The equilibrium between carbon monoxide and water on the one hand, and formic acid dissolved in water containing hydrochloric acid on the other, was measured at 218° C. and at 156° C. The partial pressure of formic acid from a similar solution was also measured.

From these data, and those given by G. N. Lewis and M. Randall for the free energies of carbon monoxide and water, the free energy of formic acid was calculated.

In conclusion, I wish to express my indebtedness to Professor G. N. Lewis for valuable suggestions and assistance in the prosecution of this research.

[CONTRIBUTION FROM THE RICHARDSON CHEMICAL LABORATORY OF THE TULANE UNIVERSITY OF LOUISIANA.]

THE PHENOMENON OF PASSIVITY IN CONNECTION WITH FERROUS ALLOYS OF DIFFERENT COMPOSITION AND STRUCTURE.[1]

BY HAL WALTERS MOSELEY.

Received July 12, 1915.

Introduction.

The literature dealing with the phenomenon of passivity of iron has very little to say about the chemical composition of the samples used in the experiments and nothing to say about their physical structure. A careful examination of iron and steel from a metallographical point of view reveals the fact that there is a tremendous difference in its character, due to slight changes in chemical composition and to the method of treatment, whether mechanical or thermal or both.[2] The physical structure of a sample is dependent upon, and greatly influenced by, each of these factors. The study of its physical structure more often gives a sample's character than an ultimate chemical analysis, and it is therefore highly important that this factor be given due consideration in any study made upon commercial irons and steels. We were led to believe, therefore, that many of the apparently conflicting results recorded in experiments upon the passivity of iron and steel were due in part, at least, to the indistinct understanding of the nature of these differences, and that a study of the influence of these variables, if any, upon the phenomenon in a comparative way might lead to a more general conclusion as to its character.

The fact that iron will become passive has suggested at least a possible solution to the problem of corrosion. Cushman[3] in a comparatively

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[1] A paper read before the Section of Inorganic and Physical Chemistry, American Chemical Society, at the New Orleans meeting, April 2, 1915.

[2] Sauver, "Metallography of Iron and Steel," 1912.

[3] Cushman and Gardiner, "Corrosion and Preservation of Iron and Steel;" Cushman, U. S. Dept. Agric., *Bull.* 30, 29 (1907).

recent work states that "small quantities of inhibitive substances in boilers should be highly efficacious in preventing pitting." The inhibitive substances referred to are passivifying in character. In his work upon passivity of iron under boiler conditions, Byers[1] verifies Cushman's general conclusion, at least in so far as anodic conditions are concerned, and establishes the fact that iron (99.8%) can be made passive when the anode under steam boiler conditions. Byers also suggests the use of certain concentrations of potassium dichromate solutions in boiler waters as an inhibitor of corrosion. It, therefore, seemed of interest in this connection to study, in a comparative way, the behavior of irons and steels of known composition and structure when passivifying conditions were imposed, and if possible to make a statement which would be general for all classes of irons and steels.

Experimental.

Alloys Used in the Experiments.—We had at our disposal an unusually large collection of ferrous alloys. This material was prepared for Professor Rugan of Tulane University while research fellow in metallurgy in the University of Manchester, England, and contains a large variety of samples with carbon, silicon, manganese, sulfur, and phosphorus as variables. In addition, there were others which had been subjected to various thermal treatments with corresponding modifications in physical structure. We also secured a set of Carnegie Commercial steels from the open hearth process, ranging from 0.11% to 1.12% carbon, with manganese, sulfur, phosphorus fairly constant for the series. All these were normalized samples.

Comparative Study of Transition Points from Active to Passive when Samples were Made the Anode in a Definite Electrolyte, and in Different Electrolytes.—This study was carried out with the following points in view: first, to prove that samples of very different composition and structure could be made passive with a definite current density when the anode in an electrolytic cell, the other factors being constant; second, to determine the relative positions of the transition points, *i. e.*, current density required for passivifying, for the various samples; third, to study the influence of the various electrolytes upon the transition points; and fourth, to trace any relation between these transition points and the composition and structure of the samples.

The apparatus employed was essentially that used by Byers[2] in the experiments upon the influence of the magnetic field on the passive state of iron, with the exception of the electromagnet and the form of the electrodes. The anode was a highly polished button of iron having an exposed surface area of 3.45 sq. cm. A polished copper wire was wound

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[1] THIS JOURNAL, 34, 1368 (1912).

[2] *Ibid.*, 32, 750 (1910).

tightly around the circumference of the button and extending out some 10 cm. to make connection with the external circuit. The whole surface of the iron and copper except that prepared for exposure was coated over completely with hard paraffine for insulation.

The electrodes were put in series with the current source, a rheostat, and a Weston ammeter reading directly to 0.01 of an ampere. A voltmeter was connected across the circuit between the electrodes. When the iron was active the voltmeter would indicate the small differences of potential between the electrodes, and the ammeter would show a varying amperage with the change in resistance; when the iron became passive there was a sharp rise in the voltmeter readings and a corresponding drop in the ammeter readings. At this point oxygen was liberated from the anode.

TABLE I.—SAMPLES WITH C AND SI AS VARIABLES, MN, S, AND P FAIRLY CONSTANT.

	Chemical composition.					Current density in amperes per 3.45 sq. cm. necessary for transition from active to passive condition.		
Sample.	Per cent. C.	Per cent. Si.	Per cent. Mn.	Per cent. P.	Per cent. S.	10% nitric acid.	5% nitric acid.	*N* sodium sulfate.
A	4.03	0.243	0.15	0.15	0.108	1.10	1.00	0.10
B	3.70	0.233	0.16	0.011	0.018	2.10	1.35	0.26
C	3.08	0.172	0.13	0.01	0.019	1.90	1.00	0.40
D	2.59	0.146	0.12	0.012	0.016	2.10	1.35	0.36
E	1.96	0.215	0.20	0.015	0.013	1.90	1.35	0.50
F	1.58	0.168	0.17	0.014	0.015	2.00	1.35	....
G	0.99	0.233	0.19	0.012	0.015	2.05	1.40	0.48
H	0.55	0.182	0.20	0.014	0.013	1.75	1.25	0.52
I	0.15	0.186	0.15	0.017	0.040	2.00	1.50	....

TABLE II.—SAMPLES WITH COMPOSITION AND HEAT TREATMENT AS VARIABLES.

	Chemical composition.					Transition densities.		
Sample.	Per cent. C.	Per cent. Si.	Per cent. Mn.	Per cent. P.	Per cent. S.	10% nitric acid.	5% nitric acid.	*N* sodium sulfate.
D	2.59	0.146	0.12	0.012	0.016	2.10	1.35	0.36
D11	2.59	0.146	0.12	0.012	0.016	2.15	1.35	0.50
D16	2.59	0.146	0.12	0.012	0.016	1.65	1.25	0.45
D26	2.59	0.146	0.12	0.012	0.016	2.00	1.25	0.50
E	1.96	0.215	0.20	0.015	0.013	1.90	1.35	0.50
E11	1.96	0.215	0.20	0.015	0.013	1.90	1.20	0.47
E16	1.96	0.215	0.20	0.015	0.013	1.85	1.25	....
E26	1.96	0.215	0.20	0.015	0.013	2.00	1.25	0.50
F	1.58	0.168	0.17	0.014	0.015	2.00	1.35	....
F11	1.58	0.168	0.17	0.014	0.015	2.00	1.75	....
F16	1.58	0.168	0.17	0.014	0.015	2.05	1.45	....
F26	1.58	0.168	0.17	0.014	0.015	2.10	1.50	....
I	0.15	0.186	0.15	0.017	0.040	2.00	1.50	....
I11	0.15	0.186	0.15	0.017	0.040	2.25	1.50	....
I16	0.15	0.186	0.15	0.017	0.040	2.25	1.50	....
I26	0.15	0.186	0.15	0.017	0.040	2.35	1.45	....

TABLE III.—SPECIAL SAMPLES WITH C, SI, AND HEAT TREATMENT AS VARIABLES.

	Chemical composition.					Transition densities.		
Sample.	Per cent. C.	Per cent. Si.	Per cent. Mn.	Per cent. P.	Per cent. S.	10% nitric acid.	*N* phosphoric acid.	*N* sodium sulfate.
J........	4.60	0.79	0.126	0.016	0.018	1.50	0.34	0.52
J17......	4.60	0.79	0.126	0.016	0.018	1.75	....	....
O........	3.98	1.79	0.23	0.010	0.013	2.03	0.34	0.56
O2......	3.98	1.79	0.23	0.010	0.013	1.71	....	0.55
P........	3.79	2.96	0.25	0.010	0.012	1.57	0.37	0.57
P1......	3.79	2.96	0.25	0.010	0.012	1.80	....	0.57
Q2......	3.76	4.20	0.27	0.010	0.012	1.80	0.38	0.55
Q3......	3.76	4.20	0.27	0.010	0.012	1.59	....	0.52
R1......	3.79	4.83	0.30	0.010	0.012	2.02	....	0.57
R3......	3.79	4.83	0.30	0.010	0.012	1.70	....	....
S1......	3.38	6.14	0.30	0.010	0.013	2.92	....	....

TABLE IV.—CARNEGIE STEELS WITH CARBON AS THE PRINCIPAL VARIABLE.

	Composition.				Transition densities.		
Sample.	Per cent. C.	Per cent. Mn.	Per cent. P.	Per cent. S.	10% nitric acid.	*N* phosphoric acid.	0.5 *N* phosphoric acid.
T...........	0.11	0.36	0.011	0.038	2.38	0.31	0.28
U...........	0.24	0.45	0.016	0.040	2.17	0.34	0.27
V...........	0.47	0.50	0.013	0.033	2.38	0.32	0.27
W...........	0.60	0.38	0.011	0.033	2.17	0.35	0.27
X...........	1.04	0.42	0.048	0.035	2.38	0.30	0.25
Y...........	1.12	0.37	0.042	0.034	2.04	0.34	0.27
Z...........	0.20	....	High	High	2.24	0.30	0.25

Note: Where the single letter occurs—A, B, C, etc.—it refers to the original sample, and where the single letter occurs followed by numerals—D11, D16, D26, etc.—it refers to that many heat treatments where the sample has been heated above the critical range and allowed to cool properly the respective number of times indicated by the numerals.

The electrolytes used were: 10% nitric acid, 5% nitric acid, *N* phosphoric acid, 0.5 *N* phosphoric acid, *N* sodium sulfate. The results of these experiments are best understood by reference to the above tables.

The results conclusively prove that samples of iron of very different composition and structure can be passivified with a definite current density when the samples are made the anode in an electric circuit; they show that the passivifying current density is in no way related, at least in no simple way, to the chemical composition or structure of the samples; and they further show that the condition of passivity is intimately related to the passivifying electrolyte, and that current densities required to passivify in one electrolyte do not hold for others. The results of these experiments confirm the view that the phenomenon is very much more general than the work of others has shown.

Comparative Study of the Solution of Samples in 10% Sulfuric Acid at Current Densities below that Required for Passivifying.—These experiments were carried out with the following points in view: first, to determine whether there was a gradual change from active to passive, revealing itself in the amount of iron dissolved in a given time, as the current density approached nearer and nearer the transition point; second, to determine, if possible, whether or not the general statement that passive, iron does not dissolve appreciably holds for samples as heterogeneous as these under investigation; and lastly, to determine any relation that may exist between the amount of iron dissolved and that required by Faraday's law.

The apparatus used was essentially that described elsewhere in this paper. The samples were polished and reparaffined. The dissolved iron was determined by titration with 0.1 *N* potassium permanganate solution. The time of solution was five minutes and the amperage used was known to be below and approaching that required for passivifying. The electrolyte was 10% sulfuric acid. The results follow in tabular form.

The results are not conclusive. Nine out of fifteen samples reveal the fact that less iron goes into solution as we approach the transition point; some of the remaining reveal exactly the reverse condition, and some show irregularity of solution at different current densities. We believe, however, from the results that the phenomenon of passage from

TABLE V.—HEAT TREATED SAMPLES.

Sample.	Time.	Amperes.	Gram of iron in solution, actual.	Gram of iron in solution, calculated.	Difference.
E	300 sec.	0.2	0.01906	0.0173	+0.0017
E	300 sec.	0.4	0.03490	0.0346	+0.0003
E	300 sec.	0.5	0.04511	0.04325	+0.00186
E11	300 sec.	0.2	0.01557	0.0173	—0.00173
E11	300 sec.	0.4	0.03544	0.0346	+0.0008
E11	300 sec.	0.6	0.05155	0.0519	—0.00035
E16	300 sec.	0.2	0.01611	0.0173	—0.00121
E16	300 sec.	0.4	0.03327	0.0346	—0.0014
E16	300 sec.	0.6	0.05319	0.0519	+0.0012
E26	300 sec.	0.2	0.01986	0.0173	+0.0025
E26	300 sec.	0.4	0.03812	0.0346	+0.0035
E26	300 sec.	0.6	0.05531	0.0519	+0.0034
D	300 sec.	0.2	0.01825	0.0173	+0.0009
D	300 sec.	0.4	0.03222	0.0346	—0.0024
D	300 sec.	0.5	0.03866	0.04325	—0.00459
D11	300 sec.	0.2	0.02953	0.0173	+0.0122
D11	300 sec.	0.4	0.03275	0.0346	—0.0019
D11	300 sec.	0.5	0.04027	0.04325	—0.00298
D16	300 sec.	0.2	0.01879	0.0173	+0.0014
D16	300 sec.	0.4	0.03275	0.0346	—0.0019
D16	300 sec.	0.5	0.03866	0.04325	—0.00459
D26	300 sec.	0.2	0.01611	0.0173	+0.0012
D26	300 sec.	0.4	0.03275	0.0346	—0.0019
D26	300 sec.	0.5	0.0397	0.04325	+0.0035

TABLE VI.—CARNEGIE STEELS.

Sample.	Time.	Amperes.	Gram of iron in solution, actual.	Gram of iron in solution, calculated.	Difference.
T	300 sec.	0.1	0.01235	0.00865	+0.0097
T	300 sec.	0.2	0.01879	0.0173	+0.00149
T	300 sec.	0.3	0.02685	0.02738	—0.00147
U	300 sec.	0.1	0.01020	0.00865	+0.00155
U	300 sec.	0.2	0.01986	0.0173	+0.0025
U	300 sec.	0.3	0.02738	0.02595	+0.00143
V	300 sec.	0.1	0.0102	0.00865	+0.00155
V	300 sec.	0.2	0.01986	0.0173	+0.0025
V	300 sec.	0.3	0.02738	0.02595	+0.00143
W	300 sec.	0.1	0.01074	0.00865	+0.00209
W	300 sec.	0.2	0.01986	0.0173	+0.0025
W	300 sec.	0.3	0.02738	0.02595	+0.00143
X	300 sec.	0.1	0.01181	0.00865	+0.00317
X	300 sec.	0.2	0.0204	0.0173	+0.0031
X	300 sec.	0.3	0.02738	0.02595	+0.00143
Y	300 sec.	0.1	0.01449	0.00865	+0.00584
Y	300 sec.	0.2	0.01879	0.0173	+0.0014
Y	300 sec.	0.3	0.02792	0.02738	+0.00054
Z	300 sec.	0.1	0.02148	0.00865	+0.01283
Z	300 sec.	0.2	0.01933	0.0173	+0.0020
Z	300 sec.	0.3	0.03544	0.02738	+0.00806

Note: The plus sign indicates that more iron dissolved than was calculated according to Faraday's law, the minus sign indicating less.

active to passive is not an instantaneous change in properties, but a gradual adjustment toward a new condition of equilibrium. In regard to the second point involved, we found it exceedingly difficult to maintain the condition of passivity in acids when once the circuit was broken, and we are, therefore, not able to make a statement that heterogeneous samples do not dissolve when passive. The third point regarding the relation between the actual amount dissolved and that required by Faraday's law is also not clearly brought out. It was found that local action on the surface due to its heterogeneity materially influenced the amount of iron going into solution, and from the results we should judge that while the local action itself was less when the surface was under the influence of the external current, still the amount dissolved exceeded the value given by the law to such an extent that we believe local action plays an independent part in this process of solution. In other words, we may say that iron of this character goes into solution in other ways, when the anode in a circuit, than according to Faraday's law. We intend to repeat the experiment in electrolytes other than that used.

Comparative Study of Electrode Potentials of Certain Samples in Normal Nitric Acid and in Normal Sodium Sulfate.—The electrode potential of a metal immersed in an electrolyte is directly proportional to its solution tension. This solution tension is a measure of the ability of a metal to go over into the ionic form, and since in passive metals this tendency is practically reduced to zero, a study of the electrode potentials of different samples ought to reveal a proportionality between these potentials and the ability of the samples to go into the passive state. This is equivalent to saying that those metals with low solution tension, and, therefore, low electrode potential, ought to go over into the passive state more easily than those with higher solution tension. The purpose of these experiments was to find any such relation and if possible to prove or disprove the supposition in connection with heterogeneous material.

The samples employed were those described elsewhere in this paper. The electrolytes used were normal nitric acid and normal sodium sulfate. A normal calomel electrode[1] was used as a basis for the electrode potential determinations. The apparatus was arranged after this order. The half cell was arranged in series with the electrode through the intermediate liquid and the electrolyte, and connected to a Wolff potentiometer. The potentiometer was arranged in such a way that a fall of potential of 0.0001 of a volt per ohm was established.

The results are tabulated below:

TABLE VII.

In *N* nitric acid.		In *N* sodium sulfate.	
Sample.	Single potential of electrode.	Sample.	Single potential of electrode.
A	−0.2003	A	−0.0993
C	−0.1707	C	−0.0677
D	−0.1357	D	−0.0183
D11	−0.1382	D11	−0.0667
D16	−0.1657	D16	−0.0457
D26	−0.1168	D26	−0.0460
E	−0.1170	E	−0.0177
E11	−0.1184	E11	−0.0157
E16	−0.1059	E16	+0.0333
E26	−0.1137	E26	+0.0293
H	−0.1217	H	+0.0463
J	−0.1377	J	−0.0387
O	−0.1280	O	−0.1127
P	−0.1112	P	+0.0093
Q	−0.0789	Q	+0.0973
R	−0.0714	R	+0.1073
S	−0.0787	S	+0.1603

On examination of the electrode potentials of A, C, D, E, E16, Q, R and S in normal nitric acid and comparison of their transition densities in Tables I, II and III, we see a general tendency of the transition density to go higher as the electrode potentials get larger. The same general tendency is observed in the case of samples A, C, D, E, O, P, Q, R and S

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[1] Findlay, "Practical Physical Chemistry."

in normal sodium sulfate, in Tables I, II and III. It seems, therefore, that the original supposition that metals with low solution tensions passivify at a lower current density than those with high solution tensions is in general correct for this character of material. but the statement cannot be made more definite at this time.

Summary.

1. Samples of iron of very different composition and structure can be made passive when the anode is an electric circuit. The transition density from active to passive is not related in any simple way to the composition and structure of the samples. The nature and concentration of the electrolyte are factors in bringing about passivity in samples of the character of these just as for the pure metal.

2. We believe that the phenomenon is not an instantaneous change from active to passive, but a gradual adjustment toward a new condition of equilibrium, since in the majority of the experiments less iron goes into solution as the current density necessary for passivifying is approached. No statement can be made relative to the solubility of passive iron of this character, since the samples behaved normally, *i. e.*, when the circuit was broken the anode became active.

3. The current density required for passivifying increases with the electrode potential. In general, metals with low solution tension passivify at a lower current density than those with high solution tension.

New Orleans, La.

[Contribution from the Department of Chemistry of Swarthmore College.]

DETERMINATION OF THE SOLUBILITY OF SILVER NITRITE AND ITS DEGREE OF DISSOCIATION IN A SATURATED SOLUTION.

By Henry Jermain Maude Creighton and William Hillis Ward.

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The pure silver nitrite used in the following measurements was prepared as follows: To a solution of silver nitrate, a solution containing a 25% excess of potassium nitrite was added, the precipitated silver nitrite allowed to settle, the supernatant liquid then decanted off and the crystals washed several times with cold water. These crystals were then recrystallized twice from hot, distilled water, and finally dried between filter paper. In order to ascertain the purity of these crystals of silver nitrite, which were pale, lemon yellow in color, their silver content was estimated by analysis with standard ammonium thiocyanate solution, ferric alum being used as an indicator. The results obtained were as follows: (I), 70.05% Ag; (II), 70.08% Ag; (III), 70.07% Ag. The close agreement between these values and the theoretical (70.10% Ag) is indicative of the high degree of purity of the silver nitrite used in the following measure-