CXXVII.—*Observations on the Passivity of Metals.*

By Ernest Sydney Hedges.

The question whether iron which has been dipped in concentrated nitric acid owes its chemical inertness to a protective film of oxide or to a change in the nature of the metal itself has long been a matter of controversy, but the isolation by Evans (J., 1927, 1020) of a film of ferric oxide on iron rendered passive by a variety of means leaves no doubt that in these cases the inertness is due to a protective film. Evans was unable, however, to isolate such a film on iron made passive by concentrated nitric acid, because of the spontaneous breakdown of the passivity after withdrawal of the metal from the nitric acid.

One of the objects of the present paper is to show, by the use of methods which do not involve the removal of the metal from the acid, that iron rendered passive by nitric acid also has a protective oxide film. If the passive metal is coated with an oxide film, it may be expected that this film will be washed or torn off when the metal is whirled rapidly in the liquid, so that the iron will become active and dissolve. On the other hand, according to the view advanced by Smits ("Theory of Allotropy," 1922, p. 345), the more rapid removal of ions from the metal by a high speed of rotation will produce a more violent disturbance of the inner equilibrium at the surface of the metal and the iron will tend to become more passive.

Further strong evidence for the existence of an oxide film on passive iron is afforded by the recent work of Freundlich, Patscheke, and Zocher (*Z. physikal. Chem.*, 1927, **128**, 321; *ibid.*, **130**, 289).

The Passivation of Iron by Nitric Acid.—The electrolytic iron used in these experiments was very kindly provided by Mr. U. R. Evans, and its manufacture and analysis have been described by him (*loc. cit.*). The surface of the metal had, however, become somewhat corroded by damp soda–lime, in which it had been packed: this was not a serious drawback for the present investigations. The material was cleaned in dilute sulphuric acid, and washed in water before use.

In order to conduct the " whirling " experiments under the most sensitive conditions, it was first necessary to determine the minimum concentration of nitric acid which would suffice to passivate the iron. At first, reproducible values were not obtained, but it was soon found that the iron should not be used too soon after being taken out of the sulphuric acid. In order to obtain reproducible values, the sheet of iron was dried, cut up into pieces 1 cm. × 1 cm., and kept for 24 hours before use. No doubt, the slight " air-passivity " soon reaches a constant value.

Another source of error was found to be that in solutions of nitric acid containing 7—14% of water (by vol.), the production of passivity depends on the rate at which the iron passes through the surface of the liquid: metal which was active as it passed through the surface became passive before it reached the bottom of the vessel. Reproducible results could be obtained only by throwing the metal forcibly through the liquid surface; in fact, if one piece of iron foil is gently dropped with its flat side to the liquid surface, and another piece is thrown edge-ways through the surface, the first piece dissolves with great vigour, whereas the second piece is unattacked. This phenomenon has its counterpart in the liquid-line corrosion observed when a metal is half-immersed in a corroding medium. This can be observed both in the present experiments and in anodic passivation. According to Evans (*loc. cit.*, p. 1036), this is to be explained by the protective film tending to leave the metal–liquid interface and collect at the liquid–air interface. Such an explanation seems to account for the present case, but it is doubtful whether it is generally applicable: in some cases it seems necessary to postulate an enhanced reactivity at a liquid surface (compare Hedges, J., 1926, 831). (As a further example of the modifying influence of a liquid surface, the author has recently observed that in crystallising mercuric iodide by cooling a hot saturated solution in potassium iodide, red crystals form on the bottom and sides of the beaker, but the crystals forming at the liquid–air surface are *yellow*.)

The experiments were conducted in a thermostat at 30°, the solutions being made up by mixing measured quantities of nitric acid (*d* 1·42) and water from two burettes, so that the total volume of liquid (*before* admixture) was 10 c.c. For convenience, the mixtures are designated by the volumetric percentage of nitric acid used in their preparation, a mixture prepared from 1·40 c.c. of water and 8·60 c.c. of nitric acid being referred to as 86% nitric acid.

The following results were obtained. Nitric acid of concentration 100—86% rendered iron passive, a distinct yellow colour being produced in 90—86% acid. When kept in these solutions, the passive iron dissolved so slowly that after 3 months very little dissolution had taken place.

The lowest concentration of nitric acid to passivate electrolytic iron at 30° was repeatedly determined as 86%. In 85·5% acid the iron disssolved with great vigour, and in 85·75% acid it dissolved quietly with slow evolution of bubbles.

Activation of Passive Iron by Whirling.—Pieces of iron foil 1 cm. × 2 cm. were pierced and suspended by a hook on the end of a glass rod, which could be rotated at a speed of 3000 r.p.m. in nitric acid. Iron whirled in nitric acid of any high concentration always imparted a distinct yellow colour to the solution after a short time, the more readily the greater the amount of water. The following is typical of many experiments : The iron, resting on the glass hook, was quickly passed through the liquid surface of 86% acid and was observed to be passive; it was then rotated at 3000 r.p.m., and no change occurred until after 30 seconds, whereupon the solution quite suddenly became deep yellow. After a further period of 60 seconds the iron had dissolved completely. Separate experiments showed that a similar piece of iron kept at rest in nitric acid of this concentration at 30° was completely dissolved after 8 days.

These experiments show beyond doubt that passive iron becomes active when rapidly whirled in nitric acid. The " induction period " of about 30 seconds is of exceptional interest, for it seems probable that this is the time taken to remove the protective oxide film, after which the dissolution proceeds apace.

Activation of Passive Iron by raising the Temperature.—Iron which has been made passive by concentrated nitric acid is well known to become suddenly active when the solution is heated. A study was made of this transition. The experiments were carried out in a thin-walled test-tube containing 10 c.c. of the nitric acid solution and a piece of iron foil measuring 1 cm. × 1 cm. A thermometer was suspended in the nitric acid. The whole was immersed in a large beaker of water, which was constantly stirred and heated at the rate of 1° per minute by means of a small flame. The iron was thrown into the nitric acid at 30°.

In general, in the stronger solutions of nitric acid, the following sequence of events was observed on raising the temperature. At first the iron was passive and the solution almost colourless. At about 65° a faint yellow coloration appeared in the liquid, but suddenly at 75° slow evolution of small bubbles at the surface of the metal occurred : this transition was quite sharp. The rate of gas evolution increased slowly thereafter until at a higher temperature dissolution of the metal with almost explosive violence occurred very suddenly. In the following table are given the temperatures of these two sudden changes of iron in various concentrations of nitric acid :

Conc. of acid, %	100	99	98	95	90
1st temperature	74·5°	74·5°	75·5°	74·5°	75·0°
2nd ,, ...	86·5°	85·0°	83·0°	77·5°	75·0°

The table indicates that the first transition, corresponding with the first evolution of gas, takes place at a definite temperature of 74·5—75·5° independently of the concentration of the acid. The second transition temperature falls with increasing amounts of water in the mixture, until, for 90% acid, the metal passes from the passive state directly to the state of violent dissolution at 75°.

The results may be interpreted as follows : The first transition marks the change from passive to active metal, due to dissolution of the film by the nitric acid ; the reaction is slow, however, because the rate of dissolution of the film can only just keep pace with its rate of re-formation as a result of the reaction. The second transition, or violent dissolution, denotes the complete disappearance of the film, and the temperature at which it occurs falls with decreasing concentration of nitric acid because of the greater solubility of ferric nitrate in weaker nitric acid solutions.

In order to test this hypothesis, the effect of nitric acid on ferric oxide was examined. Powdered ferric oxide was ignited in a silica crucible, cooled in a desiccator, and immediately placed in a test-tube containing 10 c.c. of nitric acid (*d* 1·42). At the ordinary temperature, no coloration was produced in the acid, and even on standing for 24 hours at 30° only the faintest yellow was formed. The rate of dissolution of ferric oxide in nitric acid under these conditions is therefore very roughly comparable with that of passive iron. When the temperature was slowly raised, as in the experiments with passive iron, the first faint yellow colour was produced at 68° ; at 75°, the solution rapidly became deep yellow, and the thin deposits on the sides of the bottom of the tube vanished between 75° and 77°. The heating was continued up to 90° without change other than a general deepening of the yellow colour. The total amount of ferric oxide dissolved was small. In an experiment carried out on freshly ignited ferric oxide in 90% nitric acid, the first faint yellow colour appeared at 64°, and the solution became deep yellow over the range 72—77°. It appears, therefore, that the temperature at which passive iron in nitric acid becomes active coincides with that at which the rate of dissolution of ferric oxide becomes appreciable.

Doubt is often expressed as to the existence of an oxide of iron capable of resisting the solvent action of concentrated acids, and statements are to be found in the literature to the effect that, apart from the inadequacy of known oxides of iron, it is necessary to assume that the oxide will be decomposed on heating in order to account for the activating effect. As shown above, the latter assumption is absolutely unnecessary, and the former objection is due to a misapprehension, for it is patent that freshly ignited ferric oxide dissolves in acids with extreme difficulty. Indeed, it is significant that the three metals which are most readily passivated (iron, chromium, aluminium) all give oxides which when freshly ignited are scarcely dissolved by acids.

Possibly the velocity of dissolution of the oxides is controlled by the existing degree of hydration of the particles. Thus, ordinary, powdered ferric oxide contains much adsorbed water and is much more readily soluble than the ignited material. If this " loosely combined " water is very great, as in a ferric hydroxide gel, the dissolution by nitric acid is immediate. These considerations also apply to the other oxides mentioned.

The reason for using freshly ignited ferric oxide in the experiments described above is that, since the protective film is formed under strictly dehydrating conditions on immersing iron in concentrated nitric acid, the water content of the ferric oxide is bound to be low and its properties will approximate to those of the ignited material.

It is also noteworthy that passive iron does slowly dissolve in concentrated nitric acid, the rate being controlled by the rate of dissolution of the oxide. This view is in complete accord with all the phenomena observed on raising the temperature.

Evidence that the Transition is not of Allotropic Nature.—In addition to the experiments described above, which directly support the oxide-film theory, negative evidence has been obtained which tends to show that the transition temperature does not mark anything in the nature of an allotropic change in the metal itself. Ordinary, active iron immediately becomes blackened when placed in silver nitrate solution, through deposition of metallic silver on its surface, whereas passive iron remains unchanged. If an allotropic change from passive iron to active iron occurs at 75°, then a piece of passive iron, placed in silver nitrate solution, should cause deposition of silver as soon as the temperature reaches 75°. Actually, it was found that iron made passive by nitric acid can be heated in 0·2N-silver nitrate solution to boiling without any deposition of silver occurring. When the iron was kept for a long time in the silver nitrate solution, glistening crystals of silver were formed at isolated spots on its surface, probably representing discontinuities in the film.

Periodic Phenomena in the Activation of Passive Iron.—Periodic phenomena in the activation of aluminium and nickel passivated by anodic polarisation have been described by the author (J., 1926, 2883) as occurring when the electrode is given equal opportunities of being passive or active. A region of periodicity was observed when any of the following three conditions were changed in the direction of increasing activity: (*a*) dilution of the reagent, (*b*) increase of temperature, (*c*) addition of an agent favouring activity.

Some support is lent to the supposition that electro-chemical passivity and that produced by purely chemical means are one and the same phenomenon, for with chemically passive iron similar periodic phenomena are observed when the passivating and activating influences are made nearly equal, by the same three methods. Herrschel (*Ann. Chim. Phys.*, 1833, **54**, 87) found that, in nitric acid intermediate in concentration between that required to passivate iron and that in which iron is rapidly dissolved, a piece of iron became alternately active and passive, gas being evolved in regular pulsations; but the present author, working at 30°, has not been able to verify this.

Periodic phenomena were observed, however, in the experiments on the activation of passive iron by raising the temperature. In every case, at the transition temperature (75°), evolution of gas started in puffs which were at regular intervals in any one experiment, but the intervals varied from 1 to 9 seconds in different experiments. With rise of temperature the frequency of the periods increased. In addition to the visible changes, these periods are accompanied by an audible "pop," evidently caused by the suddenness of evolution of gas at the commencement of each period. The bright surface of the iron darkens during each rapid evolution of gas, and when it is black the bubbles stop; as the surface brightens again, evolution slowly increases, and the cycle is then repeated continuously.

The periodic formation of this visible dark film under these conditions offers additional support to the general explanation of passivity which has been given, for, if a film is being formed under conditions such that it cannot become very protective, such a film will grow and may readily reach visible thickness. At lower temperatures, where the conditions are not inimical to the permanence of a film, it is obvious that a film, once formed, will in virtue of its protective nature cease to grow. In such a case the film will be exceedingly thin.

Periodic phenomena have also been observed in the activation of passive iron by causing it to function as a cathode. This case is analogous to the addition of chlorine ions to anodically passivated nickel, the discharged hydrogen ions being the activating agent here. Heathcote (*Z. physikal. Chem.*, 1900, **35**, 210) noticed that an iron cathode in nitric acid becomes alternately active and passive. In the present investigation, the existence of periods in activation by this means was confirmed, but a detailed study of the effect of current density was precluded by the thinness of the iron foil (0·12 mm.).

Some experiments were also performed on the periodic passivation of iron by anodic polarisation in dilute sulphuric acid, and all the phenomena described in an earlier publication (J., 1926, 2878) were confirmed with the new specimen of iron.

Passivity of Other Metals at Low Temperatures.—Since the passivity of iron immersed in nitric acid is destroyed by heating to 75°, it appeared that other metals, not showing passivity at the ordinary temperature, might become passive towards concentrated nitric acid at lower temperatures.

Cobalt dissolved with great vigour in nitric acid of *d* 1·42 at the ordinary temperature, but became passive immediately at −11°. On raising the temperature slowly, the first bubbles appeared at +9°, and at 25° a sudden vigorous dissolution set in. Thus, the phenomena are precisely similar to those observed with iron at higher temperatures.

Nickel is said to be rendered passive by nitric acid (*d* 1·42) at the ordinary temperature. Of six samples (not analysed) of nickel examined under these conditions, four were rendered passive, and two were very rapidly dissolved. A specimen of the latter variety when added to nitric acid at −11° was immediately rendered passive. Again, the phenomena on warming resembled those of iron, for evolution of bubbles started suddenly at 30°, and at 72° violent dissolution set in.

Copper, when added to concentrated nitric acid at −11°, became covered with a visible, dark grey film and was inert, very little dissolution taking place in 2 days at the ordinary temperature. On warming, sudden violent dissolution occurred at 40°. Thus, the complete analogy with iron is established. The passivity of copper produced by this method is not so permanent as that of iron, for, if the copper be removed from the nitric acid, washed with water, and replaced, it is found to be active, dissolving with vigour. The reason is that the film of cupric oxide is easily soluble in dilute nitric acid at the ordinary temperature, whilst ferric oxide is not. The fact that, in the case of copper, the oxide film has reached visible thickness is in itself an indication of its relatively poor protective value.

Zinc and magnesium were not rendered passive by nitric acid at −11°, but very slow evolution of gas occurred, suggesting that the metals were in the state between the two transition temperatures. On warming, dissolution set in at +20° with such violence as to project the acid from the test-tube.

Discussion.

Not only in the present research, but also from a general consideration of the literature, there is a large amount of evidence which suggests that passivity is a general property exhibited to various extents by all metals under suitable conditions. It therefore seems illogical to limit the term, and with it the explanation, to a few metals having peculiar electronic configurations which happen to exhibit the phenomenon particularly well at the ordinary temperature.

The author has previously pointed out (J., 1926, 2885), from a consideration of the current density–potential curves for anodes of nickel and zinc, and from the existence of periodic phenomena, that there is no essential difference between the anodic polarisation of these two metals. All the evidence appears to support the conclusion that passivity produced by anodic polarisation and by purely chemical means is the same phenomenon, that it is the result of the formation of a film of oxidised material, and that it is exhibited to different degrees depending on the protective properties of the film *under the particular conditions prevailing.*

The Formation of Visible Films in Anodic Passivity.

When Evans succeeded in isolating a normally invisible film on passive iron, difficulty was experienced in reconciling the fact with some observations made by the present author on the anodic passivation of iron (*loc. cit.*). The experiments showed that immediately *before* passivation of the electrode a visible film * appeared on the

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* In the previous publication it was suggested that the observation of this visible film was entirely new. Professor W. J. Müller, of Vienna, has pointed out to me that he had observed its formation earlier (*Z. Elektrochem.*, 1924, **30**, 401).

electrode and was thrown off as soon as evolution of oxygen started. This effect could be particularly well shown through the periodic phenomena when certain current densities were used. It was thus shown that the iron was without a visible film whilst passive, and acquired a visible film every time it became active. Clearly, the visible film is not the protective film responsible for passivity.

The facts can be reconciled completely by taking the following view of the nature of anodic polarisation. When an iron anode is dissolving in dilute sulphuric acid, there will be a certain critical current density above which sulphate ions are discharged more quickly than they can be replaced by diffusion. At this point, some hydroxyl ions will be discharged simultaneously. In addition, since hydrogen ions are repelled from the anode, the hydroxyl-ion concentration in the layer of liquid immediately contiguous to the anode will increase. The net result of these effects is the production of oxide or basic salt at the surface of the anode. Since sulphate ions are still being discharged, the film will not be continuous and thus, in virtue of its non-protective nature, will attain visible thickness. The relatively thick film will have the effect, however, of raising very greatly the effective current density at those areas of the electrode left uncovered. Consequently, at some isolated spots the discharge will consist mainly of hydroxyl ions, giving a perfectly continuous oxide film. Once this protective film has formed, it is immaterial whether sulphate ions or hydroxyl ions are discharged at its surface, for either will produce evolution of oxygen. Although the thin, invisible film cannot then grow in thickness, it will extend sideways, rapidly covering the whole electrode. At this stage, oxygen is evolved at the surface of the *invisible* film, causing the discontinuous *visible* film to be thrown off the electrode.

This view is supported by experiments which have been carried out on the influence of speed of rotation of the anode on periodic electrochemical passivity, and it is hoped to communicate the results shortly.

Meanwhile, an almost identical suggestion as to the rôle of the visible film has been published by W. J. Müller (*Monatsh.*, 1927, **48**, 61, 559; Müller and Noack, *ibid.*, p. 293), who differs from the present author, however, in supposing that the high effective current density caused by the partial covering of the electrode produces a change in the nature of the metal itself, to which passivity is due rather than to a protective film. Müller arrived at this view from a consideration of the time effect in passivation, and it is noteworthy that the same conclusions regarding the preliminary processes of electrochemical passivity have been reached by each of us from different points of view.

Summary.

Reproducible values for the lowest concentration of nitric acid necessary to passivate electrolytic iron can be obtained if care is taken to ensure that the iron passes rapidly through the liquid surface, which has an activating influence.

When passive iron is whirled at 3000 r.p.m. in nitric acid of this concentration it becomes active after a short induction period. This is shown to be in accordance with the oxide-film theory, the induction period representing the time for removal of the film, but is at variance with the theory advanced by Smits.

When passive iron in concentrated nitric acid is heated, dissolution of the metal begins at 74·5—75·5°, independently of the concentration of the acid.

Freshly ignited ferric oxide is not appreciably dissolved by concentrated nitric acid until this temperature is reached, and it is shown that this temperature does not represent an allotropic change in the metal.

Other metals can be passivated by nitric acid at lower temperatures; *e.g.*, at $-11°$ copper becomes passive in concentrated nitric acid and is covered by a visible oxide film when in this state.

Periodic phenomena were observed in the activation of passive iron, both by increase of temperature and by cathodic polarisation. It is concluded that passivity produced by anodic polarisation and by purely chemical means is the same phenomenon, that it is the result of the formation of a film of oxidised material, and that it is exhibited to different degrees, depending on the protective properties of the film under the particular conditions prevailing.

A theory of the mechanism of anodic polarisation is advanced.

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