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THE CORROSION OF IRON AND STEEL.[1]

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Some time ago an investigation was undertaken in this laboratory with
a view to throwing some light upon the much discussed question as to
whether wrought iron is more resistant to corrosion than is steel.   To
this end a relatively large quantity of pure iron was prepared, and with
this as a basis, alloys of iron and varying amounts of the different ele-
ments occurring in commercial iron and steel were made by melting the
constituents in alumina crucibles heated by an electric furnace operating
under a high vacuum.   In studying the specimens so produced, it early
became apparent that a more complete understanding of the factors
which occasion corrosion and the conditions under which corrosion pro-
ceeds was necessary in order that our results could be intelligently inter-
preted.   A study of the literature on the subject showed it to be so
voluminous and so altogether contradictory, that as a first step in our
investigation of the general subject of the influence of the constituents
of iron or steel upon its corrosion, we decided to determine, if possible,
the mechanism of the reactions by reason of which corrosion takes place.[2]

Theories of Corrosion.

The more important theories of the corrosion of iron and steel which
seem to be worthy of discussion may be considered under three heads,
the first, when taken up chronologically, being the *carbon dioxide theory*.
Although the subject of corrosion had been investigated by a number of

[1] Read before the New York Section, May 1907.
[2] Since this part of the work was undertaken we have learned that Dr. Allerton
S. Cushman, Assistant Director, Office of Public Roads, Washington, has also been
investigating this subject.   Although contemporaneous, the investigations have been
carried on entirely independently, except in regard to the ferroxyl indicator, and it is
believed that Dr. Cushman's work will be found to confirm in many respects the
results herein recorded.

workers, Dr. Grace Calvert in 1871 seems to have been the first to have carried on a systematic study of the factors entering into the reaction. and concludes that at least three reagents are essential, viz. water, oxygen and carbon dioxide. This work received a complete endorsement at the hands of Crum Brown in 1888, who summarized the successive changes in the process of corrosion in the following equations:

$$4(Fe + H_2O + CO_2) = 4FeCO_3 + 4H_2$$
$$4FeCO_3 + 6 H_2O + O_2 = 2Fe_2(OH)_6 + 4CO_2$$
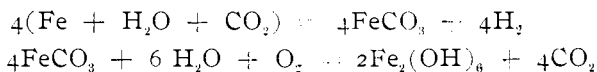
Two important facts regarding corrosion may be so easily explained by this theory that it has been very generally accepted by textbook writers and thus gained credence. These facts are. first, that the presence of carbon dioxide accelerates corrosion, and, second, that alkalies such as calcium hydroxide entirely prevent corrosion.

The latest and possibly most convincing work to be done on this subject is that of Gerald T. Moody[1], which apparently proves that no corrosion of iron will take place without carbon dioxide.

Moody's principal experiment consisted in exposing a bright piece of pure iron immersed in water to a stream of oxygen. the utmost precautions having been taken to exclude the presence of carbon dioxide. The different parts of the apparatus were connected by glass seals and in order to free them from carbon dioxide. air, after passing through a most elaborate washing and purifying system, was drawn for three weeks through the apparatus. Notwithstanding these precautions. rust in small amounts was found to develop on the specimens after a few days. When, however, air from which the carbon dioxide had not been absorbed was drawn through the water in which the iron was immersed. corrosion rapidly increased.

Moody concluded that the very small amount of rust which he had observed before the unwashed air was led in, was due to a trace of carbon dioxide which had been introduced with the piece of iron. He therefore immersed his specimens in a one per cent. solution of chromic acid in order that they might be protected from the carbon dioxide until the apparatus had been swept entirely free from this gas. After again drawing carbon dioxide-free air through the system for three weeks, the chromic acid was displaced by passing through the tube containing the iron a large quantity of pure water, introduced in such a manner as to insure no contamination with carbon dioxide. This water entirely removed all traces of this protective chromic acid solution. Carbon dioxide-free air was then drawn through the water and over the iron for five weeks and at the end of that period no rust could be observed. The connection between the washing system and the specimen was then

[1] J. Chem. Soc., (London) 89, 720.

broken and unwashed air drawn through the water.   Very considerable corrosion was observed after three days.

Electrolytic Theory.—In 1903, W. R. Whitney[1] published the results of an investigation, which furnished data on which he based a theory of corrosion in accordance with the conceptions of Nernst and the modern theory of solutions.   In accordance with this theory metals can dissolve only by entering the solution as electrically charged ions.   This escaping tendency of a metal is measured by a force known as the electrolytic solution pressure, which will operate in any solution until counterbalanced by the osmotic pressure of the metal already in solution.   In passing into the ionized state, the ions assume their positive charges while the residual negative charges remain upon the metal.   Action is therefore immediately arrested on account of the difference of potential which would exist between the positively charged ions and negatively charged metal.   In the case when iron is immersed in a solution of copper sulphate, there are present the positively charged copper ions which have a smaller solution pressure than the positively charged iron ions, and hence when the former are attracted to the negatively charged metallic iron their charges are neutralized and metallic copper is precipitated.   Since its solution pressure is less than that of the iron, there is little tendency for the copper ions to again dissolve in the presence of iron, and the action continues.

Hydrogen acts as a metal and has an electrolytic solution pressure which places it between iron and copper in the series of metals.   Iron placed in a solution containing hydrogen ions will therefore dissolve at a velocity dependent in general upon the concentration of the hydrogen ions and the ease with which the gas can be liberated upon the iron surface.   Water is dissociated to a small extent into hydrogen and hydroxyl ions and hence, if this theory holds, iron should pass into solution to a slight extent, with the liberation of an equivalent amount of hydrogen.   Any reagent which increases the concentration of the hydrogen ions, such as an acid, will increase the corrosive action, while any agent which will decrease this hydrogen concentration will inhibit corrosion.   In this way is explained the protecting effect of the alkalies and of any substance, for example, borax, which by hydrolysis yields hydroxyl ions, inasmuch as the product of the hydrogen and hydroxyl ions must remain a constant.   The formation of rust is thus seen to be a secondary action brought about by the oxidation of the already dissolved iron by the action of atmospheric oxygen.   The role of carbon dioxide is but that of any acid, increasing by its presence the concentration of the hydrogen ions and to this extent accelerating the action.

[1] This Journal, **25**, 394.

Hydrogen Peroxide Theory.—Dunstan. Jowett and Goulding[1] repeated the work of Whitney and failed to get any evidence that iron dissolved in pure water free from oxygen and carbon dioxide. They therefore considered this theory untenable and advanced a theory based upon the fact that when some metals oxidize in water. hydrogen peroxide is frequently formed. The chemical action taking place when iron corrodes in water with access of oxygen is represented by these authors as follows:

$$Fe + H_2O = FeO + H_2$$
$$H_2 + O_2 = H_2O_2$$
$$2FeO + H_2O_2 = Fe_2O_2(OH)_2 \text{ (rust)}$$
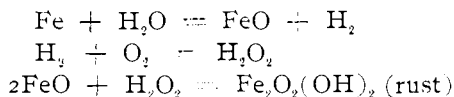
Although a great deal of experimental work was done, these investigators failed in every instance to get evidence of the presence of hydrogen peroxide in the oxidation of iron. This theory explains the fact that when zinc corrodes in water hydrogen peroxide may be detected, by the supposition that hydrogen peroxide can exist upon the surface of zinc, while when iron corrodes the hydrogen peroxide is incapable of existence on the surface of the iron long enough to make detection possible. Support for this idea is found in the fact that in every case, those reagents which inhibit rusting, are also substances which decompose hydrogen peroxide.

Experimental.

Evidently the first question to be settled is—Is carbon dioxide essential to corrosion? To this end we repeated the experiments of Moody, duplicating his apparatus and method in every possible particular. In general, our observations coincide with his. Our explanation of the phenomena observed, however, differs radically from his. It is well known that pure water attacks with considerable ease all glass except that which has been most carefully prepared, producing an alkaline solution. It is also well established that in pure water a relatively small amount of free alkali will inhibit rusting. We therefore again repeated Moody's experiment, but constructed the apparatus so that a little phenol-phthalein could be introduced after the water had been passed through the tube containing the iron. Both the water which was on the iron and also that which had passed over the iron into a flask beyond showed a distinct bright red when the indicator was added. When air containing carbon dioxide was passed through the solution this alkali was converted into the acid carbonate and the corrosion accelerated. When Jena glass which had been steamed for two days was employed, the iron corroded almost as readily as when left in the open air. We feel satisfied that in our experiments (and we believe the same to be true of Moody's) the tardy corrosion of the iron was due to the inhibiting effect of the free

[1] Chem. Soc. (London) 84, 1584. (1905.)

alkali present, and that iron does rust in the presence of air containing no carbon dioxide.

All those experiments of Moody in which chromic acid was used are rendered worthless, so far as showing the preservation of iron in the absence of carbon dioxide is concerned, by the fact, apparently overlooked by Moody, that immersing iron in chromic acid or potassium dichromate will render it relatively passive. We have repeated these experiments a number of times, carrying on simultaneously a check experiment in which we treated a specimen of the same iron with a portion of the same chromic acid solution, but drew ordinary unwashed air through the apparatus. No difference could be observed in the latter case. The fact that iron is preserved by solutions of the chromates was mentioned by Wood[1] in 1894, and later by a number of writers including Moody himself. No one seems to have noticed, however, that the passivity imparted to iron by such a solution is retained by the specimen after it is washed with pure water and dried. Without going further into this phenomenon we can but give it as our opinion that the apparent noncorrosion of iron in the absence of carbon dioxide, is due, not to the fact that no carbon dioxide is present, but to the fact that the iron is protected by the as yet not clearly understood condition of passivity, brought about by its immersion in a chromic acid solution.[2] A further proof that carbon dioxide is not essential to corrosion will be given later under the consideration of the influence of oxygen on corrosion.

The failure of the writers already noted to duplicate the results of Whitney, probably accounts for the fact that the electrolytic theory has not been more generally accepted. Even so valuable a textbook as '' General Inorganic Chemistry '' by Alexander Smith, does not mention the possibility of this explanation, although it makes very general use of the newer theories of chemistry involved in Whitney's work. The carbon dioxide theory and the peroxide theory of Dunstan are given sufficient space, while the electrolytic theory is ignored.

Evidently the theory of Whitney must stand or fall with the truthfulness of his statement that iron dissolves in pure water entirely free from oxygen and carbon dioxide. Although we employed a number of types of apparatus in studying this question, the following is both very simple and satisfactory. A round bottom Jena flask of about one liter capacity is inverted on a nozzle supplying live steam, for at least twenty-four hours. This insures the removal of any easily soluble alkalies, which

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[1] Trans. Am. Soc. Mech. Eng. 16, 384.

[2] Since the above was written, a short notice of an article by Wyndham R. Dunstan appeared in Chem. Soc. 22, 63, in which the experiments of Moody without chromic acid have been repeated. Dunstan confirms his previous results and those stated above, in that iron rusts freely in the presence of oxygen and water containing no carbon dioxide.

would otherwise destroy the neutrality of the liquid. The flask is fitted with a carefully cleaned rubber stopper through which extends a glass tube drawn down to a moderate-sized capillary at its upper end. The flask is three-fourths filled with ordinary distilled water (not conductivity water) which has previously been boiled for several hours in a block-tin heater. The water in the flask is boiled for about ten minutes and while steam is still rapidly passing out of the opening, the stopper is removed and a piece of bright iron introduced. The stopper is again inserted, the boiling continued for another ten minutes and while boiling the capillary is sealed. The flask is allowed to cool after thickly coating the stopper with molten paraffin. If this experiment be carefully performed, no action will be observed. the iron remaining bright and the water clear even after standing several days. When the stopper is removed and the water concentrated in a platinum dish, using every precaution to prevent contamination from dust, a strong test for iron can always be obtained by the addition of a drop of ferrocyanide or sulphocyanate of potassium solution.

Thinking that possibly enough gas had been occluded in the iron to effect the reaction, the above experiment was repeated a number of times under conditions which allowed of introducing pieces of iron which had been heated to low redness and cooled in hydrogen. In every case the presence of iron was easily detected when the content of the flask was evaporated to a few drops.

This experiment was again repeated with the additional precaution of using water which had been allowed to stand for a number of days over a large quantity of spongy metallic iron, the water being introduced into the reaction flask by distilling it from the iron in an atmosphere of hydrogen. Notwithstanding all these precautions, a distinct test for iron was obtained after the water had been concentrated. In all these experiments "blanks" were run which in no case showed that sufficient iron had been dissolved either from the glass or from the platinum to furnish the test which was obtained.

We therefore support Whitney in his statement that iron will dissolve in water which contains not more than a trace of electrolyte, no oxygen, and only that amount of carbon dioxide which is not retained by a strong alkaline hydroxide. In explanation of the failure of the investigators previously cited to detect dissolved iron, we would state that usually it is not possible to obtain an indication of iron with potassium ferricyanide, for example, in the water as it comes from the flask; concentration is generally necessary.

Ferroxyl Indicator.—That the corrosion of iron is an electrolytic phenomenon is shown by a very simple experiment devised by Dr. Allerton S. Cushman and ourselves. A piece of iron is immersed in ordinary

water to which has been added a little phenolphthalein and a trace of potassium ferricyanide. Within a very few minutes the iron is seen to divide itself into zones or surfaces which exhibit opposite polarity. Those portions where the iron is anodic will become coated with a precipitate of Turnbull's blue, owing to the escape of the iron ions at those points. Those portions on which hydrogen is being liberated, acting as cathodes, will become bright red owing to the formation of hydroxyl ions. This action may be more easily studied if this reagent (for which Dr. Cushman has proposed the name "ferroxyl") be thickened by the addition of neutral gelatin or agar-agar. We will return to this phenomenon later in this paper.

Function of Oxygen.—The rapidity with which iron will pass into solution in water depends not only upon the electrolytic solution pressure of the iron and hydrogen, and the osmotic pressure of the iron ions already in solution, but also upon the " excess voltage" (überspannung) which is required in order that the hydrogen ion which passes from the ionized condition may be set free.[1] In this case there is a counter electromotive force which must be overcome before the hydrogen can be liberated. It is possible, therefore, that the quantity of iron which can dissolve in water is limited to that amount which is equivalent to the hydrogen necessary to polarize that portion of the specimen which acts as the cathode. If this is the case, we should be able to make this solvent action continuous by the addition of any reagent which will depolarize the hydrogen-covered cathode portion. This reaction may be shown by the following very simple apparatus.

Two unglazed porcelain cups are placed concentric with each other and within a small Mason fruit jar, in the zinc top of which is soldered a small piece of copper tubing. The three vessels are filled with hundredth-normal potassium chloride solution free from oxygen and carbon dioxide, and the whole placed upon a hot plate of a temperature to insure continuous boiling. Two pieces of clean, pure iron, joined by an iron wire, are introduced into the central and outside compartment and the whole while still boiling is sealed by screwing on the metallic cap. Hydrogen is allowed to enter the jar as it cools in order to relieve the vacuum and prevent leakage of air. Such a cell may be maintained many hours without dissolving enough iron in either compartment to be detected by potassium ferricyanide in its unconcentrated condition. When reduced to a few drops, however, iron may always be shown to be present. Portions of each iron plate may be assumed to be anodic with iron tending to go into the ionized form, and other portions cathodic, being polarized by a film of hydrogen. If, now, a substance which will dissolve away the hydrogen be added to one compartment, the cathodic portion of the iron

[1] Nernst, Theoretische Chemie, 5th Ed., p. 712.

contained therein should be depolarized and the action should result in the solution of the anodic portions. Since the two pieces of iron are short-circuited above by a wire and below by the electrolyte, that piece which is continually depolarized would be expected to become the cathode. and the other the anode. Hydroxylamine serves as such a depolarizer and from an apparatus as above described. after standing for forty-five hours at room temperature the following results were obtained :

		Blank	Hydroxylamine
Increase in weight of cathode.	....	0.0005 grs.	0.0380 grs.
Decrease " " anode	....	0.0002 grs.	0.0393 grs.

When a five per cent. solution of potassium dichromate is used as a depolarizer, and the cell allowed to stand at room temperature for 40 hours the results were:

		Blank	$K_2Cr_2O_7$
Increase in weight of cathode	....	0.0001	0.0212
Decrease " " " anode	....	0.0000	0.0217

By passing a stream of hydrogen gas through all three cups iron will not dissolve in six hours sufficiently to give directly the ferricyanide test. If the hydrogen stream in one compartment be replaced by oxygen, iron will immediately begin to dissolve at an appreciable rate in the other compartment, separated though it is by the intermediate compartment through which hydrogen is passing. The dissolved iron in the anode compartment remains in solution as a ferrous salt while the cathode compartment becomes strongly alkaline. If the porous cells be withdrawn, the iron at once oxidizes and is precipitated as brown ferric hydroxide.

Mr. J. A. Collins. in a thesis presented at the Institute in 1898, noted the fact that if a piece of iron and a piece of magnetic oxide be immersed in water and connected through a voltameter, a very appreciable current would flow through the system with the iron as anode. To determine whether oxygen was a factor in this process the following experiment was performed: In a Jena flask containing hundredth-normal potassium chloride were suspended by fine platinum wires a piece of pure iron and a piece of magnetic oxide. These suspending wires were connected through a silver voltameter. By fitting the flask with a stopper containing gas inlet and outlet tubes, the operation could be carried on in either a vacuum, or in any desired atmosphere. When all air and carbon dioxide were expelled by long boiling. and the flask cooled under conditions which preserved the vacuum. no current passed through the voltameter upon closing the switch. When connected through a Lippman electrometer, however, a difference of potential between the two pieces was apparent. The electromotive force of the system is obviously not sufficient to furnish the " excess voltage " necessary to liberate the hydrogen on the magnetic scale, and while there exists this marked difference of potential,

no appreciable current passes. If the concentration of the hydrogen ions be increased, as can be accomplished by saturating the water with carbon dioxide, the electromotive force is then sufficient to overcome this resistance and a measurable current is obtained, the iron passing into solution. If, on the other hand, air free from carbon dioxide be passed into the flask, the cathodic film is depolarized by the oxygen and the iron dissolves. As a secondary reaction, the oxygen oxidizes, and the hydroxyl set free at the cathode precipitates the dissolved iron with the deposition of rust; this formation of rust is a factor in corrosion, however, only in so far that the concentration of the iron ions is kept very low and hence its osmotic pressure is negligible.

The influence of the depolarizing action of oxygen may be conveniently studied by using the ferroxyl indicator. For example, in a beaker may be placed a porous earthen-ware cell and the whole filled with ordinary water containing phenolphthalein and a very little ferricyanide. If a piece of iron be placed within the cell and connected by means of an iron wire with a piece of platinum in the outside compartment, immediate action takes place, deep red appearing on the platinum and a coating of blue precipitating on the iron. If, however, the platinum be heated in an alkaline pyrogallate solution, washed in boiling distilled water, and while wet used as the cathode in the cell, no action will take place for a number of hours. Only as the platinum takes up oxygen from the atmosphere, does the reaction become apparent.

The influence upon the rate of solution of iron which different metals exercise when connected by a metallic conductor with the iron, is also easily shown by this method. Those metals in the electrochemical series more negative than iron influence the action, not in proportion to their relative position in the series, but rather in proportion to some other property, possibly their ability to occlude or condense oxygen. On the other hand, aluminum is much less active in protecting iron than is zinc although it is more electro positive, while manganese completely reverses the polarity, making the iron the cathode and itself dissolving rapidly with the formation of brown manganese hydroxide.

Another conception of this action which differs only in the point of view from the above, is to consider the metal which acts as a cathode, for example, the platinum, as an oxygen electrode, and that the current flowing through the circuit (on account of which the iron dissolves) is due to the solution of oxygen and the formation of hydroxyl ions charging the solution negatively, and thereby requiring a solution of iron at the other electrode to bring about electrostatic equilibrium. When viewed in either of these two lights, the action should be proportional to the concentration of oxygen in the solution, and hence, according to the laws of Henry and Dalton, to the partial pressure of the oxygen in the

atmosphere above the solution. An experiment to test this conclusion was performed as follows: A number of Jena flasks were partly filled with boiled water and connected by means of a by-pass to a reservoir filled with definite mixtures of oxygen and nitrogen. freed as far as possible from carbon dioxide by being washed through strong potassium hydroxide and stored over barium hydroxide solution. When the water in the flasks was boiling violently. equal weights of pure iron were introduced and after ten minutes further boiling. the exit tubes were sealed, and by means of the by-passes. each flask as it cooled drew from the reservoir with which it was connected an atmosphere of known composition. Two or three times each day the gas over the solution was changed by passing through the flask a quantity of gas from the reservoir. At the end of a few hours the difference in the rapidity with which the iron was attacked was easily apparent. and after standing for four or five days the wire in each flask was cleaned and weighed. Any oxide which adhered to the wire was reduced in hydrogen and the wire again weighed. The loss of iron was in this way calculated and the results shown in the plot. The rate of the reaction is thus seen to be a direct function of the oxygen pressure and it is to be noted that the curve passes through the zero point. Only that amount of carbon dioxide which will not be absorbed by strong caustic alkalies could have been present, and this amount must have been constant in each flask. If the presence of carbon dioxide is an important factor in corrosion. it is difficult to understand why the solvent action should be so independent of the amount of carbon dioxide present. Although the same weight of iron was added to each flask there was not the same area undergoing active corrosion in each case. There were always clearly defined cathodic portions on each wire, which remained perfectly bright and on which the hydrogen was being deposited and the oxygen absorbed. These differed markedly in the different specimens but did not seem to bear a definite relation to the pressure of oxygen. When phenolphthalein was present, the bright spots were seen to continue to maintain a red zone in the solution around them. This irregularity in the area of iron actually attacked, accounts in some measure for the irregularities in the position of points not falling on the straight line in the plot.

The fact that the accelerating action of increased pressure of oxygen may be looked upon as due to an oxygen electrode. has an interesting bearing upon Dunstan's theory of the intermediate formation of hydrogen peroxide. Richarz and Lonnes[1] decomposed water saturated with air by passing through it, between platinum electrodes, a current of low electrode density. They found that at the cathode the hydrogen was to a large extent not liberated as such but that it combined with the dis-

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[1] Z. physik. Chem. 20, 145.

solved oxygen to form hydrogen peroxide. These are exactly the conditions which obtain upon the cathodic portions of iron undergoing corrosion, except that here we have iron instead of platinum. The appearance of hydrogen peroxide is therefore to be expected, provided it can exist on an iron surface. Dunstan could detect it when zinc corroded but failed to get a positive reaction in the case of iron. Dunstan explains the generally recognized inhibiting effect of the alkalies, potassium dichromate, etc., by the fact that they all instantly decompose hydrogen peroxide. If some condition already exists upon the surface of the iron such that hydrogen peroxide cannot exist, and if hydrogen peroxide is a step in the formation of rust, it is difficult to see what influence either for or against corrosion substances can have which also destroy hydrogen peroxide. The peroxide if formed at all, can be formed only when hydrogen is being oxidized by the dissolved oxygen, and the latter reaction takes place, as we have shown, on points separated from the points at which iron is passing into solution, and where if the water is still, rust patches will not form. The formation of hydrogen peroxide must be considered, therefore, incidental to and not necessary for corrosion.

It is a generally known fact that strong solutions of hydrogen peroxide will entirely protect iron from corrosion. If iron be placed in a solution of pure hydrogen peroxide, oxygen is liberated upon its surface but no rusting occurs. Moody takes this as a positive proof that oxygen alone cannot occasion corrosion. Assuming that hydrogen peroxide is a cathodic product of the action of iron on water, we would expect the presence of this reagent to inhibit the reaction, inasmuch as the law of mass action demands that the formation of a substance be limited by the concentration of that already formed.

Another possible explanation of the protective effect of hydrogen peroxide may be found in the formation of a kind of passive condition analogous to that produced by potassium dichromate, already referred to. Although much has been written upon this interesting subject there is as yet no perfectly satisfactory theory of passivity. We have noted that in the action of iron on water, when the concentration of the hydrogen ions is not sufficiently large to overcome the excess voltage of the iron surface, no action takes place unless a depolarizing substance such as dissolved oxygen is present, and then the surface divides itself into zones of different polarity. It may be possible that when iron is placed in a dichromate solution or hydrogen peroxide solution it absorbs or occludes so dense a film of oxygen upon its surface as to render the entire piece of metal so strongly cathodic that no corrosive action can take place.[1]

When bright iron is heated in the air, oxygen attacks the iron directly,

[1] A. S. Cushman, Bulletin No. 30, Office of Public Roads, U. S. Dept. of Agriculture.

forming a closely adhering layer of oxide even if it be of but micro-scopic thickness. That oxygen does not unite directly with iron in aqueous rusting, is shown by the experiment already referred to with the porous cell and also by the fact that the rust formed is never adherent to the surface of the iron. The slightest rubbing with the hand pro-duces a clean, bright surface of pure iron. Only when this layer of fer-ric hydroxide dries on the surface of the iron is an adherent scale pro-duced. Moody,[1] in a very recent communication. describes an experiment in which he shows that iron does dissolve before being precipitated as rust. He uses this fact as a further proof that carbon dioxide is essential to rusting. We see ample grounds for concluding that carbon dioxide was absent in the experiments already outlined, and yet the iron surely passed into solution before precipitating.

If a piece of chemically pure iron free from mechanical strains and without evident crystallization. be immersed in the ferroxyl indicator, the positive and negative zones will be apparent after a few moments. There appears to be an unequal concentration of oxygen or segregation of oxygen upon the surface, which cannot be explained by discernible differences in the character of the surface. If the ferroxyl indicator be removed, the surface cleaned by rubbing with a dry towel and the indi-cator again applied, the same separation into zones is seen. though in an entirely different configuration. The indicator is apparently a very deli-cate one and susceptible to changes in equilibrium, which up to the pres-ent have not been detected by other means.

Since corrosion is manifestly an electrochemical action. it seemed probable that if two specimens of iron were selected, one of which had proven itself in practice as especially resistant to corrosion. and another which had shown itself to be very susceptible to corrosion. certain differ-ences in the electrochemical behavior should be discernible. Two sets of such specimens were obtained. The first consisted of two pieces of sheet metal which had been used as culverts in road building. one of which had given way in but a short time while the other was practically intact. The second set consisted of two strands of wire from a piece of ordinary barbed wire fencing, one of which was badly corroded upon an exposure of but six months while its neighbor was apparently in its original condition. Nothing is known of the history of the two wires; the good piece of sheet was known to be from an open hearth steel ingot containing but a trace of manganese, and in the heating and rolling of which extra precautions had been taken to prevent segregation. The poor piece was known to be from an ingot of ordinary Bessemer steel.

If corrosion be an electrochemical phenomenon depending upon the formation of an anode portion and a cathode portion and the passage of

[1] Pr. Chem. Soc. **23**, 84.

a current between these two, the rate of this corrosion may be assumed to be proportional to the difference of potential between the two surfaces. In order to determine whether there was any marked difference in the samples of iron above referred to, in regard to variation in potential between points taken at random over the surface of each, the following method was employed: In the case of the sheet metal, specimens were machined to an area of about three square inches in the form of a rectangle one inch wide by three inches in length. A block of paraffin $\frac{1}{4}$ inch thick was cut to have the same surface as the sheet metal. A number of small holes about $\frac{1}{8}$ inch in diameter were drilled in the paraffin and the latter pressed upon the sheet after warming the same. A number of small electrically insulated cells were thus formed, the bottom of each being a definite portion of the surface of the metal. The physical condition of the different pieces of metal experimented with, was made as uniform as possible before applying the paraffin block, by polishing each upon a fine, dry sandstone. When any electrolyte, for example, hundredth-normal potassium chloride solution was placed in these cells, a difference of potential between any two could readily be measured by means of Poggendorf 's compensation method. The composition of the cell was Pt-KCl-Fe-Fe-KCl-Pt. In many cases a current of sufficient intensity was set up to rapidly polarize the platinum wire electrodes which were used to complete the circuit from the electrolyte in one cell, through the measuring instrument to the electrolyte in the other cell. In order to eliminate any effect which a difference in the surface of the platinum wires might introduce, these were heated in a Bunsen burner before each measurement. By taking a measurement and then interchanging the platinum wires in the respective cells, no difference in the reading was observed, and therefore the potential found was independent of the platinum. A cell for investigating the samples of wire was made in an analogous way, using a long wooden trough in which the wires were inserted, and forming cells by building up partitions of paraffin at intervals along the length of the wire.

The differences in the average variation of any two cells taken at random over the surface of sheet metal in the one case and the two wires in the other, are very marked, a typical set of readings being shown in the following table, the figures representing differences in potential, expressed in millivolts, between various cells :

Poor Sheet.			Good Sheet.		
I	II	III	I	II	III
— 56	—60	+ 47	— 5	— 5	— 8
+ 48	+21	— 86	0	— 8	0
+ 39	+30	— 48	+ 4	0	—20
— 26	—93	— 69	0	0	—20
+ 56	—31	—177	+18	— 8	0
— 30	+ 8	— 58	+ 2	+ 8	0
+ 21	+81	— 32	0	0	— 5

Corroded Wire.			Good Wire.		
+161	—13	— 30	0	— 2	+ 8
+ 93	—24	+ 38	— 4	—13	0
— 21	—13	— 63	—13	0	+ 4
— 43	—21	±103	0	0	—13
— 8	—56	— 26	+17	4	— 4
— 30	—64	— 43	— 8	5	8
+ 55	—43	— 47	0	+ 9	0
— 16	52	+119	— 5	0	0
+ 78	—21	8	— 8	+26	5

After measuring the difference of potential as above, the paraffin was in each case removed, a fresh surface obtained and the experiment repeated. No two cells ever reacted alike but there was always the marked difference between the two pieces of metal indicated above.

It is as yet too early to decide that measurements of this kind indicate the tendency of iron to corrode, but by investigating a large number of specimens of known resistance to corrosion we hope to obtain definite information on this point.

SUMMARY.

We have

(1) Proven again that carbon dioxide is not essential for the corrosion of iron :

(2) Substantiated the work of Whitney and shown that iron does dissolve in pure water in the absence of carbon dioxide and oxygen;

(3) Shown that the primary function of oxygen in the corrosion of iron is in depolarizing those cathodic portions of the iron upon which hydrogen tends to precipitate, and that a secondary function is the oxidation of the ferrous iron ion to the ferric form, with its subsequent precipitation as ferric hydroxide;

(4) Shown that the rapidity of corrosion in water is a linear function of the partial pressure of the oxygen in the atmosphere above the water :

(5) Shown that an electric current can pass between bright iron and iron covered with scale, (1) if the concentration of the hydrogen ions be increased by the presence of an acid, or (2) if oxygen or some other depolarizing substance be present ;

(6) Shown that in certain instances, areas having marked difference in potential exist in far greater number upon the surface of a piece of iron prone to corrosion than upon iron which is resistant to corrosion.

This investigaton is being continued, and in a subsequent paper the more practical phases of the subject will be dealt with.