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I. An X-ray investigation of the iron-copper system II. A study of the corrosion of galvanized sheet iron

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I. AN X-RAY INVESTIGATION OF THE IRON-COPPER SYSTEM

II. A STUDY OF THE CORROSION OF GALVANIZED SHEET IRON

By

James Hal Carter

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In charge of Major work

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TABLE OF CONTENTS

PART I.

PART II.

I. AN X-RAY EXAMINATION OF THE IRON-COPPER SYSTEM

I. INTRODUCTION

The iron-copper phase diagram has been the subject of much controversy. The greatest difference in opinions occurs concerning the miscibility of iron and copper in the liquid state.

The usual methods of thermal and microscopic analyses have formed the basis of previous investigations of this system. Each of these methods detects the presence of two or more phases but neither of them definitely establishes the identity of all phases present.

The object of the present study was to apply x-ray methods of examination to certain solid alloys of iron and copper with the view of locating the region of immiscibility. The rate of cooling of the alloys was fairly rapid. The region of immiscibility detected, therefore, corresponds to that which existed in the liquid state at the time of solidification. More rapid rates of cooling and also higher temperatures will be employed in future work.

II. HISTORICAL

A review of the literature shows no previous work on the application of x-ray methods to the study of any portion of the iron-copper system. The work that has been done on this system was based entirely upon thermal and microscopic observations.

Considerable controversy has occurred between some experimentors using the same methods. Chief among these was the heated argument between Ruer (1) and Muller (2) concerning the miscibility of liquid iron and liquid copper at temperatures represented by points just above the liquidus curve on the phase diagram.

Ruer and Goerens (3) have determined that the mutual solubility between iron and copper in the liquid state decreases with increasing temperature. Seemingly apparent contradictions to the phase rule exhibited by their experimentally determined diagram are explained on the basis of the system acting as a ternary one. The limits of miscibility of iron and copper in the liquid state at the melting point are given as 23.8 % and 85% copper. Separation into two layers takes place only when the system is heated 20° or more above its melting point. Otherwise the two metals remain emulsified. This type of diagram, shown in Figure I, would result from the intersection of a miscibility gap in the liquid phase with the liquidus line of the phase diagram. The phase diagram offered by these authors is identical with the one given in the International Critical Tables.

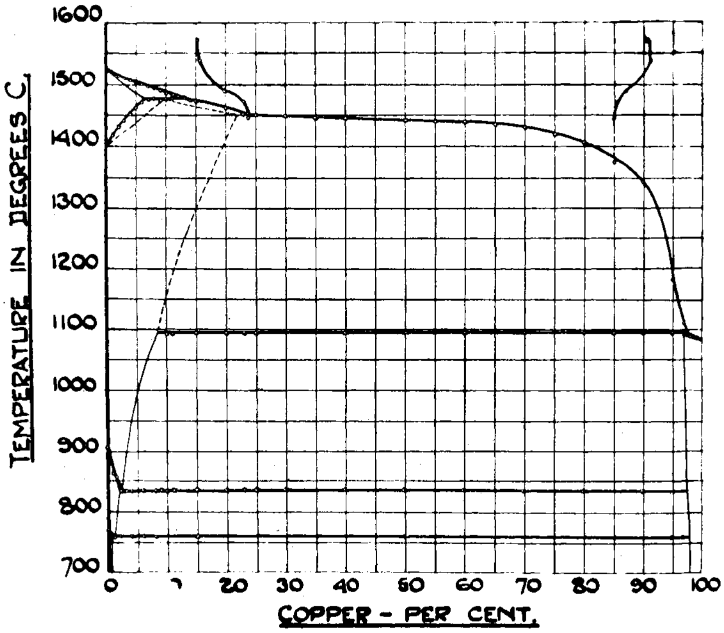


Fig. I

On the other hand, Muller (2),(4) came to the conclusion that there was a miscibility gap in the liquid state which had a lower critical point at about 1500° C. Muller's proposed diagram is shown in Figure II.

Ruer claims that Muller's results are due to the presence of impurities. If a lower critical point existed, then the two phases separating should become identical in composition at this temperature. On slow cooling to 1445° C. and with vigorous stirring, Ruer Goerens did not succeed in obtaining complete miscibility.

Benedicks (5) points out that an intersection of the miscibility curve with the liquidus curve appears absolutely possible. The decrease in mutual solubility with increase in temperature is explained on the basis of a larger temperature coefficient of atomic volume for copper than for iron. At low temperatures the atomic volume of copper is smaller than that of iron. However, the possibility exists that by increasing the temperature the difference in volume becomes important enough to cause a reduction of the mutual solubility.

Benedicks proposed the diagram shown in Fig. III which, he says, confirms the interpretation of Muller without conflicting greatly with the observations of Ruer and Goerens.

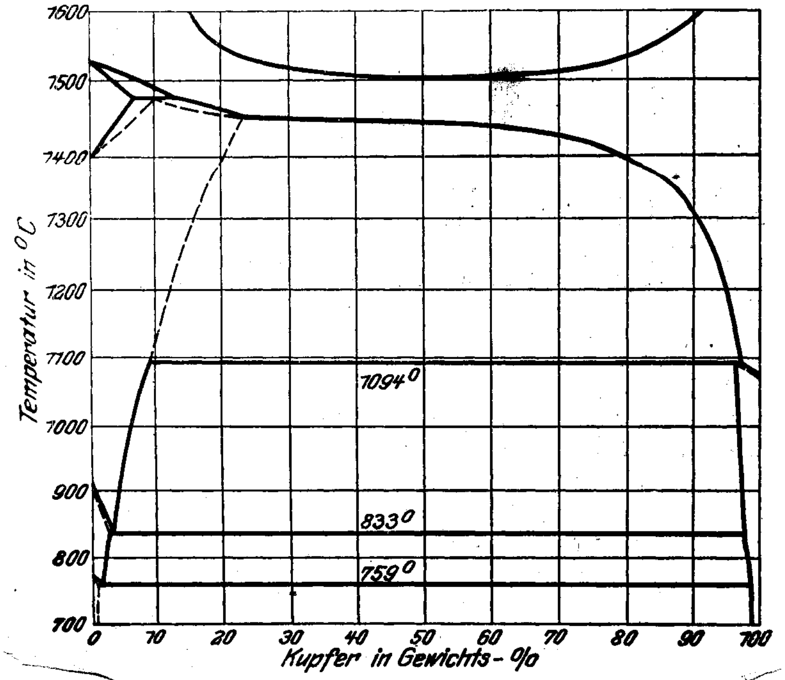


Abbildung 2. Zustandsschaubild
Eisen-Kupfer mit abgeänderter Mischungslüc

Fig. II

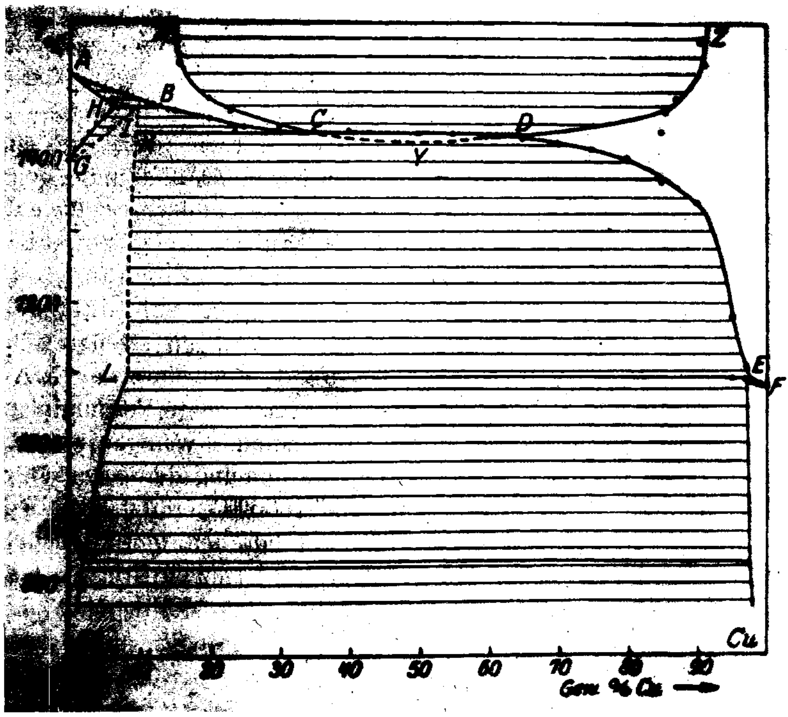


Fig. III

III. EXPERIMENTAL

A. Preparation of Alloys.

The alloys used in this work were made by melting together pieces of Armco iron rods and electrolytic copper of high purity. The melting was carried out in a magnesia crucible in connection with an Ajax induction furnace. The magnesia crucibles were made by molding moistened magnesia into form inside a graphite crucible and then, after drying, the crucibles were baked at about 1700° C. for approximately one hour. A modification of this method , using 10% $MgCl_2$, has been suggested by Jordan, Peterson, and Phelps (6). The graphite crucibles were 4 inches in length and 1 1/2 inches in inside diameter. The walls and bottom of the magnesia lining were about 3/8 inches thick.

About 150 grams of iron and copper, in the approximate ratio in which they were desired in any particular melt, were charged into the magnesia crucible and melted. A continuous stream of nitrogen gas was passed over the surface of the melt to prevent oxidation of the charge. This method was used by Ruer and Kushman (7) and also by Ruer and Fick (8) in the preparation of their samples.

The low per cent copper alloys were prepared by melting the iron separately and then adding the copper.

This proceedure lessened the danger of oxidation of the copper by shortening the time during which it remained in the crucible. After the charge was completely molten and the copper had been added, about 10 to 15 minutes were allowed for the melt to become uniformly mixed. The current was then shut off and the melt allowed to cool until it could be removed from the furnace. The samples were then ground on an emery wheel in order to remove the outside surface. The finished sample was about 2 inches in length and 3/4 inches in diameter.

A qualitative chemical analysis of several of the alloys showed that no impurities had been introduced during their preparation.

B. Analysis of Alloys.

The alloys were analyzed for per cent copper according to the method given by Lord and Demorest (9). The iron was removed as $Fe(OH)_3$ and the copper determined by the iodide method. Three check determinations were made and the average per cent recorded. The results of this analysis are given below.

TABLE I.

Alloy No.	% Cu	Alloy No.	% Cu
1	1.15	55	54.84
2	1.48	60	62.22
3	2.59	65	72.52
4	4.43	70	74.91
6	4.64	75	82.31
15	13.02	80	83.39
22	15.05	85	87.85
30	26.11	90	90.12
50	52.68	96	96.26

C. Heat Treatment of Alloys.

In order to determine the effect of heat treatment on the structure of the alloys, each sample was cut into two pieces and one piece of each sample was placed in a Hump annealing furnace. The temperature of the furnace was maintained at 1700° C. for a period of twelve hours. Then the current was shut off and the samples were left in the furnace until they had cooled to room temperature before being removed.

The furnace temperature was regulated and recorded by means of a Leeds and Northrup automatic recorder in conjunction with an iron-constantan thermocouple.

D. X-Ray Photography of Alloys.

An x-ray photogram was made of each alloy as cast and of representative alloys after they had been heat treated. The photograms were made by the Hull-Debye-Sherrer method on a General Electric Multiple Diffraction apparatus. The x-rays were generated by a Coolidge-type x-ray tube having a Molybdenum target. The samples were obtained in the form of filings and were mounted on the casettes by means of thin glass tubes about one or two millimeters in diameter. The average length of exposure was 24 hours.

The photograms of the original alloys, as cast, are shown in Figures IV to XII. Photograms of the heat treated samples are shown in Figures XIII to XVIII.

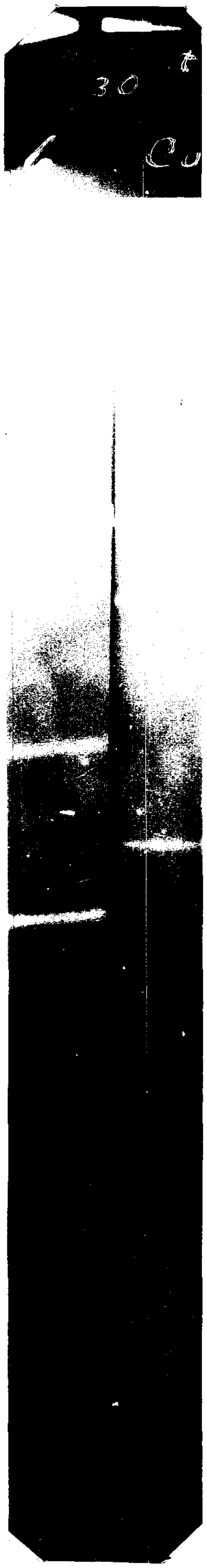
The following table gives the composition of the various alloys and the number of the photogram corresponding to it.

TABLE II.

Alloy Number	% Cu	Figure Number	Remarks
6	4.64	IV a	As cast
Cu	100.00	IV b	As cast
1	1.15	V a	As cast
2	1.48	V b	As cast
3	2.59	VI a	As cast
4	4.43	VI b	As cast
22	18.05	VII a	As cast
30	26.11	VII b	As cast
50	52.68	VIII a	As cast
55	54.84	VIII b	As cast
70	74.91	IX a	As cast
75	82.31	IX b	As cast
80	83.39	X a	As cast
15	13.02	X b	As cast
85	87.85	XI a	As cast
90	90.12	XI b	As cast
Fe	0.00	XII a	As cast
96	96.26	XII b	As cast
6	4.64	XIII a	Heated
15	13.02	XIII b	Heated
22	18.05	XIV a	Heated
30	26.11	XIV b	Heated
50	52.68	XV a	Heated
55	54.84	XV b	Heated
70	74.91	XVI a	Heated
75	82.31	XVI b	Heated
80	83.39	XVII a	Heated
85	87.85	XVII b	Heated
96	96.26	XVIII a	Heated
90	90.12	XVIII b	Heated

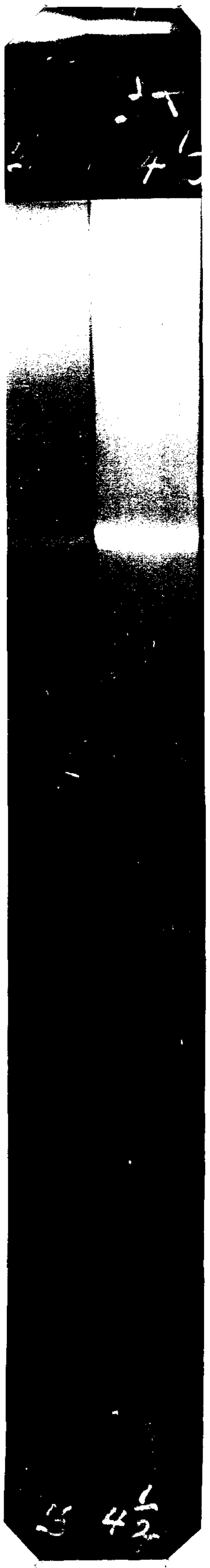
E. Photomicrographs of Alloys.

Photomicrographs were made of each alloy for which a photogram was taken. These photomicrographs are shown in Figures XIX to XXV. Each sample was etched with 5% nitric acid in alcohol solution for 8 seconds. The magnification in each case is 220 diameters.



(a) (b)
Fig. IV

(a) (b)
Fig. V



(a) (b)
Fig. VI

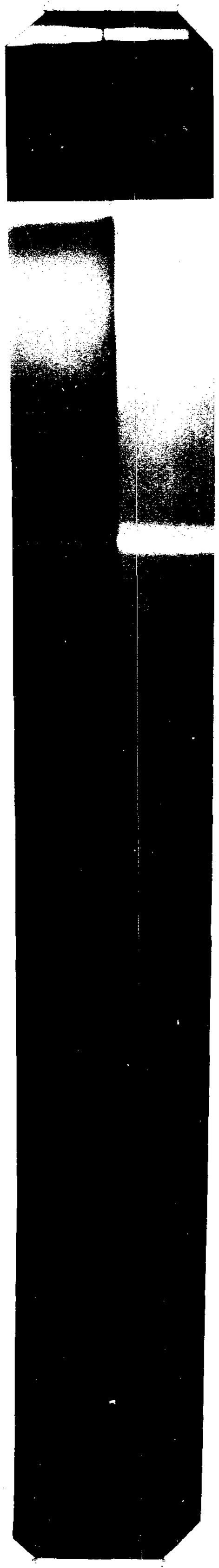


Fig. VII

Fig. VIII

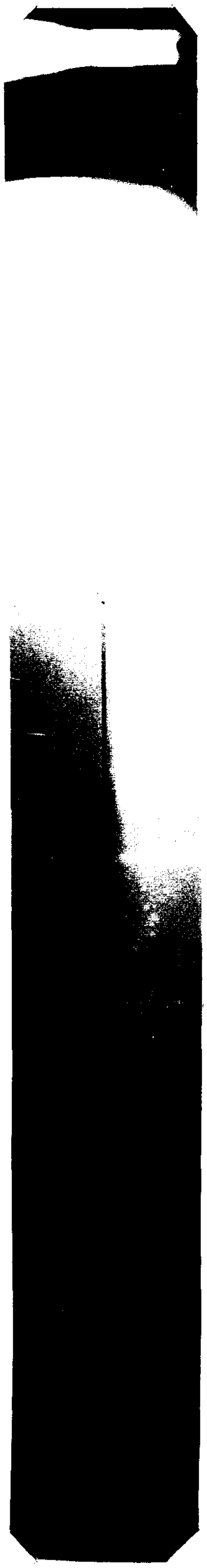


Fig. IX

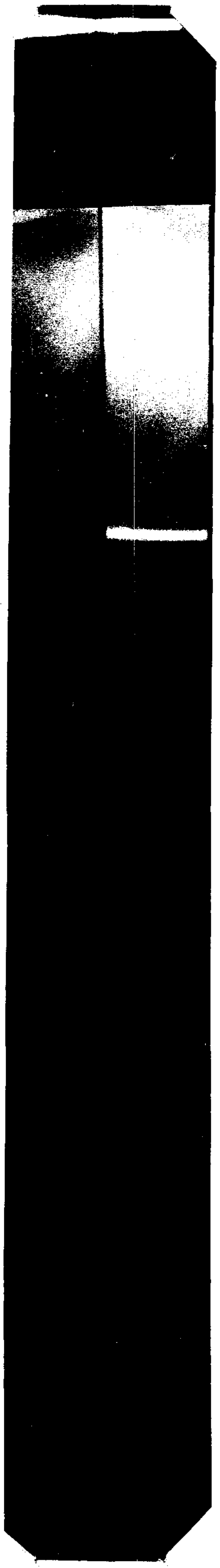


Fig. X

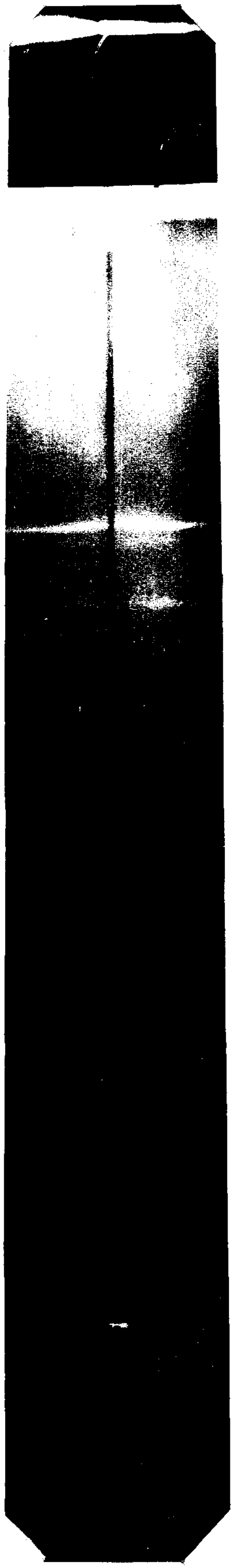


Fig. XI

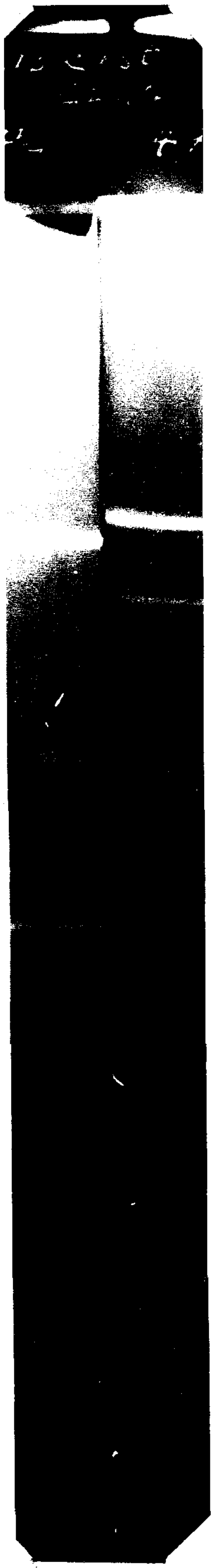
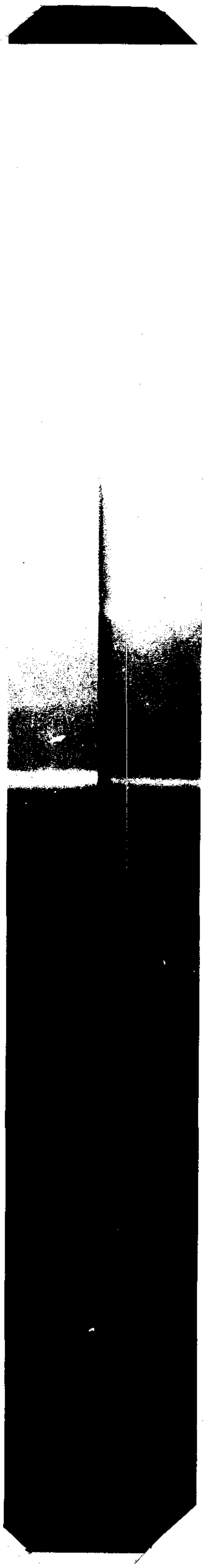
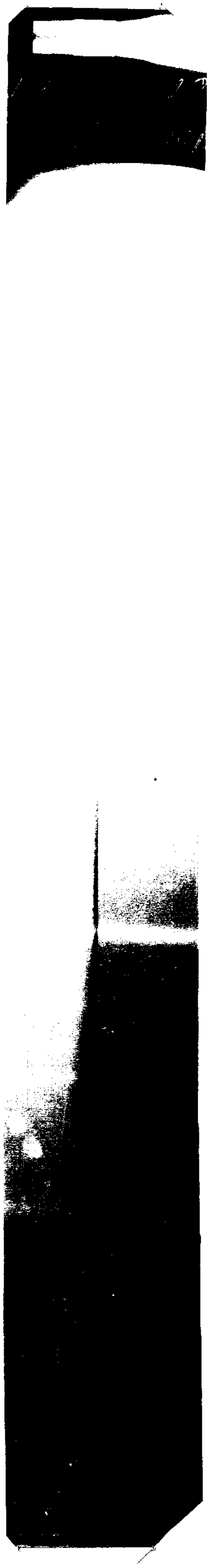


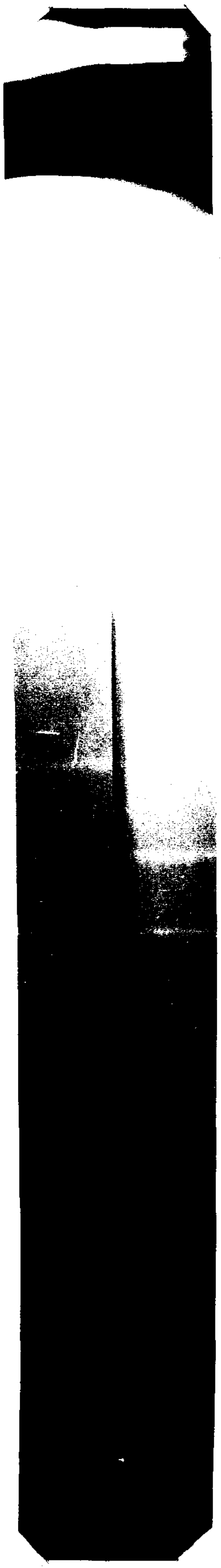
Fig. XII



(a) (b)
Fig. XIII



(a) (b)
Fig. XIV



(a) (b)
Fig. XV

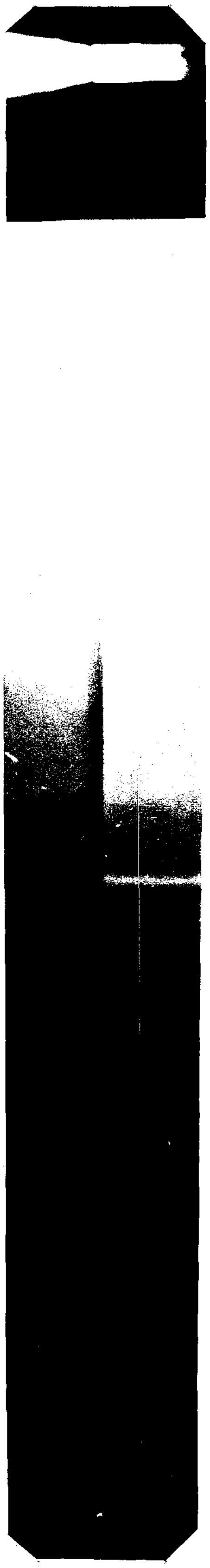


Fig. XVI

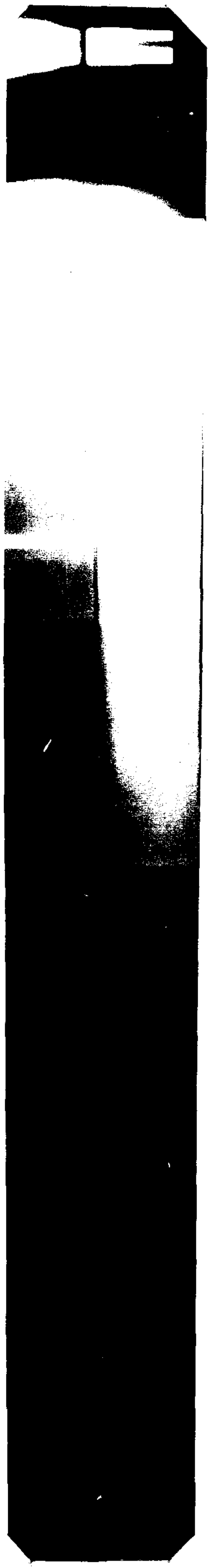


Fig. XVII

Fig. XVIII

Fig. XIX Sample 15
As cast 13.02% Cu

Fig. XIX Sample 15
Heated 13.02% Cu

Fig. XX Sample 22
As cast 18.05% Cu

Fig. XX Sample 22
Heated 18.05% Cu

Fig. XXI Sample 30
As cast 26.11% Cu

Fig. XXI Sample 30
Heated 26.11% Cu

Fig. XXII Sample 55
As cast 54.84% Cu

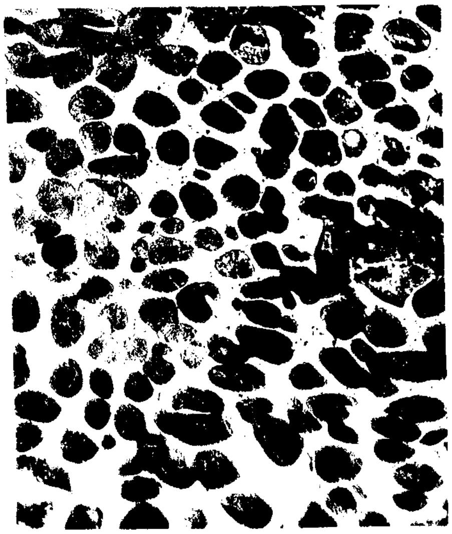


Fig. XXII Sample 55
Heated 54.84% Cu

Fig. XXIII Sample 70
As cast 74.91% Cu

Fig. XXIII Sample 70
Heated 74.91% Cu

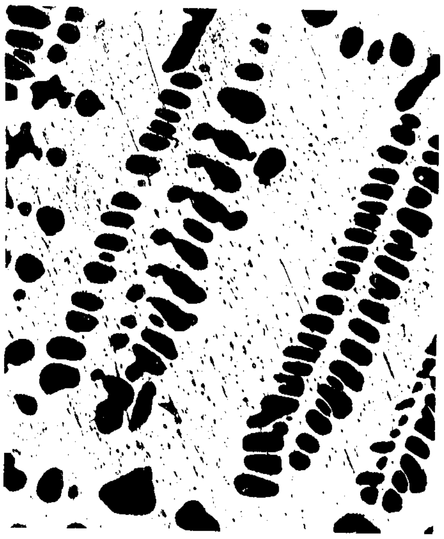


Fig. XXIV Sample 80
As cast 83.39% Cu

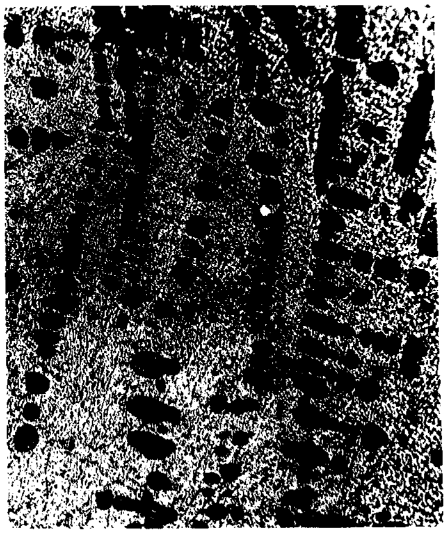


Fig. XXIV Sample 80
Heated 83.39% Cu

Fig. XXIV Sample 90
As cast 90.12% Cu

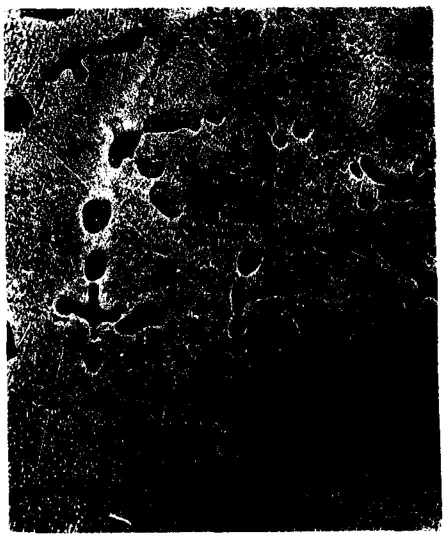


Fig. XXV Sample 90
Heated 90.12% Cu

IV. TREATMENT OF RESULTS AND CONCLUSIONS

An examination of the photograms of the samples as cast reveals three distinct types of results. The high per cent copper alloys do not give any indication of iron lines in the photograms. The low copper alloys show only iron lines. Then there is a region, of approximately equal per cent composition, over which the photograms show both iron and copper lines.

As standards for reference, photograms were made of pure iron and pure copper. When checked against these standards, the photograms of the iron-copper alloys show no lines which are not given by one or the other of the pure metals. Hence only two patterns, that of pure copper and that of pure iron, are to be considered.

It is evident from a study of the x-ray photograms that the copper lines make their first appearance in the case of sample number 22. No trace of copper lines is noticeable for sample number 15. This indicates a change of structure in passing from sample number 15 to sample number 22. These samples contain 13.02% Cu and 18.05% Cu respectively. The photogram of sample number 22 shows all the lines of both iron and copper.

As we examine the high per cent copper alloys, we find only copper lines for the samples numbering above 80.

The change is somewhat more difficult to detect than it was for the low per cent copper. This is probably due to the fact that copper shows more lines than iron. A close examination, however, shows the first appearance of iron lines as we pass from sample number 80 to sample number 75. These samples correspond to 83.39% Cu and 82.31% Cu respectively.

These results indicate that a miscibility gap does exist. The region of immiscibility begins between 13 and 18% copper on the low per cent copper side of the diagram and continues up to between 82 and 84% copper on the high per cent copper side of the diagram. These results are in fair agreement with those of Ruer and Goerens (3) for the upper limit but vary considerably for the lower limit. Ruer and Goerens gave the limits as 23.8% Cu and 85% Cu respectively.

Copper crystallizes in a face-centered cubic system. Clark (10) gives the value of the edge of the unit cube for copper as equal to 3.603 A.U. The corresponding value for gamma iron, which also crystallizes in the face-centered cubic system, is 3.63 A.U. These cubes, therefore, are not very much different in size and solution of each element in the other is not surprising. Evidently the x-ray pattern of the solvent, in this system, is the only one shown until the concentration of the solute reaches approximately 15% by weight. This marks the appearance of a new phase.

An examination of the photograms made of the heat treated samples shows results identical with those of the samples as cast. From this, we conclude that either the time of annealing was insufficient or that heat treatment had no effect on the structure of the alloys.

In order to obtain further information concerning this last mentioned point, samples of the alloys, both before and after heat treatment, were examined microscopically. A study of the photomicrographs shown in Figures XIX to XXV indicates that the annealing process has started some changes. Evidently the time of annealing was not sufficient. Lack of time has prevented further work on this point, but it is hoped that future work may be done to determine the effect of heat treatment on the limits of miscibility as found by examination of the unheated samples.

Summarizing, we may say that the results obtained seem to confirm the results of Ruer and Goerens as to the existence of an immiscibility gap. A fair agreement as to the limits of miscibility was obtained. Annealing at 1700° Centigrade for twelve hours evidently starts some change of structure, but the change is not sufficiently advanced to be detected by x-ray methods.

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II. A STUDY OF THE CORROSION OF GALVANIZED SHEET IRON

I. INTRODUCTION

The large and increasing tonnage of metals subject to corrosion in the industries has brought the question of conservation to the front as a major engineering problem. In the oil industry alone, losses and cost of main² tenance of pipe lines, tanks, and oil refineries amount to millions of dollars per year. Considerable losses have been experienced by the manufacturers of sheet metal to be used for culverts, water tanks, etc.

Prevention of corrosion may be worked out along three lines: (1) by developing more resistant metals, (2) by reducing the corrosive character of the environment, or (3) by the use of more stable protective layers of materials which are cheaper and much more resistant than the metal.

The present study is concerned with the second of these methods and was undertaken with the object of isolating a certain range of gas compositions most favorable to the progress of localized, or "buckshot", corrosion. This type of corrosion, sometimes referred to as pitting, occurs quite generally on galvanized sheet iron. Rust spots form on the surface of the metal and the corrosion gradually advances until a small hole, about the size of a shot, has been formed. In the case of large water tanks, these holes appear first near the bottom of the tank. The corrosion products usually collect around the pit in the form of a tubercle, or they may stream from the pit and start corrosion at other points. Evans (1) describes this phenomenon as point corrosion.

II. HISTORICAL

A review of the literature reveals but very little information concerning the effect of subjecting a metal to varying compositions of the atmospheric gases, oxygen, carbon dioxide, and nitrogen. Carbon dioxide (2), oxygen (3), and electrochemical action (4) have been regarded as the cause of the corrosion of iron. Arndt (5) states that when rusting begins it spreads with increasing rapidity, by the galvanic action between the rust and the metal. A surface covered with rust is not necessarily protected from further corrosion because the coating is usually porous and the oxygen of the air penetrates it. Gunderson (6) found that, in order to inhibit corrosion, the hydrogen ion concentration should be reduced to a low value, or oxygen should be removed from the water in which the metal was submerged.

The work of Shipley and McHaffie (7) also shows qualitatively the influence of oxygen. At a pH of 9.4 and in the absence of oxygen, they found that corrosion occurs and that the rate of corrosion increased directly as the hydrogen ion concentration. The presence of oxygen accelerated the corrosion due, they say, to the oxidation of ferrous ions to form ferric hydroxide, thereby increasing the hydrogen ion concentration.

Friend (8) exposed a cylinder of polished iron or steel to air enclosed in a flask over potassium hydroxide solution. The surface was not tarnished although it was kept constantly moist by condensation of the water vapor rising from the warmed potassium hydroxide solution.

In an investigation of the influence of oxygen and carbon dioxide on the corrosion of iron in water Inamura (9) has shown that the corrosion depends on the presence of oxygen in water free from carbon dioxide and that carbon dioxide accelerates corrosion in the presence of oxygen. Corrosion may proceed in water containing carbon dioxide in the absence of oxygen.

Bablik (10) holds that the protective action of zinc coatings does not depend on the formation of a galvanic couple between the zinc and the base metal, as none of the latter should be exposed if the galvanizing has been properly done. It is most probably due, he says, to the formation of a thin, tenuous film of zinc hydroxide and basic zinc carbonate on the surface of the coating. The presence of any substance in the atmosphere which will dissolve this coating tends to cause local perforations of the zinc and the setting up of local currents which eventually destroy the metal.

After watching the development of rust by means of a binocular microscope, Hanson (11) came to the conclusion that electrolytic action begins in the presence of water according to the equation:

$$Fe + 2H^{+} \text{ (ionic) } + 2(OH)^{-} = Fe^{+++}\text{(ionic) } + 2(OH)^{-} + H_2$$

The product of this reaction, $Fe(OH)_2$, forms a film on the metal and protects it from further corrosion. Carbon dioxide then reacts with this film forming ferrous carbonate which is later precipitated in the form of ferric hydroxide, when oxygen of the air dissolves in the water.

Hicks (12), using Malin's number 10 Music Wire , tried the effect of dry oxygen, dry carbon dioxide, moist oxygen, and moist carbon dioxide on the rate of corrosion. His results are given in the following table.

From the table it will be seen that the moist mixture of oxygen and carbon dioxide is the most active. However, no attempt was made to determine the optimum concentrations.

TABLE I.

Gas in Flask	Days to reach constant weight		Increase in weight mg/sq.cm.		Remarks
	25°	0°	25°	0°	
Dry O_2	5	5	None	None	From tanks dried by H_2SO_4
Dry CO_2	5	5	None	None	Same as above
Dry O_2 + CO_2	5	5	None	None	Equal volumes
Dry air, CO_2 free	5	5	None	None	Dried as above
H_2O vapor	6	6	None	None	Test piece hung over H_2O; air removed by H_2
Moist O_2	10	7	0.3	2.0	Hung over H_2O sat. with O_2
Moist CO_2	12	9	1.1	5.6	Hung over H_2O sat. with CO_2
Moist O_2 +CO_2	10	8	2.7	13.2	Hung over H_2O Gas-flow rates equal
Moist air	15	13	1.2	1.1	Air bubbled through H_2O

Recent results of Cox and Roetheli (13) led these authors to the conclusion that "corrosion rates of steel in oxygenated water are approximately proportional to the oxygen concentration below concentrations of 5.5 c.c. per liter, while at higher concentrations the rates of corrosion are considerably lower than those demanded by a strict adherence to the linear relationship."

III. EXPERIMENTAL

A. Preparation of Experimental Set-Up.

The corrosion set-up included three sets of twenty sample cans each. The sample cans were made from 18 gauge galvanized Armco sheet iron. The sheets, after being cut to the desired size, were rolled into shape. The sides were lapped one inch, riveted, and then soldered. The bottom was soldered to the can and the top was held in position by means of twelve 3/16 inch bolts. A 2-inch hole through the top, fitted with a rubber stopper, served as the inlet and the outlet for the gases. A double rubber gasket was used to make the top water tight. The cans were filled to within two inches of the top with conductivity water. Four watch glasses were placed symmetrically, convex side downward, on the bottom of each can. Each sample can, when finished, measured 23 inches in height by 9 1/4 inches in diameter.

Each set of sample cans was immersed in a thermostat tank which was made of the same material as the cans. The size of each of these tanks was 60 inches in length by 45 inches in width by 28 inches in height. Each tank was equipped with a heater and a stirring device.

The corrosion samples were also made from 18 gauge galvanized Armco sheet iron. The size of each sample was

9 inches in length by 2 inches in width. Each sample was perforated at five points on each side by means of a small power drill. It was intended that the perforations should just penetrate the zinc coating. Sixteen of these corrosion samples were placed in each can and were supported, by means of glass hooks, on a framework suspended from the top of the sample can. Eight of the samples were arranged circularly at the top of the sample can and the other eight placed likewise at the bottom. A photograph of this arrangement is given in Figure I.

Pressure cans for holding the gaseous mixtures were made similarly to the sample cans with the exception that both the top and the bottom were soldered to the can. These cans were soldered extra heavy in order to withstand a pressure of two atmospheres.

A photograph of the entire set-up is shown in Figure II.

Fig. Ia

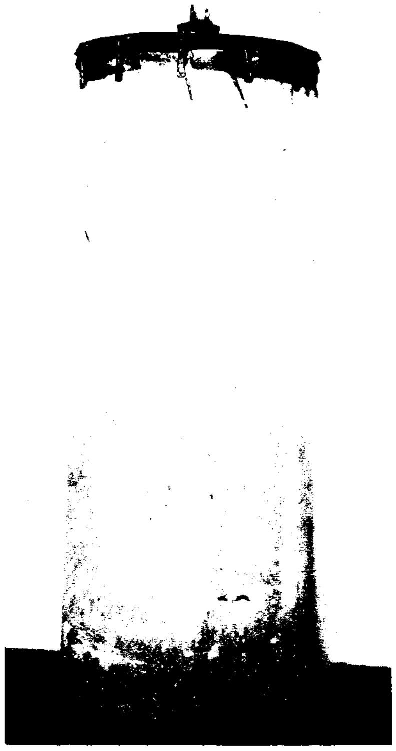

Fig. Ib

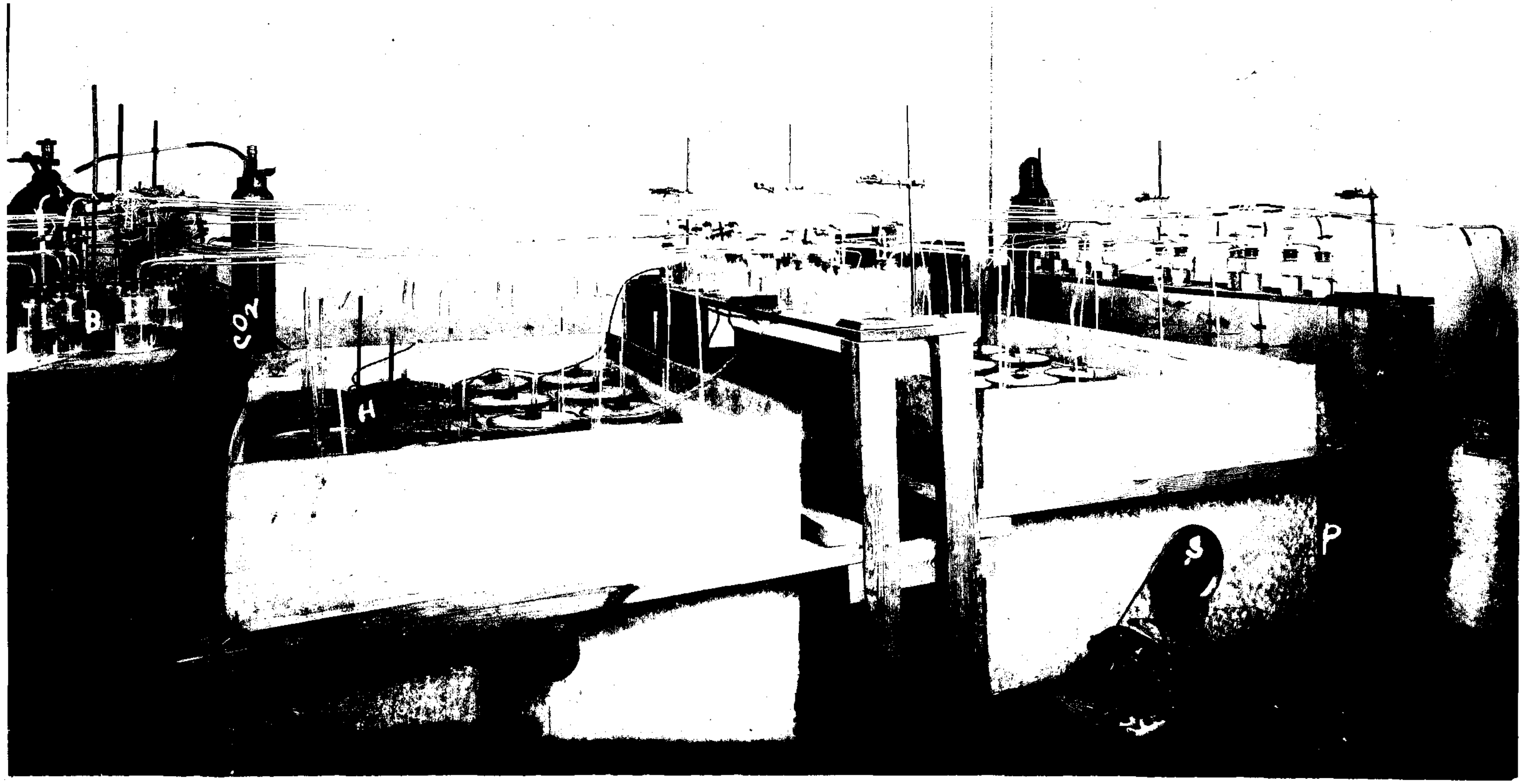

Fig. II

B. Operation of the Corrosion Set-Up.

The corrosion experiment extended from March 1, 1931 to July 24, 1931. In general, the experiment consisted in exposing samples of 18 gauge galvanized Armco sheet iron, submerged in conductivity water, to the action of certain mixtures of carbon dioxide, oxygen, and nitrogen gases. The compositions of the different gaseous mixtures used are given in the following table. The gases were taken directly from the commercial steel cylinders.

TABLE II.

Mixture number	% CO_2	% O_2	% N_2
1	0.00	5.00	95.00
2	0.00	10.00	90.00
3	0.00	15.00	85.00
4	0.00	20.00	80.00
5	0.00	25.00	75.00
6	0.03	5.00	94.97
7	0.03	10.00	89.97
8	0.03	15.00	84.97
9	0.03	20.00	79.97
10	0.03	25.00	74.97
11	0.06	5.00	94.94
12	0.06	10.00	89.94
13	0.06	15.00	84.94
14	0.06	20.00	79.94
15	0.06	25.00	74.94
16	0.10	5.00	94.90
17	0.10	10.00	89.90
18	0.10	15.00	84.90
19	0.10	20.00	79.90
20	0.10	25.00	74.90

The compositions of the different gaseous mixtures and the rate of bubbling of the gases through the sample cans were checked daily. The gases were forced through the sample cans by means of the pressure reservoirs which were kept at about two atmospheres. The rate of bubbling was adjusted so that the gases entered the sample cans at the rate of one bubble per second, as measured by glass tips with an inside diameter of about one millimeter.

The gases entered the sample cans through the small glass tips placed midway between the upper and lower samples. In order tp prevent any bubbles of the gases from becoming attached to the upper set of samples, sections of galvanized pipe were suspended (by a chromel wire) around the gas inlets. These sections of pipe were 9 inches in length by 2 inches in diameter and they extended from the level at which the gases entered to within 2 1/2 inches of the water level. Figure IIb shows the pipe in its position.

The temperature of the samples was held within two degrees either side of 26° C. On the average, the temperature was quite constant at 26° C.

IV. OBSERVATIONS

A. Corrosion of Samples.

An examination of each corrosion sample was made. The number of perforations which had been attacked on each sample and the degree of corrosion were noted.

The pH values of samples of water from both top and bottom portions of the sample cans from set-ups one and two were determined. The pH values were determined colorimetrically by the use of a set of LaMotte standards.

Samples of water from the middle portion of the sample cans from set-up two were tested for total dissolved solids.

The results of these observations are given in the following table.

TABLE III.

The notation for sample numbers is as follows:

25 = set number 1
40 = set number 2
55 = set number 3
T_4 = Top sample from can number 4
B_1 = Bottom sample from can number 1
N = New sample
O_{40}= Old sample which had been used previously at 40° for three months

Thus 40 T_4 O_{40} represents a top sample from can number 4 of set number 2 and which had been used previously at 40° for three months.

TABLE III (continued)

Sample Number	CO_2	O_2	N_2	pH	Points of Corrosion	Relative Corrosion
25 T_1 N	0	5	95	7.0	0-0-0-0	0
25 T_1 O_{25}					5-0-9-10	24
25 B_1 N				7.1	0-0-0-0	0
25 B_1 O_{25}					0-0-0-4	4
40 T_1 N	0	5	95	6.9	10-8-10-5	33
40 T_1 O_{40}					10-10-9-8	37
40 B_1 N				6.9	10-2-9-5	26
40 B_1 O_{40}					10-9-10-10	39
55 T_1 N	0	5	95		9-10-8-6	33
55 T_1 O_{40}					7-6-8-5	26
55 B_1 N					4-6-9-8	27
55 B_1 O_{40}					9-10-8-6	33
25 T_2 N	0	10	90	7.2	0-0-4-0	4
25 T_2 O_{25}					9-9-9-9	36
25 B_2 N				7.1	0-0-0-0	0
25 B_2 O_{25}					0-0-2-2	4
40 T_2 N	0	10	90	7.0	4-4-2-4	14
40 T_2 O_{40}					10-9-9-8	36
40 B_2 N				6.9	4-3-0-0	7
40 B_2 O_{40}					4-4-2-2	12
55 T_2 N	0	10	90		4-10-6-8	28
55 T_2 O_{40}					5-8-10-7	30
55 B_2 N					7-2-10-8	27
55 B_2 O_{40}					6-5-7-7	25
25 T_3 N	0	15	85	7.1	0-0-0-0	0
25 T_3 O_{25}					9-5-8-9	31
25 B_3 N				7.15	0-0-0-0	0
25 B_3 O_{25}					8-8-5-0	21
40 T_3 N	0	15	85	7.15	3-9-9-4	25
40 T_3 O_{40}					10-10-9-8	37
40 B_3 N				7.0	0-0-0-0	0
40 B_3 O_{40}					4-0-6-0	10
55 T_3 N	0	15	85		0-2-3-0	5
55 T_3 O_{40}					0-0-3-4	7
55 B_3 N					2-2-3-0	7
55 B_3 O_{40}					2-0-7-2	11

TABLE III (continued)

Dissolved Solids	Remarks
	No action
	Medium - only 1 real tubercle
	No action
	Very slight - just started
0.0185	Strong - 10 tubercles starting
	Strong - no closed tubercles - much streaming
	Very slight - rust just started
	Very slight - rust just started
	Medium - 12 small tubercles
	Medium - 3 small tubercles
	Medium - 6 small tubercles
	Medium - 1 small tubercle
	Very slight - rust just started
	Medium - 4 small tubercles
	No action
	Very slight - rust just started
0,0385	Medium
	Medium - 1 tubercle - streaming
	Very slight - rust just started
	Very slight - rust just started
	Medium - 8 tubercles
	Medium
	Slight - 3 tubercles
	Slight - rust just started
	No action
	Medium - streaming - 10 small tubercles
	No action
	Slight
0.0050	Medium - 2 tubercles
	Strong - streaming - 17 tubercles
	No action
	Slight - rust just started
	Slight - rust just started
	Slight - rust just started
	Slight - rust just started
	Slight - rust just started

TABLE III (continued)

Sample Number	CO$_2$	O$_2$	N$_2$	pH	Points of Corrosion	Relative Corrosion
25 T$_4$ N	0	20	80	7.1	0-0-0-2	2
25 T$_4$ O$_{25}$					8-10-8-8	34
25 B$_4$ N				7.0	0-0-0-0	0
25 B$_4$ O$_{25}$					0-0-0-0	0
40 T$_4$ N	0	20	80	7.15	8-3-4-4	19
40 T$_4$ O$_{40}$					9-7-6-8	30
40 B$_4$ N				7.1	0-0-0-0	0
40 B$_4$ O$_{40}$					0-0-0-0	0
55 T$_4$ N	0	20	80		0-2-5-1	8
55 T$_4$ O$_{40}$					4-4-2-6	16
55 B$_4$ N					2-1-1-4	8
55 B$_4$ O$_{40}$					7-5-6-1	19
25 T$_5$ N	0	25	75	7.1	7-10-9-9	35
25 T$_5$ O$_{25}$					10-10-10-9	39
25 B$_5$ N				6.8	0-3-0-0	3
25 B$_5$ O$_{25}$					9-10-9-7	35
40 T$_5$ N	0	25	75	7.2	6-5-7-3	21
40 T$_5$ O$_{40}$					9-8-8-8	33
40 B$_5$ N				7.2	0-0-0-0	0
40 B$_5$ O$_{40}$					0-0-0-0	0
55 T$_5$ N	0	25	75		0-0-5-3	8
55 T$_5$ O$_{40}$					8-6-1-3	18
55 B$_5$ N					7-1-5-5	18
55 B$_5$ O$_{40}$					5-6-10-7	28
25 T$_6$ N	0.03	5	95	7.3	0-1-5-0	6
25 T$_6$ O$_{25}$					10-9-8-8	35
25 B$_6$ N				7.0	0-0-0-0	0
25 B$_6$ O$_{25}$					10-3-2-10	25
40 T$_6$ N	0.03	5	95	7.2	1-3-3-0	7
40 T$_6$ O$_{40}$					6-7-6-3	22
40 B$_6$ N				7.2	0-0-0-0	0
40 B$_6$ O$_{40}$					0-0-0-0	0
55 T$_6$ N	0.03	5	95		3-3-7-2	15
55 T$_6$ O$_{40}$					3-2-3-4	12
55 B$_6$ N					3-2-4-1	10
55 B$_6$ O$_{40}$					8-7-8-6	29

TABLE III (continued)

Dissolved Solids	Remarks
	Slight - rust just started
	Medium - 10 tubercles
	No action
	No action
0.0100	Slight - 2 tubercles
	Medium - 3 tubercles - streaming
	No action
	No action
	Very slight - rust just started
	Slight
	Slight
	Slight
	Medium - 15 tubercles
	Medium - 25 tubercles
	Very slight
	Medium
0.0123	Medium - 1 tubercle
	Medium - 3 tubercles - streaming
	No action
	No action
	Slight - rust on edges
	Slight
	Very slight
	Very slight
	Very slight
	Medium - 6 tubercles - streaming
	No action
	Slight
0.0036	Slight
	Slight - 1 tubercle
	No action
	No action
	Very slight - rust just started
	Very slight - rust just started
	Very slight - rust just started
	Slight

TABLE III (continued)

Sample Number	CO_2	O_2	N_2	pH	Points of Corrosion	Relative Corrosion
25 T_7 N	0.03	10	90	7.1	8-10-8-9	35
25 T_7 O_{25}					10-10-10-10	40
25 B_7 N				7.1	6-6-8-5	25
25 B_7 O_{25}					9-9-10-10	38
40 T_7 N	0.03	10	90	7.0	7-6-4-8	25
40 T_7 O_{40}					8-7-6-6	27
40 B_7 N				7.0	0-0-0-0	0
40 B_7 O_{40}					2-8-4-6	20
55 T_7 N	0.03	10	90		3-4-5-3	15
55 T_7 O_{40}					1-1-2-5	9
55 B_7 N					4-6-4-2	16
55 B_7 O_{40}					3-2-6-7	18
25 T_8 N	0.03	15	85	7.4	2-0-3-2	7
25 T_8 O_{25}					8-3-8-4	23
25 B_8 N				7.2	0-0-0-0	0
25 B_8 O_{25}					0-0-1-0	1
40 T_8 N	0.03	15	85	7.3	10-3-5-3	21
40 T_8 O_{40}					6-6-8-7	27
40 B_8 N				7.1	0-0-0-0	0
40 B_8 O_{40}					2-0-2-0	4
55 T_8 N	0.03	15	85		2-4-0-2	8
55 T_8 O_{40}					2-2-1-0	5
55 B_8 N					0-0-0-0	0
55 B_8 O_{40}					1-4-5-5	15
25 T_9 N	0.03	20	80	7.1	2-0-0-0	2
25 T_9 O_{25}					0-1-4-1	6
25 B_9 N				7.1	0-0-0-0	0
25 B_9 O_{25}					0-0-0-0	0
40 T_9 N	0.03	20	80	7.1	0-0-0-5	5
40 T_9 O_{40}					1-0-6-6	13
40 B_9 N				7.15	0-0-0-0	0
40 B_9 O_{40}					0-0-0-0	0
55 T_9 N	0.03	20	80		0-0-0-0	0
55 T_9 O_{40}					2-1-2-1	6
55 B_9 N					5-0-0-0	5
55 B_9 O_{40}					0-1-0-0	1

TABLE III (continued)

Dissolved Solids	Remarks
	Medium - 21 tubercles
	Strong - 37 tubercles - streaming
	Slight
	Medium - 29 tubercles - streaming
0.0100	Medium - 9 tubercles
	Medium - 16 tubercles
	No action
	Slight - 2 tubercles
	Slight - rust just started
	Slight - rust just started - 1 tubercle
	Slight - rust just started
	Slight - rust just started
	Very slight - rust just started
	Medium
	No action
	No action
0.0186	Slight - 2 tubercles
	Medium
	No action
	Very slight - rust just started
	Very slight - rust just started
	Very slight - rust just started
	No action
	Slight - rust just started
	Very slight - rust just started
	Slight
	No action
	No action
0.0085	Very slight
	Slight
	No action
	No action
	Slight - rust just stated
	Very slight - rust just started
	Very slight - rust just started
	Very slight - rust just started

TABLE III (continued)

Sample Number	CO_2	O_2	N_2	pH	Points of Corrosion	Relative Corrosion
25 $T_{10}N$	0.03	25	75	6.9	1-1-1-0	3
25 $T_{10}O_{25}$					5-5-8-5	23
25 $B_{10}N$				7.1	1-5-3-0	9
25 $B_{10}O_{25}$					1-0-0-0	1
40 $T_{10}N$	0.03	25	75	7.1	1-1-2-0	4
40 $T_{10}O_{40}$					0-0-0-0	0
40 $B_{10}N$				7.1	1-1-0-0	2
40 $B_{10}O_{40}$					1-0-0-0	1
55 $T_{10}N$	0.03	25	75		0-4-3-2	11
55$T_{10}O_{40}$					5-4-0-5	14
55 $B_{10}N$					0-2-3-1	6
55 $B_{10}O_{40}$					7-3-3-3	16
25 $T_{11}N$	0.06	5	95	7.0	0-2-2-2	6
25 $T_{11}O_{25}$					6-8-5-7	26
25 $B_{11}N$				7.2	0-0-0-0	0
25 $B_{11}O_{25}$					1-0-6-3	10
40 $T_{11}N$	0.06	5	95	7.15	0-0-0-0	0
40 $T_{11}O_{40}$					0-0-0-1	1
40 $B_{11}N$				7.4	0-0-0-0	0
40 $B_{11}O_{40}$					0-0-0-0	0
55 $T_{11}N$	0.06	5	95		0-1-0-0	1
55 $T_{11}O_{40}$					4-4-4-2	14
55 $B_{11}N$					2-1-0-1	4
55 $B_{11}O_{40}$					4-3-2-0	9
25 $T_{12}N$	0.06	10	90	6.9	0-0-0-0	0
25 $T_{12}O_{25}$					2-8-8-3	21
25 $B_{12}N$				7.0	0-0-0-0	0
25 $B_{12}O_{25}$					1-0-3-0	4
40 $T_{12}N$	0.06	10	90	8.0	0-0-0-0	0
40 $T_{12}O_{40}$					6-8-1-1	16
40 $B_{12}N$				7.4	0-0-0-0	0
40 $B_{12}O_{40}$					0-0-0-0	0
55 $T_{12}N$	0.06	10	90		3-4-3-1	11
55 $T_{12}O_{40}$					5-5-4-6	20
55 $B_{12}N$					0-1-4-2	7
55 $B_{12}O_{40}$					0-3-0-0	3

TABLE III (continued)

Dissolved Solids	Remarks
	Slight - rust just started
	Medium - 15 small tubercles
	No action
	Slight - rust just started
0.0290	Very slight - rust just started
	No action
	Very slight - rust just started
	No action
	Slight - rust just started
	Slight - rust just started
	Slight - rust just started
	Slight - rust just started
	Slight - 2 small tubercles
	Medium - 18 tubercles
	No action
	Slight - rust just started
0.0096	No action
	No action
	No action
	No action
	No action
	Slight - rust just started
	Very slight
	Very slight - rust just started
	No action
	Medium - 12 tubercles
	No action
	Slight - rust just started
0.0160	No action
	Slight
	No action
	No action
	Slight - rust just started
	Slight - rust just started
	Slight - rust just started
	Slight - rust just started

TABLE III (continued)

Sample Number	CO_2	O_2	N_2	pH	Points of Corrosion	Relative Corrosion
25 $T_{13}N$	0.06	15	85	7.5	0-0-1-2	3
25 $T_{13}O_{25}$					7-4-3-2	15
25 $B_{13}N$				7.15	0-0-0-0	0
25 $B_{13}O_{25}$					0-0-0-0	0
40 $T_{13}N$	0.06	15	85	7.7	0-0-0-0	0
40 $T_{13}O_{40}$					4-6-9-5	24
40 $B_{13}N$				7.4	0-0-0-0	0
40 $B_{13}O_{40}$					5-0-0-2	7
55 $T_{13}N$	0.06	15	85		0-0-0-0	0
55 $T_{13}O_{40}$					10-7-6-8	31
55 $B_{13}N$					3-0-1-1	5
55 $B_{13}O_{40}$					1-4-5-0	10
25 $T_{14}N$	0.06	20	80	6.9	0-0-0-0	0
25 $T_{14}O_{25}$					1-7-5-2	15
25 $B_{14}N$				7.4	0-0-0-0	0
25 $B_{14}O_{40}$					4-3-0-0	7
40 $T_{14}N$	0.06	20	80	7.25	1-3-7-0	11
40 $T_{14}O_{40}$					0-2-2-7	11
40 $B_{14}N$				7.0	0-0-0-0	0
40 $B_{14}O_{40}$					0-0-0-0	0
55 $T_{14}N$	0.06	20	80		4-1-2-1	8
55 $T_{14}O_{40}$					1-0-0-0	1
55 $B_{14}N$					5-1-0-1	7
55 $B_{14}O_{40}$					1-3-0-0	4
25 $T_{15}N$	0.06	25	75	7.0	8-4-7-7	26
25 $T_{15}O_{40}$					6-10-10-10	36
25 $B_{15}N$				6.9	7-9-10-8	34
25 $B_{15}O_{40}$					8-10-10-10	38
40 $T_{15}N$	0.06	25	75	7.1	8-10-7-8	33
40 $T_{15}O_{40}$					9-6-9-8	32
40 $B_{15}N$				6.9	0-0-0-0-	0
40 $B_{15}O_{40}$					0-0-0-0-	0
55 $T_{15}N$	0.06	25	75		0-1-2-1	4
55 $T_{15}O_{40}$					4-5-4-4	17
55 $B_{15}N$					0-1-1-1	3
55 $B_{15}O_{40}$					0-1-1-2	4

TABLE III (continued)

Dissolved Solids	Remarks
	Slight - rust just started
	Slight - 1 tubercle
	No action
	No action
0.0126	No action
	Slight - rust just started - streaming
	No action
	Slight - rust just started
	No action
	Slight - 3 tubercles
	Very slight - rust just started
	Slight - rust just started
	No action
	Slight - 4 tubercles
	No action
	Very slight - rust just started
0.0133	Very slight - rust just started
	Slight
	No action
	No action
	Very slight - rust just started
	No action
	Very slight - rust just started
	Very slight - rust just started
	Very strong - 24 large tubercles
	Very strong - 23 large tubercles - streaming
	Medium - 15 small tubercles
	Medium - 23 small tubercles - streaming
0.0092	Medium
	Medium - streaming
	No action
	No action
	Slight - rust just started
	Medium
	Slight
	Slight - rust just started

TABLE III (continued)

Sample Number	CO_2	O_2	N_2	pH	Points of Corrosion	Relative Corrosion
25 $T_{16}N$	0.10	5	95	6.9	1-2-2-2	7
25 $T_{16}O_{25}$					7-9-9-8	33
25 $B_{16}N$				7.0	0-0-0-0	0
25 $B_{16}O_{25}$					0-1-5-2	8
40 $T_{16}N$	0.10	5	95	6.85	3-6-2-4	15
40 $T_{16}O_{40}$					9-8-9-9	35
40 $B_{16}N$				6.85	0-0-0-0	0
40 $B_{16}O_{40}$					0-0-0-0	0
55 $T_{16}N$	0.10	5	95		0-1-0-1	2
55 $T_{16}O_{40}$					0-2-0-0	2
55 $B_{16}N$					1-0-1-1	3
55 $B_{16}O_{40}$					2-0-0-1	3
25 $T_{17}N$	0.10	10	90	7.1	3-2-0-4	9
25 $T_{17}O_{25}$					8-7-8-8	31
25 $B_{17}N$				7.0	0-0-0-0	0
25 $B_{17}O_{25}$					0-0-1-1	2
40 $T_{17}N$	0.10	10	90	7.3	5-9-4-8	26
40 $T_{17}O_{40}$					8-6-10-8	32
40 $B_{17}N$				6.8	0-1-0-0	1
40 $B_{17}O_{40}$					8-7-6-5	26
55 $T_{17}N$	0.10	10	90		0-0-0-0	0
55 $T_{17}O_{40}$					7-4-7-5	23
55 $B_{17}N$					2-4-0-0	6
55 $B_{17}O_{40}$					1-0-0-0	1
25 $T_{18}N$	0.10	15	85	7.1	2-0-1-3	6
25 $T_{18}O_{25}$					8-6-7-5	26
25 $B_{18}N$				6.9	0-0-0-0	0
25 $B_{18}O_{25}$					1-5-1-0	7
40 $T_{18}N$	0.10	15	85	7.15	1-1-1-1	4
40 $T_{18}O_{40}$					4-2-5-6	17
40 $B_{18}N$				7.0	0-0-0-0	0
40 $B_{18}O_{40}$					0-0-0-0	0
55 $T_{18}N$	0.10	15	85		2-4-1-1	8
55 $T_{18}O_{40}$					8-4-7-6	25
55 $B_{18}N$					2-3-1-2	8
55 $B_{18}O_{40}$					2-3-1-1	7

TABLE III (continued)

Dissolved Solids	Remarks
	Slight - 3 small tubercles
	Medium - 7 small tubercles
	No action
	Slight - rust just started
0.0123	Very strong
	Strong - 21 tubercles - streaming
	No action
	No action
	Slight - rust just started
	Very slight - rust just started
	Very slight - rust just started
	Very slight - rust just started
	Very slight - rust just started
	Medium - 18 medium tubercles
	No action
	Very slight - rust just started
0.0642	Medium - 11 small tubercles
	Very strong - 11 tubercles - streaming
	No action
	Slight - rust just started
	No action - edges rusting
	Slight - rust just started
	Slight - rust just started
	No action - edges rusting
	Very slight - rust just started
	Medium
	No action
	Very slight - rust just started
0.0120	Very slight - rust just started
	Very slight - rust just started
	No action
	No action
	Medium - 2 medium tubercles
	Medium - black oxide
	Slight - rust just started
	Slight - rust just started

TABLE III (continued)

Sample Number	CO_2	O_2	N_2	pH	Points of Corrosion	Relative Corrosion
25 $T_{19}N$	0.10	20	80	7.1	10-7-8-6	31
25 $T_{19}O_{25}$					10-9-8-10	37
25 $B_{19}N$				6.9	7-8-7-9	31
25 $B_{19}O_{25}$					10-10-10-10	40
40 $T_{19}N$	0.10	20	80	7.25	0-0-0-0	0
40 $T_{19}O_{40}$					0-0-0-0	0
40 $B_{19}N$				7.4	0-0-0-0	0
40 $B_{19}O_{40}$					0-0-0-0	0
55 $T_{19}N$	0.10	20	80		9-9-5-6	29
55 $T_{19}O_{40}$					5-4-5-7	21
55 $B_{19}N$					8-3-6-3	20
55 $B_{19}O_{40}$					5-3-4-6	18
25 $T_{20}N$	0.10	25	75	7.1	6-3-7-5	21
25 $T_{20}O_{25}$					7-8-7-8	30
25 $B_{20}N$				7.0	8-7-5-6	26
25 $B_{20}O_{25}$					10-9-6-8	33
40 $T_{20}N$	0.10	25	75	7.15	0-2-1-5	8
40 $T_{20}O_{40}$					1-1-3-1	6
40 $B_{20}N$				7.4	3-3-0-1	7
40 $B_{20}O_{40}$					1-0-1-1	3
55 $T_{20}N$	0.10	25	75		4-0-1-0	5
55 $T_{20}O_{40}$					4-5-4-4	17
55 $B_{20}N$					5-5-3-4	17
55 $B_{20}O_{40}$					2-3-6-5	16

TABLE III (continued)

Dissolved Solids	Remarks
	Very strong - 24 tubercles
	Very strong - 35 tubercles
	Slight - black oxide
	Medium - 23 small tubercles
0.0107	No action
	No action
	No action
	No action
	Medium - 6 small tubercles
	Medium - 4 small tubercles
	Slight
	Slight
	Very strong - 19 large tubercles
	Very strong - 23 large tubercles
	Very strong - 19 large tubercles
	Very strong - 28 large tubercles
0.0410	Medium - 37 small tubercles - black oxide
	Medium - 3 tubercles - just starting
	Slight - rust just started
	Slight - rust just started
	Medium - edges rusting badly - 1 tubercle
	Medium - edges rusting badly - 3 tubercles
	Slight - rust just started
	Slight - edges rusting - 2 large tubercles

A study of the photographs, pages 30 to 50 inclusive, shows the comparative results of the corrosion of the samples. A representative sample from the top and one from the bottom of one can subjected to each gas composition were photographed.

TABLE IV.

Index to Photographs of Representative Samples.

Gas composition	Figure number	Sample T	 B
1	III	1	2
2	IV	3	4
3	V	5	6
4	VI	7	8
5	VII	9	10
6	VIII	11	12
7	IX	13	14
8	X	15	16
9	XI	17	18
10	XII	19	20
11	XIII	21	22
12	XIV	23	24
13	XV	25	26
14	XVI	27	28
15	XVII	29	30
16	XVIII	31	32
17	XIX	33	34
18	XX	35	36
19	XXI	37	38
20	XXII	39	40

Figure XXIII shows samples as taken from cans for observations.

Fig. III

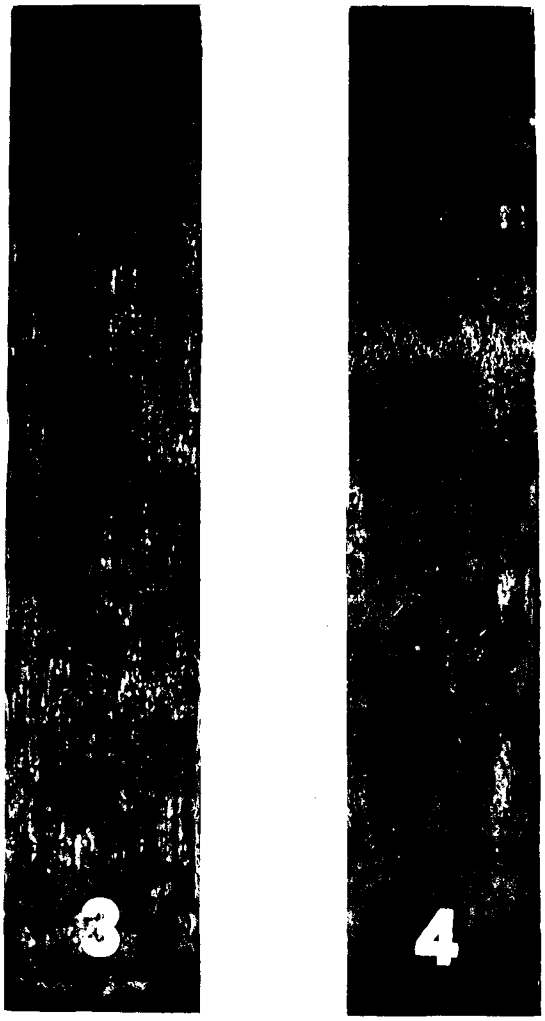

Fig. IV

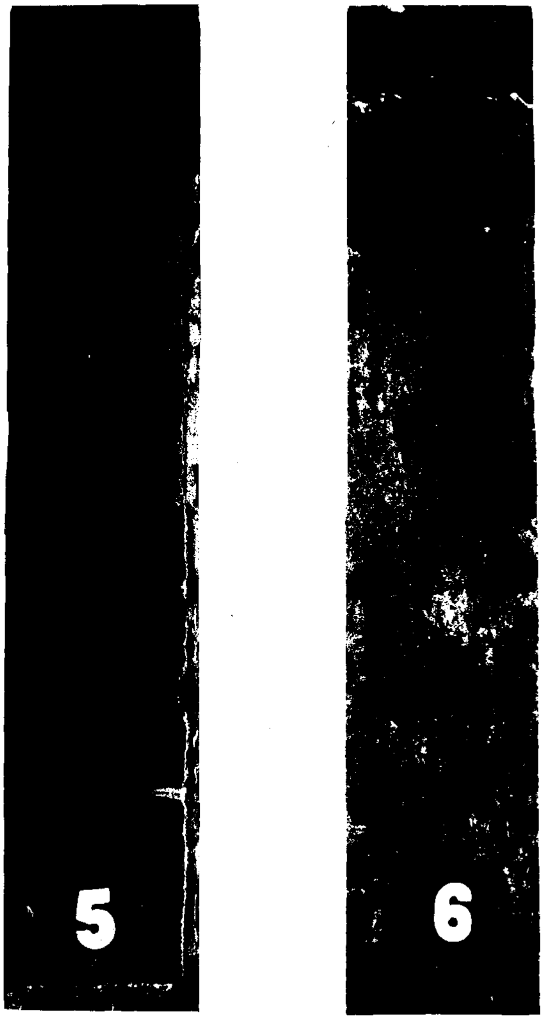

Fig. V

Fig. VI

Fig. VII

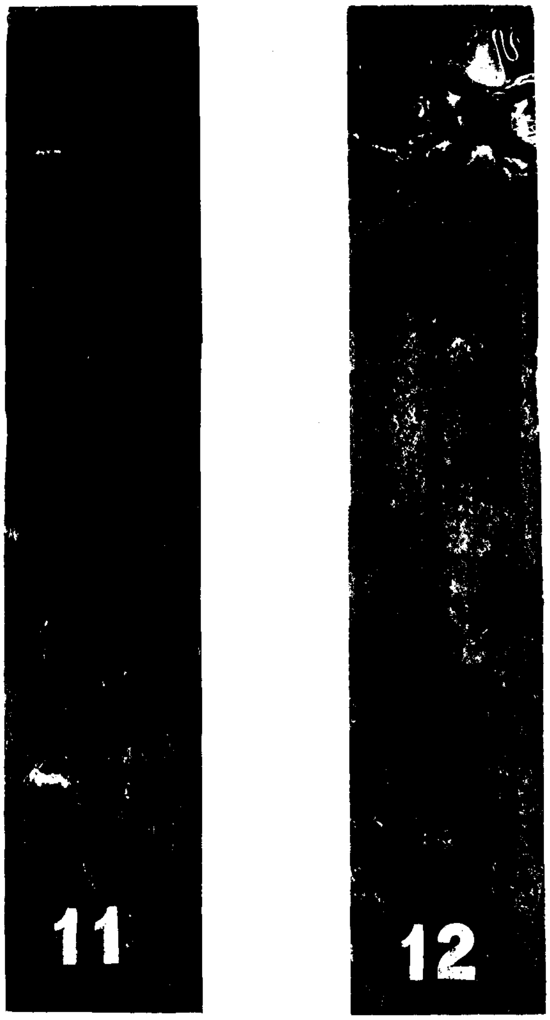

Fig. VIII

Fig. IX

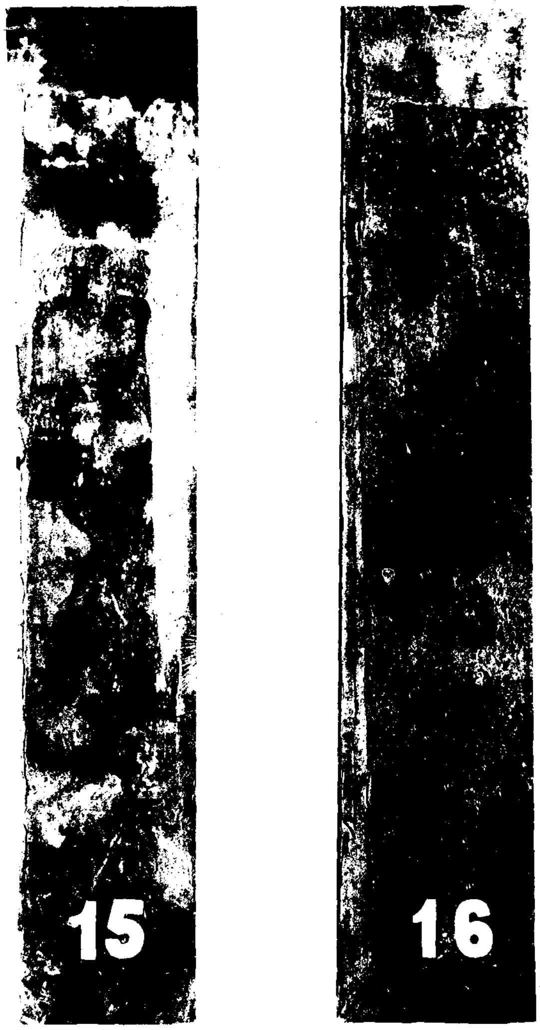

Fig. X

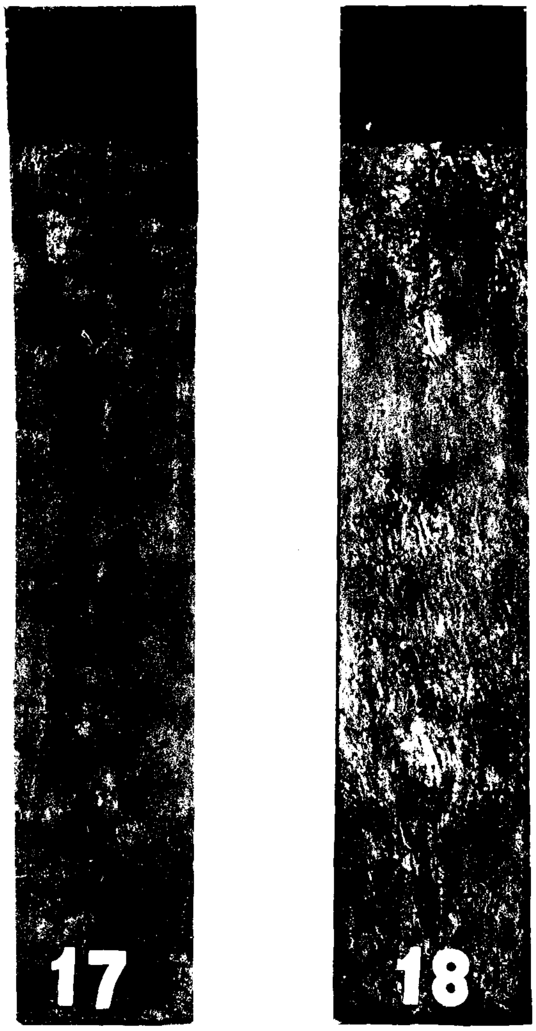

Fig. XI

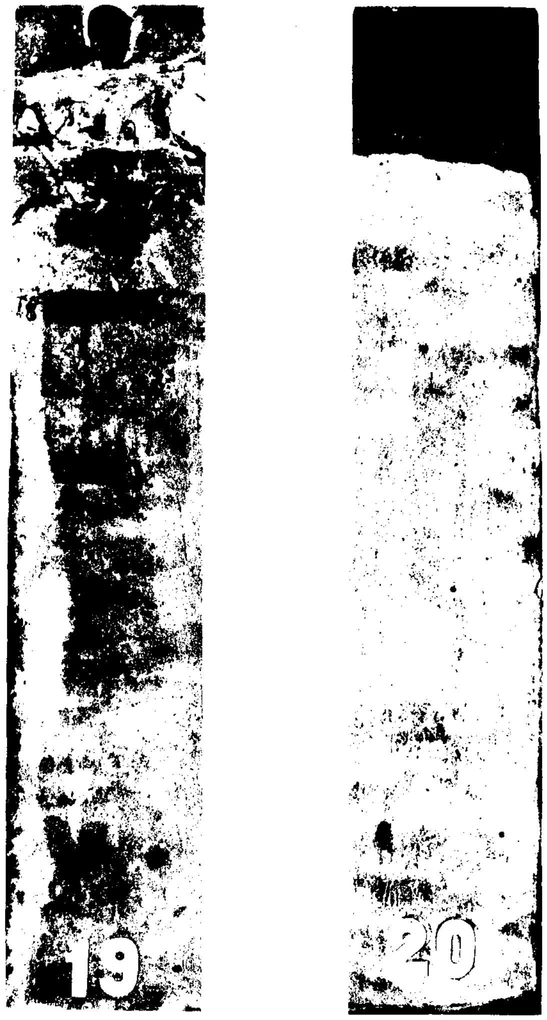

Fig. XII

Fig. XIII

Fig. XIV

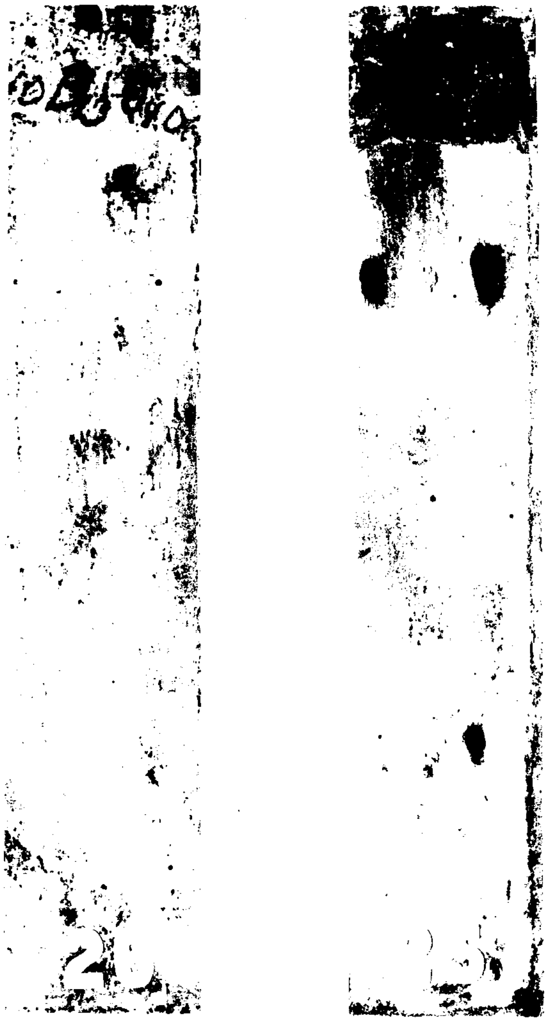

Fig. XV

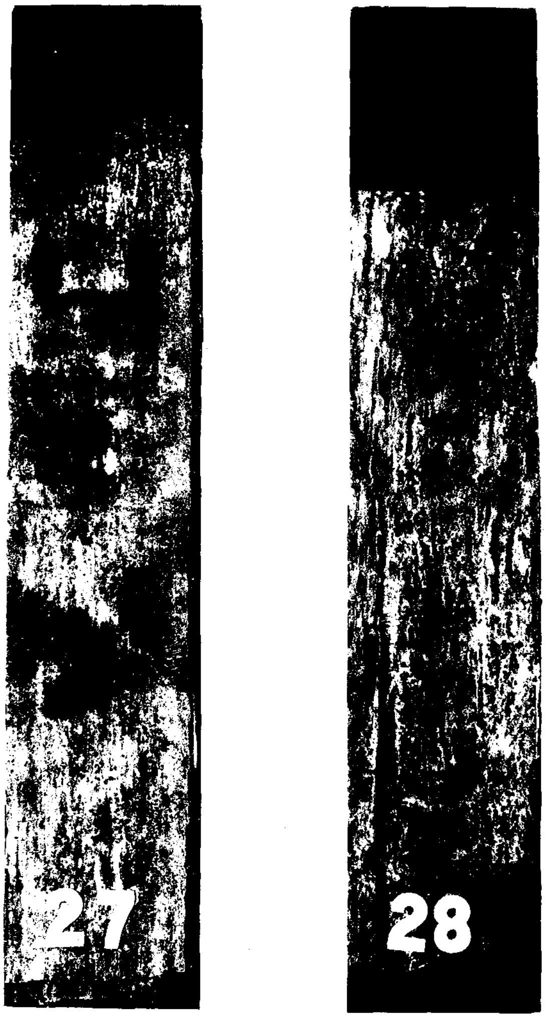

Fig. XVI

Fig. XVII

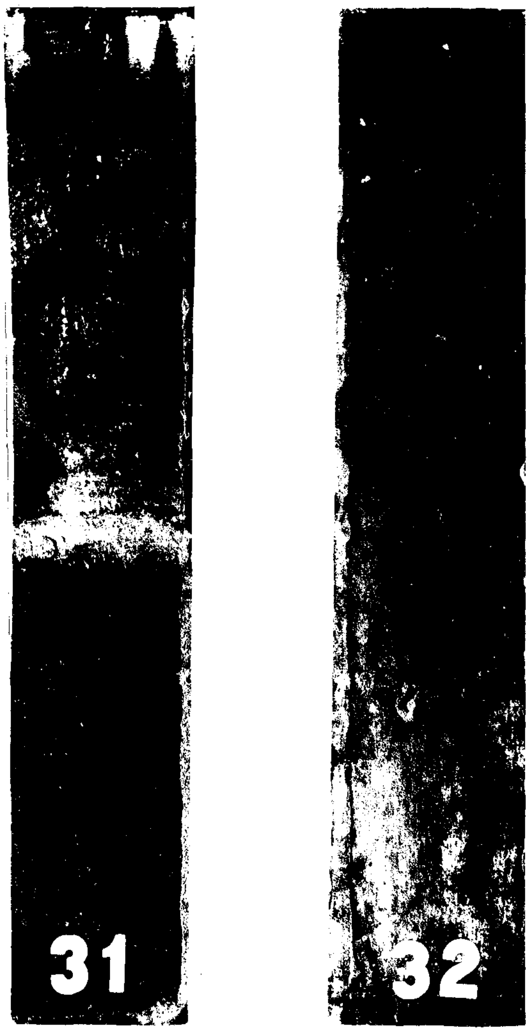

Fig. XVIII

Fig. XIX

Fig. XX

Fig. XXI

Fig. XXII

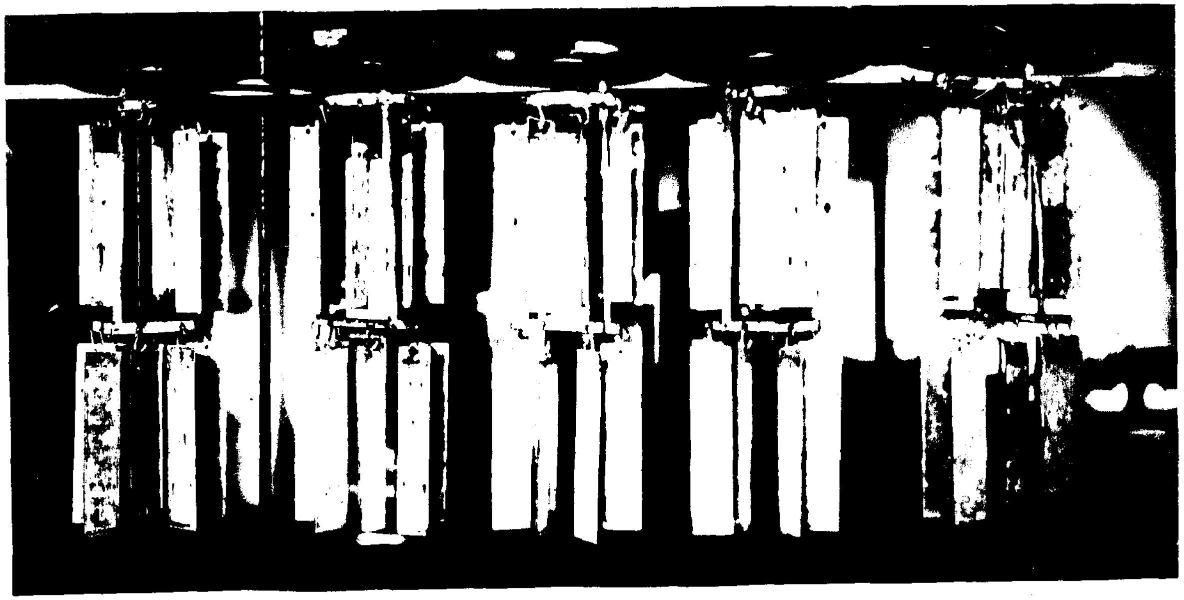

Fig. XXIII

B. Corrosion of Sample Cans and Thermostat Tanks.

The sample cans were divided into three sets of twenty cans each. The first set was made up of old cans which had been paraffined on the inside at the water line and on the rivets during a previous run and were reparaffined for this experiment. The paraffin prevented corrosion of all parts which it covered. The second set was also made up of old cans which had been paraffined inside. These cans were not reparaffined for the present experiment. This set showed considerable corrosion at the water line and on the rivets. The third set was made up of new cans and were not paraffined. This set showed much less corrosion than the second set.

The corrosion of the inner walls of the sample cans took place either at the water line or on the rivets (when not covered with paraffin). The degree of corrosion varied from weak to strong. The results of an observation of the corrosion at the water line, of cans of the second set, are given in Table V.

TABLE V.

Can No.	Corrosion	Can No.	Corrosion
1	Medium	11	Strong
2	Medium	12	Strong
3	Very Strong	13	Medium
4	Medium	14	Very Strong
5	Medium	15	Very Strong
6	Weak	16	Medium
7	Medium	17	Strong
8	Medium	18	Strong
9	Weak	19	Medium
10	Weak	20	Weak

The bottoms of the cans were not corroded in any can at the time of this observation. Apparently the only effect of the watch glasses was to prevent a deposition of sludge on that part of the bottom which they cover.

The outsides of the sample cans were not corroded. In all cases, however, a white deposit of basic zinc carbonate had formed about the water line.

At the time these observations were made none of the sample cans had corroded very badly. At the present time (four months later), however, large tubercles may be found on the inside and outside walls and on the bottoms of the sample cans. These cans have been standing open in the thermostat tanks and still have the conductivity water in them. Thus far none of the sample cans have corroded to the extent of being completely perforated at any point.

The condition of the thermostat tanks at the time the set-up was dissembled was the same as that of the outsides of the sample cans. The same remarks apply to their present condition as were applied to the sample cans. These tanks have been in use now for about two years.

C. Observations of Sludge.

A qualitative chemical analysis of the sludge taken from can number 20 of the third set-up showed that iron, zinc, and a small per cent of carbonate were present.

Apparently this sludge is, for the most part, a mixture of iron and zinc oxides and hydroxides with a small per cent of carbonates.

The weight of the sludge from cans numbers 2 and 20 of the third set-up was found to be 118.85 grams and 159.83 grams respectively. The amount of sludge in the other cans appeared to be within this range.

Since the color of the sludge in different sample cans was found to vary considerably, an examination of set-up number 2 was made. The results are given in Table VI.

TABLE VI.

Can Number	Color of Sludge	Can Number	Color of Sludge
1	Dark red	11	White
2	Light red	12	White
3	Dark red	13	Light red
4	Light red	14	light red
5	Light red	15	Light red
6	White	16	Light red
7	Light red	17	Dark red
8	Light red	18	Light red
9	White	19	White
10	White	20	Light red

V. CORRELATION OF DATA

The relative corrosion values given in Table III were summed up for all cans having the same gas compositions. The results are given in Table VII.

TABLE VII.

	5% O_2	10% O_2	15% O_2	20% O_2	25% O_2
0.00 % CO_2	282	224	151	136	240
0.03 % CO_2	161	268	111	38	91
0.06 % CO_2	71	82	95	64	227
0.10 % CO_2	100	157	117	227	189

It can be seen from the table that, for any constant carbon dioxide content, the degree of corrosion passes through a minimum as the oxygen content increases. If the oxygen content is held constant, the degree of corrosion also passes through a minimum as the carbon dioxide content increases. The minimum corrosion occurs at 20% oxygen and 0.03 % carbon dioxide.

Relative values were assigned to the degree of attack as recorded in Table III under "Remarks". The results were summed for all cans having the same gas compositions and this data tabulated in Table VIII.

TABLE VIII.

No action = 0 Slight = 2 Strong = 4
Very slight = 1 Medium = 3 Very strong = 5

	5% O_2	10% O_2	15% O_2	20% O_2	25% O_2
0.00 % CO_2	26	23	21	17	22
0.03 % CO_2	15	31	14	10	17
0.06 % CO_2	11	15	13	9	31
0.10 % CO_2	21	19	17	24	41

This table shows results identical with those of Table VII with the exception that the minimum is found at 20% oxygen and 0.06% carbon dioxide. The regions of low values correspond exactly in the two tables.

An examination of the data on dissolved solids, color of sludge, and pH values gave no correlation that could be detected. It is the opinion of the writer that the data on these observations are insufficient to warrant the drawing of any conclusions. Although there may be enough observations on the pH values, the differences of these values are small compared to the degree of accuracy of the method of determining them.

VI. THEORETICAL TREATMENT AND CONCLUSIONS

Recent work on the fundamental processes of corrosion has been done mainly on the study of metal surface films and potentials. Films can either inhibit or accelerate corrosion, depending upon their physical properties, potentials, and continuity.

Speller (14) was led to believe from his investigations that the corrosion rate varied linearly with the oxygen concentration. This linear relationship has been accepted in the past and used as a basis for calculating corrosion rates at different oxygen concentrations from known rates at other concentrations. Later, Speller (15) modifies his conclusions to allow for the protective action of the corrosion films.

In order for the corrosion rate to be a linear function of the oxygen concentration, (1) the rate of diffusion of oxygen from the main body of the liquid to the surface of the metal would have to be slow in comparison with the rate at which the oxygen was consumed by reaction at the metal surface: and (2) the resistance of the film formed by the corrosion products should not change with varying oxygen concentration.

In the work of Forrest, Roetheli, and Brown (16) it is shown that the film formed in the corrosion of steel in oxygenated water in a system permitting a low rate of stirring is considerably less protective than the film formed in a similar system in which the liquid is kept rapidly stirred. These authors conclude that the corrosion rate is dependent largely upon the character and composition of the corrosion film. The composition of the film is dependent upon the pH of the liquid near the metal surface.

Cox and Roetheli (13) find that the corrosion rates are approximately proportional to the oxygen concentration below concentrations of 5.5 c.c. per liter, while at higher concentrations the rates are lower than they would be if they adhered strictly to a linear relationship. Their maximum oxygen concentration was 20 c.c. per liter.

Hicks (12) was led, by his experiments, to offer the following mechanism of corrosion:

1. Metallic iron dissolves in water in an adherent film of liquid water as $Fe(OH)_2$ until pH = 9.4 .
2. The presence of oxygen insures maximum E.M.F., and therefore acts as an accelerator.
3. The system of equilibria

   $$Fe(solid) = Fe(dissolved) + 2H_2O = Fe(OH)_2 + H_2$$

   is shifted to the right, and corrosion maintained by oxygen and carbon dioxide as follows:
   - (a) O_2 removes $Fe(OH)_2$ by oxidation to less soluble $Fe(OH)_3$, also H_2 by oxidation.
   - (b) CO_2 removes $Fe(OH)_2$ by conversion to less soluble $FeCO_3$, also forms H_2CO_3, the H^+ of which dissolves metallic iron and favors corrosion.

In the present experiment it was noted that the corrosion of both the top and the bottom samples was uniform with respect to the points of perforation. This indicates that there was no oxygen or carbon dioxide gradient noticeable in that portion of the water which bathed each sample.

The top samples were decidedly more corroded than the bottom samples in practically all cases. Evidently the gases diffused to the top and there was not enough stirring action, nor enough gas, to maintain as high concentration in the lower part of the can as in the upper part.

In all cases the old samples showed much more corrosion than did the new ones. The cases in which streaming of the corrosion products occurred were restricted entirely to the old samples. This is probably due to the previous exposure of part of the samples. These old samples were not perforated during the first exposure but considerable amounts of the zinc coating had been dissolved away. These results agree with those of Bablik (10) previously mentioned. The new samples would probably show streaming action if the time of exposure had been longer.

Wherever corrosion had proceeded to the extent of the formation of a tubercle, it was found that the greatest amount of corrosion had occurred at a point immediately below the original perforation. This fact may be explained on the basis of the differential aeration theory of Evans (1). If two electrodes of the same material, joined to a galvanometer, are immersed in the solution of a salt such as sodium chloride and air is passed over one electrode only, a current is recorded, the aerated electrode being the cathode and the unaerated electrode being the anode. This differential aeration principle has been found capable of explaining numerous cases of intense localized corrosion at points to which oxygen has little direct access.

At first, corrosion products form about the perforated points on the corrosion samples and stream downward. In the presence of relatively high oxygen concentrations the $Fe(OH)_2$ formed is oxidized to $Fe(OH)_3$. The less soluble $Fe(OH)_3$ forms a film over the metal surface which, according to the experiments of Forrest, Roetheli, and Brown, is highly resistant to the diffusion of oxygen and thereby causes a region of low oxygen concentration beneath the film. This unaerated portion is anodic to the surrounding aerated portions and thus electrochemical action results. Iron goes into solution at the anode as $Fe(OH)_2$ and is deposited as $Fe(OH)_3$ at the cathodic areas. This deposition of $Fe(OH)_3$ results in the formation of a membranous wall, or mantle, around the anode. When once the walls of the mantle have formed around the anodic point they will protect it from oxygen, and thus the anodic attack will persist indefinitely.

An important feature of this type of corrosion is that the anodic portion is often small compared to the cathodic area and thus the whole effect is concentrated on a small area. Corrosion localized at one or two points, leading to pitting and perforation, is a much more serious thing than general corrosion. So long as corrosion is spread uniformly over the entire surface, its effects may be neglected; it is the localized type of attack, of which pitting is merely an extreme example, that causes the most trouble.

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