257. *The Reductive Dissolution of Ferric Oxide in Acid. Part II. The Reductive Dissolution of Powdered Ferric Oxide.*

By M. J. Pryor and U. R. Evans.

Experiment shows that both the rate and the current efficiency of reductive dissolution of α-ferric oxide powders diminish with an increase in the temperature of previous ignition, with an increase in the time of reduction, and with an increase in pH of the electrolyte. It is concluded that, at pH values below 2·0, the rate of reductive dissolution is controlled by surface conductivity of the oxide and hence by the number of surface defects. When the electrolyte is de-aerated the current efficiency greatly increases, although the rate of reductive dissolution is not significantly changed. Evidently, the rôle of dissolved oxygen as a cathodic depolariser is most pronounced at low current densities.

The study of the reductive dissolution of films of α-ferric oxide present on iron, described in Part I (preceding paper), was complicated by the facts that: (1) any attempt to grow films thicker than about 700 A. was accompanied by the formation of a layer of magnetite next to the metal; (2) thin films of α-ferric oxide were probably in a strained condition when in contact with the iron. Consequently, an attempt was made to study the reductive dissolution of powdered samples of α-ferric oxide, prepared by ignition of the precipitated, hydrated oxide.

Since the bulk conductivity of this oxide is low (Bevan, Shelton, and Anderson, *J.*, 1948, 1729), considerable difficulty was encountered in developing a suitable form of cathode. The one used eventually consisted of a fixed mass of oxide floating on a pool of redistilled mercury; electrical contact to this electrode was made by means of a shielded platinum wire dipped into the mercury.

By using this electrode in conjunction with a sheet iron anode, the influence of the temperature of ignition of the oxide, its surface condition, the pH of the electrolyte, and the presence of different acids on the rate of autoreduction was determined. The current flowing in the cell was measured continuously throughout the experiments so that the current efficiency of the oxide reduction could be calculated.

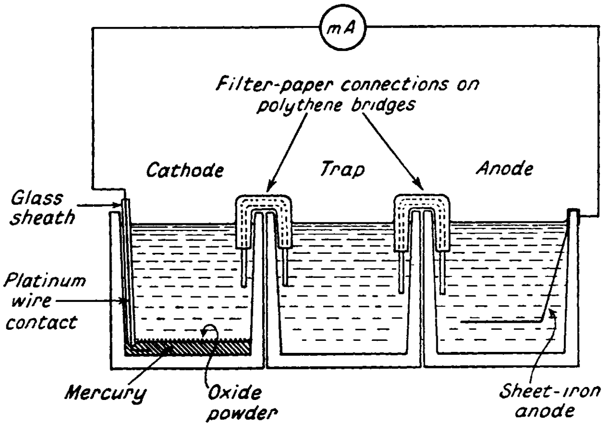
The experiments mentioned above were carried out in electrolytes containing dissolved oxygen. The cell, however, was suitable for experiments under anærobic conditions since the autoreduction of oxide powders was much slower than that of oxide films. Many of the previous experiments were repeated under anærobic conditions in order to study the rôle of oxygen as a cathodic depolariser.

EXPERIMENTAL.

Materials.—The oxides under examination were prepared by precipitating a boiling acidified solution of ferric ammonium sulphate with ammonia, and igniting the precipitate at different temperatures varying between 200° and 1000°. The oxides ignited above 300° consisted of rhombohedral α-ferric oxides ($\bar{3}m$), but those ignited below 300° were amorphous to *X*-rays. Full details of the preparation and *X*-ray examination of these oxides have been recorded by the authors (*J.*, 1949, 3330).

FIG. 1.

The mercury cell.



The iron anodes were cut from a sheet, 0·02 cm. thick, of the same composition as that used in Part I. All chemicals were of " AnalaR " quality.

The Mercury Cell.—The mercury cell (Fig. 1) consisted of three compartments, each being a square glass vessel, measuring approximately 4 × 4 × 4 cm., and holding about 60 ml. of solution. The cathode compartment contained 50 ml. of electrolyte together with 0·25 g. of the oxide under examination floating on a pool of redistilled mercury, which was chosen mainly on account of its high overpotential of hydrogen evolution. Electrical connection to the mercury was secured by a platinum wire shielded from direct contact with the electrolyte by a glass tube. The anode compartment contained a sheet of iron, the edges of which were screened with several coats of polystyrene lacquer, leaving an area of 1 sq. in. exposed to the electrolyte. The two compartments were connected together by means of filter-paper strips carried on small bridges made from polythene, through a central compartment which acts as a trap, to prevent mixing of the respective solutions. The edges of the vessels in contact were smeared with vaseline to prevent " siphoning away " of the electrolyte. The cell could be short-circuited by joining the platinum wire contact to the iron anode through a switchboard and sensitive milliameter. Measurements of the electrode potential of the anode, and of the potential differences across the cell were made by means of a valve potentiometer and a silver–silver chloride electrode. Experiments were carried out with the cell contained in an asbestos-lined steel box, placed inside a room thermostatically controlled at 25° ± 0·25°.

Characteristics of the Cell.—The current was found to diminish with time; reproducible results were only obtained after special precautions had been taken to exclude vibrations. Typical current–time curves obtained with different acids containing dissolved oxygen in the cell

Mercury (cathode)|Acid|Iron (anode)

are shown in Fig. 2. The potential difference–time curves had exactly the same form as the current–time curves. The ohmic resistance of the cell, calculated from the ratio of potential difference to current, varied between 105 ohms in 1·0N-solutions of hydrochloric, sulphuric, or perchloric acid, and 140 ohms in 0·01N-solutions of the same acids. As the resistance of the valve potentiometer was of the order of 10^9 ohms, it could divert only a negligible fraction of the total current from the milliameter. The actual values of the electrode potentials of the anode and cathode, in 0·1N-hydrochloric acid, were measured against a standard silver–silver chloride electrode. The lowest potential reached by the cathode was −0·28 volt.

FIG. 2.

Currents generated by the cell
Hg|*Acid*|Fe
at 25°.

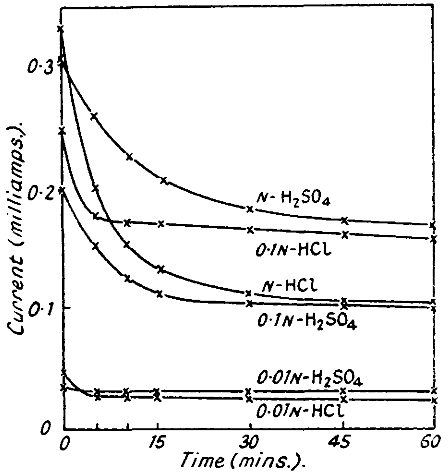
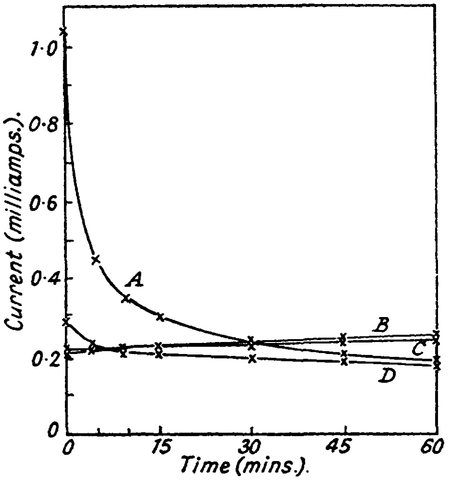


FIG. 3.

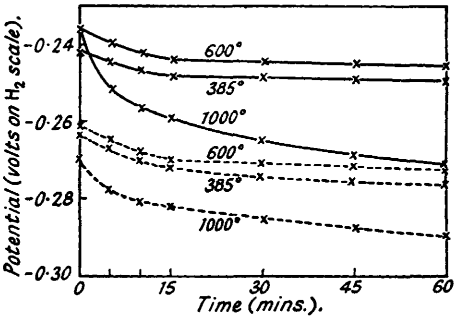
Currents generated by the cell
Fe_2O_3,Hg|*Acid*|Fe
at 25°.



A = *Oxide ignited at* 1000° *in* 1·0N-HCl.
B = *Oxide ignited at* 385° *in* 0·1N-HCl.
C = *Oxide ignited at* 600° *in* 0·1N-HCl.
D = *Oxide ignited at* 1000° *in* 0·1N-HCl.

FIG. 4.

Relation between time and the potentials of the anode and cathode of the cell Fe_2O_3,Hg|*Acid*|Fe *using oxide ignited at different temperatures and* 0·1N-*hydrochloric acid, containing dissolved oxygen at* 25°.



×——× *Potential of cathode.*
× - - - - × *Potential of anode.*

When 0·25 g. of the oxide ignited at 1000° was placed in the cathode compartment, the initial value of the current was usually slightly higher (Fig. 3) in 0·1N-acids and many times larger in 1·0N-acids. The initial current usually diminished within 15 minutes, to nearly the same value as that obtained in the absence of oxide. The ratio of potential difference to current was approximately constant and gave a value of 110—130 ohms for the resistance of the cell Fe_2O_3, Hg (cathode)|Acid|Fe (anode). The actual values of the anodic and cathodic potentials are shown in Fig. 4.

With oxides ignited at 600° and below, the initial current in 0·1N-hydrochloric acid was approximately 0·22 milliamp., and increased steadily throughout the period of the experiment (curves *B* and *C* in Fig. 3). The ratio of potential difference to current remained constant, giving a value of 120 ohms for the resistance of the cell containing the oxide ignited at 385°. Measurements of the anodic and cathodic potentials (Fig. 4) showed that, although both fell with time, the potential of the anode decreased more rapidly than that of the cathode. This is in direct contrast to the oxides ignited at 700° and above.

FIG. 5.

Relation between temperature of ignition and the percentage reductive dissolution, in one hour, of ferric oxide in 0·1N-*hydrochloric acid, containing dissolved oxygen, at* 25°.

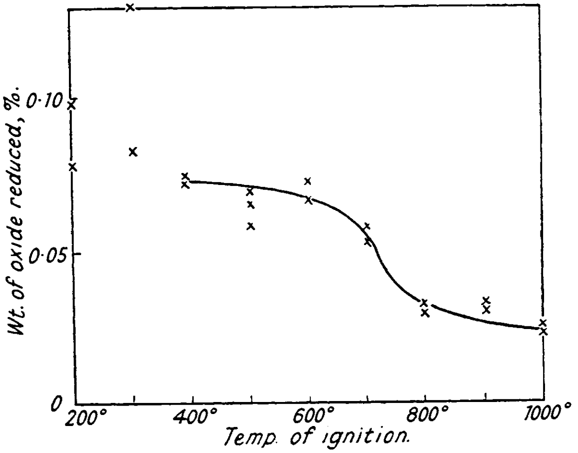
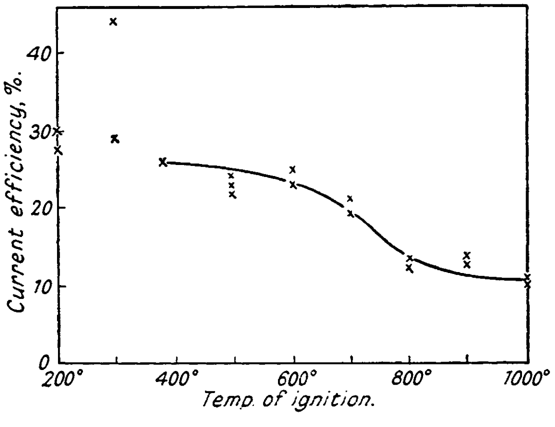


FIG. 6.

Relation between temperature of ignition of ferric oxide and the current efficiency of reductive dissolution in 0·1N-*hydrochloric acid, containing dissolved oxygen, at* 25°.



Procedure.—0·250 G. of the oxide under examination was carefully weighed out and introduced into the cathode compartment in the manner described by Pryor and Evans (*loc. cit.*). During the experiments, the variation of current, anodic potential, and potential difference across the cell, with time, was measured. At the end of the experiment the solution in the cathodic compartment was filtered rapidly, under reduced pressure, through three layers of Whatman No. 42 filter-paper, and iron determined colorimetrically by the thioglycollic acid method (Swank and Mellon, *Ind. Eng. Chem. Anal.*, 1938, **30**, 7). The quantity of oxide dissolved directly during the period of the experiment was derived from blank readings obtained in the absence of a cathodic current. This correction was subtracted from the total iron content of the solution in the cathodic compartment; the balance was expressed as the percentage by weight of oxide reductively dissolved.

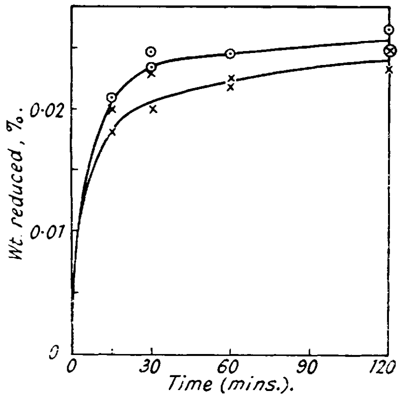
The number of coulombs flowing during the experiment was estimated by Simpson's rule and the percentage efficiency of the reductive dissolution calculated.

Results in the Presence of Oxygen.—The manner in which the weight percentage of oxide reductively dissolved by one hour's treatment with 0·1N-hydrochloric acid, varied with the temperature of ignition of the oxide is shown in Fig. 5; the relation between cathodic efficiency and temperature of ignition is illustrated in Fig. 6. The results obtained with oxide, ignited at temperatures of 300° and below, are probably not reliable owing to the comparatively high rate of direct dissolution in 0·1N-acid.

FIG. 7.

Relation between time and the percentage reductive dissolution of the oxide ignited at 1000° in 0·1N-hydrochloric acid

(a) *containing dissolved oxygen,*
(b) *de-aerated*
at 25°.

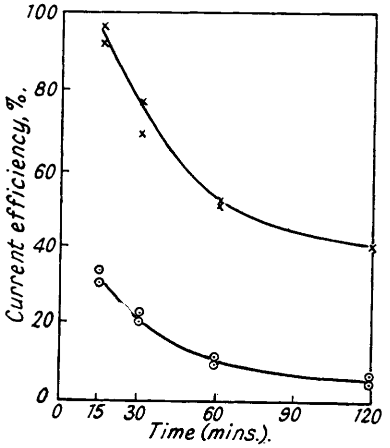


○———○ *Results in solutions containing dissolved O_2.*
×———× *Results in de-aerated solutions.*

FIG. 8.

Relation between time and the current efficiency of the reductive dissolution of the oxide ignited at 1000° in 0·1N-hydrochloric acid

(a) *containing dissolved oxygen,*
(b) *de-aerated*
at 25°.

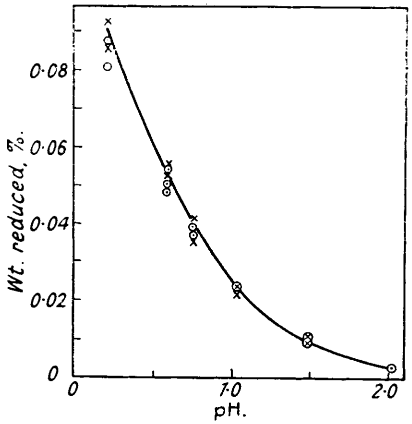


○———○ *Results in solutions containing dissolved O_2.*
×———× *Results in de-aerated solutions.*

FIG. 9.

Relation between pH and the percentage reductive dissolution of the oxide, ignited at 1000°, in solutions of hydrochloric acid

(*a*) *containing dissolved oxygen,*
(b) *de-aerated*
at 25°.

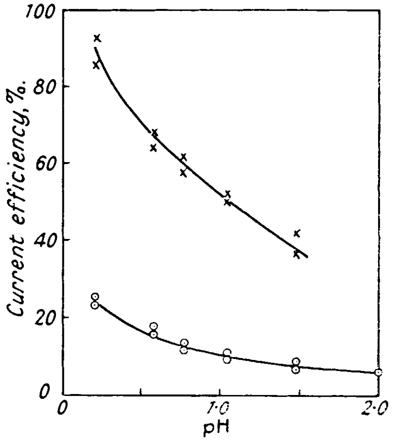


○ *Results obtained in solutions containing dissolved O_2.*
× *Results obtained in de-aerated solutions.*

FIG. 10.

Relation between pH and the current efficiency of the reductive dissolution of the oxide, ignited at 1000°, in solutions of hydrochloric acid

(a) *containing dissolved oxygen,*
(b) *de-aerated*
at 25°.



○———○ *Results obtained in solutions containing dissolved O_2.*
×———× *Results obtained in de-aerated solutions.*

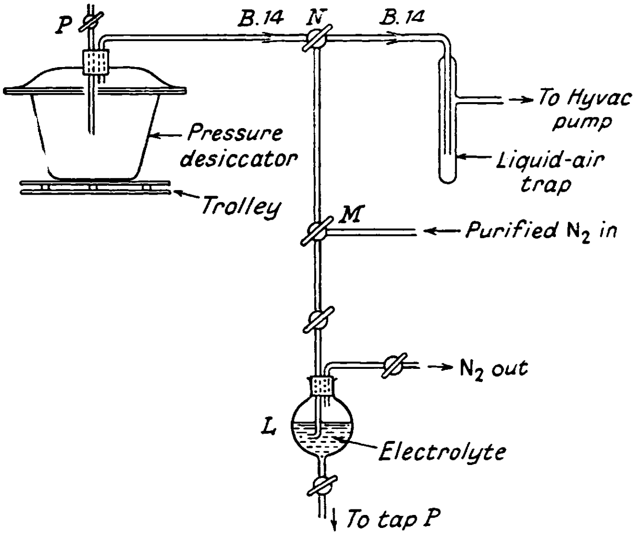
The variation with time of the reductive dissolution in 0·1N-hydrochloric acid of the oxide ignited at 1000° is shown in Fig. 7, and Fig. 8 gives the corresponding variation of the cathodic efficiency.

The effect of pH on the reductive dissolution in solutions of hydrochloric acid and the efficiency of reduction of the oxide ignited at 1000° are shown in Figs. 9 and 10; the range of pH covered in this examination was 0·0—2·0, the cell being too insensitive for higher values.

Effect of Different Acids.—The experiments determining the effect of pH on the reductive dissolution of the oxide ignited at 1000° were repeated, different solutions of sulphuric and perchloric acids being used. The results were the same, within the limits of experimental error, as those previously obtained with hydrochloric acid.

Two-stage Experiments.—It was now thought that reductive dissolution of ferric oxide powders was influenced by surface conductivity and consequently, according to Bevan, Shelton, and Anderson (*loc. cit.*), by the number of surface defects. It was shown by Pryor and Evans (*loc. cit.*) that certain acid pre-treatments, which were believed to alter the number of surface defects, greatly altered the rate of direct dissolution of α-ferric oxide powders. Two-stage experiments were, therefore, carried out to ascertain whether similar treatments had any effect on the rate of reductive dissolution.

FIG. 11.



In a typical experiment 1·0 g. of the oxide ignited at 1000° was exposed to 0·1N-hydrochloric acid for 20 hours, followed by filtration, careful washing, and drying in a desiccator. A 0·250-g. sample of the residue was subjected to direct attack by 0·1N-hydrochloric acid in the mercury cell for 1 hour and was found to lose 0·022%. A second sample subjected to reductive dissolution lost an additional 0·012% at a current efficiency of 6·5%. A sample of the oxide, which had not received any acid pre-treatment, would have suffered reductive dissolution to the extent of 0·023% at a cathodic efficiency of 10% under similar conditions.

In another typical experiment, 0·250 g. of oxide ignited at 1000° was subjected to cathodic treatment in 0·1N-hydrochloric acid for one hour. The current was then turned off, and direct dissolution allowed to proceed for a further hour. The quantity of oxide autoreduced in the first hour, calculated from previous experiments, was subtracted from the total iron content of the cathodic solution; the results showed that, in the second hour, only 0·005% of the oxide was dissolved by direct acid attack. A similar two-stage experiment, carried out without cathodic treatment, produced approximately 0·015% dissolution during the second hour's exposure to acid.

Reductive Dissolution under Anærobic Conditions.—Experiments were carried out in de-aerated solutions with the mercury cell placed in a vacuum apparatus (Fig. 11). The cell was contained in a pressure desiccator, mounted on a movable trolley, so that it could be easily removed from the rest of the apparatus. Electrical connection was made to the cell through four stout brass rods forced through the rubber bung in the lid of the desiccator. All rubber joints in the apparatus were coated with picein wax to minimise access of air.

The electrolyte was partially freed from oxygen in the flask, *L*, by bubbling in nitrogen, previously purified by passing through reduced copper, nickel, and iron turnings at 450° for two hours; during this period the desiccator was thoroughly flushed out with nitrogen. The flask was then connected by a rubber tube to the tap *P*, in the desiccator lid, and the solution run into the mercury cell under reduced pressure. The desiccator was then evacuated with a "Hyvac" two-stage pump for ten minutes. During this operation the electrolyte boiled vigorously and expelled the gases dissolved in the solution. After ten minutes' pumping, purified nitrogen was readmitted, through tap *N*, and the desiccator flushed out for a further ten minutes. Taps *P* and *N* were then closed, and the desiccator isolated from the rest of the apparatus.

The oxide was introduced into the cell by a clockwork tipping device. The small tube, containing 0·25 g. of oxide, was supported in a horizontal position by a rubber band stretched between two pins. The tube could be released by movement of the minute finger of the clock, which was attached to the rubber band by a hook and a length of thread. Once released, the tube jettisoned its contents into the cell and the experiment could commence.

Results in the Absence of Oxygen.—The majority of the anaerobic experiments were carried out on oxide ignited at 1000°—the type mainly used in previous experiments.

The variations, with time, of the percentage of reductive dissolution and the cathodic efficiency in 0·1N-hydrochloric acid are shown in Figs. 7 and 8. The rates of reductive dissolution are identical, within the limits of experimental error, with those previously obtained in solutions containing dissolved oxygen; the cathodic efficiency, however, is very much higher (Fig. 8) and in the first 15 minutes approaches 100%.

The relation between pH and both the percentage of reductive dissolution of the oxide ignited at 1000° and the cathodic efficiency, in different solutions of hydrochloric acid, is shown in Figs. 9 and 10. Again the rates of reductive dissolution are almost identical with those obtained in solutions of equivalent concentration containing dissolved oxygen, whilst the cathodic efficiencies are much higher.

An experiment on the oxide ignited at 385° showed that 0·14% was reductively dissolved, in one hour, in 0·1N-hydrochloric acid, at a current efficiency of 55%, as compared with 0·073% reductive dissolution at an efficiency of 25% in a solution of the same acid containing dissolved oxygen.

DISCUSSION.

During the experiments previously described the electrode potential of the cathode never fell below −0·28 volt. Since Frumkin's results (*Discussions of Faraday Soc.*, 1947, **1**, 57) show that, at the experimental current density (approx. 10^{-4} amp./sq. cm.) the overpotential of hydrogen evolution in 0·1N-hydrochloric acid is approximately 0·95 volt, only a negligible fraction of the total cathodic current can be accounted for by this reaction.

It appears, therefore, that the two most important reactions taking place at the cathode are: (*a*) the reductive dissolution of ferric oxide; (*b*) the reduction of oxygen dissolved in the electrolyte.

In solutions containing dissolved oxygen it has been observed that the efficiency of the first process never exceeded 50% and seldom even 25%. Conditions present in this cell, however, favour the reduction of oxygen as this reaction takes place at the mercury surface. Reductive dissolution, on the other hand, involves the transference of electrons across the mercury–oxide interface and through the oxide itself. During the study of the reductive dissolution of ferric oxide films both alternative cathodic reactions occurred at the oxide–solution interface and so it is probable that, in this case, the efficiency of reductive dissolution was higher.

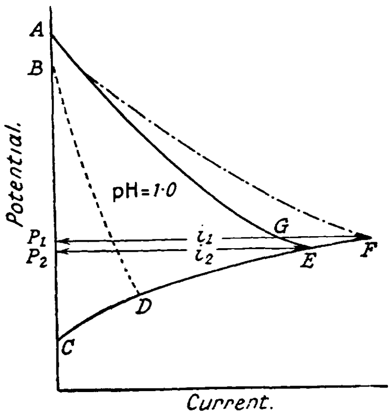
The rate of reductive dissolution and the percentage efficiency decrease as the temperature of ignition increases from 385° to 1000° (Figs. 5 and 6). The rate appears to be higher for oxide ignited at or below 300°, but the correction for the direct dissolution of these oxides is so high that the values are unreliable. According to the results obtained in Part I, conditions of pH should be favourable for rapid reductive dissolution, but in spite of this, both the efficiency and the rate of reduction are fairly low, and it may be that this is caused by low electronic conductivity of the oxide. Bevan, Shelton, and Anderson (*loc. cit.*) showed that the surface conductivity of massive α-ferric oxide was much higher than its bulk conductivity and depended largely on the number of defects present in the surface layers. Reductive dissolution must involve the conduction of electrons through the oxide, and so it is probable that surface conductivity is a most important factor. It was suggested by Pryor and Evans (*loc. cit.*) that the rate of direct attack on α-ferric oxide of acids which do not form soluble complexes with ferric ions depended on the number of defects in the surface; furthermore, increase of the temperature of ignition from 385° to 1000° resulted in a steady decrease in the rate of direct dissolution in 0·1N-hydrochloric acid owing to the fact that the oxides ignited at comparatively low temperatures contained a high number of defects "frozen-in" at the phase change at 300°; the powdered oxides ignited between 385° and 600°, which presumably contain this comparatively high number of defects, are fairly readily auto-reduced in the mercury cell (Fig. 5), and it can be seen, from Fig. 4, that the cathodic potentials during reductive dissolution of oxides ignited at 385° and 600° remain practically constant with time. Heating above the Tammann temperature—approximately 650° for α-ferric oxide—should result in a decrease in the number of defects, and it can be seen that the rate of reductive dissolution drops between ignition temperatures of 600° and 800°. It appears that the cathodic polarisation during autoreduction of the oxide ignited at 1000° increases continuously with time, probably owing to a progressive exhaustion of surface defects and consequently a reduction of the surface conductivity.

Practically all the reductive dissolution of the oxide ignited at 1000° occurs during the first 15 minutes' exposure to 0·1N-hydrochloric acid (Fig. 7). In direct dissolution also the rate is quickest during the first 15 minutes of the experiment, and so this additional close parallelism between direct and reductive dissolution supports the view that they both depend on the number of defects in the surface of the oxide; further confirmation was provided by two-stage experiments which showed that, once the surface defects originally present in the oxide surface had been largely removed by acid treatment, the rate of reductive dissolution decreased from 0·023% to 0·012%, in one hour, and the efficiency from 10% to 6·5%.

Direct dissolution in non-complex-forming acids was found to be independent of the acid radical, and a similar result was obtained during a study of reductive dissolution.

The rate of reductive dissolution and the efficiency increased with a decrease in pH value, as shown by Figs. 9 and 10. Since it was also found that higher currents flowed at lower pH values, this observation agrees with that of Campbell and Thomas (*Nature*, 1938, **142**, 253; *Trans. Electrochem. Soc.*, 1939, **76**, 303) who showed that, at high current densities, the importance of oxygen as a cathodic depolariser was smaller. Presumably at high current densities and rapid rates of reductive dissolution, the oxygen immediately surrounding the cathode is rapidly exhausted. Any subsequent reduction of oxygen will then be controlled by the rate at which it can diffuse to the cathode from the bulk of the solution. If the rate of reductive dissolution is high, this rate of diffusion will be slow by comparison and so the efficiency of reductive dissolution should be high.

FIG. 12.



CDEF = Anodic polarisation curve.
BD = Oxygen reduction curve.
AE = Reductive dissolution curve.
AF = Total cathodic curve.
(*Not to scale.*)

Reductive dissolution probably involves two stages, *i.e.*, reduction and direct dissolution of the product of reduction. The fact that cathodic reduction of oxide films, by means of a small constant current, can be achieved at higher pH values than autoreduction indicates that the overall reductive dissolution is not controlled by the direct dissolution of the product of reduction—at least at low pH values. The results of the two-stage experiments on the reductive dissolution of oxide powders are also in accord with this view.

In general, it can be seen that the removal of dissolved oxygen has practically no effect on the rate of reductive dissolution of ferric oxide ignited at 1000° but increases the cathodic efficiency of this process very considerably. These results are in accordance with high polarisation of the cathodic reaction and low polarisation of the anodic reaction. If the currents resulting from the two simultaneous cathodic reactions are summed graphically by Akimov's method (*Acta Physicochem. U.S.S.R.*, 1945, **20**, 809), it will be seen from Fig. 12 that in the presence of dissolved oxygen the total corrosion current is i_1 of which P_1G is devoted to reducing oxide and GF to reducing oxygen. If the oxygen is removed from solution the total corrosion current i_2 is all devoted to reducing oxide. The rate of reduction, which depends on the current flowing, is little different from that in the presence of oxygen (P_1G) provided that the slope of the anodic curve is low compared with that of the cathodic curve. The current efficiency, however, increases in this case from $100P_1G/P_1F\%$ to 100%. Thus it can be seen that the fact that oxygen removal only influences the efficiency of reduction of the oxide at 1000° is due to high polarisation of the cathodic reaction.

The rate of reductive dissolution of the oxide ignited at 385° appears to be increased by removal of oxygen. In this case, however, the polarisation of the cathodic reaction is smaller (Fig. 4), probably owing to the comparatively high number of defects. It would therefore be expected, in this case, that removal of oxygen would increase the rate of reductive dissolution of this oxide as well as the cathodic efficiency—as was found to be the case.

Conclusion.—A cell has been developed suitable for investigating the reductive dissolution of powdered samples of α-ferric oxide. A fixed mass of oxide is floated on mercury, and both the rate and the current efficiency of reductive dissolution are measured. It was shown that both the rate and the current efficiency of reductive dissolution decrease with an increase in the temperature of ignition of the oxide, with increasing duration of the experiment, and with an increase in pH of the electrolyte. The results obtained with solutions of sulphuric and perchloric acid are identical, within the limits of experimental error, with those obtained in solutions of hydrochloric acid. When the solutions are de-aerated the current efficiency increases, but the rate of reductive dissolution is not significantly altered. This is believed to be due to the facts that reductive dissolution is highly polarised and that the influence of pH on the unpolarised potential of reductive dissolution is given by a term $(3\boldsymbol{R}T/\boldsymbol{F}) \log_e [H^+]$, while that on the alternative reduction of dissolved oxygen is given by $(\boldsymbol{R}T/\boldsymbol{F}) \log_e [H^+]$. The rôle of dissolved oxygen as a cathodic depolariser becomes more pronounced as the pH increases and the current density decreases.

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