258. *The Reductive Dissolution of Ferric Oxide in Acid. Part III. The Mechanism of Reductive Dissolution.*

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This paper summarises the conclusions of the two previous papers on reductive dissolution and suggests the mechanism of the reaction. It is believed that the reductive dissolution of ferric oxide involves the combination of hydrogen atoms, discharged at the oxide surface, with oxygen ions, belonging to the oxide lattice, to form either hydroxyl ions or water molecules which pass into the bulk of the solution. This reaction liberates electrons which reduce an equivalent number of ferric ions to the ferrous condition, thus creating a series of the "metal-excess" type of defects in the oxide surface which will then become particularly susceptible to direct acid attack.

It was shown in Part I (*J.*, 1950, 1259) that, on dissolution of thin films of α-ferric oxide on iron, the rate of autoreduction increases with a decrease in film-thickness, with a decrease in pH and with an increase in temperature of the electrolyte. Potential measurements show that reductive dissolution is highly polarised and that the polarisation increases with a rise in pH. The activation energy determined from the temperature coefficient is about 8·5 kcals./g.-mol.

The reductive dissolution of powdered samples of α-ferric oxide was investigated in Part II. It was concluded that, at pH values below 2·0, reductive dissolution is controlled mainly by surface conductivity and hence by the number of surface defects. The removal of dissolved oxygen from the electrolytes produces no significant change in the rate of reductive dissolution, but results in much higher current efficiencies of reduction; the effect of dissolved oxygen as a cathodic depolariser becomes more pronounced as the current density decreases.

The reductive dissolution of ferric oxide was represented in Part I by the equation

$$Fe_2O_3 + 6H^+ + 2e = 2Fe^{++} + 3H_2O \quad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

and it was considered that the reaction occurred in three simultaneous steps: (*a*) the conduction of electrons through the oxide; (*b*) the reduction of surface layers of the oxide to the ferrous condition; (*c*) the rapid direct dissolution of the product of reduction. In the majority of experiments the overall reaction is not controlled by the first step; in fact the only examples in which this step largely controls the overall reaction are during the reductive dissolution of silvery hiatus and thicker films and during the reductive dissolution of oxide powders, the conductivity of which is confined mainly to surface layers.

The results of the two-stage experiments described in Part II, and the fact that cathodic reduction of oxide films can take place at pH values as high as 5·0, indicate that, within the pH range of rapid autoreduction, the overall reaction is not controlled by stage (*c*).

Thus it appears that the step mainly controlling the rate of reductive dissolution of α-ferric oxide is step (*b*). Miley (*Carnegie Schol. Mem. Iron and Steel Inst.*, 1936, **25**, 197) pictured this step as the reduction of ferric oxide to ferrous oxide, but the author believes that the mechanism of the reduction is essentially similar to that suggested by Bevan, Shelton, and Anderson (*J.*, 1948, 1729) for the high-temperature reduction of semi-conducting oxides by gaseous hydrogen.

During autoreduction, electrons necessary for reductive dissolution are provided by the anodic dissolution of iron, and it was shown by Evans and Miley (*J.*, 1937, 1295) that one molecule of ferric oxide required two electrons for reduction. It is believed that the electrons discharge hydrogen ions at the oxide surface according to the equation

$$2H^+ + 2e = 2H \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

Since the electrons have to pass through the oxide to the oxide–solution interface, it is this step that is influenced by the electronic conductivity of the oxide. The two hydrogen atoms, adsorbed on the oxide surface, then react with one oxygen ion, belonging to the oxide lattice, to give a water molecule which passes into the bulk of the solution :

$$\underset{\text{(adsorbed on the oxide)}}{2\mathrm{H}} + \underset{\text{(belonging to the oxide lattice)}}{\mathrm{O}''} = \mathrm{H_2O} + 2\boldsymbol{e} \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

The two liberated electrons combine with the two neighbouring ferric ions and reduce them to the ferrous condition :

$$2\mathrm{Fe}^{+++} + 2\boldsymbol{e} = 2\mathrm{Fe}^{++} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

Thus two hydrogen atoms, discharged by two electrons produced at the anode, have created a defect of the " metal excess " type in the oxide surface. In the experiments of Bevan, Shelton, and Anderson (*loc. cit.*), the temperature was usually sufficiently high to allow these defects to diffuse into the interior of the oxide. Under the experimental conditions studied by the author, however, the temperature was never high enough to permit rapid self-diffusion and so it is believed that the defects created by this series of reactions remain in the surface layer.

The chemical composition of the product of reduction produced in reactions (3) and (4) is roughly that of ferrous oxide. The crystal structure will, however, be very different from that of the face-centred cubic ferrous oxide and will approximate to that of α-ferric oxide with one oxygen ion per molecule missing and the ferric ions replaced by ferrous ions.

It was suggested (Pryor and Evans, *J.*, **1949**, **3330**) that direct acid attack on α-ferric oxide took place mainly at isolated surface defects of this type, and that once the original surface defects were largely destroyed, the rate of attack rapidly decreased. During reductive dissolution, a large number of similar defects are continually produced in the oxide surface by the mechanism previously described; hence it would be expected that direct acid attack upon the reduced surface layers would be extremely rapid. The reactions believed to occur during reductive dissolution of one molecule of α-ferric oxide may be summarised by the sequence (2) and (3), followed by (4) and (5), the total result being (1).

$$(2\mathrm{Fe}^{+++} + 2\mathrm{O}'') + 2\boldsymbol{e} = \underset{\text{(product of reduction)}}{(2\mathrm{Fe}^{++} + 2\mathrm{O}'')} \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$(2\mathrm{Fe}^{++} + 2\mathrm{O}'') + 4\mathrm{H}^{+} = \underset{\text{(in solution)}}{2\mathrm{Fe}^{++}} + 2\mathrm{H_2O} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

This leads to an explanation of the remarkable difference in the rates of the direct and reductive dissolution of α-ferric oxide. The direct dissolution of the so-called α-ferric oxide is a slow process depending on lattice defects originally present in the oxide; their frequency depends on the previous history of the oxide, but in all cases they are few in number. The initial and comparatively rapid attack takes place at defects near to the surface, but, once these are destroyed, the rate of dissolution falls off as the more perfect parts of the oxide lattice are attacked. Since these defects not only involve the presence of ferrous ions but also loosen the lattice forces around neighbouring ferric ions, the iron in solution is partly in the ferrous and partly in the ferric condition. The reductive dissolution of α-ferric oxide is a much more rapid process since, here, a large number of defects are produced in the surface at a rate determined by the applied current. The entire surface of the oxide is continually converted into defects, with the result that the iron passing into solution is wholly in the ferrous condition.

It has been shown previously that the reductive dissolution of ferric oxide is mainly controlled by the production of defects in the surface as shown in equations (3) and (4); it is probable that this step, and in particular, the reaction between adsorbed hydrogen atoms and oxygen ions belonging to the oxide, *i.e.*, equation (3), is responsible for the high polarisation of the overall reaction. The comparatively high value of the activation energy of autoreduction, *i.e.*, 8·5 kcals./g.-mol., determined in Part I, probably refers mainly to this step in the overall reaction.

Several of the reactions that can take place at an iron cathode in solutions of low pH values are : (1) the reductive dissolution of the oxide film; (2) the reduction of dissolved oxygen; (3) the evolution of hydrogen. The first step in all these reactions is probably the discharge of hydrogen ions. These discharged ions may react with oxygen ions belonging to the ferric oxide lattice, in which case the oxide film will suffer reductive dissolution, they may reduce oxygen dissolved in solution, or they may combine together to form molecules of hydrogen. Alternative cathodic reactions are, in fact, alternative reactions of hydrogen atoms discharged cathodically.

The mechanism suggested for the reductive dissolution of α-ferric oxide can be extended to include the cathodic reduction of cuprous and cupric oxides, and the sulphides of copper and silver. In these cases, however, the electrons liberated by the combination of adsorbed hydrogen atoms with oxygen (or sulphide) ions, belonging to the oxide (or sulphide) lattice, will probably reduce cuprous or silver ions directly to the metal, and cupric ions first to the cuprous condition and then to the metal.

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