The theory, in the form of Equations C and D, has been tested out here by direct experiment. It would, however, be superfluous to publish the results, seeing that the theory is based on no other principles than those involved in Equation A, and that the validity of the latter is, sufficiently indicated by the cases discussed in the preceding section.

In conclusion, we will mention that the above is one of a series of studies (mostly experimental) that have been made possible by a grant from the Rumford Fund of the American Academy of Arts and Sciences. It is a pleasure to again express our thanks to the Rumford Committee for their generous interest in this work.

WORCESTER. MASS.

PASSIVITY OF METALS.

BY HORACE G. BYERS AND SETH C. LANGDON.

Received July 18, 1914.

Introduction.

In a previous paper by one of us,[1] the term passivity was defined as properly applying to an element when it "shows abnormal electrochemical relations, and a chemical inactivity not corresponding to its ordinary behavior and not in accord with its position in the electromotive series of the elements." These characteristics are exhibited by a number of elements under a variety of circumstances and to varying degrees, but the passivity of iron has been most carefully studied and the present paper is limited to a study of one phase of its behavior. Iron becomes passive when immersed in certain electrolytes, which are always oxygen compounds. It also becomes passive under certain conditions when used as an anode. In this case also, the electrolyte is almost always an oxygen compound in solution in water. The most apparent evidences of transition from the active to passive condition of iron, as an anode, are: the metal no longer dissolves, its surface brightens, oxygen is evolved from its surface and, coincident with these changes, an ammeter, in series in the circuit, shows a sudden drop in the current. Considerable work has been done in this laboratory on this behavior and the conclusion reached,[2] that the following factors influence the establishment of the passive state in iron used as an anode: (*a*) the character and condition of the metal; (*b*) the electrolyte employed; (*c*) the temperature; (*d*) the curent *density;* (*e*) the duration of passage of the current; and (*f*) the character of movement of the electrolyte.

In the hope that the above variables represented a complete catalogue, it was thought that light could be thrown upon the subject by a study of the behavior of an anode when *two of the factors were allowed to vary mutually while all others were held constant.* Below, is given, briefly, the experi-

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[1] THIS JOURNAL, **30**, 1718 (1908).

[2] *Ibid.*, **35**, 759 (1913).

mental method employed and results obtained when the attempt was made to determine the relation between the current density and the time required to induce passivity.

Experimental.

The arrangement of the apparatus is shown in Fig. 1. The electrolyte used was 0.2 N sulfuric acid contained in a small glass cell immersed in ice water. The anode was a piece of iron wire "for standardization," diameter 0.720 mm., sealed with paraffin into a glass tube so that a length of exactly 10 mm. was exposed. The cathode was a platinum wire sealed in a glass tube. The electrodes were connected in series with six storage batteries, a resistance box, a Weston milliameter and a key.

The external resistance is first adjusted so that a current of the required density will flow through the circuit, and the time required to convert an active anode to the passive condition is determined by a stopwatch, the time recorded being the interval between the closing of the key and the appearance of the phenomena above described. If the current be not too small, the time required is fairly small and, therefore, iron is dissolved to an extent insufficient to materially affect the diameter of the wire. It was, therefore, possible to make a series of determinations on one section of wire. In order that these should be comparable, the circuit was broken as soon as the iron became passive and allowed to remain open 30 seconds before closing the circuit for the next determination. This interval is quite sufficient for, in 0.2 N sulfuric acid, iron rendered

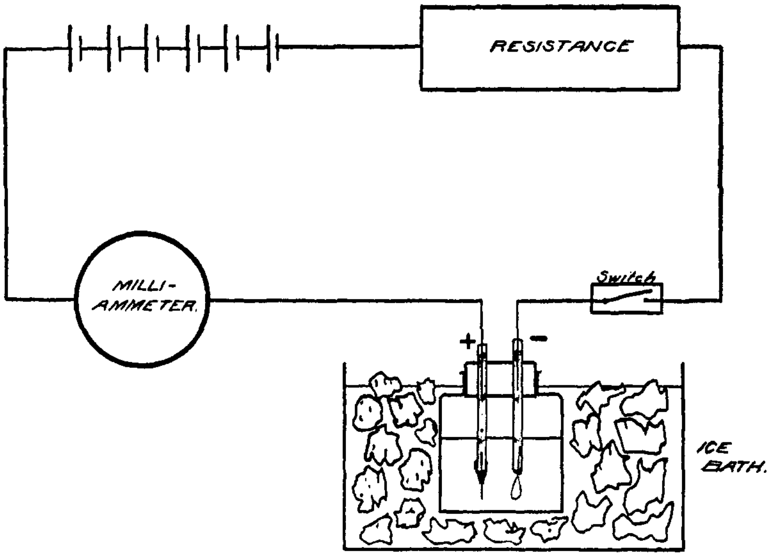

Fig. 1.

passive as an anode almost instantly becomes active when the current is stopped. The character of the results is shown in Table I.

TABLE I.

0.2 N H_2SO_4; temperature, 0°; 10 mm. wire exposed.

Milliamperes current.	Time in seconds to passivify the iron.	Diameter of the wire.
30	12	0.709
30	22	0.707
30	24	0.705
30	26	0.703
30	25	0.797
30	28	0.695
30	28	0.693
30	30	0.687
30	29	0.685
30	29	0.680
30	38	0.675
30	31	0.670

Disregarding the first determination, there is a range of difference from the mean time of 28 seconds which is not to be accounted for by the small variation of current density due to change in the surface of the wire exposed. A large number of similar determinations were made, using current densities ranging from 15 to 80 milliamperes with a corresponding time required to passivify the iron varying from 21 minutes to 3 seconds. All experiments showed a similar lack of agreement between individual measurements. Sets of determinations were also made at 18° and at 25°, using the cell in a thermostat. These gave even less satisfactory results, due, in part, to the greater loss of iron while rendering the anode passive, greater current densities being needed at higher temperatures. These somewhat extended experiments failed to show the desired uniformity of relation between two variables and the suspicion that all the factors influencing the passive condition were not yet at hand grew more pronounced.

During the progress of the work it was noted that minute bubbles of oxygen occasionally adhered to the surface of the iron even after it became wholly active and that in such cases the metal became passive more readily. Jarring the electrode, or stirring the electrolyte, partially obviated this difficulty, but when minute bubbles were allowed to persist, the results still varied widely. This suggested that *dissolved* oxygen in the neighborhood of the electrode might be a factor in our problem.

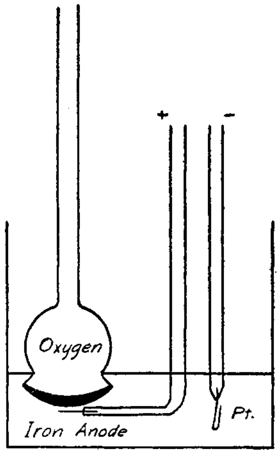

Fig. 2.

To test the question an apparatus, Fig. 2, was so arranged that the iron anode could be held close beneath an atmosphere of oxygen which was kept at constant pressure in the thistle tube. By rotating tube bearing the anode, it could be readily removed somewhat distant from this concentration of oxygen. The results obtained (Table II) indicate clearly that iron is much more readily made passive near the oxygen surface. When hydrogen gas or nitrogen was substituted for oxygen no such effect was produced.

TABLE II.

N/5 H_2SO_4; room temperature; 5 mm. iron wire exposed.

No.	Time in sec. for 30 m. amps. to passivify.	Diam. of wire in mm.	Relation of iron to oxygen bubbles.	No.	Time in sec. for 30 m. amps. to passivify.	Diam. of wire in mm.	Relation of iron to oxygen bubbles.
1	10	0.710	Under	13	37	0.700	Not under
2	11	0.709	Under	14	17	0.700	Under
3	16	0.708	Under	15	23	0.700	Under
4	17	0.708	Under	16	24	0.697	Under
5	13	0.708	Under	17	45	0.693	Not under
6	13	0.707	Under	18	19	0.693	Under
7	27	0.706	Not under	19	47	0.692	Not under
8	26	0.706	Not under	20	25	0.688	Under
9	15	0.705	Under	21	63	0.688	Not under
10	22	0.705	Under	22	30	0.680	Under
11	22	0.704	Under				
12	20	0.702	Under				

Nos. 3–6 show an average a little above 15 seconds.

Nos. 7 and 8 not under the oxygen required about twice the time.

No. 9 under the oxygen, goes down to 15 seconds again.

After No. 9, the iron was removed from the electrolyte, washed and dried and the experiment discontinued for about 20–25 minutes and after this more time was required to render the iron passive but in general the time required under the oxygen was about half that required when not directly under the bubble of oxygen.

The effect of higher concentrations of oxygen was next investigated with the apparatus arranged as in Figs. 3 and 4. A tank of oxygen was connected to a manometer and thence to the cell, which was closed by a rubber stopper held in place by a pressure clamp. The anode and cathode were arranged as before, except that the anode was held in place by Khotenski's wax and then coated with paraffin. A length of 5 mm. was exposed. The electrical connections were as before. The cell was placed in an ice bath not shown in the cut. All factors known to influence passivity were thus held constant except the concentration of the oxygen above, and consequently in, the solution. After a desired oxygen pressure had been established and sufficient time to secure saturation had elapsed, the cell was shaken with a circular motion to insure freedom from anode bubbles. After 30 seconds the circuit was closed and the time required for a current of 15 milliamperes to passivify the iron was measured. The circuit was then opened and measurements repeated. Table III shows

TABLE III.

No.	Time in seconds to passivify the iron.	Oxygen pressure in pounds per square inch.
1	?	air that is oxygen, 3 pounds
2	40	
3	45	
4	45	
5	45	
6	20	15 pounds
7	21	
8	22	
9	20	
10	20	
11	12	51 pounds
12	11	
13	12	
14	$10^1/_2$	
15	11	
16	11	
17	11	
18	7	57.4 pounds
19	$6^1/_2$	
20	7	
21	$6^1/_2$	
22	7	
23	5	65.88 pounds
24	6	
25	5	
26	5	
27	4	81.34 pounds
28	$4^1/_2$	
29	5	
30	4	
31	4	
32	34	Here fresh electrolyte substituted. Saturated with air, *i. e.*, oxygen, 3 pounds
33	45	
34	45	

0.2 *N* sulfuric acid. 5 mm. length of iron wire exposed. Initial diameter 0.710 mm. Final diameter 0.680 mm. 15 ma. current employed while rendering iron passive.

such a series for pressures of oxygen ranging from 3 lbs. per sq. in. to 81 lbs. with one section of wire. The values so obtained represent a very satisfactory constancy and are typical of a large number of series which are not detailed.

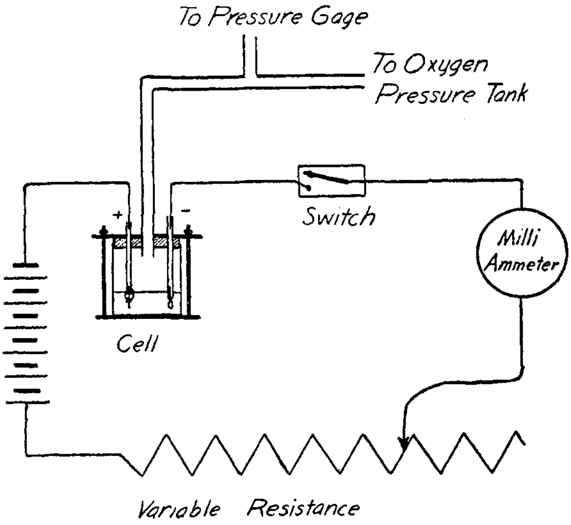

Fig. 3.

It will be observed that loss of surface area, due to solution of the iron, is not a seriously disturbing factor since the decrease of diameter of the iron in succesive determinations is about 0.0009 mm., and only 0.03 mm. in the whole series of 34 determinations. When oxygen pressures of 0.2

atmosphere, secured by air pressure were used no such uniform agreement in time, required to render iron passive, could be obtained. This accounts to us fully for our long-continued failure to secure quantitative results under atmospheric pressures. When 0.2 N nitric acid was used as the electrolyte, other conditions being otherwise the same as those above detailed, the results were different; the iron becomes active much less readily in nitric acid. It was finally found necessary to remove the iron after each determination, wash with 0.2 N sulfuric acid and with water before a satisfactory repetition could be obtained. With nitric acid also, the factor of continued passage of the current is less marked in its effect than with sulfuric acid, and a critical density is more apparent. Below this critical density, even long-continued passage of the current only infrequently produced passivity. If the current density is sufficiently great, passivity is established practically instantly. For 0.2 N nitric acid solution at atmospheric pressure, *i. e.*, about 3 lbs. per sq. in. of oxygen pressure, the critical current was found to be 20 milliamperes. At 56 lbs. oxygen pressure, the critical current was 13 milliamperes. It will be observed that increase of oxygen pressure here lowers the current density required to render the iron passive.

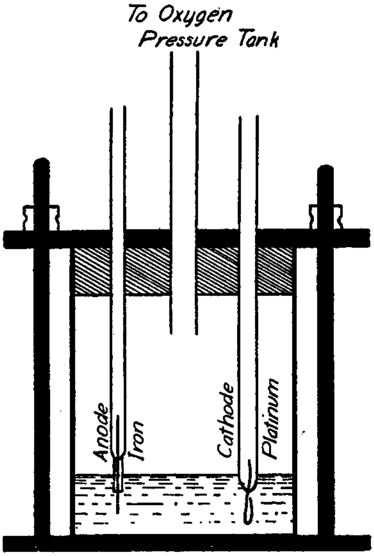

Fig. 4.

In 0.01 N hydrochloric acid with 53 lbs. oxygen pressure, oxygen was evolved freely and the other phenomena of passivity appeared when the current density was relatively high. When the other conditions, except the pressure of gas imposed, were similar, there was only a very slight evolution of gas at the anode. With 0.02 N hydrochloric acid less oxygen was evolved, and with 0.05 N and 0.1 N solutions no indications of passivity either with or without oxygen pressure, could be observed. It appears that with a sufficient dilution of chlorine ions the passive state can be induced in halogen solutions: a fact not heretofore demonstrated.

Summary and Conclusions.

From the foregoing results it appears that to the six factors, mentioned in the introduction, which condition the passive state is to be added a seventh: The concentration of dissolved oxygen about the anode. Indeed, this is apparently *the* determining factor. When all these factors are taken into account, constant results are obtainable with respect to the time required to render iron passive with a given current in sulfuric acid and in nitric acid a critical current density is determinable.

In a previous paper by one of us[1] it was stated that of the various theories concerning passivity none were satisfactory and that the writer had none to offer. It is desired here to formulate the ideas which have been developed by several years more or less of continuous investigation of the problem.

It would appear that of the various views offered several are correct so far as they go and for that reason were to a certain extent justified. The most satisfactory explanation of passivity is that furnished by Faraday —not the so-called Faraday explanation as perverted by Beetz and Wiedeman, but rather his statement that the state is one of a "very delicate equilibrium" between oxygen and iron. According to Le Blanc[2] iron has a limited rate of ionization at a given temperature. This may be taken as at least a reasonable hypothesis. If, now, a current is tending to leave an anode at a rate which requires solution of the metal, in accordance with Faraday's law, at a rate greater than the anode can ionize, then either the current pressure must increase the rate of ionization, anions must separate on the anode, or the current is retarded. If the anion is liberated and is of a type which when liberated covers the anode, one of two things occurs: 1st, When the anodic covering is highly non-conducting material, the current is cut off and the anodic deposition slows up or ceases. This is the type furnished by the reactions with cyanides, oxalates, etc. 2nd, In the case of compounds which readily liberate oxygen under anodic conditions, deposition of the gas on the surface takes place. When such deposition begins in effect, the surface of anode exposed is lessened and the rate of deposition is consequently increased. This explains the "spread of passivity" over an iron anode, which is a visible phenomenon. The anode being covered by a film of oxygen is no longer an iron anode but a gas electrode. The single potential measurements recorded by Schoch and others,[3] are then simply measurements of the potential of oxygen electrodes and have no relation whatever to the potential of iron itself.

It appears that oxygen *is occluded by the iron.* This conclusion is reached not alone from the fact that single potential measurements of iron and nickel, etc., when passive, are different but because maximum potentials are so reached. Also from an uncompleted investigation in this laboratory it appears that increase of oxygen pressure does not, at least at small pressures, increase the anodic potential shown by iron anodes.

The appearance of the passive condition on metals when they are simply immersed in electrolytes, as iron immersed in concentrated nitric acid,

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[1] *Loc. cit.*

[2] *Z. Elektrochem.*, 11, 9 (1905).

[3] N. T. M. Wilsmore, *Z. physik. Chem.*, 35, 291–332 (1900).

chromate solutions, etc., is to be accounted for by the presence of *pure oxygen* in these solutions. That such is the case is scarcely to be questioned if the principles of equilibrium reactions are taken into account. In the experimental portion of this paper it is shown that iron as an anode may be rendered passive in highly dilute hydrochloric acid. This is as it should be, when it is recalled that in the electrolysis of hydrochloric acid the proportion of oxygen liberated at the anode increases with dilution.

While the facts shown by Muthman, Heathcote and others, with respect to air or in a vacuum, argue strongly against the existence of an oxide film, they are to be expected if occluded oxygen is the real passive anode. It is, perhaps, not desirable to enter further upon a discussion designed to show how completely the facts accord with the view just presented, but we will content ourselves with a brief and clear restatement.

We consider passivity, not associated with a visible film, to be due to the rate of ionization of certain metals, being insufficient to carry currents of greater than certain densities. When such current density is exceeded, oxygen electrodes, consisting of occluded oxygen, are formed in oxygen electrolytes. Non-anodic passivity is likewise due to occlusion of oxygen and consequent protection of the metal from attack.

UNIVERSITY OF WASHINGTON.

LEAKAGE PREVENTION BY SHIELDING, ESPECIALLY IN POTENTIOMETER SYSTEMS.

BY WALTER P. WHITE.

Received July 20, 1914.

This paper describes methods of making insulation more effective in electrical measuring systems by diminishing the influence of disturbing electromotive forces, both external and internal.

These methods, whose principles were known for at least ten years before their application to the potentiometer, are no more needed by the potentiometer than by other instruments of equal delicacy, but are exceptionally effective with it. They are not needed where insulation is quite adequate, as it usually is in dry weather, and an enormous amount of excellent work has certainly been accomplished without them, so that they are sometimes regarded, on first acquaintance, as an unnecessary complication. But in damp weather they have often proved both indispensable and very efficient, yielding results of the highest precision under conditions that would have been nearly hopeless without their aid; while as to complication, the arrangements, once installed, require no attention whatever, and the time of installation, an hour or two, is less than may be required to even locate one of the leakages that might occur through their absence.

The general principle of the methods appears most simply in the prevention of external leakage, that is, of disturbances due to stray currents