(Translated from the German.)

A Paper on "The Hydrogen Theory of Passivity," by Professor G. C. Schmidt (Münster), [experimental part by Dr. W. Rathert], was communicated by Dr. G. Senter.

1. Introduction.

Although the abnormal chemical and electrochemical behaviour of iron and certain other metals has been known for more than 100 years, up to the present no explanation of the cause of passivity has met with general acceptance. In course of time many theories have been suggested and subsequently given up. At the present time only two theories deserve serious consideration : (a) the oxide theory of Faraday, according to which passivity is due to a coating of oxide or oxygen on the metal-a theory which still finds supporters in spite of the many serious objections put forward against it-and the hydrogen theory, according to which the metals in question are normally passive and become active only in the presence of dissolved hydrogen acting as a catalyst. The latter view has recently been strongly supported by my pupils Grave * and Adler † on the basis of experimental investigations. Flade ‡ does not regard their results as conclusive, and considers that his own investigations lend support to the oxide theory. In the present Paper the results of further experiments designed to decide between these two theories are described.

2. Criticism of Flade's Results.

Flade found that iron rendered passive by anodic polarization in dilute sulphuric acid immediately returns to the active state when the polarizing e.m.f. is removed. When, however, it is in a circuit and forms the anode under the influence of an external, not too great, e.m.f., the potential gradually becomes more negative, until at a certain potential, the "transition point," it suddenly becomes active. Flade regards this point as the long sought limit between the active and passive states.

The arrangement used by Flade is practically identical with that of Fredenhagen, \S and the question arises whether the transition point discovered by Flade is not the "activation potential" of Fredenhagen. If this should prove to be the case it follows, since Fredenhagen has shown that the "activation potential" and the "passivation potential" are quite different, that the formation of well-defined oxides is excluded. This point was first investigated.

^{*} Grave, Zeitsch. physikal. Chem., 1911, 77, 513.

[†] Adler, ibid., 1912, 80, 385. † Habilitationsschrift, Marburg, 1910; Zeitsch. Electrochem. 1912, 17, 335.

[§] Fredenhagen, Zeitsch. physikal. Chem., 1908, 63, 1.

3. Experimental Results.

As a result of investigations which will be fully described elsewhere, it was found that the "transition point" is in fact identical with the activation potential of Fredenhagen, and, further, that in all cases the activation potential and the passivation potential are different. The transition point does not form a boundary between the active and the passive states, since iron can remain active at a potential which is much more positive (more noble) and passive at a potential much more negative than that corresponding with the transition point. Further, experiments with wires of different lengths show that the transition point has not always the same value. In fact, the determining factor in these investigations is the current density, or in other words, the amount of oxygen set free by the current. The investigations of Flade furnish evidence against the oxide theory, since, as Fredenhagen has pointed out, the activation and passivation potentials must coincide if oxides are formed. On the other hand, the results in question can readily be accounted for on the basis of the hydrogen theory. When iron is rendered passive by anodic polarization, the oxygen combines with the hydrogen diffusing through the iron towards the surface and thus retards solution of the metal. The iron remains passive as long as the oxygen is being liberated freely. As the amount of oxygen liberated falls off with diminishing current density a point is reached when it is no longer sufficient to combine with all the hydrogen. The iron becomes active at one point; hydrogen is immediately set free at this point, neighbouring regions become active as a consequence of local currents, and thus the whole surface becomes active with explosive rapidity. When the attempt is now made to reverse the condition of the metal, considerable resistance is met with on account of the considerable content of hydrogen and its high absorptive power for this gas. As the rate of liberation of oxygen increases, the potential gradually becomes more positive (nobler), the metal becoming passive at certain points : at other points solution of the metal proceeds and the evolved hydrogen tends to remove the passivity. As the current density and the consequent liberation of oxygen are further increased, more and more of the metal is rendered passive, until a point is ultimately reached at which the tendency to activity is overcome and the whole of the metal becomes passive. This change cannot proceed with the same rapidity as the converse one, on account of the strongly marked tendency of iron to remain active, and it is therefore not to be anticipated that the activation and passivation potential will coincide-a conclusion fully confirmed by experiment.

The behaviour of chromium is the converse of that of iron, the active condition in this case being the normal. Corresponding with this the transition point with evolution of hydrogen is quite sharp.

4. The Effect of Polishing.

Although the results of Flade and those subsequently obtained in the Münster laboratory can be explained on the hydrogen theory, they do not constitute a conclusive proof of the validity of that theory. The results described below allow, in my opinion, a definite decision between the two theories.

The guiding principle in these investigations is as follows : According to Muthmann and Frauenberger* passivity is brought about by the presence of oxygen dissolved in the metal. Flade accepts this view only as regards the action of air in causing passivity; all other passivity phenomena are ascribed

* Sitzungsber. Kgi. Bayr. Akad., 1904, 24, 201.

to the formation of oxide films on the metal. On either of these assumptions any metal the surface of which is cleaned in the entire absence of oxygen must be active, whilst according to the hydrogen theory it is to be anticipated that iron, which always contains hydrogen, would be active, and chromium and nickel, which do not contain hydrogen, would become passive.

In order to test these conclusions an apparatus was constructed in which the metals could be subjected to friction in an atmosphere of hydrogen or nitrogen and the potentials then determined at once. The gases were very carefully purified and air was completely excluded. It was found that when subjected to friction in hydrogen, chromium and nickel became rather more positive (nobler) but remained completely passive. These results show conclusively that metals may remain passive in the absence of oxygen, under circumstances in which the formation of an oxide film is impossible-results which cannot be reconciled with the oxide theory. The small differences of potential observed when metals are subjected to friction in different gases are due to adhering layers of gas. Iron, on the other hand, was always found to be active even in neutral solutions of ferrous sulphate : it is naturally a less noble metal than chromium or nickel, and, as the investigations of Belloc* and others have shown, always contains considerable amounts of hydrogen.

5. Effect of a Hydrogen Charge on the Potential and Activity of a Metal.

In the foregoing sections it has been proved that metals which contain no alloy with oxygen and are free from coatings of oxide can retain the passive condition, but in order to show the validity of the hydrogen theory it is further necessary to prove that dissolved hydrogen can transform metals from the passive to the active form. For this purpose metals prepared by electrolytic methods and therefore containing hydrogen were examined ; and, further, hydrogen was liberated at a point and conveyed by diffusion to other passive portions of the surface, under which circumstances the passive portions regained their activity.

As already mentioned, ordinary iron is active in ferrous sulphate solution, probably owing to the large proportion of hydrogen it contains. Electrolytic iron is also active under these conditions, showing a less noble potential than ordinary iron. The potential $\epsilon_h = -0.66$ volt found by Muthmann and Frauenberger, + is, as shown by Richards and Behr, ‡ too high; it represents the potential of iron supersaturated with hydrogen. The value $\epsilon_{k} = -0.4232$ volt obtained by us in good agreement with that given by Richards and Behr, is also that of a metal containing hydrogen. Muthmann and Frauenberger found that the potential can be made more negative (less noble) by adding more hydrogen, and it seems plausible to assume that by the withdrawal of hydrogen the potential will become more positive, and that finally the metal will become passive. These conclusions cannot be satisfactorily tested experimentally, as the amount of hydrogen in iron in any given case is not known and the gas cannot be completely removed from the metal.

The matter can, however, be tested in the case of nickel and of chromium. Ordinary nickel in nickel sulphate and chromium in dilute sulphuric acid are completely passive. On the other hand, electrolytic nickel and chromium, which are both highly charged with hydrogen, are active and go into solution with evolution of hydrogen.§ If chromium is deposited electrolytically on a

Richards and Behr, 1907, 58, 301.
§ According to Carveth and Curry, J. Physical Chem., 1905, 9, 353, electrolytic chromium contains 250 times its volume of hydrogen.

^{*} Ann. Chim. Phys., 1909, 18.

[†] Loc. cit.

sample of the same metal prepared by the Goldschmidt process, and which is quite inactive, the latter under the influence of the hydrogen also dissolves in dilute sulphuric acid. Our results are in entire agreement with those of Hittorf, who showed that even the minute trace of hydrogen liberated at a chromium electrode by making it a cathode for a moment renders the metal active. In my investigations just described the hydrogen which starts the reaction is contained in the electrolytic iron. The phenomena just described, at least as far as chromium and nickel are concerned, must be regarded as "experimenta crucis" in favour of the hydrogen theory. When the metals are prepared electrolytically or by reduction at a high temperature and subsequent rubbing in an atmosphere of hydrogen, they differ only in electrochemical behaviour and in the extent to which they are charged with hydrogen. The assumption that these two factors are in causal connection cannot be avoided, especially as the possibility of the formation of oxides or alloys with oxygen is excluded.



FIG. I.

The experiments with iron are, however, not decisive, since it always remained active. The following investigations supply the evidence required:

6. Proof that a Metal is rendered Active by Diffusion of Hydrogen Ions.—Iron.

In order to transform passive iron into the active condition by diffusion of hydrogen, advantage was taken of the discovery of Grave* that when hydrogen is liberated at one side of a piece of iron foil, it rapidly diffuses through and alters the e.m.f. The arrangement of the apparatus was as follows: A and B are two glass troughs, one side of each having been removed and replaced by a thin sheet of iron, Fe. P is a platinum cathode connected with two accumulators. The iron is earthed. The two troughs are filled with dilute potassium hydroxide, which has a slight passivating action. N is the normal electrode. The p.d. between the iron and the normal electrode is measured by means of a sensitive Dolezalek electrometer, The alkali renders the metal passive, and it was anticipated that when E. hydrogen is liberated on one side of the iron the gas will pass through by diffusion and render the iron active. The result of an experiment is shown in Fig. 2, the times being represented as abscissæ and the e.m.f.'s as ordinates. The letters H and O indicate the moment when the liberation of these gases began. The rapidity with which the hydrogen acts is remarkable. The

* Loc. cit., p. 570.

commencement of its evolution is followed almost instantly by alteration of e.m.f. on the other side.

The investigations did not, however, lead to conclusive results; the iron remained passive under all circumstances. The probable reason is that the amount of hydrogen which passes through is too small to counteract the



passivating action of the potassium hydroxide. The solution in the trough A was therefore replaced by another electrolyte, chromic acid. The latter is a strong oxidizing and passivating agent as well as an acid. If the hydrogen



theory is correct and the iron is highly charged with hydrogen, it ought to be possible so to oppose the two properties of chromic acid that one of them prevails. Preliminary investigations showed that in chromic acid any potential through a wide range can be imparted to iron. The more concentrated the

solution the more positive (more noble) is the potential; the more dilute the solution the less noble is the potential. If an acid is chosen the concentration and oxidizing power of which is just sufficient to render the iron passive, it should be possible to render the metal active by hydrogen reaching it by diffusion. The result of such an investigation is represented in Fig. 3, which shows that the iron is at first passive, but the moment that hydrogen begins to be liberated (at H) the potential falls very rapidly and the metal becomes active. If the evolution of hydrogen is now interrupted (in the second trough B, Fig. 1) the metal remains active and dissolves with evolution of hydrogen.

Quantitative investigations showed that more iron is dissolved than corresponds with Faraday's law. This is not surprising, since iron not only goes into solution according to the law in question, but is also acted upon directly by chromic acid. This behaviour is analogous to that of a zinc electrode in



sulphuric acid; more zinc is dissolved than corresponds with Faraday's law unless the metal is protected by amalgamation against the direct attack of the acid.

These results, in combination with the above theoretical considerations, are practically conclusive in favour of the hydrogen theory. On the basis of the oxide theory, however, it might be supposed that the metal under the action of the acid becomes coated with oxide which is reduced by the hydrogen so that the electrode again becomes active. To this it might

be objected that passive iron remains quite bright in chromic acid. Further, if a layer of oxide is formed at first there would appear to be no reason why this process should not continue. This, however, is not the case, since, as was shown above, when the metal is activated by means of hydrogen it continues active even when the evolution of hydrogen is interrupted. The latter fact can readily be accounted for on the hydrogen theory as follows : When iron is in process of being dissolved and is passivated at certain points by the chromic acid, local currents are immediately set up and the passive regions again become active under the influence of the liberated hydrogen.

Moreover, according to the oxide theory, iron in chromic acid should be rendered active by rupture of the surface film by scratching, which is



FIG. 5.

not the case. Further, an oxide of definite composition, such as is presumably postulated in this case, should show a definite potential, whilst it was found that iron in chromic acid shows all possible potentials, depending on the concentration of the acid.

All these results and arguments constitute so powerful support to the hydrogen theory as to put its validity practically beyond question, more particularly as the most delicate methods have failed to detect a trace of the hypothetical oxide.

7. Chromium.

The successful results obtained in the activation of passive iron by diffusing hydrogen induced me to make analogous experiments with chromium. The metal was electrolytically deposited on thin sheets of iron or steel. After about 14 days the initially active metal became passive—

probably owing to gradual loss of hydrogen. The experiments were made as described above. The results are given in the accompanying table and are represented graphically in Fig. 4.

TABLE I.

Chromium deposited on Steel and allowed to stand 14 Days exposed to the Air. Potential in 0.1 N Sulphuric Acid.

Potential.	Time.	Evolution of Gas.
$\begin{array}{c} - 0.0336 \\ - 0.0262 \\ - 0.3059 \\ - 6.2909 \\ - 0.2321 \\ - 0.2174 \\ - 0.4310 \\ - 0.4530 \\ - 0.4780 \end{array}$	min. 0 4 6 7 9 11 12 13 14	Hydrogen " " " " "

The chromium electrode was at first passive. Under the influence of the diffusing hydrogen the potential fell at first rapidly, then more gradually till it reached a value of -0.2174 volts and finally fell within a minute to -0.4310 volts. The electrode was then active, as shown by the fact that it began to dissolve with a vigorous evolution of hydrogen, and it continued active when the cathodic polarization was interrupted. Of the other experiments, which gave analogous results, only one is quoted, as it shows the rapidity of action of the hydrogen.

Chromium deposited on a Steel Foil 0.08 mm. thick. Electrolyte 0.1 N H₂SO₄.

Potential.	Time.	Evolution of Gas.
	min. o 3 6 5 7 5 8 5 13 5	Hydrogen

The results are represented in Fig. 5. The electrode was originally passive; within $\frac{1}{2}$ minute of the commencement of the evolution of hydrogen it became active and began to dissolve with rapid evolution of gas. The dissolution continued after interruption of the cathodic polarization till all the chromium had disappeared.

Conclusion.

In the foregoing a series of observations have been described which in our opinion cannot be explained on the oxide theory, but are in best accord with the hydrogen theory. The views of the author on the phenomenon of passivity have already been briefly described by Grave. Just as water or other liquids do not boil, even when their vapour pressure is equal to that of the superincumbent pressure, unless a catalyst such as air is present, so the metals which can be passivated dissolve rapidly only in the presence of a catalyst. The most important of such catalysts is hydrogen, since it is dissolved readily and in large amount by metals. Whether other gases are also catalytically active cannot at present be stated, since they are only absorbed to a very small extent by metals. Just as relatively small amounts of air initiate rapid evaporation in large quantities of liquid, so a small quantity of hydrogen can activate large amounts of iron, nickel, and chromium. It might be supposed that the hydrogen, like air in the case of boiling, forms a nucleus round which the ions of metal collect. Further investigation must decide whether this hypothesis is in accord with the facts.

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