XV.—*The Electrical Behaviour of Surfaces of Corroding Iron.*

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The corrosion of iron is usually the result of electrochemical action caused by the passage of currents between portions of the metal which are at different potentials with respect to an electrolyte in contact with them. The differences of potential are produced by differential aeration (Evans, " Corrosion of Metals," Chap. VI), but the conditions under which they are produced generally depend on such a variety of factors that it has not been possible to obtain much information as to the mechanism of their production and behaviour, and this lack of knowledge necessarily limits our control of the phenomenon.

The present investigation was initiated with a view to elucidate the mechanism giving rise to corrosion currents, but it immediately became evident that an important part of the work must be the attainment and recognition of a standard condition for metal and solution. It was found that two apparently identical pieces of electrolytic iron, cut from the same sheet and having similarly ground surfaces, gave widely different potentials on immersion in an electrolyte and had distinctly different subsequent histories. This point is illustrated by Curves 1 and 2, Fig. 2, in which the potential of an electrode immersed in an electrolyte is plotted against time of immersion.

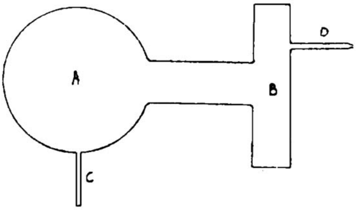
As a result of our work, we reach the following conclusions. When a piece of iron is placed in an air-free electrolyte, there is a stable potential to which it tends, probably ultimately determined by the hydrogen-ion concentration of the solution. It does not immediately acquire this potential, but after prolonged immersion the stable condition, which proved to be easily reproducible, is attained, and the behaviour of the metal when subjected to experiments using this condition as a starting point is also reproducible.

Curves 3, 4, 5, and 6 of Fig. 2 are of a similar type to 1 and 2, but relate to an electrode first brought into this standard state, the nature of which was found to be almost independent of the composition of the iron. Iron corroding in a neutral electrolyte not rendered air-free is in a stable condition which has most of the characteristics of that just described, although it depends to some extent on the degree of aeration of the electrolyte.

EXPERIMENTAL.

Apparatus.—The apparatus used (Fig. 1) consisted of a Pyrex-glass flask, A, and a tube, B, forming a T-piece with the neck; B was the half-cell containing the iron electrode, and A served as a reservoir of air-free electrolyte. The apparatus was first placed with B above A and the solution was boiled for about ½ hour to free it from air. Towards the end of the boiling, oxygen-free nitrogen was admitted sparingly through the capillary tube, C. After the boiling, the side tube, D (which later served to make contact with the calomel electrode), was blocked with filter-paper, the apparatus was turned on its side, B and D were filled with solution, and the whole was maintained under a pressure of nitrogen of about one foot of water. The iron electrodes were inserted through rubber bungs into the ends of B. Two electrodes were sometimes used in order to carry out two experiments at the same time. It was found possible to make the changes from electrode-bearing bungs to plain bungs quickly and without contaminating the solution noticeably with oxygen (see below). The pressure applied gradually through C made it easy to get rid of any bubbles of air that might tend to lodge under the bungs. This cell was connected through D to a calomel electrode and the potentials of the electrodes were measured against it by a potentiometer in the usual way.

FIG. 1.

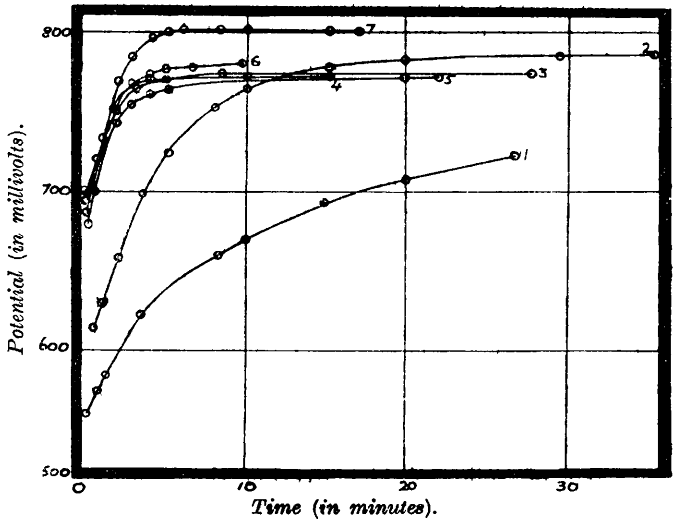


Earlier experiments with more complicated apparatus had shown (1) that it was possible to expose the surface of the air-free electrolyte for a few moments to air, as when changing bungs to make an exposure or insert an electrode, without producing contamination, and (2) that it was highly desirable to have the reservoir containing the air-free solution in direct communication with the cell without the intervention of rubber-tube connexions.

The Standard State.—Curves 3, 4, 5, and 6 of Fig. 2 are typical of a series of 20 obtained with several electrodes which had all been previously immersed for at least 12 hours in an air-free *N*/2-potassium sulphate solution and then exposed for 1 minute to air and replaced in the solution. All potentials are given against the saturated calomel electrode, but no corrections were made for liquid–liquid junction potentials, etc., so the values are not to be considered as absolute. Except where stated to the contrary, all the electrodes were made from a sheet of electrolytic iron kindly given to us by Mr. U. R. Evans, and having the following impurities: C, 0·04: Mn, 0·025; Si, 0·010; S, 0·013; P, 0·017; Ni, 0·09%; Cr, nil.

The similarity of these four curves and their wide difference from curves 1 and 2 is striking. The last two curves represent the behaviour of electrodes from the same sheet of metal, ground with emery paper under the same conditions, and then immersed in air-free $N/2$-potassium sulphate. Curves 3 and 4 were given by the same electrode, but the surface had been reground between the two experiments; Curves 5 and 6 were obtained with separate electrodes. Different samples of electrolyte were used in each of these four cases. Curve 7 shows the result of similar treatment when the condition of the solution is slightly altered. It is intended to investigate further the cause of the different equilibrium potentials obtained with different solutions. The indications at present are that the completeness with which the solution is freed from oxygen partly determines these potentials, but it is also fairly certain that hydrogen-ion concentration exercises a marked effect. For solutions thoroughly boiled and left standing in contact with iron for 12 hours or more, the extreme variation observed is about that shown by the gap between Curves 3, 4, 5, and 6 and Curve 7. It will be noticed that the general form of all five curves is the same.

FIG. 2.



Curves 1 *and* 2 *show the attainment by the electrode of the standard state afte being polished with emery paper and immediately immersed in electrolyte. Curves* 3, 4, 5, 6, 7 *show recovery of electrode to standard condition after an exposure of* 1 *minute in each case. (All potentials are on the saturated calomel scale.)*

The condition to which the electrodes used in these and similar experiments have attained was taken as a standard. It could always be achieved by the immersion for many hours of an electrode in an air-free electrolyte. No other treatment gave such reproducible surface conditions, although qualitative reproducibility could be obtained with electrodes which had been immersed for a long time in an electrolyte not rendered air-free. Here the potential reached was not so base as in the standard state, and the time required to regain that potential after exposure to air was greatly increased.

The standard state is a direct result of action by the electrolyte and is not a spontaneous disappearance of the air-formed modification of the iron. This was tested by keeping the electrode for about ½ hour in oxygen-free nitrogen after a minute's exposure to air. Its subsequent behaviour was exactly the same as that of one of which the only treatment was a minute's exposure to air.

The interpretation of the above facts is as follows. The well-known and very variable electric condition of iron surfaces is due to the formation of a surface film of oxide, which is more or less cracked and remains in a state of continuous cracking and repair for a long time after the grinding of the surface (see Evans, J., 1927, 1020). This is probably further complicated by a greater or less adsorption of gas and other impurities in the surface. On immersion in an electrolyte such as potassium sulphate, the oxide film is gradually undermined and broken up, and any adsorbed material is removed, so that after the lapse of several hours the surface behaves electrically as a clean iron surface. In order that this should be the case, the film is not necessarily destroyed, for it is possible to achieve the standard state with a visible and apparently adherent coat of yellow oxide covering the electrode, and the subsequent electrical history of such an electrode on exposure to air and re-immersion is the same as that of one which is bright. This is demonstrated by Curve 6, Fig. 2, which was obtained with an electrode brought into the standard state after a previous treatment of alternate oxidation and reduction: it was covered with a visible yellow film on which were large grey patches.

The Effect of Oxidation on Iron in the Standard State.—A series of experiments was made with iron electrodes, brought to the standard state and then exposed to air for a few seconds, 1 minute, 5, 10, 30, 45, 120, 250, or 1125 minutes. The "effect" was measured by the changes of potential with time on immersion of the electrode, after exposure, in air-free electrolyte. In the shortest exposure, the electrode was taken wet from the solution and immediately returned to it, so that any slight amount of air which did reach it had to diffuse through a layer of solution and the effective exposure was probably extremely short. Even this exposure made the iron sensibly more noble, and the potential only returned to its original value after 2 or 3 minutes; presumably this represents the time needed for the destruction of the film by the electrolyte. Longer exposures resulted in a greater change of the potential and greater resistance of the film to subsequent destruction.

The curves obtained showed (i) that the potential immediately after immersion measures in some sense the state of the iron surface at immersion, and (ii) that the time required for the restoration of the normal state measures the resistance of the film to destruction.

After about 2 hours' exposure to air the change in condition of the surface produced by further exposure is small as measured by the time taken to recover the standard state. The obvious conclusion is that the film in this time has reached a state in which it protects the metal beneath from further action. It appears, however, as though the outside layer of the protective film were still undergoing modification.

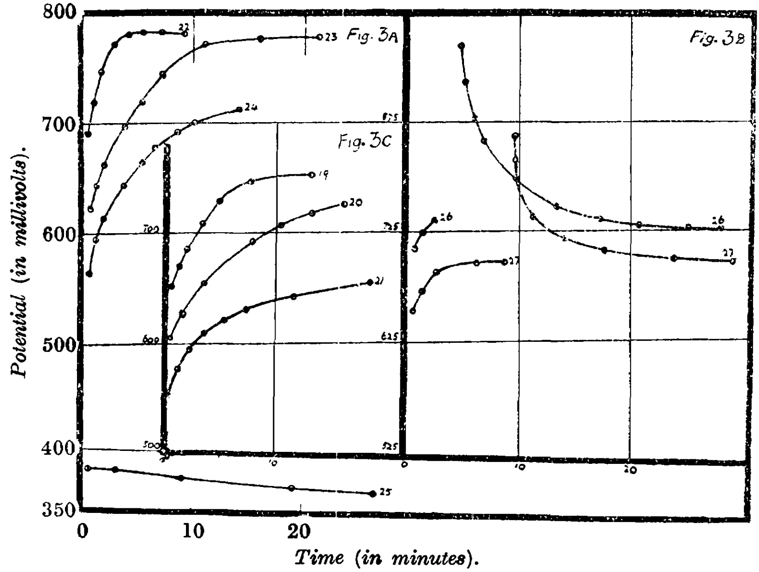
The curves obtained after exposure to a powerful oxidising agent such as potassium chromate or anodic treatment in sodium hydroxide solution indicated the existence of a film which is more resistant to attack by electrolyte than that given by the longest air exposure. Prolonged immersion in air-free electrolyte restored the electrode to the standard state, although the restoration was much slower.

As the currents responsible for the corrosion of iron immersed in a normally aerated electrolyte are due to potential differences produced similarly to those described above, it might be thought probable that their passage would destroy the film producing these potential differences, the energy for the current coming from the cathodic reduction of the oxide. The following experiments were made with a view to test this.

The Effect of the Passage of Current on the Destruction of the Ennobling Film on Iron.—When an electrode is immersed in electrolyte after exposure to air, the passage of currents of density about 40 microamps. per sq. cm. to the electrode as cathode seems to have no effect on the form of the time–potential curve, beyond a temporary polarisation. Two electrodes were exposed to air for 10 minutes prior to making the experiment; in one case, no current was passed, but in the other, 3 minutes after immersion, 40 microamps. per sq. cm. were passed to the iron as cathode for 1 minute. The polarisation effect was found to disappear after about 1 minute. This can only be interpreted as meaning that the air-formed modification of the iron is unaffected by the passage of corrosion currents. Anodic treatment (40 microamps. for 1 minute) was found to have scarcely any effect at all on the electric condition of the surface.

Experiments on Cast Iron, Mild Steel, and "Stainless" Steel.—Experiments with cast iron and mild steel indicate that their general behaviour is very similar to that of electrolytic iron. The curves for corresponding exposures, though not of exactly the same form, follow the general lines of those obtained with electrolytic iron. Fig. 3C shows curves for exposures of 1, 5, and 54 minutes on mild steel (19, 20, 21), and Fig. 3A those of 1, 10, and 100 minutes on cast iron (22, 23, 24). The electrodes come to a standard state after prolonged immersion in electrolyte, but in this state they are much more sensitive and go out of the standard state much more easily.

FIG. 3.



(A) *Curves* 22, 23, *and* 24 *show recovery of cast-iron electrode to the standard condition after exposure to air of* 1, 10, *and* 100 *minutes. Curve* 25 *shows effect of a* 5*-minute exposure to air on a stainless steel electrode.*

(B) *Curves* 26 *and* 27 *show effect of passing a current of* 40 *microamps. for* 1 *minute on electrodes of mild steel and cast iron.*

(C) *Curves* 19, 20, *and* 21 *show recovery of mild-steel electrode to the standard condition after exposure to air of* 1, 5, *and* 54 *minutes.*

Experiments with current indicate that cast iron and mild steel are more easily polarised, the polarisation effect being large compared with that of pure iron. This renders the task of finding the effect of passage of current upon the passifying film more difficult. The indications are that it is unaltered. Curves 26 and 27, Fig. 3B, show the effect of passing a current of density about 40 microamps. per sq. cm. for 1 minute to electrodes of mild steel and cast iron, respectively.

"Stainless" steel, as was anticipated, gave a completely different result—Curve 25, Fig. 3A, shows its behaviour when given an exposure to air of 5 minutes. After immersion in the electrolyte for 12 hours it was still in the same condition as when first put in. It behaved like a noble metal in having no definite potential of its own in the solution and in being extremely easily polarised so as to take up almost any potential.

Summary.

Iron when corroding is in a stable and reproducible state, and, provided that the electrodes are first aged by prolonged immersion in an electrolyte and the condition of aeration of the electrolyte is standardised, reproducible results can be obtained.

The behaviour of pure electrolytic iron is also typical of that of mild steel and cast iron; difference in composition has but little effect provided that it is not such as to produce air passivity, as in the case of "stainless" steel. Such steel shows completely different behaviour: it resembles a noble metal, is easily polarised by minute currents, and shows no very definite normal potential.

The potential which an iron electrode reached after prolonged immersion in an air-free electrolyte was taken as standard. In $N/2$-potassium sulphate this is between 0·75 and 0·80 volt on the saturated calomel scale, the actual value probably depending on the p_H of the solution. Electrodes in this condition were given various exposures to air and re-immersed in the same electrolyte; the resulting potentials were measured, and their change with time observed. The curves showing this change with time, *i.e.*, the rate of recovery of the standard state, demonstrate that the film which is responsible for the corrosion current increases in protective power and resistance to destruction with time of exposure of the iron to air up to about 2 hours, after which but little further change takes place on further exposure.

When this stage is reached immersion of the iron in air-free $N/2$-potassium sulphate causes a destruction of the ennobling film in about an hour, and a consequent return of the metal to the standard state in this time. Some film is formed even in the shortest exposures it was possible to give. The destruction of the film is due to action by the electrolyte; it is not destroyed if the electrode is merely left in contact with an inert gas after exposure.

More drastic oxidation, such as anodic treatment in alkali, produces a film which takes considerably longer to destroy on exposure to electrolyte than any that are air-formed; eventually, however, the same standard state is achieved in each case.

The passage of corrosion currents has no effect on the ennobling film that gives rise to the potential differences which produce them. The potentials are modified temporarily owing to polarisation effects, but these effects rapidly disappear when the current is stopped, leaving the film unchanged except for the action of the electrolyte.

In conclusion, we wish to express our gratitude to Mr. U. R. Evans, without whose interest and encouragement this work would probably not have been carried out. We are particularly indebted to him for corresponding with us during the progress of the work, and so to some extent mitigating the disadvantages of distance from other laboratories where similar work is being carried out.

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