -perchloric acid. The results, Table I, are identical, within the limits of experimental error, with those previously obtained with hydrochloric acid.

In experiments with hydrofluoric acid, carried out in square glass vessels lined with paraffin wax, the rate of dissolution (Fig. 3) of  $\alpha$ -ferric oxide was much higher than in any of the other three acids.

TABLE I.

*Variation, with time, of the wt.-percentages of various oxides dissolved by 0.1N-hydrochloric, -sulphuric, or -perchloric acid, under stagnant conditions.*

Temp. of ignition of oxide.	Time, hrs.	Mass of oxide, 0.25 g. Thermostat temp., 25°.			
		(a) in HCl		(b) in H <sub>2</sub> SO <sub>4</sub> .	
600°	0.25	0.032, 0.035	0.035, 0.037	0.034, 0.036	
	0.5	0.050, 0.054	0.052, 0.054	0.050, 0.052	
	1	0.072, 0.072	0.070, 0.071	0.070, 0.073	
	2	0.089, 0.086	0.090, 0.088	0.084, 0.085	
	24	0.187, 0.185			
	168	0.465, 0.456			
800°	0.25	0.028, 0.028	0.030, 0.029	0.030, 0.031	
	0.5	0.0365, 0.0385	0.045, 0.039	0.039, 0.042	
	1	0.056, 0.054	0.055, 0.056	0.054, 0.055	
	2	0.072, 0.070	0.074, 0.072	0.071, 0.068	
	24	0.176, 0.172			
	168	0.450, 0.438			
1000°	0.25	0.021, 0.025	0.030, 0.027	0.031, 0.025	
	0.5	0.037, 0.039	0.044, 0.042	0.041, 0.040	
	1	0.0475, 0.050	0.055, 0.050, 0.052	0.046, 0.047	
	2	0.063, 0.065	0.064, 0.0625	0.056, 0.058	
	24	0.160, 0.160, 0.164			
	168	0.235, 0.257			

TABLE II.

*Effect, on the wt.-percentage of ferric oxide dissolved in 1 hour, of the addition of extra chloride ions to 0.01N- and 0.1N-hydrochloric acid.*

Concn. of acid, N.	Concn. of extra chloride ions added, N.	pH.	Oxide ignited at 1000°. Mass of oxide, 0.25 g. Thermostat temp., 25°.	
			Wt.-% of oxide dissolved in 1 hr.	
0.01	—	2.02	0.014, 0.018, 0.015	
	0.01	2.01	0.018, 0.017	
	0.05	2.03	0.016, 0.018	
	0.1	2.04	0.019, 0.015	
	0.5	2.04	0.018, 0.018, 0.016	
0.1	—	1.03	0.0475, 0.050	
	0.1	1.04	0.051, 0.050	
	0.5	1.04	0.047, 0.049	

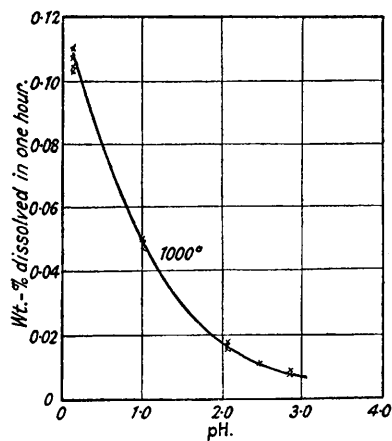
In tests to determine whether the dissolution was affected by additional chloride ions (as potassium chloride), extra chloride ions (0.01—0.5N-potassium chloride) in hydrochloric acid (0.01 and 0.1N.) produced no significant change in the dissolution of the oxide ignited at 1000° (see Table II).

No dissolution of oxides, ignited at 600°, 800°, or 1000°, could be detected if the pH of the solution exceeded 3.2 (Fig. 8). Experiments at higher pH were continued for as long as 14 days, with chloride ion concentrations up to 1.5N., but gave no iron detectable by thioglycolic acid.

*Two-stage Experiments.*—It was at this point felt that the dissolution in dilute solutions of hydrochloric acid was connected with a loosened structure around surface-lattice defects. Experiments were carried out to ascertain whether these defects could be replenished at the surface by diffusion from the interior. 1 g. of the oxide ignited at 1000° was exposed to 0.1N-hydrochloric acid for 1 hour, filtered off, washed carefully, and dried in a desiccator. Portions of this residue were then allowed to stand at 25° for different times; 0.250-g. samples were then exposed for a further hour to 0.1N-hydrochloric acid. It was found, that, after ageing of the material for 29 hours at 25°, 0.0185% (by weight) of the oxide was dissolved by 0.1N-hydrochloric acid in 1 hour. Previously 0.0445% of the oxide had been dissolved in an hour, making a total of 0.063% dissolved in the two separate 1-hour periods.

FIG. 8.

Relation between the percentage dissolution, in 1 hour at 25°, of the oxide ignited at 1000°, and the hydrogen-ion activity of different solutions of hydrochloric acid.



chloric acid for 1 hour, thus indicating an average recovery of 28%.

#### DISCUSSION.

The X-ray examination (Fig. 1) shows that oxides ignited at not less than 385° consist of  $\alpha$ -ferric oxide, but those ignited at not more than 300° are amorphous. This amorphous structure is similar to that obtained in the X-ray researches of Böhm (*Z. anorg. Chem.*, 1925, 149, 203) and reported by Griffith and Morcom (*loc. cit.*) and is doubtless characteristic of the hydrated oxide. It appears, therefore, that dehydration of the precipitate, and a consequent phase change, results from ignition at temperatures above 300°; this is in accordance with the observations of Griffith and Morcom, who also found that the "percentage solubility" of the resulting  $\alpha$ -ferric oxide was only one-quarter of that of the hydrated oxide. The marked drop in the percentage dissolution observed by the authors above 300° (Fig. 2), is doubtless connected with the same loss of water. A similar drop in the dissolution rate with dehydration was noted by Blitz and Lemke (*Z. anorg. Chem.*, 1929, 184, 373) with precipitated hydrated aluminium oxides, whilst Williams and Thewlis (*loc. cit.*) showed that  $\gamma$ -hydrated ferric oxide (artificial lepidocrocite) became completely dehydrated when heated above 350°, giving  $\gamma$ -oxide.

It appears from the results in Fig. 2 that the oxides studied in the present research can be divided into two classes :

- (1) Those ignited at 300° and below, which still contained "combined" water and whose crystal structure is undetermined.
- (2) Those ignited between 385° and 1000° which consist of anhydrous  $\alpha$ -ferric oxide.

The following discussion deals mainly with the second, anhydrous group.

Fig. 3 shows that the rate of dissolution of  $\alpha$ -ferric oxide ignited at 1000° is comparatively high only in solutions of hydrofluoric and concentrated hydrochloric acid. The anomalous

effect of hydrofluoric acid has been observed by Clay and Thomas (*J. Amer. Chem. Soc.*, 1938, **60**, 2384) with hydrated alumina and it appears probable that this acid is effective in dissolving  $\alpha$ -ferric oxide because of the ease of formation of soluble ferrifluoride complexes. Similarly, high concentrations of hydrochloric acid will be favourable for the formation of complexes between ferric and chloride ions. It is probable, therefore, that if the anion of the acid is one that readily forms soluble complexes with ferric ions the oxide will dissolve fairly readily.

Dilute solutions of sulphuric, perchloric, and hydrochloric acid most probably do not form soluble complexes with ferric ions and it can be seen from Fig. 3 that the rate of dissolution of  $\alpha$ -ferric oxide in these acids is low. The remainder of the discussion will be devoted to the mechanism of dissolution in non-complex-forming acid solutions. Fig. 3 also indicates that the oxide ignited at 1000° contains a surface constituent that is comparatively easily removed by dilute acids, as the curve relating the percentage (by weight) dissolved to the acid concentration rises sharply from zero and then flattens out as the concentration increases from 0.1N. to 1.0N. The shape of the curve between 0.1N. and 1.0N. is also found with oxides ignited at 600° and 800° (Fig. 4), but not with the oxide ignited at 300° (Fig. 5).

The falling off in the dissolution rate with time (Figs. 6 and 7)—even under conditions of agitation—points to the depletion of some readily soluble constituent in the oxide. This preferentially soluble constituent might be mainly associated with the presence of defects in the oxide lattice—a conclusion supported by the detection of ferrous ions in the filtrates.

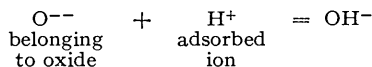
Recent work by Garner (*Chem. and Ind.*, 1947, 132) and by Bevan, Shelton, and Anderson (*J.*, 1948, 1729) shows that  $\alpha$ -ferric oxide is a semi-conductor of the metal-excess type, containing vacant sites in the oxygen lattice. To maintain electrical neutrality these oxygen defects must be associated with the presence of ferrous ions in the oxide lattice. It is probable, furthermore, that around these defects the O-O and Fe-O distances will be slightly different from those in the "perfect" ferric oxide lattice.

The fact that the total dissolution in two separate one-hour periods (separated even by 15 days) is practically the same as that obtained by two hours' continuous treatment suggests that the diffusion of defects from the interior of the oxide to the surface is extremely slow at 25°. This result is in accordance with the views of Tammann (*Z. anorg. Chem.*, 1925, **149**, 67), who held that below the Tammann temperature (half of the absolute melting point, *i.e.*, approx. 650° for  $\alpha$ -ferric oxide), self-diffusion was so slow that the surface defects were not in equilibrium with those in the interior. By heating, at 1000°, oxide whose surface defects had been removed by acid pretreatment, it was found to be possible to restore the rate of dissolution to its original value. This indicates that a high-temperature treatment can restore the number of defects at the surface of the oxide to the original value. A different result was obtained by heating for 24 hours at 385°; in this case the rate of dissolution recovered to only 28% of the original value. These observations are of interest in connection with the results recorded in Fig. 2. It can be seen that raising the ignition temperature from 385° to 1000° results in a steady decrease in the percentage dissolution in 0.1N-hydrochloric acid. The equilibrium number of defects in a solid increases with temperature, and so it might be expected that ignition at high temperatures would favour more rapid dissolution; that this is not so is due to two additional factors. First, the density of the powder increases with the temperature of ignition, owing to sintering. Thus, although the particle size is approximately constant, the specific surface area decreases as the ignition temperature rises. Secondly, the two-stage experiments show that the surface defects in the oxide cannot be replenished by heat-treatment at 385°. Consequently it appears that the original surface defects in the oxide ignited at this temperature resulted from the method of preparation, *i.e.*, these defects were probably "frozen in" at the phase change caused by the dehydration at 300°. Only when the temperature of ignition appreciably exceeds 650° would true equilibrium be expected. The oxide ignited at 1000°, however, appears to contain the equilibrium number of defects "frozen in" by rapid cooling to room temperature, as subsequent heating to 1000° of samples of this oxide whose surface defects have been largely removed by an acid treatment results in the restoration of the dissolution rate to its original value.

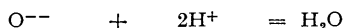
The relatively large amount of ferrous iron in the acid extract strongly suggests that dissolution takes place most readily at the lattice defects where the energy needed for dislodging ions will be smaller than elsewhere. A picture of the more detailed mechanism—somewhat more speculative—may now be offered.

It is widely believed that the first step in any dissolution process is the adsorption of ions, from solution, on the surface of the material in question; in dilute solutions of acids which do not readily form soluble complexes with ferric ions, the rate of dissolution appears to be independent both of the acid used (Fig. 3, Table I) and of the presence of additional chloride

ions (Table II). Changes in the concentration of hydrogen ions, however, have a marked effect on the rate of dissolution (Fig. 8). It appears probable, therefore, that under these conditions the important step in the dissolution of  $\alpha$ -ferric oxide is the combination of adsorbed hydrogen ions with oxygen ions belonging to the oxide lattice. The removal of oxygen ions, from the oxide lattice, is likely to be considerably easier at surface defects where the O-O and Fe-O distances are slightly different from their normal values. The removal of one oxygen ion, as a hydroxyl ion, or as water, does not involve any production or consumption of electrons:



or



Consequently this reaction cannot create defects, in the form of ions of "abnormal" charge, as does the reaction of these oxides with gaseous hydrogen, illustrated in the work of Bevan, Shelton, and Anderson (*loc. cit.*). Thus the rate of dissolution should be controlled by the number of defects originally present in the oxide surface. If the oxygen ions, situated at a surface defect, move into the solution as hydroxyl ions (or as water) unaccompanied by iron, the surface of the oxide will remain positively charged. This charge can be dissipated only by iron ions passing into solution, since the temperature is too low to permit rapid self-diffusion. It will be considerably more difficult to remove oxygen ions from points in the lattice not associated with defects, as there the interionic forces will probably be much stronger. Consequently the initially rapid removal of the oxide surrounding the surface defects is followed by a slower attack on the more perfect parts of the crystal lattice.

The shortest time for the detection of ferrous ions with 2 : 2'-dipyridyl was twenty-four hours. The total iron content of the solution after that period was 0.278 mg. in 50 ml., *i.e.*, 1 : 210,000. According to Feigl (*op. cit.*) the limit of sensitivity of the 2 : 2'-dipyridyl test is about 1 : 1,660,000. On the assumption that only after dissolution has proceeded for 24 hours does the concentration of ferrous ions become sufficiently high for detection, it can be seen that the ratio of  $\text{Fe}^{++}$  :  $\text{Fe}^{+++}$  in the filtrates is of the order of 1 : 8; this suggests that not only the ferrous ions, but also the neighbouring ferric ions around each defect, pass into solution. Such a ratio is consistent with the rhombohedral structure of  $\alpha$ -ferric oxide ( $\bar{3}M$ ) in which the co-ordination number of the iron ions is six.

The reason why dissolution of these oxides cannot be observed at  $\text{pH} > 3.2$  (Fig. 8) can now be explained. The minimum concentration of iron detectable by thioglycollic acid is approximately  $2 \times 10^{-6}$  g.-ion/l. The concentration of ferrous ions in the filtrates after one hour's exposure to 0.1N-hydrochloric acid will be considerably smaller than this, and so dissolution will not be detected unless ferric ions also pass into solution. If, however, conditions of pH are such that ferric ions would be precipitated as hydroxide, then no dissolution will be detectable by measurements of the iron content of the filtrates. Thus the factor that decides whether dissolution will be detectable is the solubility product of ferric hydroxide. Britton's value of  $10^{-37.7}$  (*J.* 1925, 1204) gives 3.3 as the maximum pH at which dissolution should be detectable; this is in good accord with the experimentally determined value of 3.2.

The dissolution characteristics of oxides ignited at 300° and below are quite different from those of anhydrous  $\alpha$ -ferric oxide. Fig. 5 shows that the curve relating dissolution to acid concentration has a different shape from that obtained with the anhydrous oxides (Fig. 4). Presumably these hydrated oxides can dissolve at points other than those associated with the presence of defects, probably owing to the presence of hydroxyl bonds in the lattice; the existence of this bond, in these hydrated oxides, has been shown by Wells ("Structural Inorganic Chemistry," 1945, p. 356). The weak hydroxyl bonds should facilitate the removal of the surface oxygen ions by adsorbed hydrogen ions. This factor—along with the higher specific surface area—may serve to explain why hydrated oxide dissolves so much more quickly than the anhydrous variety.

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