

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

## ANODIC RELATIONS OF PASSIVE IRON WITH NOTES ON POLARIZATION POTENTIALS AS INFLUENCED BY EXTERNAL GAS PRESSURES.

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In a series of researches previously carried out in this laboratory,<sup>1</sup> it was determined that the establishment of anodic passivity in iron is influenced by the seven following factors: (1) the condition and previous treatment of the iron, (2) the nature and concentration of the electrolyte, (3) the stirring of the electrolyte, (4) the temperature, (5) the current density, (6) the time of flow of the current, and (7) the concentration of oxygen dissolved in the electrolyte.

The last factor was of striking interest, for it was found that with a pure iron anode, of 0.71 mm. diameter and 5 mm. in length, immersed in 0.2 *N* H<sub>2</sub>SO<sub>4</sub> at a temperature of 0° C., with negligible stirring influences, and with 15 milliamperes flowing, it required 45 seconds for passivity to be established, that is, if the electrolyte was saturated with oxygen at 13 pounds, pressure per square inch, but only 4 seconds were required if the electrolyte was saturated with oxygen supplied at a pressure of 81 pounds per square inch.

That the effect was due to the high concentration of dissolved oxygen, and not to the mechanical pressure, was shown by the failure of other gases, supplied at high pressure, to produce any corresponding effect.

Since it has been assumed that the anodic potential is a measure of passivification, it was expected that illuminating results would be obtained by a study of the effect of oxygen pressure on the potential of iron.

In order that the results obtained might be of greater value in interpreting the work already done, conditions analogous to those outlined above were chosen, *i. e.*, the same electrolyte, temperature, concentration, similar electrodes, etc.

In order to work with the high gas pressure the normal calomel electrode was modified somewhat in form, as shown in Fig. 1. The absence of air space within the cell prevents liquids from being forced back into the cell when pressure is applied. The fine capillary minimizes diffusion, and as fresh normal potassium chloride was introduced through the stopcock, after each set of measurements, any contaminated solution in the capillary was thus forced out. During the six months that the cell was in use its value was checked from time to time and showed very satisfactory constancy. Throughout the work a potentiometer, capable of detecting potential differences of one ten-thousandth of a volt, was

<sup>1</sup> Byers, *THIS JOURNAL*, 30, 1718 (1908); Byers and Langdon, *Ibid.*, 35, 759 (1913); 36, 2004 (1914).

used, but readings were taken only to the third decimal, for in most cases the potential fluctuates slightly from moment to moment. The instrument used was very satisfactory as it allowed very quick and accurate adjustment.

The initial electromotive force of different sections of wire, immediately after immersion in 0.2 *N* sulfuric acid was not always the same, but ranged between the limits +0.522 and +0.506 volt. This behavior, which is probably to be ascribed to variations in the material and surface of the electrodes, finds analogy in the variation of the time required for a given current to passivify different sections of wire.

As iron stands in contact with the acid its potential gradually changes, as shown in Table I, though the variations here are of a more uniform character and of greater magnitude than were shown in all cases.

TABLE I.

Time in minutes.....	Start	2	19	31	37	45
E. M. F. Volts.....	+0.511	+0.513	+0.523	+0.524	+0.524	+0.527
60	72	87	125	140	150	152
+0.530	+0.536	+0.536	+0.539	+0.542	+0.544 <sup>1</sup>	+0.549
					+0.549	+0.550

An exactly similar set of figures appears in Table II where at the end of seven minutes hydrogen gas, at 50 lbs. pressure per sq. inch, was applied. As a comparison of Tables I and II shows, the gas at this pressure caused no noticeable deviation from the normal behavior. Oxygen pressure showed a corresponding lack of effect (see Table II) on prolonged application, thus allowing the electrolyte to become saturated with the gas.

TABLE II.

Time in minutes.	E. M. F.		Time in minutes.	E. M. F.	
Start	0.507	No	Start	0.510	No
2	0.510	ext.	4	0.514	ext.
4	0.511	gas	7	0.515	pressure
7	0.513	pressure	8	0.517	
10	0.515		9	0.519	
12	0.517	Hydrogen	13	0.521	Oxygen
13	0.518	pressure	18	0.523	pressure
15	0.518	50 lbs.	19	0.524	53 lbs.
18	0.519	per sq.	20	0.524	per sq.
20	0.520	in.	25	0.526	in.
			27	0.527	

It may therefore be concluded that neither mechanical pressures nor the saturation of the electrolyte with hydrogen or oxygen produces a pronounced effect on the electromotive force of iron when immersed in 0.2 *N* sulfuric acid.

The second step was to obtain the electrode potential of iron electrodes held in the passive condition by a small current, and subsequently to de-

<sup>1</sup> Iron changed to fresh electrolyte.

termine the effect of oxygen and other gaseous pressures. The apparatus is shown in Fig. 1, and requires but little explanation. The iron electrode was in series with a platinum electrode, a milliammeter, five lead storage

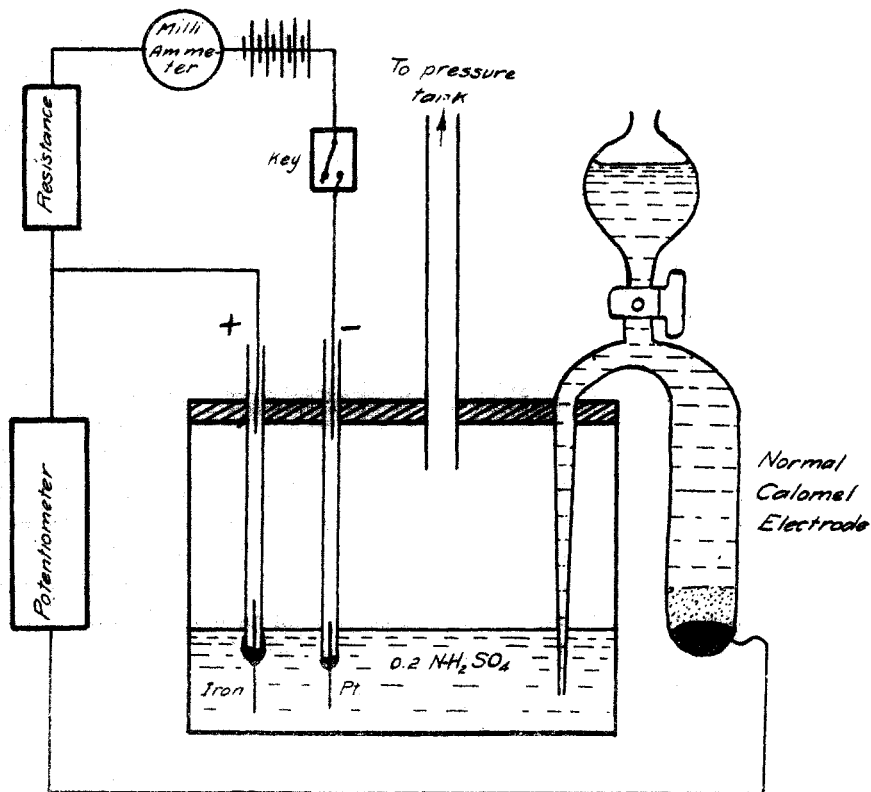


Fig. 1.

batteries, a variable resistance and a key. The potential difference between the normal calomel electrode and the iron electrode could be measured at any time by the potentiometer which was connected through a commutator.

With the arrangement just described, a section of wire was rendered passive at high current density and then the resistance of the external circuit increased until the polarizing current had dropped to 10 milliamperes. The first readings of the potential just after passivification were always higher than subsequent values. These changes, as appears in Table III, show that a polarized passive electrode becomes less noble on standing, even though a small external current is maintained to sustain the polarization. This is exactly analogous to the behavior of the active iron when no external current is used. (Compare Table I.)

TABLE III.

Iron passive. 10 M. A. flowing.								
Time	Start	4	7	10	16	20	22	24 min.
E. M. F.	+0.510	+0.512	-1.790	-1.789	-1.785	-1.782	-1.783	-1.781

The effect on this polarization potential produced by the application to the surface of the electrolyte, of oxygen gas under pressure, is shown in Table IV, where it is clearly evident that, coincident with the rise in pressure, there is a fall in potential, and that with the release of the pressure the potential again rises, but not as high as it was when the pressure was first applied.

TABLE IV.

Time in minutes.	E. M. F.	Ext. current.	O pressure applied. Lbs. per sq. in.	Time in minutes.	E. M. F.	Ex. current.	O pressure applied. Lbs. per sq. in.
Start	+0.506	None	None	30	-1.788	10 M. A.	42
1	+0.560	"	"	32	-1.786	"	"
2	+0.507	"	"	33	-1.788	"	"
Iron rendered passive and then current reduced to 10 M. A.				36	-1.796	"	None
3-5	Varying	10 M. A.	"	38	-1.798	"	"
7	-1.820	"	"	39	-1.796	"	"
10	-1.816	"	"	41	-1.796	"	"
12	-1.818	"	"	43	.....	"	48
15	.....	"	42	44	-1.786	"	"
17	-1.806	"	"	46	-1.787	"	"
22	-1.807	"	"	48	-1.788	"	"
23	.....	"	None	53	-1.793	"	"
25	-1.811	"	"	54	+0.518	None	None

This is not surprising in view of the fact just established in the previous experiment, that for an anodically polarized passive iron electrode the value of its potential gradually decreased with time.

That the change in potential is due to the mechanical pressure and is independent of the nature of the gas is also made clear by the data in Table V. A range of oxygen pressures was used and then a corresponding treatment using hydrogen pressure. The results as shown here are more uniform than those exhibited by most electrodes. The measurements in the table were all made on one section of iron wire but the data indicated were previously ascertained on divers sections and the results as shown are typical and are confirmed by numerous independent tests. The table shows the most complete and satisfactory single series of measurements.

When this work was undertaken it was expected that if the gas pressure produced any effect it would be after the electrolyte had become saturated with the gas, and that if the hydrogen produced any result at all that it would be opposite to that caused by oxygen. The fact that the change

TABLE V.

Time in minutes.	E. M. F.	Ext. current.	O press. applied. Lbs. per sq. in.	Time in minutes.	E. M. F.	Ext. current.	O press. applied. Lbs. per sq. in.
Start	+0.510	None	None	27	-1.770	10 M. A.	None
3	+0.510	"	"	28	-1.760	"	25.8
5	+0.510	"	"	30	-1.751	"	30.5
Iron rendered passive current then lowered to 10 M. A.				31	-1.740	"	34.6
8	-1.784	10 M. A.	"	32	-1.730	"	43.9
12	-1.771	"	"	34	-1.767	"	None
13	-1.771	"	"	35	+0.520	None	"
14	-1.730	"	43.9	38	+0.520	Iron active	
15	-1.768	"	None	Iron rendered passive and current lowered to 10 M. A.			
17	-1.771	"	18.7	40	-1.775	10 M. A.	
18	-1.730	"	43.9	41	-1.776	"	H press.
19	-1.730	"	43.9	44	-1.728	"	43.9
20	-1.730	"	43.9	48	-1.747	"	34.0
21	-1.768	"	None	50	-1.755	"	30.5
23	-1.730	"	43.9	51	-1.761	"	25.8
25	-1.748	"	30.5	53	-1.770	"	None
26	-1.760	"	25.8				

of potential was coincident with the application of the pressure and independent of the gas led to the suspicion that perhaps the phenomena were not characteristic of passive iron alone. To test this, potential determinations were made, under analogous conditions, on the following electrodes: an iron cathode, platinum anode and cathode, and a copper anode. Table VI shows the changes produced. The data for cathodes are only approximate, due to lack of constancy, so that the results are only qualitative, although the change with pressure is quite evident and it becomes clear that *on application of gaseous pressure, anodes, from which gas is being evolved, become more positive and cathodes more negative.* Nernst's equation for the potential of metal electrodes can be extended to the effects just described if the anode is considered as coated with an oxygen film or charged with oxygen, as by occlusion. In the equation  $E = (RT/Fn) (\text{nat log } P/p)$ ,  $P$  would represent the solution tension of the oxygen which is associated with the metal, and  $p$  would represent the osmotic pressure of oxygen ions in the solution. The application of any external pressure would then immediately increase the concentration of the oxygen associated with the metal and thus raise the solution tension  $P$  and the value of  $E$  the potential. On the other hand, the increase of the value of the osmotic pressure  $p$  would be a slow process, so that on application of external pressure the value  $P$  increases faster than  $p$  and there results the rise in anode potential. Exactly analogous relations exist in the case of the cathode and a similar explanation of the increased negativity of cathodes can be made. From the form of

the factor ( $\text{nat log } P/p$ ) it is to be expected that the change of potential with pressures, such as those used, would be small. Taking into consideration the facts indicating the presence of an oxygen film, this is the most useful hypothesis to apply in this case where the change in potential is small, such as would be expected if a gas film were considered. If occluded oxygen or an oxygen charge is assumed we are at loss for satisfactory explanation due to lack of knowledge of the coefficient of occlusion. The effects of pressure on potential, as above detailed, are new and merit fuller investigation. The potential measurements led directly to the studies which follow.

TABLE VI.

Platinum anode.			Iron cathode.		
0.2 N H <sub>2</sub> SO <sub>4</sub> , temp 0°.					
Polarizing current 8 M. A.					
Time in minutes.	E. M. F.	Hydrogen pressure. Lbs. per sq. in.	Time in minutes.	E. M. F.	Pressure. Lbs. per sq. in.
Start	-1.899	0	Start	+0.069	None
1	-1.898	0	4	+1.069	"
2	-1.879	50	7	+1.058	40 (hydrogen)
3	-1.882	40	9	+1.057	"
7	-1.884	38	10	+1.057	"
9	-1.885	35	15	+1.065	None
12	-1.890	28	20	+1.069	"
13	-1.898	0			
15	-1.898	28			
18	-1.893	34			
21	-1.886	46			
24	-1.882	57			
26	-1.882	57			
27	-1.903	0			
Copper cathode.			Platinum cathode.		
Start	+1.141	None	Start	+1.680	None
2	+1.140	"	2	+1.680	"
4	+1.127	29 (oxygen)	5	+0.685	"
6	+1.050	41 "	7	+0.673	43 (oxygen)
7	+1.160	None	8	+0.697	None
			10	+0.673	43 (oxygen)
			11	+0.676	43 "
			13	+0.793	None

In the hope of obtaining a more intimate knowledge of the processes of passivation a study was made of the changes of the potential of iron while it was passing from the active to the passive state, and the reverse. The conditions and apparatus used were exactly the same as in the work just detailed. The field of polarization potentials is one of unusual difficulty, because an electrode in contact with an electrolyte shows great variation in behavior, especially when an external current is impressed. Using the potentiometer previously described, the changes in potential when the iron was used as an anode were found to be interesting, but when attempts were made to get accurate readings of the momen-

tary values it was found that satisfactory and reproducible values could not be obtained.

The potential behavior of iron in contact with 0.2 *N* sulfuric acid, when no external current is flowing, has been previously described, and, as was shown in Table I, the potential gradually became more positive on standing. This value does not attain constancy in the course of two hours. Different specimens of iron wire on immersion in the acid show potentials ranging from +0.506 to +0.522 volt. When the external current, 10 milliamperes was applied, the potential quickly became less positive and at the end of two seconds it had generally passed through the value +0.11 volt. (See Fig. 2.) Then the change became slower and there was a continuous fall to about -0.15, and this was soon followed

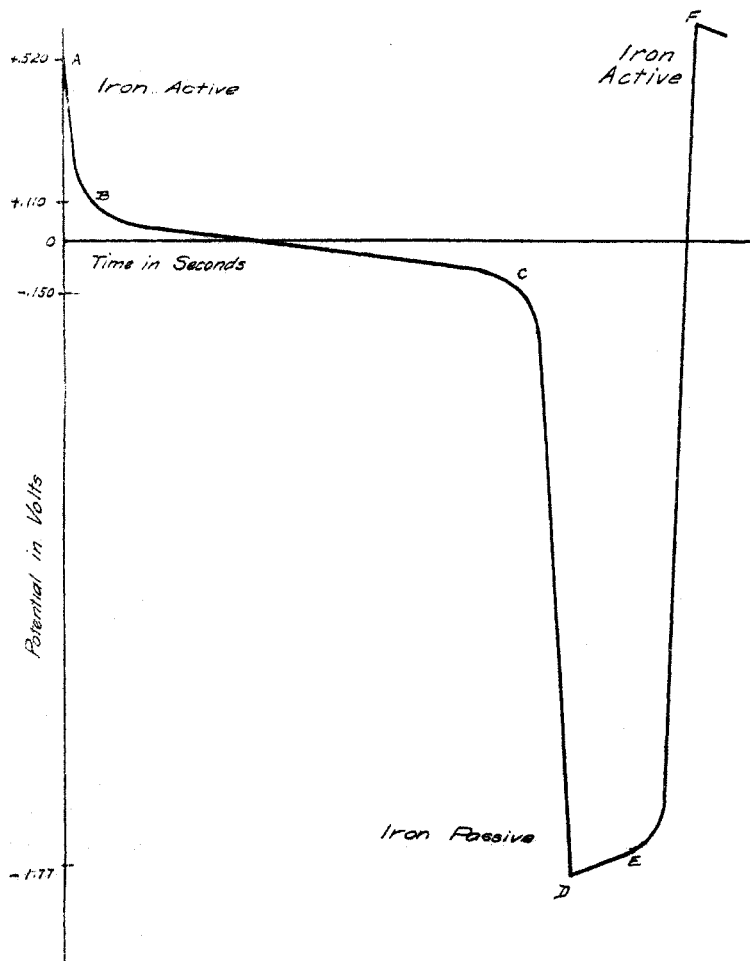


Fig. 2.

by a very rapid fall to the neighborhood of  $-1.85$ . Coincident with this last sudden drop the iron became passive and the resistance at the anode surface increased, as was shown by the fall in polarizing current.

When the external current was stopped the potential did not change greatly for a little while and then there was a very sudden rise as the iron became active. The time elapsing before activation sets in is longer when the passive electrode has been polarized for a greater length of time or when a high current has been used. On becoming active, with no external current flowing, the potential usually rose to a value slightly above 0.6 volt, which is higher than the initial value on first immersing the iron in the electrolyte. Potentiometer readings could not be made in the ordinary way, since during the processes the values were constantly changing. The current through the external circuit was changing in an analogous manner and this tends to show that the change of potential is associated with a change in resistance at the electrode surface. The external resistance was so arranged that there was, as nearly as possible, a current of 10 milliamperes flowing during the period shown in the curve by the length B to C. Using these conditions the method adopted was to choose a time, for instance five seconds, after the external current was applied, and then attempt to get as good readings of the potential at this time as was possible. The potentiometer circuit was closed with the instrument set at the estimated potential, then by the vigor and direction of the galvanometer throw the setting was estimated and, after the iron had been rendered active again, another trial was made at the end of the fifth second. Thus a value was approached; but there was always the difficulty that the potential of any particular specimen of wire was always changing and different samples gave different values, so that exact quantitative results were impossible. However, the graph gives a very good idea of the trend of events and the failure to obtain concordant results is characteristic of work in this field. Heathcote,<sup>1</sup> attempted to obtain a similar set of values with even less success, although he arrived at a somewhat similar curve for the changes of potential as iron becomes passive. The form of the curve (see Fig. 2) is such that it presents rather strong evidence in favor of the idea that the establishment of passivity is the result of two processes. The first of these would consist of the formation of a layer of insoluble material such as ferrous oxide. This would not be, of necessity, a firmly adherent coating and might be pierced by holes or pores. Its initial formation would correspond to the part of the curve from A to B. The other process would be the establishment of a film of oxygen gas which would form a complete cover over the electrode. The transition between these two processes is represented by the slow drop in potential shown between B and C, after which the

<sup>1</sup> *J. Soc. Chem. Ind.*, 26, 899 (1907).



cover rapidly becomes complete and potential drops from C to D. In a similar way the curve indicates that activification is a single process or at best practically the simultaneous removal of both the oxygen and the oxide coats. This removal is exceptionally complete as is shown by the final maximum potential. This may also be due to the removal of the occluded gases.

That the variation of anode potential is associated with a change of resistance at the anode surface is confirmed by the change in the polarizing current as the iron becomes passive. The graph (see Fig. 3) shows that

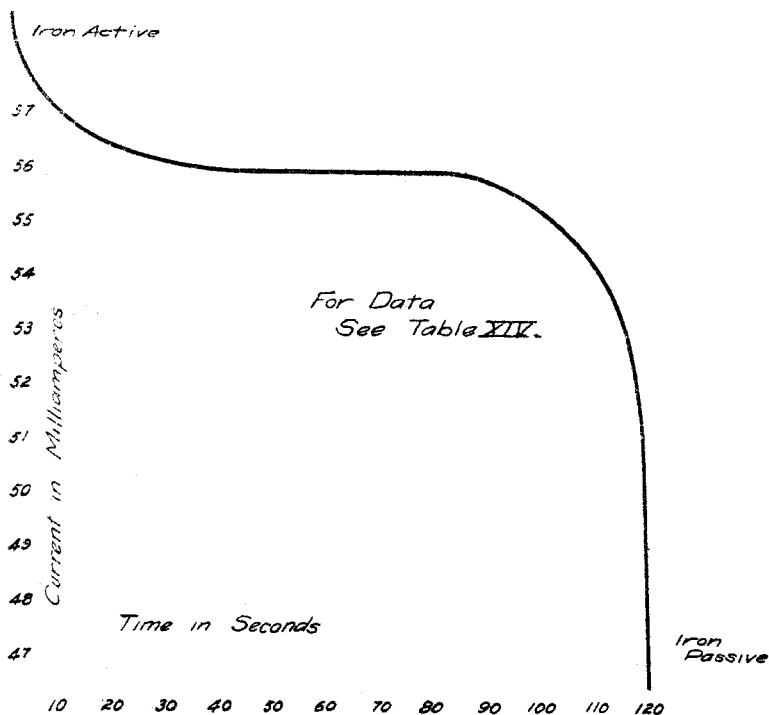


Fig. 3.

the variation in external current with time is exactly analogous to the changes in the anode potential during the process of passivification. In taking the data (Table VII) a long section of iron was used in order to obtain values of greater magnitude.

TABLE VII.

Conditions: Temperature, 18°. 0.2  $N$   $H_2SO_4$ . Diameter of iron wire, 0.770 mm. 25 mm. wire exposed. The wire had previously been rendered passive two or three times. Several successive determinations on the same section of wire gave exactly similar results. Throughout the work the external resistance was not changed.

Time in seconds.....	0	3	10	17	32	75	85	95	105	110	117	120
Current milliamps.....	59	58	57	56 $\frac{1}{2}$	56 $\frac{1}{4}$	56	56	55 $\frac{1}{2}$	55	54	53	46 $\frac{1}{2}$

The theoretical explanations of passivity are numerous and varied, but for the sake of brevity their historical review must be omitted, as well as the discussion of the principal phenomena.<sup>1</sup> However, in consideration of the seven factors mentioned at the opening of this paper, and in view of the potential relations above detailed, a brief theoretical statement now appears to be in order.

It seems to the authors that there is no general explanation of passivity but that the loss of activity is dependent upon the conditions, and that the explanation of the mechanism of the reaction will not come at one step by the announcement of an all-embracing hypothesis. Iron anodes in sulfuric acid behave differently, depending upon the circumstances. This has been pointed out by Schulze,<sup>2</sup> who says that in "dilute sulfuric acid iron shows passivity; in concentrated acid, valve action; in intermediate concentrations an unstable valve action succeeded by passivity." The nature of valve action is made clear by the behavior of aluminium, in that when used as an anode in a suitable electrolyte a film of aluminium oxide is formed and oxygen is evolved. The film is at first so thin that it is invisible but gradually builds up to a light gray coating pierced by very numerous holes of microscopic size. This film absorbs about 5% of the current, the rest being used in the formation of the oxygen which escapes. The work and conclusion of Schulze, although bearing largely on valve action, throw interesting and valuable light on the problem of passivity. The objection is often raised that, as in the case of iron, it is difficult to understand how oxide or hydroxide coatings exist in the presence of an acid electrolyte. Let us consider the case of a metal used as an anode and it is readily seen that there is no objection to the assumption that the surface of the metal itself is in contact with a neutral or alkaline medium, for since the anode is positively charged the hydrogen ions which bear a charge of like sign would be repelled, and their concentration materially reduced, in the zone of contact between the electrolyte and anode. On the other hand, negative ions would be attracted and increase the possibility of primary anionic discharge. The relations of iron to sulfuric acid are very complex, and it will be sufficient to outline the conclusions arrived at with respect to the mechanism of the establishment of passivity in iron when used as an anode in 0.2 *N* sulfuric acid, and under the *specific conditions* which have been maintained throughout the experimental work. There is little doubt but that we are concerned with surface conditions in our study of passivity. The potential curve shows that what occurs when passivity is established is a two-process change. The external current curve agrees with this.

<sup>1</sup> For a complete discussion see *Trans. Faraday Soc.*, 1914; Byers, *THIS JOURNAL*, 30, 1718 (1908); Heathcote, *J. Soc. Chem. Ind.*, 26, 899 (1907).

<sup>2</sup> *Trans. Faraday Soc.*, 1914.

Let us now consider a reaction mechanism that would account for these changes. (See Fig. 4.) The ordinary facts of electrode potentials show that metals can and do form ions directly so that with our iron anode it is very probable that there is an equilibrium between the metal and its ions. There is also evidence that the anions may be attracted to the surface of the anode and discharge directly on the iron to form free  $\text{SO}_4$  radicals. These latter may react directly with the metal to form ferrous

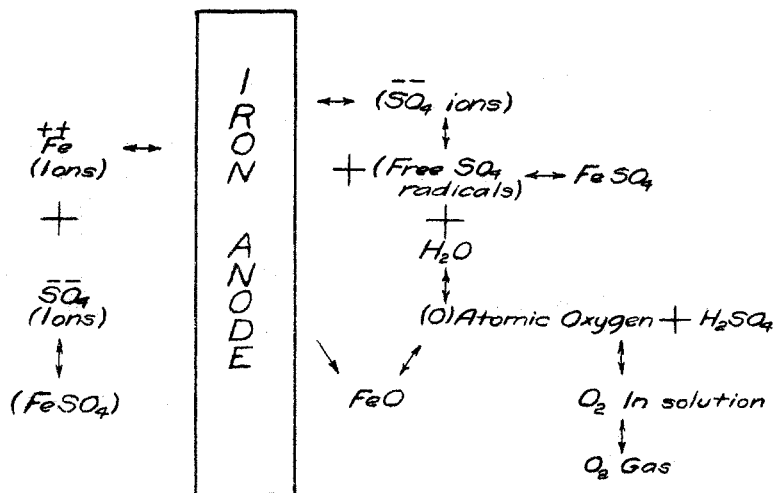


Fig. 4.

sulfate, or may react with water to form oxygen atoms. The oxygen atoms will react with the iron to form insoluble ferrous oxide or unite to form molecular oxygen. The equilibrium relations are shown diagrammatically in Fig. 4. Ferrous oxide is used in the equilibrium diagram to represent the initial step in the process of passivification, because this is the simplest assumption.

At the moment that the iron becomes an anode the greater part of the current is carried by means of iron ions entering the solution. But some anions are discharged directly on the surface of the iron and thus carry part of the current. These discharged ions can react with the iron to form ferrous sulfate, or with the water to form atomic oxygen, which in turn can form ferrous oxide or oxygen molecules. In the latter case the solution would eventually become saturated with oxygen and the gas would escape. But the formation of bubbles against an external pressure is a process that requires energy, and it seems that so long as the free iron is readily available it requires less work to form the very insoluble ferrous oxide. However, the more oxide that is formed the less free iron is available and more sulfate ions are primarily discharged, so that the concentration of free oxygen atoms would be so increased that the equi-

librium would be changed to the direction of the formation of oxygen molecules in solution. On saturation, if the intensity of the reaction is sufficient, gas will form and the electrode become covered with a film of oxygen, the high resistance of which accounts for the last final drop in the potential and current curves. On account of the surface tension this formation of the gas film will be quick and complete.

This hypothesis fits the facts which are characteristic of the behavior of passive iron anodes under the conditions studied. Particular attention is called to the strong confirmatory evidence given by the fact, established in the previous research, *that dissolved oxygen increases the speed with which passivity is established*, but does not materially affect the potential. With the high oxygen pressures the equilibrium conditions are made more favorable for the formation of the ferrous oxide and for the formation of the oxygen film. The fact that stirring retards the establishment of passivity is in perfect accord with the explanation given, for it certainly would tend to tear off the film of oxide, thus keeping fresh iron constantly exposed. However, after the passivity has been once established, the tendency of stirring to destroy the condition would be reduced to a minimum by the tendency of surface tension to keep the gas film intact. The re-establishment of activity occurs when, after the external current has been stopped, the gas film becomes ruptured in any way. Then the iron and oxide layers are in relation to each other very much as in a short-circuited cell and the activation occurs almost at once. The retarding influence of higher temperatures offers no difficulty. The fact that very low current densities do not passivify is not surprising in view of the equilibrium conditions which have to be established. It is here unnecessary to review all of the facts of passivity of iron to show that they accord with the explanation offered.

#### Summary.

The work previously done, in which seven critical factors bearing on passivity were established, has been extended to a study of the electro-motive behavior of polarized passive electrodes.

A special modified calomel cell for working at high pressures is described.

On application of gaseous pressures, anodes of passive iron, or any other metal anode from which oxygen was being evolved, became more electro-positive and cathodes more electronegative. The change was a function of the mechanical pressure and not of the degree of saturation of the electrolyte with dissolved gas.

Measurements of the variations of polarizing current and of anodic potential during the process of passivification gave curves which indicated that passivification was here a two-process operation.

It is pointed out that there is no one general explanation of passivity,

but rather that in each case the loss of activity is dependent upon the conditions.

A theoretical explanation is offered for the conditions studied.

SEATTLE, WASHINGTON.

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#### NOTE.

**A Simple Bath Used for the Solution of Samples in an Oxygen-free Atmosphere.**—The apparatus here described has for its application the solution of materials requiring heat in the absence of air. If a non-aqueous bath is desired it should be planned on smaller dimensions to avoid undue loss of liquid used.

An eight-inch porcelain evaporating dish is used for the bath. (See Fig. 1.) In the evaporating dish are placed some glass beads and a five-inch porcelain desiccator plate having under supports. On this plate is placed a heavy circular, square or triangular glass rod support for the dish which is to contain the sample. This support holds the dish in position. (A small porcelain desiccator plate can be inverted and used for the same purpose, the supports serving as points which partially enclose

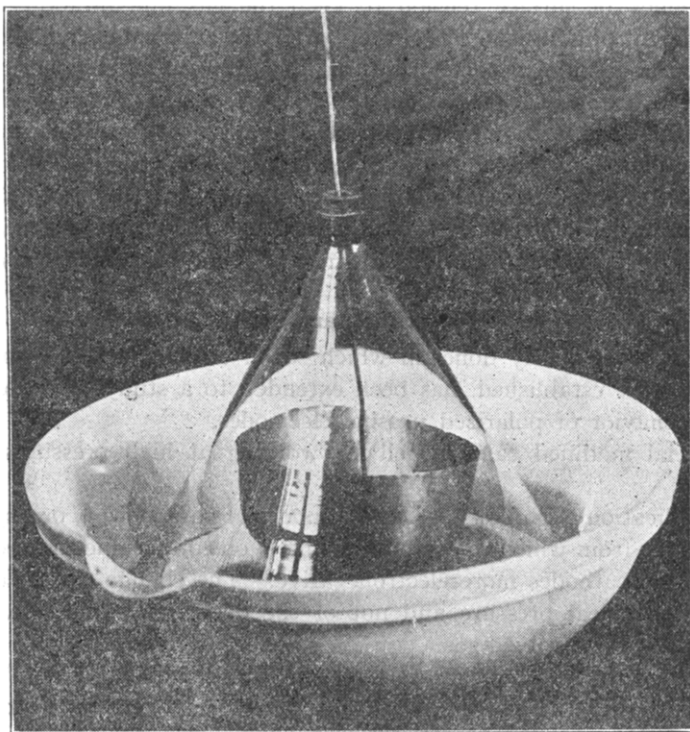


Fig. 1.