# 630. *The Mechanism of Inhibition of the Corrosion of Iron by Sodium Hydroxide Solution.*

By J. E. O. MAYNE, J. W. MENTER, and M. J. PRYOR.

When iron, freed from its original air-formed oxide film, is immersed in 0·1N-sodium hydroxide, containing dissolved oxygen, it becomes covered with a thin film of $\gamma$-$Fe_2O_3$; the view is put forward that this film is responsible for passivity and results from a heterogeneous reaction between oxygen, dissolved in the solution, and the iron. A de-aerated solution of 0·1N-sodium hydroxide attacks iron very slowly; the reaction is controlled mainly by high polarisation of the cathodic discharge of hydrogen ions.

AN investigation into the mechanism of inhibition of the corrosion of iron by a solution of sodium hydroxide was carried out by Travers and Aubert (*Compt. rend.*, 1932, **194**, 2308) who measured the potential of electrolytic iron immersed in N-sodium hydroxide. In the presence of air they obtained a potential of $+0·002$ v., but when the solution was de-aerated by the prolonged bubbling of purified nitrogen, the potential was $-0·718$ v. (Throughout this paper all potentials are expressed on the standard hydrogen scale.) They concluded that inhibition was due to dissolved oxygen and not to hydroxyl ions, although they made no measurement of the rate of corrosion in the de-aerated solution. Lochte and Paul (*Trans. Electrochem. Soc.*, 1933, **64**, 169) repeated these measurements, using 0·1N-sodium hydroxide and a method of de-aeration which involved an apparatus open to the air. They recorded a potential of −0·025 v. in the presence of air and −0·400 v. when the solution was de-aerated. U. R. Evans (" Metallic Corrosion, Passivity and Protection," Edward Arnold & Co., 1946, p. 543) discussed these results and concluded that " The passivity resulting from the simultaneous presence of oxygen and alkali is connected with the diminished solubility of ferrous hydroxide in solutions rich in hydroxyl ions; instead of passing into solution, the ferrous hydroxide forms a solid film and is converted to a hydrated ferric oxide in physical contact with the metal."

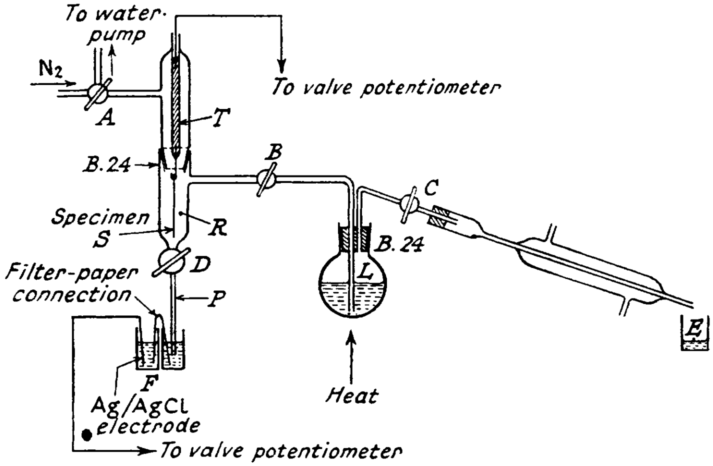
Kabanov and Leikis (*Acta Physicochem. U.S.S.R.*, 1946, **21**, 769) subjected iron, previously reduced in hydrogen at 700—900°, to anodic polarisation with a small constant current density, in 2N-sodium hydroxide saturated with hydrogen. The examination was extended in a later paper (Kabanov, Burnstein, and Frumkin, Faraday Soc. Discussions, 1947, **1**, 259) which showed that the anodic polarisation curve had two arrests corresponding to processes which take place at constant potentials. The first arrest, at the most negative potential was shown to be characteristic of the formation of ferrous hydroxide, and the second, which is half as long as the first, to the oxidation of ferrous hydroxide to ferric hydroxide. If more current was passed, the potential then rose rapidly by about 1 v. and the specimen became passive, an effect attributed to the formation of a " passivating oxide."

It was shown recently by Mayne and Pryor (*J.*, 1949, 1831) that the film formed on initially film-free iron by solutions of chromic acid and potassium chromate, containing dissolved oxygen, consisted mainly of $\gamma$-$Fe_2O_3$. Since exposure of iron to air would result in the formation of films of similar composition (Iitaka, Miyake, and Iimori, *Nature*, 1937, **39**, 156; Nelson, *J. Chem. Physics*, 1937, **5**, 252; Vernon, *Trans. Faraday Soc.*, 1935, **31**, 1677) some doubt existed as to how much of the oxide film, formed during passivation, was produced by the chromate rather than by the dissolved oxygen. In order to obtain further information regarding the part played by dissolved oxygen during inhibition by potassium chromate and by sodium hydroxide solutions, the following investigation was carried out.

## EXPERIMENTAL.

*Materials.*—The iron used in these experiments had the same composition as that used in a previous investigation (Mayne and Pryor, *loc. cit.*). Each specimen was cut from sheet 0·02 cm. thick and was degreased in benzene, abraded with 3/0 emery, swabbed with acetone, and dried; the size of the specimen varied according to the apparatus used.

FIG. 1.

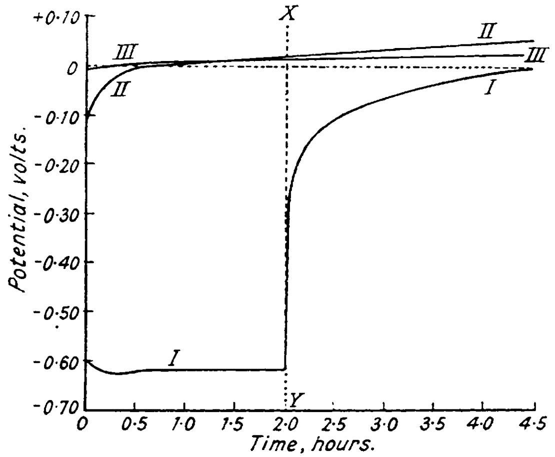


*Preliminary Investigation.*—Removal of oxygen from water is a slow process, and the work of Evans and Mears (*J. Soc. Chem. Ind.*, 1933, **52**, 349T) has indicated that the degree of de-aeration obtained by previous workers may not have been very high. Consequently our solutions were de-aerated by boiling accompanied by the continuous bubbling of purified nitrogen in a closed apparatus (Fig. 1).

The specimen *S* (5 × 0·5 cm.; degreased and abraded) was suspended in the reaction chamber *R* from a stout platinum wire; this wire was sealed into the tube *T*, which was partly filled with mercury during the experiments in order to obtain electrical contact with the specimen. 50 Ml. of the solution under examination were placed together with 50 ml. of distilled water in the flask *L*. The apparatus was flushed out with nitrogen, purified by passage over reduced copper turnings at 450° and then over soda lime. The nitrogen entered the apparatus through the tap *A*, bubbled through the solution in the flask *L*, and finally ran to waste through the condenser. After 30 minutes the solution was heated to boiling and water distilled into the beaker *E*. When approx. 15 ml. had collected, the solution was cooled and the procedure repeated three times, continuously in a current of nitrogen, until the 50 ml. of water originally added to the solution had been distilled over into *E*. The solution in *L* was then allowed to cool to room temperature, tap *C* was closed, *A* was opened to the water-pump, and 10 ml. of solution were sucked over into the reaction chamber *R* so that four-fifths of the specimen was immersed. Nitrogen was then re-admitted through *A*, the tap *D* in the reaction chamber opened, and solution forced down the capillary tube *P*. The vessel *F* contained a silver/silver chloride electrode in 0·1N-potassium chloride solution bridged by a filter-paper strip to a similar chloride solution in contact with the liquid in *R*; values of the potential difference between this electrode and the iron specimen could be measured by means of a " Cambridge " valve potentiometer, after the tap *D* had been rotated several times so that the grease on it was wetted with a layer of the conducting electrolyte. Since junction potentials in these decinormal solutions were only of the order of 10—15 mv. they were neglected throughout the investigation.

After the potential measurements in the de-aerated solution were complete, usually after 2 hours, the flask *L* was removed and air sucked over the surface of the solution in *R* by means of the water-pump. The tap, *B*, was inserted in the apparatus so that it could be used for film stripping experiments.

FIG. 2.



*I. De-aerated* 0·1N-NaOH. *Air admitted at X–Y after* 2 *hours.*
*II.* 0·1-NaOH, *in contact with air for whole experiment.*
*III. De-aerated* 0·1M-$K_2CrO_4$. *Air admitted at X–Y after* 2 *hours.*

Some of the results obtained in this apparatus are shown in Fig. 2; it can be seen from curve III that the potential of an iron specimen immersed in de-aerated 0·1N-potassium chromate is unchanged on the admission of air, whereas the potential of an iron specimen immersed in 0·1N-sodium hydroxide rises by some 600 mv. in a comparatively short time upon the admission of air to the apparatus (curve I). In experiments with 0·1N-sodium hydroxide the potential of the iron was found to rise slowly during 20 hours and it was concluded that the de-aeration of the solution was insufficiently complete. Consequently it was decided (1) to investigate the reactions taking place between iron and sodium hydroxide solutions containing dissolved oxygen (corresponding to the upper portion of curve I) by an electron-diffraction examination of the stripped film, and (2) to investigate the reactions taking place between iron and de-aerated sodium hydroxide solution under conditions of more complete de-aeration.

*Reaction between Iron and Sodium Hydroxide in the Presence of Air.*—An iron specimen, 5 × 1 cm., was passivated for 2 days in 0·1N-sodium hydroxide, containing dissolved oxygen, by a similar method to that previously described for chromate solutions (Mayne and Pryor, *loc. cit.*), in which the air-formed film was first destroyed by treatment with dilute hydrochloric acid. The passivated specimen was dipped in a 0·1% solution of Formvar 1595, in a 3 : 2 mixture of trichloroethylene and acetone, and allowed to dry; this technique, which facilitates the manipulation of the stripped film, was developed by Vernon, Nurse, Clews, and Calnan (*Nature*, 1949, **164**, 909). The reinforced film was then stripped from the specimen by the method of Vernon, Wormwell, and Nurse (*J.*, 1939, 621), in the apparatus shown in Fig. 1. Portions of the stripped film were floated on to copper grids and examined by electron diffraction, using the transmission method. This was carried out in the Metropolitan Vickers EM3 Electron Microscope, operating at 75 kv. By reducing the magnification of the first projector lens of this microscope it is possible to obtain a focused image of the transmission diffraction pattern of a specimen. An additional aperture may be inserted above the first projector which selects an area of approx. 10-$\mu$. diameter for examination. It is thus possible by the operation of a switch to pass from the microscopical examination of a particular area of the specimen to the diffraction pattern of the same area. The instrument thus permits a more sensitive analysis of the structure of the film than does the conventional electron-diffraction camera. (The differences between the results obtained with the two types of instrument will be discussed in a later publication.)

Examination of the stripped film in the electron microscope shows that there are large areas which are very homogeneous. In some places, however, there are collections of more dense particles of the order of 1 $\mu$. in diameter. The diffraction pattern from the homogeneous areas consists of continuous rings agreeing very well with the $\gamma$-$\mathrm{Fe_2O_3}$ or $\mathrm{Fe_3O_4}$ structure. A typical pattern is shown in Fig. 5. The sharpness of the rings varies from one part of the film to another, showing that there is some variation in crystal size in the film. The rings are sometimes arced, indicating a preferred orientation of the grains in the film. The observed spacings for such a film are compared in Table I with the *X*-ray values. As the size of the diffraction pattern is a function of the magnification of the various lenses, the lattice spacings have been calculated by selecting a prominent known line of the $\gamma$-$\mathrm{Fe_2O_3}$ pattern as standard.

TABLE I.

| Ring radius, *R* (cm.). | Intensity. | Lattice spacing *d* (A.). | $\gamma$-$\mathrm{Fe_2O_3}$ spacing * (A.). | Ring radius, *R* (cm.). | Intensity. | Lattice spacing *d* (A.). | $\gamma$-$\mathrm{Fe_2O_3}$ spacing * (A.). |
|---|---|---|---|---|---|---|---|
| 1·27 | vs | 2·935 | 2·935 | 2·20 | w | 1·695 | 1·70 |
| 1·415 | w | 2·63 | 2·63 | 2·35 | ms | 1·585 | 1·60 |
| 1·48 | ms | 2·52 | 2·51 | 2·56 | vs | 1·46 | 1·47 |
| 1·80 | ms | 2·065 | 2·08 | 2·95 | ms | 1·26 | 1·27 |
| 2·04 | w | 1·83 | 1·86 | 3·24 | w | 1·15 | 1·15 |

vs = very strong, s = strong, ms = medium, w = weak.

* Calculated from $a_0 = 8{\cdot}32$ A.

If, however, an area of the film containing the denser particles is brought into the field the pattern shows a striking change. There is often pronounced arcing of the rings and sometimes even a cross grating pattern of spots superimposed on the ring pattern (see, for example, Fig. 6). It is found that the cross grating spots coincide with rings of the $\gamma$-$\mathrm{Fe_2O_3}$ pattern. Thus these massive particles have the same structure as the bulk of the film. Spacings calculated from a photograph of this type are tabulated in Table II.

TABLE II.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Ring radius, *R* (cm.) ......... | 0·765 | 0·90 | 1·255 | 1·48 | 1·537 | 1·80 | 1·935 | 2·20 | 2·335 |
| *d* (A.) .......................... | 4·86 | 4·13 | 2·96 | 2·51 | 2·42 | 2·065 | 1·925 | 1·695 | 1·60 |
| $\gamma$-$\mathrm{Fe_2O_3}$ * ..................... | 4·82 | 4·16 | 2·935 | 2·51 | 2·41 | 2·08 | 1·91 | 1·70 | 1·60 |
| Ring radius, *R* (cm.) ......... | 2·52 | 2·65 | 2·93 | 2·97 | 2·09 | 3·22 | 3·35 | 3·45 | 3·59 |
| *d* (A.) .......................... | 1·48 | 1·31 | 1·27 | 1·25 | 1·21 | 1·16 | 1·11 | 1·08 | 1·035 |
| $\gamma$-$\mathrm{Fe_2O_3}$ * ..................... | 1·47 | 1·315 | 1·27 | 1·25 | 1·20 | 1·16 | 1·11 | 1·08 | 1·04 |

* Calculated from $a_0 = 8{\cdot}32$ A.

Closer examination of some photographs has disclosed a number of weaker sharp spots scattered in random radial directions over the plate, many of which do not lie on rings and do not coincide with $\gamma$-$\mathrm{Fe_2O_3}$ spacings. The spacings of these spots are listed for a number of different plates in Table III.

TABLE III.

*Calculated spacings of spots* (A.).

| Plate 1. | Plate 2. | Plate 3. | Plate 4. | Lepidocrocite *X*-ray spacing (A.).* | Index. | Plate 1. | Plate 2. | Plate 3. | Plate 4. | Lepidocrocite *X*-ray spacing (A.).* | Index. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3·86 | 3·91 | — | — | 3·87 | 100 † | — | — | 1·535 | — | 1·54 | 071 |
| 3·31 | 3·35 | — | — | 3·29 | 120 | — | 1·525 | 1·525 | — | 1·53 | 002 |
| R | R | R | R | 2·97 | 011 | 1·515 | 1·51 | 1·515 | — | 1·52 | 231 |
| — | — | 2·42 | 2·44 | 2·43 | 140 | 1·48 | — | 1·485 | — | 1·49 | 022 |
| 2·355 | 2·365 | — | 2·365 | 2·36 | 111 | — | 1·43 | — | 1·435 | 1·43 | 171 |
| 2·31 | 2·30 | — | 2·315 | — | — | — | — | 1·41 | 1·41 | 1·42 | 260 |
| R | R | R | R | 2·08 | 131, 060 | 1·395 | — | 1·395 | 1·40 | — | — |
| 1·96 | — | — | — | — | — | 1·375 | — | — | — | 1·37 | 122, 042 |
| 1·915 | 1·90 | 1·92 | 1·92 | 1·93 | 051, 200 | 1·35 | 1·345 | 1·335 | — | — | — |
| — | — | — | 1·84 | 1·85 | 220 | 1·28 | — | — | — | — | — |
| — | — | — | 1·815 | 1·83 | 160 | 1·26 | — | 1·27 | — | 1·265 | 091 |
| 1·71 | — | 1·72 | — | 1·73 | 151 | — | 1·24 | — | — | 1·23 | 062 |
| — | 1·57 | — | — | 1·56 | 080 | — | — | 1·185 | — | 1·18 | 222 |

* $a_0 = 3{\cdot}87$ ; $b_0 = 12{\cdot}51$ ; $c_0 = 3{\cdot}06$.

† Prohibited reflection.

It is difficult to attribute an incomplete set of spacings unambiguously to any particular structure. The only course open is to find out how the spacings which are observed compare with those of possible chemical constituents of the specimen. In this instance the only possible compounds are sodium carbonate (arising from sodium hydroxide incompletely washed out of the film) and lepidocrocite ($\gamma$-$\mathrm{Fe_2O_3,H_2O}$). No satisfactory fit could be obtained with sodium carbonate, whereas nearly all the spots observed show good agreement with possible spacings of lepidocrocite.

The pattern of lepidocrocite is difficult to distinguish from that of $\gamma$-$\mathrm{Fe_2O_3}$, as a number of prominent spacings in each pattern are almost identical. Many spots are in fact observed on the $\gamma$-$\mathrm{Fe_2O_3}$ rings

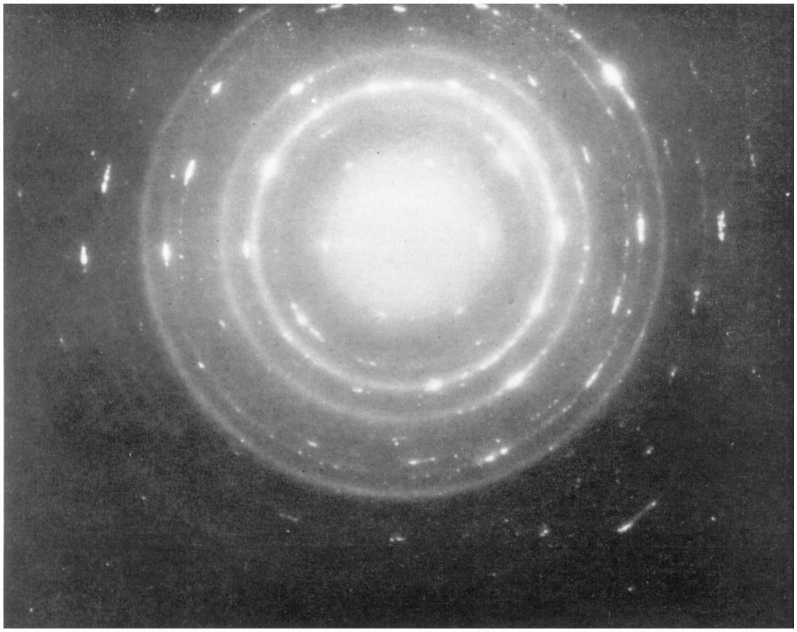


Fig. 6.

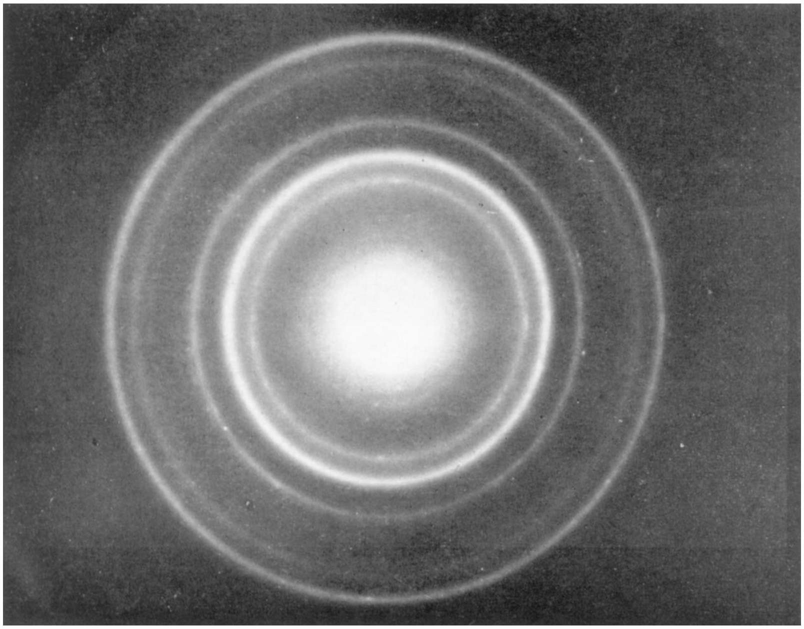


Fig. 5.

[*To face p.* 3232.

and, while some of these certainly arise from the massive particles mentioned above, some of them could be due to lepidocrocite particles if these are present. The lattice spacings of such spots have therefore been included in Table III and indicated by the letter R.

The two most prominent lines of the lepidocrocite patterns are at 6·25 A. (relative intensity 100%) and 3·29 A. (relative intensity 90%). The distinction between lepidocrocite and $\gamma$-$Fe_2O_3$ is most readily shown by the presence or absence of these spacings. The latter spacing is clearly observed on several plates, but the former never. 6·25 A. is the spacing of the (020) planes which lie in a direction of very easy cleavage. It is possible, therefore, that the particles are only a few molecular layers thick in a direction perpendicular to the (010) planes so that the diffracted intensity from these planes is very small.

Another group of lines 1·556, 1·54, 1·53, 1·522, 1·433 A. are found in lepidocrocite but not in $\gamma$-$Fe_2O_3$, and the occurrence of these is further evidence in support of the presence of lepidocrocite.

FIG. 3.

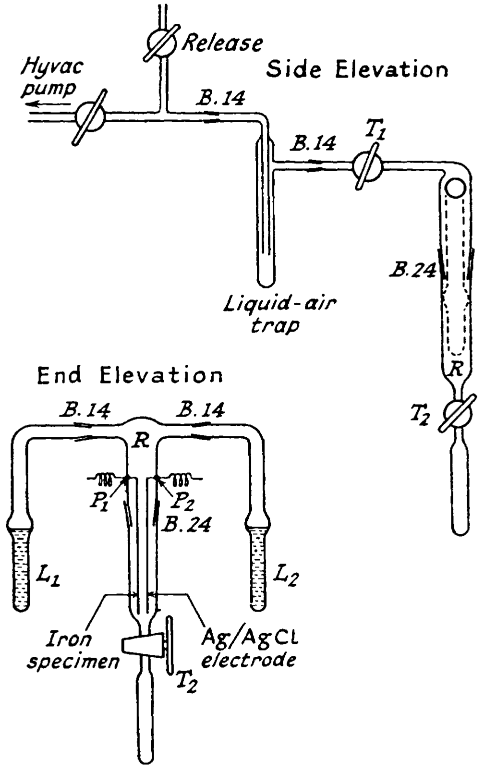
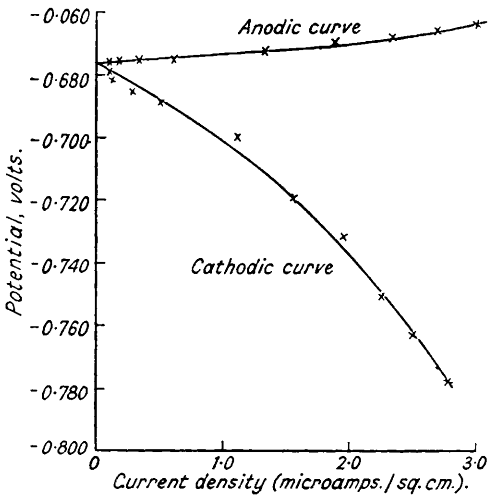


FIG. 4.



It is difficult to give an upper estimate of the relative quantity of lepidocrocite in the film. The limited number and intensity of the spots suggests that it must be very small; there is often only one spot on a plate corresponding to a particular lattice spacing.

In summarising, we may say that the bulk of the stripped film consists of $\gamma$-$Fe_2O_3$. In addition, there are a considerable number of particles of the same material of the order of 1 $\mu$. in diameter scattered on the film. Finally, there is indirect but satisfactory evidence for the presence of very small quantities of lepidocrocite ($\gamma$-$Fe_2O_3,H_2O$).

*Reaction between Iron and De-aerated Sodium Hydroxide Solution.*—In order to obtain improved de-aeration, a vacuum technique was evolved, based on the fact that the solubility of gases in solids is very appreciably lower than that in liquids.

The apparatus, Fig. 3, was made from soda-glass, except the parts that were to be dipped into liquid air, which were made from Pyrex. 20 Ml. of 0·1N-sodium hydroxide were placed in the side arm, $L_1$, and 20 ml. of 0·04N-hydrochloric acid in the other, $L_2$. The iron specimen (degreased and abraded) was suspended from a platinum wire $P_1$ sealed into the side of the reaction-vessel $R$ so that an area measuring 2 × 0·5 cm. was exposed to the solution. A silver/silver chloride electrode was similarly suspended from the platinum wire $P_2$. All connections in the apparatus were effected by means of either B.14 or B.24 " Quickfit " joints; the taps used were of the 6-mm.-bore vacuum type. The joints were all carefully greased with Apiezon L grease. The experimental procedure was as follows :

The solutions in $L_1$ and $L_2$ were carefully frozen from the bottom by liquid air, taps $T_1$ and $T_2$ were opened, and the system was evacuated by a Hyvac two-stage pump capable of reducing the pressure to

$3 \times 10^{-4}$ mm. of mercury. After 10 minutes' pumping, $T_1$ was closed, and the frozen solutions in $L_1$ and $L_2$ were allowed to melt. Under reduced pressure, dissolved air was rapidly expelled from the solutions. These were then refrozen, the system was evacuated for 10 minutes, and the procedure was repeated. In the first experiments carried out in this apparatus, the cycle was repeated three times. In the later cycles, it was observed that evolution of gas from the solutions on melting was practically imperceptible. In the subsequent experiments, however, de-aeration was achieved by carrying out six cycles, together with a desorption of oxygen from the walls of the apparatus. This was effected by heating the walls of the apparatus with a smoky flame, while $T_1$ was open and the system was being evacuated. When the de-aeration process was judged to be complete, $T_1$ and $T_2$ were closed and the solutions allowed to come to room temperature.

The air-formed film on the specimen was destroyed by 5 minutes' treatment with the dilute hydrochloric acid in $L_2$. 10 Ml. of the acid were transferred to the reaction chamber $R$ by rotating $L_2$ slowly about the joint connecting it to $R$. The acid was run out of $R$ by opening $T_2$ and was replaced by 10 ml. of 0·1N-sodium hydroxide from $L_1$. A trace of chloride from the previous treatment remained and was sufficient to allow the silver/silver chloride electrode to function. Values of the potential difference between the iron specimen and the electrode were measured with a valve potentiometer. The concentration of chloride ions was determined at the end of the experiment by bridging to another silver/silver chloride electrode in 0·1N-potassium chloride; in most experiments the concentration of residual chloride ions was within the range 0·001—0·0001N. The iron in solution was determined (after acidification) by the thioglycollic acid method (Swank and Mellon, *Ind. Eng. Chem.*, *Anal.*, 1938, **30**, 7).

When the solutions were de-aerated by three of the cycles previously described, the potential of the specimen slowly rose during 72 hours. If, however, the solutions were de-aerated by six freezing cycles, and air was desorbed from the walls as described, the potential of the specimen, which was initially −0·645 v., fell to −0·720 v. in 20 minutes, rose to −0·694 v. in 24 hours, and remained constant at this value for a further 48 hours. It was concluded, therefore, the the upward drift in potential previously observed was caused by the incomplete removal of oxygen. At the end of the experiment the vacuum was broken and the iron content of the solution was found to be 14 $\mu$g. In this experiment the original air-formed film on the specimen was removed by treatment with hydrochloric acid which left behind a small quantity of chloride ions. Further experiments were therefore carried out in which iron, carrying its air-formed film, was exposed to 0·1N-sodium hydroxide free from chloride, and the iron contents of the solutions were compared with those obtained from similar specimens exposed to 0·1N-sodium hydroxide in contact with air. In an anaërobic test lasting for 25 days, the solution contained 42 $\mu$g. of iron, whereas in the presence of air no iron could be detected after a similar exposure period.

In order to obtain further information regarding the mechanism of the reaction between iron and de-aerated 0·1N-sodium hydroxide, a second iron electrode was introduced into the apparatus shown in Fig. 3, and both anodic and cathodic polarisation curves were obtained by maintaining a small potential difference across the iron electrodes and measuring their change in potential with current density by means of the standard silver/silver chloride electrode. The results obtained are shown in Fig. 4.

## DISCUSSION

During the preliminary investigation it was found that the potential of an iron specimen still carrying its air-formed film was approximately −0·630 v. in de-aerated 0·1N-sodium hydroxide (Fig. 2, curve I); when air was admitted to the apparatus the potential rose rapidly, becoming positive on the standard hydrogen scale—a result in accordance with previous work. Using the apparatus shown in Fig. 3, in which de-aeration was more effective, and iron specimens from which the air-formed film had been removed by acid pre-treatment, it was found that (1) the solution contained a small amount of iron,* (2) the potential of the specimen fell to a minimum value of −0·720 v., and (3) the potential remained constant in the region of −0·700 v. for 48 hours.

It appears, therefore, that iron is very slowly attacked by de-aerated 0·1N-sodium hydroxide; the fact that, under these conditions, the potential–time curve is almost flat suggests that the electrochemical attack is mainly under cathodic control; had the control been anodic, *i.e.*, governed by film formation, the curve would have sloped upwards. This view is confirmed by the polarisation curves (Fig. 4), which show that the anodic curve, at very low current densities, is almost flat while the cathodic curve has a much steeper slope. It should be noted that these polarisation curves are the continuation of the curves representing a corroding specimen; see, for instance, Simnad and Evans (*Trans. Faraday Soc.*, 1950, **46**, 175).

Thus it appears that in a de-aerated solution of 0·1N-sodium hydroxide very slow electrochemical attack takes place on an iron specimen with the probable formation of ferrous hydroxide as the anodic product. Furthermore the rate of attack appears to be largely governed by the slow cathodic discharge of hydrogen ions and not by the formation of a film of ferrous hydroxide at anodic areas, which is in accordance with the views of Frumkin and his co-workers (*loc. cit.*). They state that under conditions of anodic polarisation " ferrous hydroxide was deposited as

---

* The iron could not have arisen from the acid treatment since similar quantities were found in experiments, in which no acid was used.

a gelatinous, porous, precipitate weakly bound to the metal. This was concluded from the failure to detect any ohmic resistance on an electrode covered with a deposit of $Fe(OH)_2$ although this compound is itself non-conducting." Frumkin believed that the ferrous hydroxide layer formed on iron anodes in de-aerated 2N-sodium hydroxide resulted from hydrolysis of $HFeO_2'$ ions and not from precipitation of anodically produced ferrous ions, since he was able to infer that the rate of formation of ferrous ions at the potential of the formation of $Fe(OH)_2$ was far too low to accord with his experimental results. Schrader (*Chem. News*, 1929, **138**, 354) has stated that only when the concentration of alkali exceeds 0·5N. is iron present mainly in the form of the univalent $HFeO_2'$ ions. Consequently it appears that under the conditions studied by the present authors the ferrous hydroxide results mainly from the precipitation of anodically formed ferrous ions. Furthermore it must be borne in mind that under conditions of natural corrosion in de-aerated 0·1N-sodium hydroxide the rate of attack is limited mainly by high polarisation of the cathodic discharge of hydrogen ions and that insufficient current passes to carry the anodic reaction further than the formation of ferrous hydroxide.

When iron is exposed to 0·1N-sodium hydroxide containing dissolved air the potential quickly becomes positive to hydrogen (Fig. 2, curve II). Furthermore a thin film, identified by electron diffraction as $\gamma$-$Fe_2O_3$ together with a very small quantity of lepidocrocite, is formed on the iron which is in the passive condition. The observations of Kabanov, Burnstein, and Frumkin (*loc. cit.*) that a relatively thick layer of anodically produced hydrated ferric oxide does not alone give rise to passivity and is formed at a potential of only about 100 mv. more positive than is ferrous hydroxide, suggest that the small quantity of lepidocrocite in the film does not play the major role either in instituting passivity or in developing the positive potentials observed in the presence of air. Thus the view is put forward that oxygen dissolved in solution is primarily responsible for passivity. It is considered that this oxygen becomes adsorbed on the surface of the iron and takes part in a heterogeneous reaction with surface iron atoms leading to the formation of a thin film of $\gamma$-$Fe_2O_3$. This film is believed to grow until it becomes practically impervious to oxygen and to ions, after which it prevents corrosion.

It was shown in a previous paper (Mayne and Pryor, *loc. cit.*) that the film formed on iron by a 0·1N-potassium chromate containing dissolved air, was composed mainly of $\gamma$-$Fe_2O_3$. It has now been shown that the potential of an iron specimen immersed in 0·1N-chromate is unaffected by dissolved oxygen (Fig. 2, curve III); since potentials of the order of zero (on the hydrogen scale) could hardly be obtained unless the metal is covered with an impervious film, it appears that potassium chromate, in the absence of dissolved oxygen, can oxidise the surface of film-free iron to $\gamma$-$Fe_2O_3$ by the heterogeneous mechanism previously suggested. Such is not the case with sodium hydroxide which is not itself an oxidising agent.

Schikorr (*Z. anorg. Chem.*, 1930, **191**, 322) has shown that $\gamma$-$Fe_2O_3,H_2O$ is formed by the slow interaction of oxygen and ferrous hydroxide; thus the $\gamma$-$Fe_2O_3,H_2O$ arises from the ferrous hydroxide produced either directly or indirectly by electrochemical action—a matter studied by Evans (*op. cit.*, pp. 5, 11). It should be noted that the distribution of the $\gamma$-$Fe_2O_3,H_2O$ through the film is not known; the particles may be evenly dispersed or they may be on the surface; furthermore its presence may be necessary for inhibition.

Thus it appears that when iron is immersed in water or solutions of sodium hydroxide, saturated with air, two reactions may occur: (1) electrochemical attack with the production of hydrated corrosion products, *e.g.*, ferrous hydroxide, either directly or indirectly, which then reacts with oxygen forming $\gamma$-$Fe_2O_3,H_2O$; and (2) a direct reaction between iron and dissolved oxygen with the formation of $\gamma$-$Fe_2O_3$.

Electrochemical attack will decrease as the pH of the solution rises, either by a progressive increase in cathodic polarisation, as suggested by the results obtained by Chyzewski and Evans (*Trans. Electrochem. Soc.*, 1939, **76**, 220), or by anodic polarisation brought about by the formation of lepidocrocite; on the other hand the reaction between iron and oxygen is independent of pH and will therefore become the important reaction in solutions of high pH. Conversely a fall in pH will favour the electrochemical reaction with the production of ferrous hydroxide, which will lower the concentration of oxygen at the metal surface, thereby preventing the formation of a film of $\gamma$-$Fe_2O_3$.

This tentative theory of the corrosion and inhibition produced by water and solutions of sodium hydroxide is consistent with the results obtained by Lee (*Trans. Faraday Soc.*, 1932, **28**, 707), Bengough and Wormwell (Report of the Chemistry Research Board for the Triennial Period ended 31st Dec., 1937, H.M.S.O., 1938, p. 17), and Groesbeck and Waldron (*Proc. Amer. Soc. Test Mat.*, 1931, **31**, II, 286), in their investigation into the effects of oxygen on the rate of corrosion of steel in water and in dilute chloride solutions.

The authors are indebted to the British Iron and Steel Research Association (J. E. O. M. and M. J. P.) and to the Royal Society (J. W. M.) for financial assistance, and to Dr. F. P. Bowden and Dr. U. R. Evans, in whose laboratories the work was carried out, for encouragement and advice. They thank Mr. R. F. King for help with the electron microscope, and Dr. J. N. Agar and Dr. F. Wormwell for useful criticism.

RESEARCH LABORATORY ON PHYSICS AND CHEMISTRY OF RUBBING SOLIDS,
DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF CAMBRIDGE.
DEPARTMENT OF METALLURGY, UNIVERSITY OF CAMBRIDGE.

[*Received, August 2nd*, 1950.]