256. *The Reductive Dissolution of Ferric Oxide in Acid. Part I. The Reductive Dissolution of Oxide Films Present on Iron.*

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

When oxidised iron is immersed in dilute acid and the α-ferric oxide is destroyed by autoreduction the rate of destruction diminishes with an increase in film thickness, with an increase in pH, and with a decrease in temperature. The activation energy, calculated from the temperature coefficient, is about 8·5 kcals. Potential measurements show that reductive dissolution is highly polarised and that the polarisation increases with a rise in pH—which explains why the destruction is so slow at high pH values.

It has been shown (Evans, *Proc. Roy. Soc.*, 1925, *A*, **107**, 228) that, when an iron specimen showing interference tints due to an oxide film is subjected to cathodic treatment in 0·02N-hydrochloric acid, the colours undergo uniform changes, indicating a thinning of the film It was later found (Evans, *J.*, 1930, 478) that, although tinted iron specimens dipped into 0·1M-sulphuric acid quickly lost their colour, indicating the destruction of the film, the same film, if previously stripped from the metallic basis, could be preserved in the same acid for long periods. It was suggested that the rapid destruction of the films, when in electrical contact with the iron, was due to local cells, Fe (anode) | Acid | Fe_2O_3 (cathode), set up at discontinuities in the film; the ferric oxide suffers cathodic reduction and ferrous ions pass into the liquid. This conclusion is supported by the observations (Evans, *J.*, 1930, 481) that the destruction of the films on tinted iron by 0·01M-sulphuric acid can be prevented by the application of a sufficient anodic current, whereas a cathodic current accelerates their disappearance, and that the destruction of the colours can be prevented by the presence of an oxidising agent in sufficient concentration (0·1M-chromic acid in 0·01N-sulphuric acid). Evidently the disappearance of the films is due to a combination of reduction and dissolution.

In earlier papers the rapid destruction of oxide films on cathodic areas was called " cathodic reduction " or " reductive dissolution." In the present paper the reductive dissolution occurring in a short-circuited cell Fe | Acid | Fe_2O_3 will be called " autoreduction," the term " cathodic reduction " being restricted to destruction brought about by an external E.M.F.

Cathodic reduction has been applied to the determination of the thickness of oxide films on iron (Miley, *Carnegie Schol. Mem. Iron & Steel Inst.*, 1936, **25**, 197; Evans and Miley, *Nature*, 1937, **139**, 283; Miley and Evans, *J.*, 1937, 1295). The oxidised specimen is made the cathode under a constant current in ammonium chloride solution, where the pH is too high to permit autoreduction. The weight of film destroyed can be calculated from the number of coulombs needed—provided that no alternative cathodic reaction proceeds simultaneously.

Despite much work on the application of cathodic reduction, no adequate account of the mechanism has been offered. The earlier papers suggested a reduction of ferric to ferrous oxide which was believed to dissolve instantaneously in the electrolyte; but Hoar (private communication) has argued that there is no reason why *massive* ferrous oxide should dissolve with great speed.

The present paper describes an attempt to obtain fuller information regarding the autoreduction and cathodic reduction of films on heat-tinted iron immersed in electrolytes containing dissolved oxygen; it includes studies of the influence of film thickness, pH, temperature, and the presence of complex-forming ions on the rate of reductive dissolution.

EXPERIMENTAL.

Materials.—The iron used in these experiments was in the form of annealed sheet, 0·02 cm. thick; it was kindly supplied by the British Iron and Steel Research Association; analysis showed : C, 0·005; Si, 0·0075; S, 0·013; P, 0·003; Mn, 0·007; Ni, 0·018; Cr, 0·02; Cu, 0·003; O, 0·12; N, 0·008; H, 0·00009%. The chemicals were of AnalaR quality.

Each specimen was degreased thoroughly in xylene, abraded with 3/0 emery paper, swabbed with acetone, and dried with filter-paper. Except in experiments designed to show the effect of film thickness on the rate of autoreduction, the specimens were tinted in the air-oven at 210° for 30 hours, in order to obtain an oxide film showing the first-order red-brown interference colour. This particular colour was chosen because Constable (*Proc. Roy. Soc.*, 1929, *A*, **125**, 378) had shown it to be obtained only over a fairly narrow range of film thickness.

A disc of iron of the same composition, measuring 2 cm. in diameter and 0·1 cm. thick, was treated in an identical manner, and its surface examined by electron diffraction, the reflection method being used, in order to determine the structure of the heat-tinted film; this examination was kindly carried out by Mr. J. W. Menter. The values of the spacings, based on gold-leaf as a standard, are shown in the following table. They are in good accord with those previously obtained from α-ferric oxide by *X*-ray diffraction (" Index of *X*-Ray Diffraction Constants," A.S.T.M., 1945) and suggest that the film responsible for the first-order colour is largely composed of rhombohedral α-ferric oxide.

Ring radius (cm.).	Spacing (A.).	Intensity.	A.S.T.M. *X*-ray spacings for α-Fe_2O_3.	A.S.T.M. *X*-ray intensity.	*hk. l.*	Ring radius (cm.).	Spacing (A.).	Intensity.	A.S.T.M. *X*-ray spacings for α-Fe_2O_3.	A.S.T.M. *X*-ray in tensity.	*hkl.*
0·86	3·80	W	3·68	0·18	11·0	1·89	1·73	M	1·69	0·63	321
1·19	2·74	V.S.	2·69	1·00	21·1	2·16	1·51	V.S.	1·485	0·50	310
1·29	2·53	V.S.	2·51	0·75	10·1	2·20	1·47	V.S.	1·451	0·50	211
1·45	2·19	M	2·20	0·18	20·2	2·39	1·365	W	1·381	0·03	433
1·76	1·86	S	1·84	0·63	22·0	2·66	1·23	V.W.	1·26	0·13	202

V.S. = very strong. S = strong. M = moderately strong. W = weak. V.W. = very weak.

Experimental Method.—It was observed during preliminary experiments that specimens tinted to first-order colours changed their tints uniformly when exposed to 0·1N-hydrochloric acid. Furthermore, the period needed for the disappearance of colour was independent of the area of specimen exposed to the acid; after the colour had vanished, the specimen almost certainly still carried an invisible oxide layer. The boundary between the visible and invisible films, however, represented a convenient, if arbitrary, end-point.

This " boundary method " showed good reproducibility as regards the period of immersion necessary for the autoreduction of first-order oxide films. A portion of the specimen was exposed to the acid until the visible films had disappeared; the specimen was then immersed more fully and the time required for the disappearance of the boundary between the visible and the invisible film noted. The scatter was generally less than 10%, except where the film was destroyed very quickly.

The Effect of Film Thickness.—Pure iron specimens measuring 6 × 2 cm. and 0·02 cm. thick, abraded and degreased as previously described, were heated in the air-oven at 300° for different times to give oxide films of the following interference colours :

Interference colour.	Approx. thickness (A.) (Evans and Miley, *Nature*, 1937, **139**, 283).	Time for autoreduction (secs.).
1st-Order straw	440	2—3
1st-Order red-brown	560	3—5
1st-Order violet	695	7—10
Silvery hiatus (light blue)	725	300

The times taken for the autoreduction of these films in 0·1N-hydrochloric acid (pH = 1·12) at constant temperature (20·5°) were determined by using the " boundary method ".

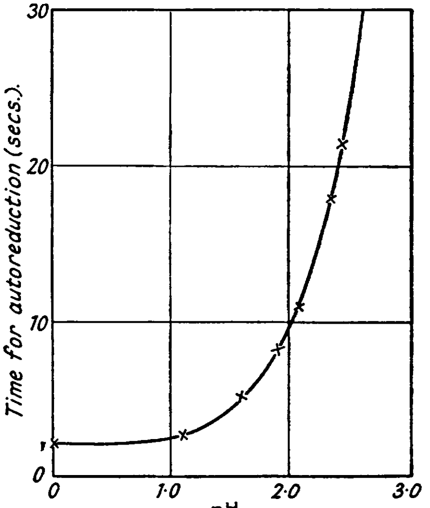
The first-order straw, red-brown, and violet films all thinned rapidly and apparently uniformly during autoreduction, disappeared sharply after a definite period of immersion (see above table), and left a clean metal surface. With films of the " silvery hiatus," autoreduction spread outward from certain points so that the destruction of the film was non-uniform; indeed, the whole range of first-order interference colours could be observed simultaneously on specimens immersed for 30 seconds; even after 300 seconds the films had not completely disappeared. These thicker films are known to be duplex (Evans, Iron and Steel Inst. Special Rep., 1938, **21**, 225), with a lower layer of magnetite next to the metal; when subjected to autoreduction they left behind a black residue which was extremely resistant to reductive dissolution. If the specimen remained in the solution for a further hour, the black film was undermined, leaving a clean metal surface. The film, which remained suspended in the solution, was highly magnetic.

These results were confirmed by a different method. If the specimen was electropolished, in the perchloric acid–acetic acid bath developed by Jacquet (*Compt. rend.*, 1948, **227**, 556), before being heat-tinted, the interference colours showed very distinctly under the microscope. It was observed that the colours differed from grain to grain and that a film which appeared red-brown to the naked eye was, in fact, composed of different grains showing such interference colours as blue, violet, red-brown, and straw, when examined under the microscope. Even light straw specimens contained a few violet and blue grains and the proportion of grains showing these colours increased with the mean film thickness. This variation of oxide thickness from grain to grain is doubtless due to the fact, pointed out by Mehl and McCandless (*Trans. Amer. Inst. Min. Met. Eng.*, 1937, **125**, 531), that the rate of growth of oxide films on iron is anisotropic.

An electropolished iron specimen, measuring 4 × 2 cm. and 0·02 cm. thick, was therefore gradient-tinted in a Bunsen flame, half-immersed lengthways in 0·1N-hydrochloric acid for 20 seconds, washed rapidly in distilled water, and dried on filter-paper. There was a shift in the colours, relative to the original tints, which were preserved unchanged above the water-line—similar to that obtained previously with an external current (Evans, *Proc. Roy. Soc.*, 1925, *A*, **107**, 228). A comparison with the original colours, at a magnification of 400, showed that the original first-order straw and red-brown regions were almost completely decolorised, with the exception of isolated grains carrying blue interference films. Evidently the blue film was more resistant to reductive dissolution than thinner films. In the first-order violet range original red-brown and straw colours were largely reduced, many grains carrying violet films were thinned and after short-time treatments appeared red-brown or straw, but the blue colours were mostly unchanged. The silvery film appeared to be composed of approximately equal proportions of grains showing second-order yellow and first-order blue tints. Film reduction in 20 seconds was so incomplete that the contrast at the " water-line " was much less sharp than in the first-order violet, red-brown, and straw ranges.

FIG. 1.

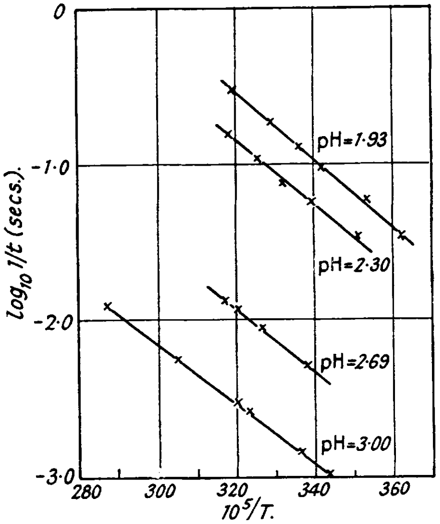
Relation between pH and the time of autoreduction of first-order red-brown films.



First-order red-brown films.
Temp. = 20·5°.

FIG. 2.

Relation between the logarithm of the inverse of the time of autoreduction and the inverse of the absolute temperature.



The Effect of Hydrogen-ion Concentration.—The effect of pH on the autoreduction of first-order red-brown α-ferric oxide films on specimens measuring 7 × 2·5 × 0·02 cm. was determined by the boundary method in eight solutions of potassium chloride and hydrochloric acid of molar chloride-ion concentration covering the pH range 0·02—5·09; all experiments were carried out in 50 ml. of solution held at constant temperature (20·5°) in a water-bath and were repeated at least six times with fresh solutions; Fig. 1 is based on the average of results obtained.

When the pH of the solution exceeded 3·0, autoreduction of the film was not observed even when the specimen was left in the solution for 24 hours. Portions of the film, however, had been undermined. probably by an extension of anodic areas on the specimen, and could be observed in suspension in the solution. Under the microscope (× 500) these fragments of film exhibited abrasion marks probably inherited from the iron. The remaining film on the specimens showed its original red-brown colour.

The Effect of Temperature.—The relation between time of autoreduction and temperature was determined by the same procedure for first-order red-brown films in four of the above potassium chloride–hydrochloric acid solutions having pH values of 1·93, 2·30, 2·69, and 3·00. The solutions were kept at the appropriate temperature in a water-bath, each determination being carried out at least six times in fresh solutions; the rate of autoreduction increased with a rise in temperature and when the logarithm of the inverse of the time was plotted against the inverse of the absolute temperature, a family of parallel straight lines was obtained (Fig. 2).

Potential Measurements during Autoreduction.—Two series of experiments were carried out in which potential measurements were taken during autoreduction of visible oxide films on heat-tinted specimens.

FIG. 3.

Relation between time and potential during the autoreduction of films of different thickness at pH = 2·37 *and at* 17·5°.

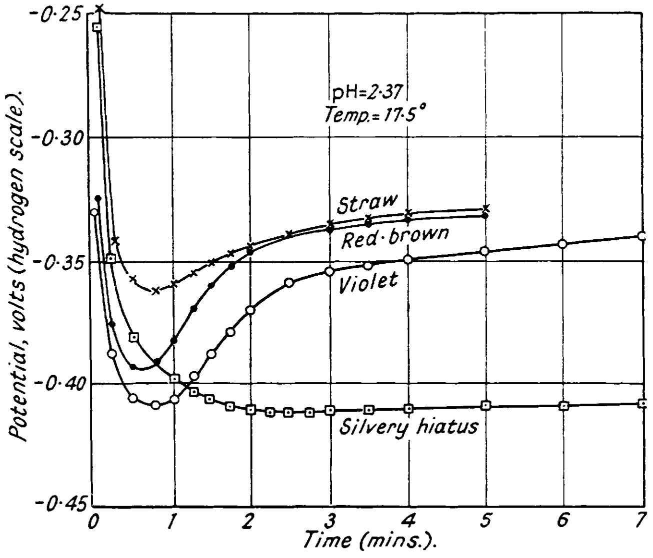
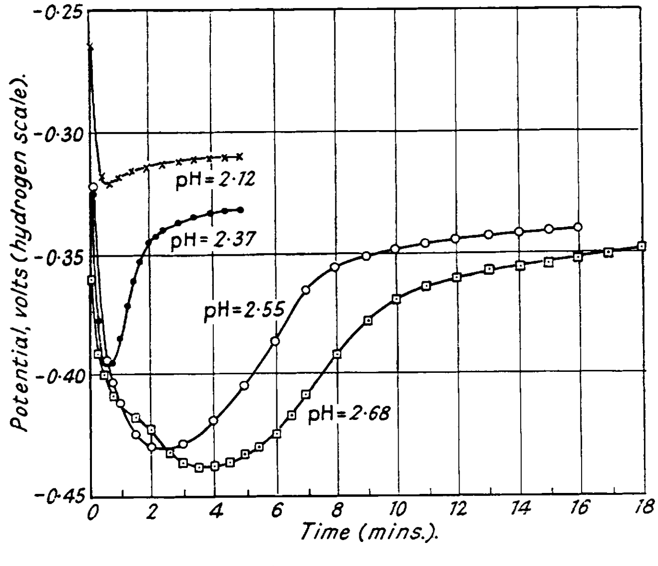


FIG. 4.

Relation between time and potential during the autoreduction of first-order red-brown films in solutions of different pH at 17·5°.



The potential was measured against a silver–silver chloride electrode enclosed in a tubulus drawn out to a tip of 0·1 cm. internal diameter. The specimen was mounted on a fibre frame (Evans, *J. Soc. Chem. Ind.*, 1928, **47**, 731), so that an area measuring 3·5 × 2·5 cm. was immersed in the electrolyte, the tip of the tubulus being situated 0·1 cm. away from the iron; in these experiments a large volume (400 ml.) of solution was used. The variation of potential difference with time was measured by means of a valve potentiometer.

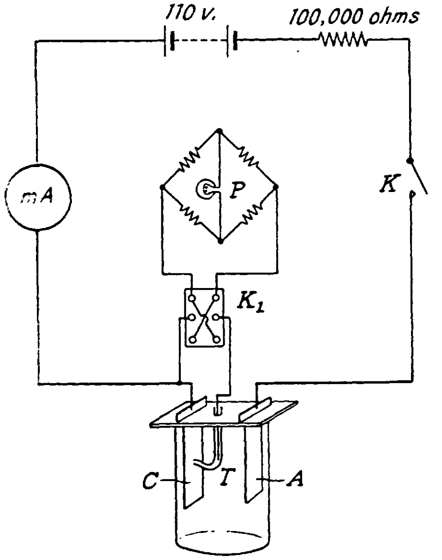
In the first series of experiments the influence of film thickness on the shape of the potential–time curves was investigated. The solution used (pH = 2·37) was maintained at 17·5° and had M-chloride-ion concentration. The specimens were tinted to straw, red-brown, violet, and silvery hiatus colours, experiments being conducted in triplicate. Typical curves relating the potential, on the standard hydrogen scale, to time are shown in Fig. 3.

In the second series the influence of the pH of solutions of M-chloride-ion concentration, at constant film-thickness (first-order red-brown) and temperature (17·5°), on the form of the potential–time curves was investigated. The range of pH covered by the solutions was 2·12—2·68. Experiments were again in triplicate and typical curves are shown in Fig. 4.

Potential Measurements during Cathodic Reduction.—Single electrode-potential determinations were carried out during cathodic reduction in 0·1N-ammonium chloride solution (pH = 4·94), containing dissolved oxygen, an electrical circuit being used similar to that of Miley (*Carnegie Schol. Mem. Iron and Steel Inst.*, 1936, **25**, 197), except that the single-electrode potential of the cathode was measured against a silver–silver chloride electrode (Fig. 5). The electrodes were iron sheets of standard size, one of which (the cathode) had been tinted to the required interference colour, whilst the other (the anode) had been freshly abraded with 3/0 emery paper. The electrodes were mounted on a fibre frame so that they were 3·5 cm. apart. A tubulus, drawn down to 0·1 cm. internal diameter, was also mounted on the frame so that its tip was situated 0·1 cm. distant from the heat-tinted cathode. 250 Ml. of 0·1N-ammonium chloride solution were used in each experiment, the electrodes being immersed to a depth of 2·5 cm.

FIG. 5.

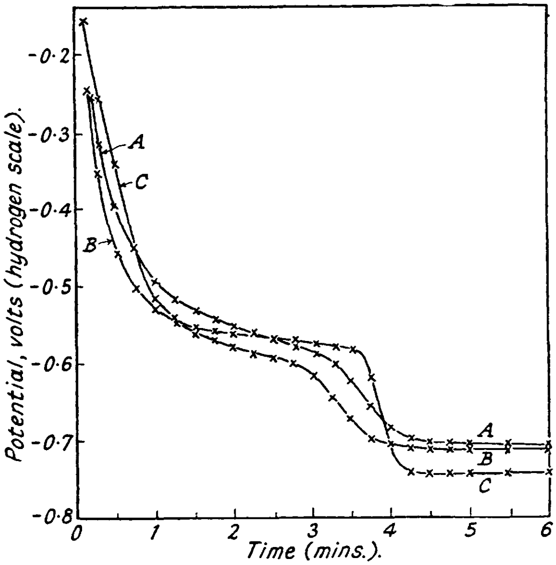
Circuit used for the cathodic reduction of oxide films.



C = Cathode. A = Anode. T = Tubulus. K and K_1 = Keys. P = Valve potentiometer. mA = Sensitive milliammeter.

FIG. 6.

Potential–time curves for first-order violet films.



A, B = In 0·1N-NH_4Cl.
C = In 0·1N-NH_4Cl + KCN (0·7 *g./l.*).

Typical potential–time curves for first-order violet films are shown in Fig. 6, curves *A* and *B*. Curve *C* was obtained with an addition of 0·7 g./l. of potassium cyanide, which raised the initial pH of the electrolyte from 4·94 to 5·05. Similar curves were obtained with oxide films of different thickness. The alteration produced by cyanide addition was also obtained with films of different thickness.

DISCUSSION.

During autoreduction the anodic areas are provided by iron exposed to the acid at discontinuities in the oxide film. The electrons, liberated by the anodic reaction, will pass from the metal, through the oxide film, and take part in the cathodic reaction at the oxide–solution interface. Consequently, one of the factors controlling the rate of reductive dissolution will be the electronic conductivity of the film.

The fact that the specimen carrying thin first-order films changes colour uniformly during autoreduction suggests that these films possess sufficient electronic conductivity to permit the rapid, uniform, conduction of electrons.

The bulk conductivity of ferric oxide is, however, known to be low (Somerville, *Chem. Met. Eng.*, 1912, **10**, 423). In the films of hiatus and second-order thickness the area of iron exposed at cracks is much smaller, particularly as a magnetite layer exists below the α-ferric oxide. Their greater thickness imposes a greater resistance to the passage of electrons, and since it has been shown by Bevan, Shelton, and Anderson (*J.*, 1948, 1729) that electrons often move more readily over the surface of semi-conducting oxides than through the lattice, it is probable that such reductive dissolution as occurs will take place at or near to discontinuities or at places where the film is abnormally thin. This may explain the slow and irregular form of autoreduction observed on these thicker films. The difference between the behaviour of thin and thick films is illustrated diagrammatically in Figs. 7(*a*) and (*b*), in which, for simplicity, the metal surface is assumed to be planar.

The rate of autoreduction was shown to increase rapidly with increasing temperature. If it is assumed that the time for autoreduction is inversely proportional to the mean rate of autoreduction, then the activation energy can be calculated from the gradient of the parallel family of straight lines in Fig. 2. The value calculated, 8·5 kcals./g.-mol., may be useful later in deciding the rate-determining step during reductive dissolution.

FIG. 7 (*a*).

Electrons liberated at an anodic area passing uniformly through a thin oxide film.

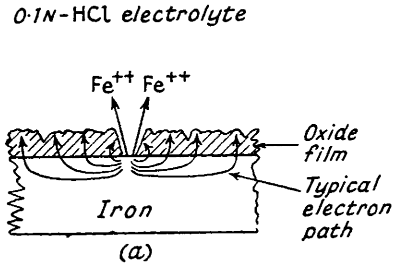
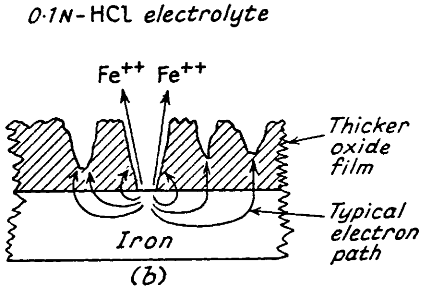


FIG. 7 (*b*).

Electrons liberated at an anodic area passing preferentially through the thinner points in a thicker oxide film.



The change in the rate of autoreduction with pH is very marked (Fig. 1); in hydrochloric acid of pH 1·0, first-order red-brown films disappear within 2 seconds, while at pH 4·0 they are unthinned even after 24 hours. The explanation may lie in the fact that the competing cathodic reactions are affected in different degrees by pH changes. The three possible cathodic reactions are: (*a*) the reductive dissolution of the oxide; (*b*) the reduction of dissolved oxygen; (*c*) the evolution of hydrogen. The fact that hydrogen evolution is never observed during the reductive dissolution of ferric oxide makes it unlikely that (*c*) is an important alternative reaction, but it is included for completeness' sake. When the films are destroyed by cathodic reduction achieved by a high external E.M.F. applied through a high resistance, a constant current is imposed, and, if no alternative cathodic reactions are possible, the destruction of the film should proceed at a rate determined by Faraday's law, even at comparatively high pH values. During autoreduction, however, the current does not necessarily remain constant, but is determined by polarisation and possibly resistance. Thus if the reductive dissolution of ferric oxide is highly polarised, the current devoted to oxide reduction will diminish and consequently the rate of film destruction must become slower.

Of the three possible cathodic reactions, (*b*) and (*c*) may be represented by the equations

$$O_2 + 4H^+ + 4e = 2H_2O \quad \ldots \quad (1)$$

$$2H^+ + 2e = H_2 \quad \ldots \quad (2)$$

The work of Miley and Evans (*J.*, 1937, 1295) leads to the conclusion that a molecule of ferric oxide requires two electrons for reductive dissolution. Since all the iron found in solution is in the ferrous condition, the reductive dissolution of ferric oxide may be represented by the equation

$$Fe_2O_3 + 6H^+ + 2e = 2Fe^{++} + 3H_2O \quad \ldots \quad (3)$$

This reaction undoubtedly takes place in steps but the value of the equilibrium potential will be independent of the mechanism.

The anodic reaction

$$Fe - 2e = Fe^{++} \quad \ldots \quad (4)$$

is not directly affected by pH. The unpolarised single-electrode potentials of the three possible cathodic reactions will be influenced respectively by pH according to the relationships

$$(1)\ E = E_0 + (\boldsymbol{RT}/\boldsymbol{F})\log_e [\mathrm{H}^+]$$
$$(2)\ E = E_0 + (\boldsymbol{RT}/\boldsymbol{F})\log_e [\mathrm{H}^+]$$
$$(3)\ E = E_0 + (3\boldsymbol{RT}/\boldsymbol{F})\log_e [\mathrm{H}^+]$$

all other products being assumed to be in the standard state. Thus the unpolarised electrode potential of the third reaction (the reductive dissolution of oxide) is affected by pH three times as strongly as the other two reactions.

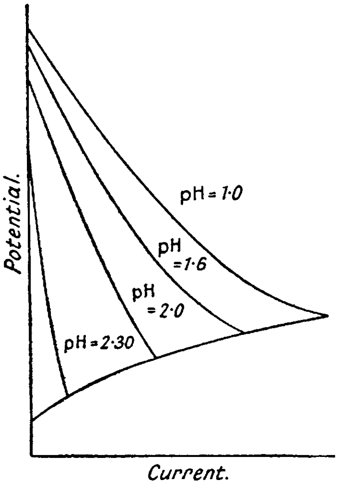
In practise, few reactions take place rapidly near their equilibrium potentials and so it becomes necessary to consider the effect of pH on polarisation. The unpolarised potential of the reductive dissolution is given by the equation

$$(3\mathrm{A})\ E = E_0 + (\boldsymbol{RT}/2\boldsymbol{F})\log_e [\mathrm{H}^+]^6/[\mathrm{Fe}^{++}]^2$$

[of which (3) is a special case corresponding to normal activity of ferrous ions]. The value of E_0 calculated from the thermodynamic data of Camps (*J. New Eng. Waterworks Assoc.*, 1946, **60**, 188) and Bichowsky and Rossini ("The Thermochemistry of Chemical Substances," 1936, p. 89, Reinhold Publishing Co.) is +1·035 volts. The unpolarised electrode potential at pH 4·0 and an arbitrary ferrous-ion concentration of 10^{-6} g.-ion/l. is +0·68 volt (this represents the concentration to be expected when a red-brown film has been half destroyed). The single potential of the anodic reaction (4) at this ferrous-ion concentration is −0·62 volt. Thus it can be seen at pH 4·0 there is an open-circuit potential difference of 1·3 volts between these anodic and cathodic reactions. In several determinations of the rate of autoreduction multiple scratch lines were ruled on the specimens after heat-tinting to expose the metal; since this produced no alteration in the rate of autoreduction, it was concluded that anodic polarisation was not high. Thus the fact that autoreduction could not be detected at this pH suggests that the polarisation of the reductive dissolution of ferric oxide is very high so that the cathodic current is carried by the alternative cathodic reactions.

FIG. 8.

Probable effect of pH on the reductive dissolution of ferric oxide.



Figs. 3 and 4 show that the compromise potential during autoreduction falls rapidly at first, flattens out, and then increases to an approximately steady value. (The compromise potential obtained in a highly conducting electrolyte represents the intersection of the anodic and cathodic polarisation curves.) The time taken to reach this steady value, which is the potential of "film-free" iron evolving hydrogen, approximates to the predicted time for the complete autoreduction of the film. During hydrogen evolution it has been suggested (Gatty and Spooner, "The Electrode Potential Behaviour of Corroding Metals," 1938, p. 253, Clarendon Press) that practically the whole metallic surface is covered with hydrogen, with anodic attack taking place at isolated points which do not remain stationary. This will result in comparatively low cathodic and high anodic polarisation, which may explain why the compromise potential during the hydrogen evolution type of corrosion is higher than during autoreduction. The low values of the compromise potential (between −0·32 and −0·45 volt) during autoreduction are consistent with high polarisation of the cathodic reaction (E_0 = +1·035 volts) and low polarisation of the anodic reaction (E_0 = −0·44 volt). Furthermore it can be seen from Fig. 4 that the minimum value of the compromise potential decreases from −0·32 volt to −0·44 volt as the pH of the solution increases from 2·12 to 2·68. Since the anodic reaction is not directly influenced by pH, and since a change in pH from 2·12 to 2·68 would change the unpolarised potential of reductive dissolution by only 49 mv., it follows that the polarisation of this reaction increases with an increase in pH; this is illustrated diagrammatically in Fig. 8. Consequently, the alternative cathodic reactions will increase in importance as the pH rises. This will be discussed more fully in Part II.

Fig. 3 shows that the width of the "well" in the potential–time curves increases with film thickness, at constant pH—a fact which accords with the view that the time taken to reach the steady value of potential is that required for the autoreduction of the oxide film. The potentials of specimens carrying silvery hiatus films, however, did not rise to that of a " film-free " specimen immersed in the same electrolyte, but remained at a value of $-0{\cdot}42$ volt, *i.e.*, approximately 0·1 volt more negative. This can be explained by the circumstance that the subsequent cathodic reaction probably now occurs at the surface of the unreduced magnetite, the distribution of which may determine the ratio of anodic to cathodic areas and consequently the relative values of the anodic and cathodic polarisations.

The arguments just set forth offer a satisfactory explanation of the remarkable effect of pH on the rate of destruction of the films.

The results of some single-electrode potential measurements carried out during the cathodic reduction of first-order violet films in 0·1N-ammonium chloride solution containing dissolved oxygen are shown in Fig. 6. The potential falls, rapidly at first, and then flattens out. This is followed by a second sharp drop to the potential of hydrogen evolution. The second drop was considered by Miley to mark the point at which the oxide reduction was complete. The addition of a small quantity of potassium cyanide, which forms soluble complexes with ferrous ions, raises the potential during reductive dissolution and emphasises the sharpness of the second drop (curve *C*, Fig. 6). This is in accordance with equation (3A) which indicates that the single-electrode potential could be raised by decreasing the concentration of ferrous ions. The low values of potential observed during reductive dissolution ($-0{\cdot}5$ to $-0{\cdot}6$ volt) provide further evidence that this reaction is highly polarised, since the unpolarised electrode potential at pH 5·0 and a ferrous-ion concentration of 10^{-6} g.-ion/l. is $+0{\cdot}504$ volt.

It was mentioned previously that the magnetite layer present in the thicker films was not destroyed during autoreduction. During the determinations of single-electrode potentials a black layer of magnetite invariably remained on the specimens after the reductive dissolution of duplex films. One of the features of electrometric determinations of film thickness—as hitherto employed—is that, in testing duplex films, only the ferric oxide layer is estimated.

Conclusion.—The destruction of ferric oxide films which occurs when heat-tinted iron is dipped in dilute acid is *not* due to *direct* dissolution as *ferric* ions, but to *reductive* dissolution as *ferrous* ions. The destruction occurs quickly and regularly when the films are thin, so that the colours change uniformly over the whole surface; probably electrons can pass through these thin films easily, permitting uniform cathodic action at all points of the outer surface. The thicker films are destroyed slowly and irregularly, probably because the reaction occurs preferentially around discontinuities.

The rate of destruction increases with temperature, and the results suggest an activation energy of 8·5 kcals. for the controlling stage. The effect of pH is remarkable; the first-order red-brown colours disappear within 2 seconds at pH 1·0, but are unchanged after 24 hours at pH 4·0. This is partly because the equilibrium potential of the reductive dissolution reaction includes the term $(3\boldsymbol{R}T/\boldsymbol{F})\log_e[\mathrm{H}^+]$, whereas the values for the two alternative reactions (liberation of hydrogen and reduction of oxygen) include the term $(\boldsymbol{R}T/\boldsymbol{F})\log_e[\mathrm{H}^+]$, so that the first reaction is more influenced by rise in pH than the other two; an even more important reason is that the first reaction is subject to high polarisation which increases with a rise in pH.

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