Adsorption of Oxygen on Iron and Influence of Adsorbed Oxygen on the Behaviour of an Iron Electrode

By *R. Burstein*, *N. Shumilova* and *K. Golbert*

In the numerous papers on the passivity of iron attention has repeatedly been drawn to the role of oxygen films in passivity phenomena. However, the minimum thickness of the oxygen film which passivates iron has not as yet been determined experimentally. Langmuir[1] presumed that the passive state of iron sets is upon adsorption of a monomolecular film of oxygen, but there are no experimental data in the literature confirming this assumption. Freundlich, Patscheke and Zocher[2], investigating the influence of oxygen on the dissolution in nitric acid of iron mirrors (obtained from iron carbonyl) showed that after brief contact with oxygen the solubility of degassed iron in acid is reduced. However, these observations are of a qualitative character. Bonhoefer[2a] is of the opinion that the passivating layer formed on iron in nitric acid is a monomolecular film of oxygen. The influence of oxygen films on passivity has also been repeatedly pointed out in papers by Tammann[3], Evans[4], Kistiakowsky[5] and others.

In studying the mechanism of platinum passivation, Ershler[6] came to the conclusion that noticeable passivity is reached when the adsorbed oxygen forms but a fraction of a monolayer. The oxygen

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[1] Langmuir, Trans. Am. Electrochem. Soc., **29**, 260 (1916).

[2] Freundlich, Patscheke u. Zocher, Z. physik. Chem., **128**, 321 (1927); **130**, 289 (1927).

[2a] Bonhoefer, Z. Elecktrochem., **47**, 147 (1941).

[3] Tammann, Z. anorg. Chem., **107**, 104 (1919).

[4] Evans, Trans. Farad. Soc., **18**, 1 (1922).

[5] Kistiakowsky, J. Russ. Phys. Chem. Soc., **57**, 97 (1925).

[6] Ershler, Thesis. The Karpov Institute of Physical Chemistry, 1941.

thus affects not only the surface areas on which it is adsorbed, but the remaining part of the surface as well. Ershler suggested that the bond between the adsorbed oxygen and the platinum bears a dipole character. The oxide film, which is composed of dipoles, modifies the structure of the ionic double layer and hence retards dissolution.

The present paper aims at a quantitative study of the influence of adsorbed oxygen on the passivity of iron during its anodic oxidation. A solution of this problem demands a knowledge of the true surface of an iron electrode.

It was also considered of interest to compare, by measuring the kinetics of oxygen adsorption, the thickness of the oxide film which passivates iron towards oxidation by gaseous oxygen with the thickness of the oxide film causing passivity towards electrochemical oxidation in the process of anodic polarization.

Haber and Goldschmidt[7] were the first to point out that upon exposure of iron to oxygen a thin oxide film forms, preventing further oxidation.

The kinetics of the adsorption of oxygen on iron were measured by Langmuir[8], who found that this process proceeds rapidly at first, then slows down considerably. Although the surface area was unknown in Langmuir's experiments, the author assumed that the rapid stage of adsorption corresponds to the formation of a monomolecular layer of oxygen on the iron. In later investigations it was shown by electron diffraction photographs[9] that when iron is exposed to oxygen at room temperature a film of $\gamma-Fe_2O_3$ or Fe_3O_4 is formed. The formation of an oxide film on smooth iron was further investigated by Gulbranson[10] by means of an extremely sensitive microbalance. Gulbranson determined the thickness of the oxide film on iron by the change in weight upon adsorption of oxygen and also upon reduction of the

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[7] Haber u. Goldschmidt, Z. Electrochem., **12**, 64 (1906).

[8] Langmuir, J. Am. Chem. Soc., **39**, 1380 (1918).

[9] Nelson, J. Chem. Phys., **5**, 1252 (1937); Winkel u. Haul, Z. Electrochem., **44**, 611 (1938); Dankov a. Shumakov, Bull Acad. Sci. USSR, **12**, 25 (1938).

[10] Gulbranson, Electrochem. Soc. prepr. 81—15 (1942); 82—12 (1942).

oxide films by hydrogen. Gulbranson's data are in good agreement with our own, which will be set forth below.

Kochetkov[11] investigated the adsorption of oxygen on iron powder by means of a McBain balance. He also showed that rapid adsorption takes place on iron. According to these data further oxidation does not occur in dry oxygen or air but in moist oxygen slow oxidation takes place.

The first part of the present paper is devoted to an investigation of the adsorption of oxygen at low pressures in the temperature range 90—473° K. A comparison of the data corresponding to the first stage of adsorption on powdered and on smooth iron with the value of the true surface determined by Emmett's method makes it possible to determine the true surface of the smooth iron and, hence, the thickness of the oxide film.

Experimental method

Measurements of the kinetics of adsorption of oxygen were made on smooth and powdered iron. For smooth iron we used rolled Armco ribbon and Hilger HS iron rods. The powdered iron studied was obtained 1) from Kahlbaum pure ferric nitrate, 2) from iron carbonyl and 3) from the substance prepared by the second method, which after dissolution in nitric acid and evaporating was reduced to metallic iron by heating to 500°. Iron obtained by method (2) contained adsorbed CO and possibly other organic impurities. To degas such iron was extremely difficult.

The iron powders were reduced in hydrogen at 500°. In order to be sure that the reduction was complete it was placed in a tube terminated by two joints. This ground joints tube was placed inside a second tube and a nitrogen-hydrogen mixture obtained by the decomposition of ammonia over an iron catalyst was passed through the whole system. In order to check the degree of reduction of the iron, the ground glass joints of the inner tube were closed in an atmosphere of hydrogen and the tube was weighed. Reduction was continued until the weight remained constant.

It should be observed that until complete reduction has set in the iron powder is pyrophoric. Only when reduction has been carried out to constant weight do the pyrophoric properties disap-

[11] Kochetkov, Bull. Acad. Sci. URSS, 320, 1944.

pear. This refers, however, only to pure iron. If the iron mass contains small quantities of sulphur it remains highly pyrophoric even after very prolonged reduction (8 days); this, as we have shown, is related to the difficulty of removing traces of sulphur.

It is known that the iron powder obtained from iron carbonyl sinters at 550—600°. It might be supposed that this sintering tendency at low temperature, is due to the peculiar structure of the iron. However, as has been shown by experiments with iron prepared from the nitrate by methods (1) and (3), such iron powder also sinters at 550—600° after reduction has been carried out to constant weight. Traces of oxide, sulphur and other admixtures in the iron considerably raise the temperature of sintering. A similar influence of oxygen on the sintering temperature was observed earlier by Frumkin and Šhlygin[12] in an investigation of the platinum electrode. The presence of iron of carbon monoxide and organic impurities mentioned above does not affect the temperature of sintering.

The surface was prepared in the following manner. A given weight of iron powder or smooth iron with given geometrical surface was introduced in a quartz vessel connected with a vacuum system. By means of stopcocks, this system could communicate with a hydrogen set up, with a reservoir containing carefully dried oxygen[13] and with a set-up for obtaining pure nitrogen. The nitrogen in our experiments was obtained by the decomposition of sodium acid.

The iron was first degassed to a high vacuum, then the powdered iron was reduced in hydrogen at 600°. After reduction for 1—2 hours the hydrogen was pumped off, a new portion of hydrogen was admitted and reduction repeated. The powdered iron was then degassed for several hours down to a pressure of 1×10^{-6} mm Hg at 500°. In the case of smooth iron the reduction was carried out at 600°, degassing at 850°; at higher temperatures noticeable sintering sets in. If coiled wire is degassed at 900° the coils sinter and can only be unwound with extreme difficulty.

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[12] A. Frumkin and A. Šhlygin, Bull. Acad. Sci. URSS, 773, 1936.

[13] Dried by phosphorus pentoxide over a period of several months. Kahlbaum phosphorus pentoxide was subjected to long evacuation to a high vacuum, such that after the vessel containing the phosphorus pentoxide had remained standing for 15 hours with the pumps shut off, the pressure did not exceed 1×10^{-5} mm.

In order to avoid self-heating of the iron and the resulting changes in the quantity of absorbed oxygen, the kinetics of oxygen absorption were investigated at low pressures (0.1—0.01 mm Hg). After a given portion of gas was adsorbed a new portion was admitted and the kinetics again measured. This was continued until the rate became so small that above 24 hours were needed for the adsorption of one portion of gas. The influence of the adsorbed gas on the activity of the iron electrode was studied in the following manner. An iron wire 0.2 mm in diameter and 5 m long, obtained by drawing out a Hilger HS rod, preliminarily reduced and degassed according to the method described, was placed in a vessel of Duran glass, represented in Fig. 1. The apparent surface of such an electrode was 30 cm². The electrode was sealed into tube *A*. To ensure an airtight seal the iron wire was welded at *B* to a tungsten wire which gives good seals with Duran glass. In cell *C* was placed an ampoule with a degassed alkali solution, cells *D* and *E* contained mercury oxide electrodes. One electrode served for polarization, the other for measurement. The apparatus was connected to a high vacuum system

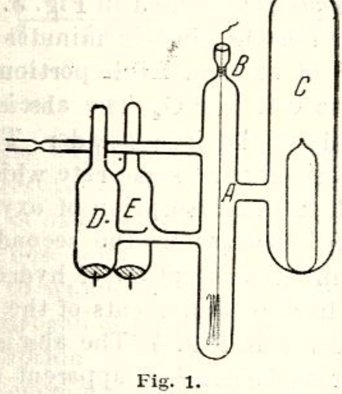

Fig. 1.

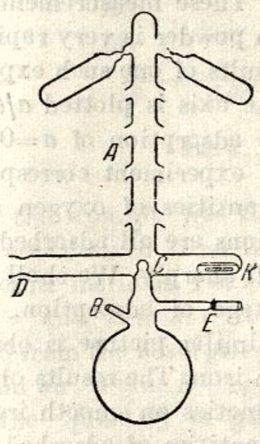

Fig. 2.

and after additional reduction and degassing at 600° was sealed off. The polarization current was turned on, the ampoule was broken by shaking the vessel and then the dependence of the potential on the quantity of electricity passed was measured.

The liquid was degassed in the set-up shown in Fig. 2. To ensure better degassing of the system the upper part of the apparatus *A* was separated from the lower part B by the bulb C. After the lower part of the apparatus and the liquid were degassed using an oil pump, and the upper part of the apparatus was degassed to a pressure of 1×10^{-6} mm Hg the apparatus was sealed off at points D and E. The bulb C was broken by means of the plunger K and the liquid entered the ampoules. The ampoules were sealed off the apparatus and used in the experiments described above.

Results of the measurements

1. Adsorption of oxygen

It was pointed out above that in measuring the adsorption of oxygen on iron the gas was admitted in small quantities. Since the pressure of the oxygen in our experiments did not exceed 0.1 mm, it was sometimes necessary to let in as many as 30 portions of gas before the surface was saturated with adsorbed oxygen. The number of portions requisite for saturation depended, of course, on the extent of the surface. The rate of adsorption was measured for each portion of gas. These measurements showed that the adsorption of oxygen on iron powder is very rapid at first, then the rate falls off sharply. The results of one such experiment are represented in Fig. 3. On the ordinate axis is plotted a/t, where t is the time in minutes needed for the adsorption of $a = 0.03$ cm^3 of oxygen. Each portion of gas in this experiment corresponded to 0.05 cm^3 O_2. The abscissae are the quantities of oxygen adsorbed on the iron powder. The first 9 portions are all adsorbed at practically the same rate which then falls off sharply. We shall term the rapid adsorption of oxygen the first stage of adsorption, the slow adsorption—the second stage.

A similar picture is observed in the adsorption of hydrogen on smooth iron. The results obtained from measurements of the adsorption kinetics on smooth iron are given in Fig. 4. The abscissae are the quantities of adsorbed oxygen on 100 cm^2 of apparent surface. It follows from the data that in the first stage the rate of adsorption of oxygen does not depend on the extent of surface covered and the kinetics correspond to a first order reaction. Measurements of the adsorption of oxygen at different pressures lead to the conclusion that the rate of adsorption is proportional to the pressure. However, since adsorption takes place very rapidly, it is not yet certain whether the measured rate in the first stage is due to the adsorption of oxygen on the iron or to diffusion of the gas to the adsorbing surface. To decide this question it is necessary to have an apparatus in which the kinetics of rapid processes can be measured. Such experiments are at present being carried out.

One might assume, following Langmuir, that the rapid stage of adsorption of oxygen is connected with the formation of a monomo-

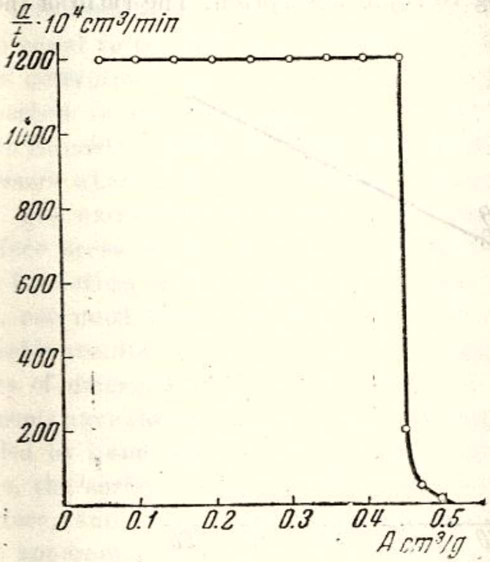

Fig. 3.

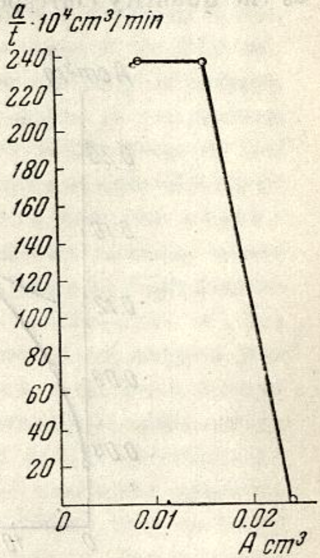

Fig. 4.

lecular oxygen film on the surface of the iron. It was therefore of interest to compare the data on surface area derived from the adsorption of oxygen with data obtained by other methods. For comparison we chose the method of Brunauer and Emmett[14], according to which the surface is determined from the adsorption isotherm of nitrogen at the temperature of liquid air. Point *B* (Fig. 5) on the adsorption isotherm corresponds to the quantity of gas forming a monomolecular layer. According to the data of Brunauer and Emmett, and also of Jura and Harkins[15], the area occupied by one nitrogen molecule is equal approximately to 15 Å^2.

The results of the measurements of the adsorption isotherms are illustrated in Fig. 5. The ordinates are the adsorbed quantities per

[14] Brunauer and Emmett, J. Am. Chem. Soc., **59**, 2682 (1937).
[15] Jura and Harkins, J. Am. Chem., Soc., **66**, 1366 (1944).

gram of iron. As appears from these data, the inflection on the isotherm corresponds to 0.15 cm^3 of nitrogen per gram of iron.

In measuring the kinetics of adsorption of oxygen on this sample of iron we found that the first stage of adsorption at 20° C corresponds to 0.45 cm^3 oxygen per gram iron (Fig. 3). Thus, the quantity of nitrogen necessary to form a monomolecular layer is one-third as great as the quantity corresponding to rapid adsorption. The ratio of the

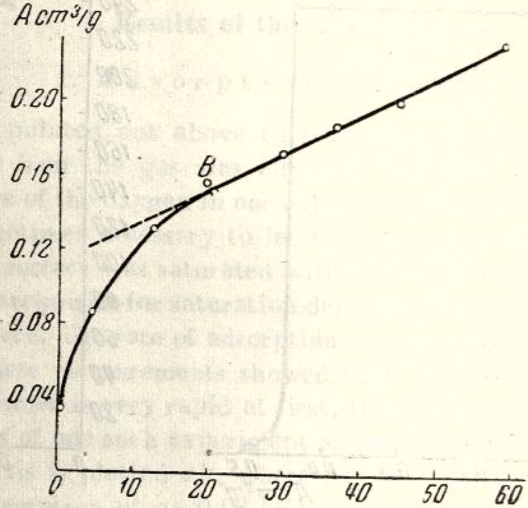

Fig. 5.

quantities of adsorbed oxygen and nitrogen remains constant in measurements of the surfaces of iron powders of different origin, *e. g.*, from the carbonyl and from the nitrate, as well as in deactivation of the surface. The latter was accomplished by prolonged heating of the iron in vacuum at 500°. Deactivation could not be carried out at higher temperatures since the iron powder began to sinter. It should be observed that in deactivating the surface we succeeded in changing it only by a factor of two.

A comparison of the results obtained for the surface of the iron powder from the adsorption isotherm of nitrogen and from the first stage of the adsorption of oxygen leads to the conclusion that if the area occupied by a nitrogen molecule equals 15 Å^2, then it may be assumed conditionally in the calculations that the area occupied by an oxygen molecule equals 5 Å^2, or that 2×10^{15} molecules are adsorbed on 1 cm^2 at 20° C. In reality, the rapid stage of adsorption probably corresponds to the formation of a film several layers thick and perhaps not entirely homogeneous. However, if the transposition factor from adsorbed nitrogen to oxygen is known and if it remains constant, the mechanism of formation of the oxide film does not affect the value found for the surface.

It follows from the data obtained that the surface of 1 gram of iron was equal to 0.5 m^2; upon deactivation it was reduced to 0.25 m^2. The determination of the surface area by the quantity of oxygen adsorbed in the first stage has several advantages in comparison with Emmett's method. In the first place the oxide film forms at low pressure which makes it possible to determine the quantity of adsorbed gas extremely accurately. By this method one can measure surface areas of 10—15 cm^2, whereas in Emmett's method, where the formation of a monomolecular layer takes place at high pressures, one must have a surface of 2×10^5 cm^2 to obtain more or less reliable results. The method of activated adsorption of oxygen permits of determining the true surface of smooth iron. Such measurements have shown that the surface of Armco iron ribbon additionally rolled by hand-operated rolls is twice as great as the apparent surface, the surface of Hilger HS iron bars is 3.5 times the apparent surface, and the surface of wire made from Hilger iron is twice the apparent surface. The ratio between the apparent and true surfaces also leads to the conclusion that the data obtained for the first stage of adsorption can be utilized to determine the surface area. To check up this ratio it would be expedient to compare the above data with the results of measurements of the double layer capacity on an iron electrode. It is proposed to carry out such experiments shortly.

The above data can also be utilized to compute the average thickness of the oxide film. Since it is known from electron diffraction data that when oxygen is adsorbed on the surface of iron Fe_3O_4 or γ—Fe_2O_3 is formed, then for an adsorption equal to 2×10^{15} molecules O_2 per 1 cm^2 of true surface, the thickness of the oxide film, if it is homogeneous, should be 6.3 Å, or 12.6 Å per 1 cm^2 of apparent surface (calculating for γ—Fe_2O_3). The value which we have obtained for the thickness of the oxide film at room temperature is thus less than what corresponds to an elementary γ—Fe_2O_3 or Fe_3O_4 cell. This circumstance may possibly be due to some inhomogeneity in the film.

Our data on the adsorption of oxygen on smooth iron are in good agreement with the findings of Gulbranson who showed that if the adsorbed O_2 is computed for Fe_3O_4, a film 15 Å thick is formed on the iron, whereas computations for γ—Fe_2O_3 give a film of 13.6 Å. Gulbranson did not determine the true surface of the iron, but a comparison of our data with his leads to the conclusion that the ratio of the true and apparent surfaces in this author's experiments was close to two.

In order to clarify the mechanism of formation of the oxide film it was considered of interest to measure the adsorption kinetics at various temperatures. The measurements were made over the range 93—473° K. The results of these measurements are depicted

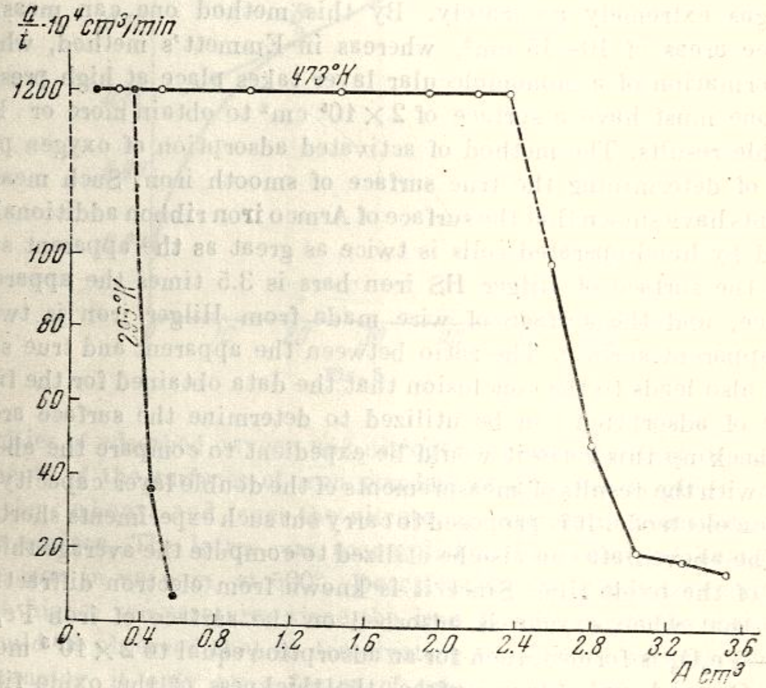

Fig. 6.

in Figs. 6 and 7. Fig. 6 represents the kinetics at 290 and 473° K, Fig. 7—the amount of gas adsorbed in the first stage of adsorption at all the investigated temperatures.

It was observed in these measurements that in the range 90—473° K the rate of adsorption of oxygen in the first stage is independent of the temperature. The quantity of adsorbed oxygen increases with rise in temperature.

If adsorption is carried out at a low temperature (90° K), and the temperature is then raised, additional adsorption takes place, the total quantity of gas adsorbed being equal to the quantity adsorbed at room temperature.

From 90 to 135°K adsorption increases, from 135 to 200° K it remains practically constant, and then with a further rise in temperature again increases. The increase in the quantity of adsorbed gas becomes especially noticeable above 290° K.

The first stage of adsorption proceeds very rapidly so that, as was pointed out above, on the basis of the experimental data available to date it is still impossible to decide whether the observed rate, independent of the temperature and the extent of surface covering, is the rate of the adsorption process on iron or the velocity of diffusion of the gas to the adsorbing surface.

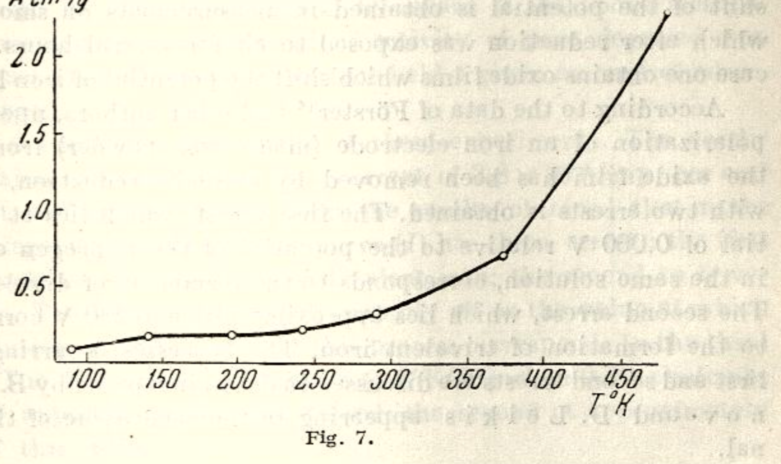

Fig. 7.

If it is assumed that at the temperature, at which adsorption remains constant, a monomolecular layer of oxygen is formed, then we find that to each adsorbed oxygen molecule corresponds an area of 8.5 Å². The decrease in the amount of adsorbed oxygen at 90° K probably means that at this temperature adsorption does not take place on the entire surface. The increase in the amount of adsorbed oxygen above 200° K can be explained by the increase with the temperature of the rate of formation of an oxide film of different structure, *e. g.* $\gamma-Fe_2O_3$. In connection with the above results it would be of interest to obtain electronograms in the temperature range where adsorption remains constant. If there is a monomolecular film of adsorbed oxygen at low temperatures the structure of the oxide film should differ greatly from that of the film formed at higher temperatures.

Information on the homogeneity of the oxide film formed on the surface of iron might be obtained by measuring the contact potential on iron covered with various amounts of oxygen.

2. The passivating action of adsorbed oxygen

It is known from investigations of the iron electrode of storage batteries that the potential of an iron electrode prepared from reduced iron powder but having been in contact with the air is shifted by 0.4—0.5 V in the positive direction relatively to an electrode which was additionally reduced electrochemically. An even greater shift of the potential is obtained in measurements on smooth iron which after reduction was exposed to air for several hours. In this case one obtains oxide films which shift the potential of iron by 0.9 V.

According to the data of Förster[16] and other authors, upon anodic polarization of an iron electrode (made from powder) from which the oxide film has been removed by cathodic reduction, a curve with two arrests is obtained. The first arrest, which lies at a potential of 0.060 V relative to the potential of the hydrogen electrode in the same solution, corresponds to the formation of divalent iron. The second arrest, which lies approximately at 0.280 V corresponds to the formation of trivalent iron. The processes occurring at the first and second arrests are discussed in detail in a paper by B. Kabanov and D. Leikis appearing in the same issue of this journal.

The electrode which was exposed for some time to the air is not electrochemically active. Electrochemical activity of the electrode corresponding to pure iron can be attained without electrochemical reduction, *e. g.* if the iron electrode is not exposed to air after reduction or, as has been shown in one of our papers, if after reduction

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[16] Förster, Z. Electrochem., **16**, 46 (1910).

the iron is treated with benzene. In the latter case the adsorbed benzene prevents the formation of a thick oxide film. Such an electrode, even after exposure to the air for several months acquires the potential of pure iron upon contact with an electrolyte at the same time retaining its electrochemical activity.

Curves similar to those described by Förster for powdered iron were obtained by Krassa[17] for smooth iron at 75°. At room temperature, according to Krassa's data, smooth iron is not electrochemically active. It is shown by Kabanov and Leikis (see this journal) that iron, which after reduction had been exposed to the air for a very short time (several minutes), showed considerable electrochemical activity at room temperature following cathodic polarization. Upon anodic polarization of smooth iron previously subjected to such treatment curves similar to Förster's for powdered iron were obtained.

It is very important for an understanding of the mechanism of passivation of iron to determine the quantity of adsorbed oxygen at which passivity is observed.

In order to solve this problem by means of the above method, we determined the electrochemical activity of pure degassed iron and the activity of iron whose surface held a given amount of adsorbed oxygen.

Fig. 8 illustrates the results of these experiments. The anodic polarization was carried out by a current of 2.8×10^{-5} amp. per cm^2 apparent surface. It appears from the results obtained that in the case of degassed iron the anodic curve (I) has three arrests: the first corresponds to the formation of divalent iron; the second to trivalent iron. The potential then falls rapidly off to the value at which the evolution of oxygen sets in; this process corresponds to the third arrest. The first arrest terminates (1 N KOH) when 0.30 coulombs per cm^2 apparent surface are passed, the second at approximately one-half this value.

When oxygen is adsorbed on the degassed electrode to the amount of 4×10^{15} molecules per cm^2 apparent surface, or 2×10^{15} molecules per cm^2 true surface, *i. e.* to an amount corresponding to the first stage of adsorption at room temperature, the electrode retains its electrochemical activity. In this case we obtain a curve similar

[17] Krassa, Z. Electrochem., **15**, 490 (1909).

to curve *1*. If this same amount of oxygen—2×10^{15} molecules per cm^2 true surface—is adsorbed on iron at 100° the electrode still retains its electrochemical activity. The behaviour of an electrode whose surface has adsorbed 4×10^{15} molecules of oxygen per cm^2 true surface at 100° will be entirely different. In this case, as appears from curves *2* and *3*, the electrode loses its electrochemical activity. The iron is completely passivated. Curves *2* and *3* are shown in Fig. 9 on another scale, and the trend of the curves, therefore, stands out more clearly.

It appears from the above findings that the presence on the surface of oxygen in an amount corresponding to the first stage of adsorption is not enough to passivate the surface towards electrochemical oxidation. This phenomenon can evidently be attributed to the

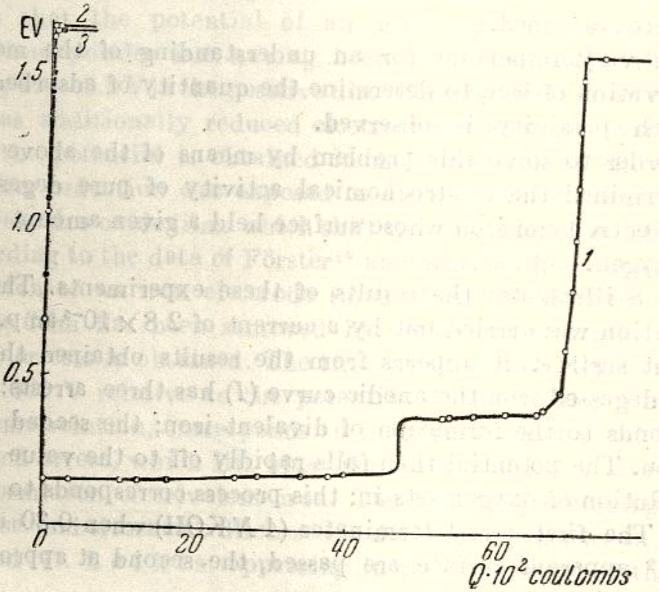

Fig. 8.

circumstance that when iron is immersed in the solution it becomes ionized as a result of which the oxide film is removed. However, at somewhat greater quantities of adsorbed oxygen the iron is passivated upon anodic oxidation.

In order to follow the process of removal of the oxide film from the surface of the iron we investigated the influence of adsorbed oxygen on the potential of the iron electrode in the absence of anodic polarization. These experiments were carried out on Armco iron.

By the above method we measured the kinetios of the setting in of a steady potential on reduced degassed iron and on iron on which was adsorbed a given quantity of oxygen corresponding to the first stage of adsorption—2×10^{15} molecules per cm^2 true surface.

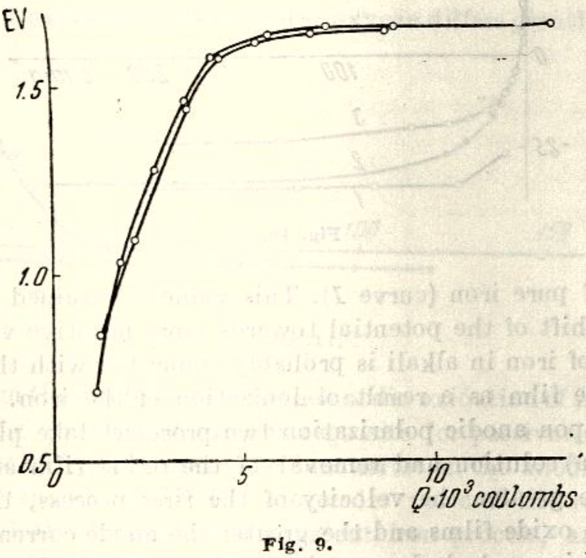

Fig. 9.

The results of these experiments are shown in Fig. 10, where curve *1* was obtained on pure iron. As appears from these data, the potential of the degassed iron electrode is 40 mV more negative than the hydrogen electrode in the same solution. However, in the process of time the potential shifts in the negative direction, approaching the potential of pure iron. The oxide film obtained at room temperature becomes stronger if it is heated at 200°. As appears from curve *3*, Fig. 10, the shift of the electrode potential in the negative direction takes place more slowly as time goes on, and even after very long contact with alkali (24 hours) it remains approximately 15 mV more positive than the potential of degassed iron.

A considerably greater shift in the potential of the iron electrode is observed if the oxide film is formed upon exposure of the iron to oxygen at a high pressure (300 mm Hg) for 25 hours[18]. In this case 3 minutes after the electrode is immersed in alkali the potential is shifted by 400 mV (curve *2*, Fig. 11); however, here too, in process of time the potential shifts to more negative values. Fifty minutes later the potential is only 30 mV more positive than the

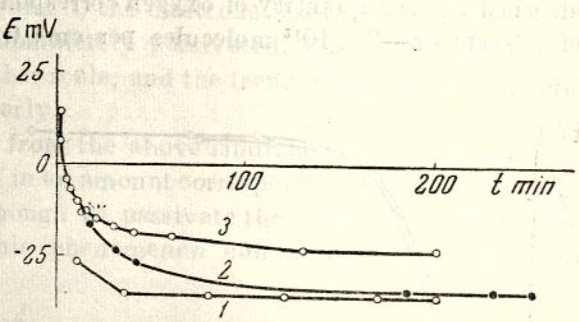

Fig. 10.

potential of pure iron (curve *1*). This value is retained for a long time. The shift of the potential towards more negative values after immersion of iron in alkali is probably connected with the removal of the oxide film as a result of ionization of the iron.

Thus upon anodic polarization two processes take place simultaneously: a) solution and removal of the oxide film and b) oxidation. The greater the velocity of the first process, the thicker will be the oxide films and the greater the anode current at which passivation is reached. Inasmuch as the process of spontaneous dissolution increases strongly with the temperature, then with rise in temperature there should be a greater and greater difference between the amount of oxygen in the gas phase which increases to form an oxide film and the amount needed for electrochemical passivation.

It is of interest to observe that if degassed iron is immersed in a degassed electrolyte and air bubbled through the solution, the potential becomes approximately 80 mV more positive than the potential of the degassed iron. This value is maintained for several

[18] Under these conditions approximately 1.5 times more oxygen is adsorbed than corresponds to rapid adsorption at low pressures, *i.e.* 3×10^{15} molecules per cm^2. The method by which the thickness of such oxide films is determined will be described in another paper.

hours and corresponds approximately to the potential of the first plateau on the anodic curve. If hydrogen is passed after oxygen, the potential again becomes more negative being only 40 mV more positive than the degassed iron. Thus, the influence of the oxygen dissolved in the electrolyte is entirely different from that of the gaseous oxygen. Dissolved oxygen affects the iron electrode similarly to anodic polarization.

The above experiments clearly show that the oxide film which forms upon exposure of iron to dry oxygen differs greatly in its pro-

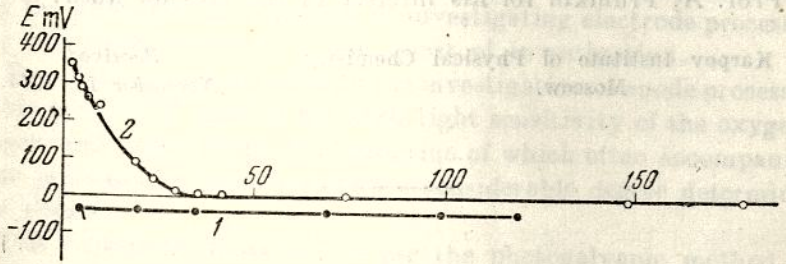

Fig. 11.

perties from the oxide formed in the anodic oxidation of iron. Indeed, whereas the quantity of oxygen requisite for passivation does not exceed 4×10^{15} molecules, the first arrest on the anodic oxidation curve corresponds to 7×10^{17} molecules per cm^2. However, as oxidation and the formation of divalent iron process, another kind of oxide evidently begins to accumulate on the surface with properties resembling those of the oxide film formed upon exposure of iron to gaseous oxygen. When a sufficient amount of such oxygen has accumulated on the surface, oxidation to divalent iron comes to an end and oxidation of divalent to trivalent iron begins.

Our data on the influence of oxygen on the passivation of iron have shown that when oxygen is adsorbed to the amount of 2×10^{15} molecules per cm^2 true surface, the electrochemical activity of the iron electrode is retained. Upon adsorption of 4×10^{15} molecules of oxygen per cm^2 complete passivation results. The indicated quantity of oxygen is not, however, the minimum for passivation of the iron electrode, for, as was pointed out above, anodic polarization is accompanied by removal of the oxide film. Were the latter process absent the amount of oxygen needed for passivation would probably be mush less.

In order to reduce the rate of removal of the oxide film it is planned to passivate the iron electrode with oxygen at low temperatures, since it is known that the evolution of gas from the iron electrode falls off greatly as the temperature is lowered.

Although our investigation has by no means been carried to completion as yet, nevertheless we feel that the method applied permits of a qualitative study of the mechanism of passivation of iron.

We take advantage of the opportunity to express our gratitude to Prof. A. Frumkin for his interest in the present work.

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Received
November 15, 1945.