CORROSION OF IRON

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The selection of material for a review on corrosion is complicated by the breadth of the field, the variety of phenomena encountered and the conflict of published opinion and theory. It therefore seems best to confine the discussion to certain features which have wide application and which have excited recent experimental research rather than to attempt anything in the nature of a complete bibliography of the subject.

ELECTROCHEMICAL THEORY

According to electrochemical concepts of corrosion, the reaction takes place through a cell between two surfaces. At the anodic surface the metal goes into solution, while one or more corresponding reactions go on simultaneously at the cathode, the current passing from anode to cathode through the solution and back to the anode through the solid.

The electrochemical theory was first developed to explain the phenomena when two metals of different solution potentials are in contact, but it was evident that the same sort of action could occur between two surfaces on a single piece of metal. Working along this line, the ferroxyl indicator test was widely used to illustrate differences in the solution potentials exhibited at different points on the surface of a metal.

The general applicability of this theory has been attacked on the ground that many cases of corrosion might be explained as direct chemical combination of oxygen with the metal, even though other cases necessitated the introduction of electrochemical conceptions. The critics failed to recognize that there is no arbitrary distance over which the cell must act in order to classify the action as "electrochemical." Corrosion phenomena between two separate pieces of metal in a solution, connected only externally are admittedly electrochemical, and the same is true for the action between a plated metal and the bare metal exposed by a pinhole in the plating. There is no reason for assuming that the action ceases to be electrochemical just because the anode and cathode areas are on the same piece of metal and may be closely adjacent. Indeed, these areas might well be contiguous molecules, and the corrosion would still be electrochemical.[1] Electrochemical action is now generally accepted as the fundamental explanation of corrosion phenomena at ordinary temperatures, even by those who formerly adhered to the theory of direct chemical attack or to that of colloidal catalytic action.

Many of the more important factors in corrosion can be predicted directly from its electrochemical nature. This can be shown by considering the simultaneous reactions occurring at the anode and at the cathode.

Anode reactions

Since metal dissolves at the anode, the two primary factors governing this reaction should be the solution potential of the metal and the concentration of metal ions in the solution adjacent to the surface. A potential for the half-cell

$$M, M^+$$

can be calculated directly from the normal potential of the metal and the metal ion concentration by the Nernst equation:

$$E - E_o = \frac{n}{RT} \ln \frac{1}{C}$$

Other things being equal, corrosion will be more rapid with metals of higher solution potential and with solutions where the metal ion concentration is low.

There are many apparent contradictions to this statement

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[1] R. J. McKay and B. D. Saklatwalla, Discussion at Detroit (1924), Meeting of Am. Electrochem. Soc.

because the "other things" are very seldom equal. As a matter of fact, solution pressure per se is frequently an unimportant factor due to supervening effects. Metals of very high potential like sodium and calcium do indeed "corrode" with great rapidity, but aluminum is generally more resistant than iron, although it has a higher potential. This case, and a great many others of the same nature, is explained by difference in the protective action of the corrosion products. Another apparent contradiction, the corrosive effect of concentrated solutions of ferric salts on iron, is readily explained by the oxidizing power of such solutions.

On the other hand although copper and gold are resistant metals they can be rapidly corroded in solutions where a complex ion forms and reduces the free metal ion concentration to an exceedingly low value—e.g., copper in ammonia and gold in cyanide solution.

Cathode reactions

The cathodic reduction may occur in many ways depending upon the corrosive conditions. For example, if iron corrodes in a solution of copper salt and metallic copper plates out, the cathode reaction is copper ion giving metallic copper.

In most cases the cathode reaction is the liberation of hydrogen gas or the reaction of dissolved oxygen, or these two in parallel.

High hydrogen ion concentration assists both reactions, in accordance with the Nernst equation. When hydrogen gas is evolved, either as a gas or dissolved in the solution, the tendency to corrode is greater as the pressure on the gas diminishes. Thus hydrogen gas may be dissolved in dilute solution more readily than it can be evolved as gas bubbles at atmospheric pressure. The rate of hydrogen gas formation is decreased by overvoltage: a resistance which is a function of many variables such as the nature and surface of the metal, the composition of the solution and the geometrical shape of the surface. Overvoltage is a factor of primary importance in the acid corrosion of iron, zinc and other anodic metals, but it will not be treated in detail in this review.

The character of the cathodic reaction of oxygen is discussed in a later section.

EFFECTS OF OXYGEN

Oxygen has long been recognized as an important factor in corrosion, but the many ways in which it determines the amount and character of corrosion are recent discoveries. The earlier theorists assigned to oxygen the rôle of oxidizing corrosion products such as ferrous hydroxide to a higher state. The full responsibility of oxygen for most natural corrosion was brought out by Walker[2] in his experiments which showed the corrosion of steel under water to be proportional to the concentration of oxygen dissolved in the water.

Corrosion can, of course, proceed in the complete absence of oxygen or other oxidizing agents. Thus iron will dissolve in hydrochloric acid, and will be appreciably corroded by water at high temperatures when the system is quite freed from oxidizing agents. Even at room temperature a slight corrosion occurs on iron in contact with deoxygenated neutral solutions.[3] However, of the total economic loss due to corrosion it is safe to estimate that over 90 per cent can be charged to the account of oxygen.

Nature of reaction

The method by which oxygen attacks metals has been explained by many theories. One which received wide acceptance was that the initial electrochemical reaction of a metal with water produced the metal hydroxide and hydrogen gas—and that the oxygen then oxidized the hydrogen gas to form water. The major obstacle to this theory was the well-known fact that dissolved oxygen gas does not react with dissolved hydrogen gas to form water. Unfortunately, the promulgation of this impossible process reacted to discredit the whole idea of electrochemical action.

This difficulty was removed by assuming that dissolved oxygen reacted with hydrogen in the atomic form, i.e., with "nascent" hydrogen which had been discharged at the surface. Such a concept has the marked advantage that it is readily presented by a logical and consistent series of reactions. In the

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[2] Walker, Cederholm, Bent J. A. C. S., **29**, 1251 (1907).

[3] Shipley and McHaffie, Can. Chem. Met., **8**, 121 (1924).

first and primary stage the metal goes into solution at the anode, and hydrogen ions discharge at the cathode, forming nascent hydrogen.

$$\begin{aligned}\text{At anode:}\quad & Fe + 2\oplus = Fe^{++}\\ \text{At cathode:}\quad & 2H^{+} = 2H + 2\oplus\end{aligned}$$

Atomic hydrogen is then removed either by the formation of hydrogen gas

$$2H = H_2$$

or by reaction with an oxidizing agent such as dissolved oxygen.

$$2H + \tfrac{1}{2}O_2 = H_2O$$

or by both reactions in parallel.[4]

While this formulation is now widely accepted, and is perhaps the simplest method of expressing the processes it is subject to the following objection. When applied to the corrosion of copper and of other metals cathodic to hydrogen, the idea that such metals will go into solution and plate out hydrogen is at first thought unreasonable. As a result, certain investigators in the past have felt compelled to discard the electrochemical theory when applied to copper, and have formulated other theories like those of direct oxidation to fill in the gaps thus created.

There is no real justification for such hesitance when we remember that the position of hydrogen in the electromotive series is determined by measurements of the potential of the half-cell, hydrogen ion against gaseous hydrogen. Now the primary reaction does not involve or imply gaseous hydrogen but produces hydrogen in an intermediate state referred to as "atomic" or "nascent." Therefore, although copper is cathodic to hydrogen in the special case where hydrogen gas is considered (and where the copper ion concentration is not abnormally low), it may legitimately be considered as anodic to hydrogen when the deposited hydrogen is removed by some oxidation reaction.

[4] Hydrogen peroxide may be formed as an intermediate product of the oxygen reaction (Bancroft, J. I. E. C., **17**, (1925) 336) but this possible step need not be introduced in considering the net result of the process.

To avoid the difficulty in visualization discussed above, the reaction of oxygen may be presented in an alternative manner.[5] Thus the cathode reaction, consisting of deposition of nascent hydrogen followed by the reaction of the hydrogen with dissolved oxygen to form water, gives as its net effect the disappearance of one mol of water (which ionized to produce the hydrogen ion), and of one-half mol of oxygen, and the production of two hydroxyl ions and of two positive charges.

$$H_2O + \frac{1}{2}O_2 = 2OH^- + 2\oplus$$

As a result, rather than picturing the discharge of hydrogen ions and their subsequent oxidation, the cathode reaction can be looked upon as the operation of an oxygen cell which produces hydroxide ions.

The choice between these two formulations is determined primarily by the relative ease with which they can be grasped. Either one is adequate if properly appreciated. Present usage favors the former, but the idea of an oxygen half-cell permits direct calculation of theoretical corrosion potentials and clarifies the consideration of the corrosion of "cathodic" metals.

It might be argued that the suggestion of an oxygen half-cell is a reversion to the theory of chemical action, which postulates direct reaction between oxygen and the metal. There is, however, one vital distinction between the chemical and electrochemical theories which is in no way vitiated by the new concept. By the former, corrosion can occur only at the place where oxygen reacts—by the latter, the metal may go into solution at a point separated from the oxygen by a finite distance. So many corrosion phenomena have been observed where the corroding metal and the corroding agent were not in contact that direct chemical action cannot possibly be regarded as a theory of universal application.

Rate of reaction

The rate of corrosion by dissolved oxygen is a function of so many variables that no single factor can be selected as deter-

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[5] Whitman and Russell, J. Soc. Chem. Ind., **43**, 1931 (1924).

mining all cases. Often the initial tendency to corrode is so slight that the rate of reaction is necessarily slow, as in the attack of noble metals by oxygen in distilled water. In most of the important cases, however, there exists so great a tendency to react that the rate is limited, not by chemical factors, but by physical ones.

Wilson[6] has stated the case for the corrosion of iron and steel in natural waters which contain dissolved oxygen. Iron has a high tendency to corrode under such conditions, the theoretical corrosion potential in neutral water at room temperature saturated with air being calculated as 1.74 volts.[7] The reactivity is therefore so great that corrosion may be considered to occur instantaneously when oxygen reaches a surface which is in effective electrochemical contact with the corroding metal. Under such conditions the only thing preventing a very rapid corrosion is the fact that the corroding agent, dissolved oxygen, cannot be supplied to the cathode rapidly enough to maintain the high corrosion rate.

It is evident that, if the corrosion rate is limited by the rate of supplying oxygen, the controlling factors are physical rather than chemical. This view is supported by numerous observations, one of the most convincing of which is that steels and irons of widely differing chemical composition show the same corrosion losses when kept under water for long periods. The importance of physical factors external to the metal itself is predominant in such cases.

The rate at which dissolved oxygen can be supplied to a surface in effective electrochemical contact with the corroding metal is, like so many other rate phenomena, a problem of diffusion. It is therefore determined by the diffusion potential and by the diffusion resistance. If the main body of the solution around the metal contains dissolved oxygen to the extent of perhaps 5 cc. per liter, and the oxygen concentration is zero at the cathode surface (because reaction there is practically instantaneous) the diffusion potential is 5 minus 0 = 5 cc. per liter. Other things being equal,

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[6] J. I. E. C., **15**, 127 (1923).

[7] Whitman and Russell, loc. cit.

and in the absence of side reactions such as hydrogen gas evolution, the corrosion rate should therefore be directly proportional to the oxygen concentration in the solution. The experiments of Walker[8] confirm this view. Wilson makes use of this proportionality in deriving a "specific corrosion rate" in order to compare the rates obtained under different conditions where the oxygen content of the solution varied. His "specific" rate is the actual rate of corrosion divided by the oxygen concentration of the solution.

The other diffusion factor—"diffusional resistance"—is somewhat more complicated. In the simplest case, where a metal corrodes without building up films of corrosion products or coatings from the solution, the diffusional resistance is due only to the quiet surface film of solution against the metal. This liquid film is sometimes spoken of as a "friction skin" of fluid, and is always present when two phases are in contact. The effective thickness of such films under definite conditions is known for some cases from studies of heat transfer, fluid friction and related processes. In a few instances it has been possible to correlate corrosion rates with the rate of oxygen diffusion calculated from the diffusivity of oxygen through water, the diffusion potential, and the effective film thickness as determined by such indirect methods.[9]

In most practical cases of corrosion, however, solid films form on the surface of the metal and influence the rate of diffusion. This brings up the whole question of solid coatings, a subject of utmost importance in corrosion which is still largely a matter of speculation. Certain types of corrosion products, such as the rust formed on iron in distilled water, seem to have very little effect on the corrosion rate because of their porous non-adherent nature. This statement deserves the qualification that the initial rate, before rust has formed on the surface, is usually high, but once the film has attained appreciable thickness subsequent increases in thickness do not have any marked effect. Now since the very presence of such rust should increase the thickness of the

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[8] Walker, Cederholm and Bent, loc. cit.

[9] For example of such calculation see Wilson, loc. cit.

fluid "friction skin" this means that the dissolved oxygen, as such, does not have to diffuse completely into the underlying metal in order to find an effective cathode surface. Such a view is substantiated by the observation that films of rust on submerged iron are highly oxidized on the outer surface, but are in the ferrous form on the side in contact with the metal. It seems probable that the oxygen reaches an "effective cathode area" in electrochemical contact with the corroding metal within the rust film itself. The exact mechanism is unknown, but may well involve an oxidation of ferrous to ferric rust in the layer of corrosion products.

It is well known that natural waters vary greatly in their corrosive action on metals. In most cases the effect is not attributable directly to acidity and the formation of hydrogen gas, although acidity may have a vital influence on the character and amount of solid coating formed on the metal. Thus, experiments[10] in a soft natural water where the pH was varied from 9.5 to 5.0 by adding sodium hydroxide or hydrochloric acid, showed no change in corrosion rate with pH value within these limits. Conversely, the corrosiveness of the water supply of the City of Baltimore has been greatly decreased by the addition of sufficient lime to precipitate carbonate scale on the pipes.[11] In the soft water experiments the addition of alkali up to a pH of 9.5 did not cause scale formation, while with the Baltimore water supply the results were quite the opposite.

Additions of alkali to give a pH higher than 9.5 to the soft water reduced corrosion, the rate diminishing progressively as pH was increased. However, it has been observed that the initial corrosion rate in dilute alkali is just as rapid as the initial rate[12] with neutral water. The effect of alkalies is therefore to build up protective films which reduce corrosion. This is of particular importance, since it contradicts the earlier opinion that alkalies were effective retarders because they cut down the concentration of hydrogen ions necessary for corrosion. As a matter

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[10] Whitman, Russell, Altieri, J. I. E. C., **16**, 665 (1924).

[11] Baylis, Chem. Met. Eng., **32**, 874 (1925).

[12] Speller and Texter, J. I. E. C., **16**, (1924) 393.

of fact, the theoretical corrosion potential in dilute alkali when iron is corroding is just as great as it is in natural waters, and the "insufficient hydrogen-ion" theory had no theoretical basis.

The action of protective films is intimately connected with oxygen diffusion since they set up barriers aganst the free access of oxygen to an effective cathode surface. They may be considered as more or less effective insulators preventing electrochemical contact between the metal and the corroding agent in the solution.

Localization of corrosion

Aston,[13] investigating the effect of wet rust on a surface, found that the metal beneath this rust was anodic and explained this as due to the low concentration of dissolved oxygen under the rust. Since that time many similar experiments have been performed, the work of Evans[14] being particularly noteworthy. Evans, studying the corrosion under a drop of water on a clean surface of steel, noted that the outer ring of metal under the drop was relatively unattacked, but that corrosion proceeded rapidly under the center of the drop and formed a pit there. He explained this as caused by differences in the concentration of oxygen dissolved in the water at the outer surface of the drop and in the center. Since the oxygen supply for corrosion came from the air by a process of dissolving in the water, the surface of the drop should be most nearly saturated and the interior should be most deficient in oxygen.

Several explanations of the phenomena have been suggested, each of which has considerable basis for argument. It is probable that the following series of steps, combining certain features of each, approximates the actual mechanism.

Initially the oxygen concentration throughout the drop is uniform and the tendency for localized corrosion is haphazard. As soon as an appreciable amount of oxygen has been consumed, however, the oxygen concentration is lower at the center and remains so during the rest of the experiment. Now a difference of

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[13] Aston, Trans. Am. Electrochem. Soc., **29**, 449 (1916).

[14] U. R. Evans, J. Soc. Chem. Ind., **43**, 15 T (1924).

oxygen concentration at two points does not mean per se that the corrosion will be localized at the point of lower concentration. It is true that a potential measurement between those two points would show the one of lower concentration to be anodic, but that is merely because the measurement is between two oxygen half-cells of unequal force. The tendency for iron to corrode is the same at both points unless there is some difference in the surface coating or composition of the solution *apart from* concentration of dissolved oxygen.

A slight amount of corrosion will therefore occur on each surface. The greater concentration of oxygen at the outside will, however, result in more vigorous corrosion around the circumference, and in the rapid formation of a film of corrosion products, and a local alkaline condition. The protective effect thus exercised over the corroding metal will diminish its rate of solution, and cause the oxygen which is depositing there to search farther afield for a reactive anodic surface. This tendency is progressive because continued oxygen reaction, unaccompanied by an equivalent corrosion of metal over the same area, maintains an alkaline condition and a protective film. Conversely, the metal at the center of the drop has not had opportunity to build up its alkaline solution and protective film before all the corrosive action is localized upon it as the least protected surface available. Consequently the metal goes into solution without a corresponding formation of hydroxide in its immediate vicinity, the solution becomes acidic, no protective film can be built up, and all the corrosive action is localized towards the formation of a pit. Further aid to this tendency is furnished by a mantle of corrosion product built up where ferrous ions diffusing from the center meet hydroxide ions from the outside. This mantle shuts off oxygen which is diffusing in towards the center, but it is too far away from the metal to have any protective action.

Localized corrosion due indirectly to differences in oxygen concentration is of considerable practical importance. Familiar examples which are caused by this, at least in part, are the pitting of pipe threads and of steel covered with mill scale.

EFFECT OF VELOCITY

The experimental evidence on the effect of velocity in corrosion of steel by natural waters is contradictory. Heyn and Bauer[15] found that corrosion increased with velocity up to a certain critical point but that above this point there was a sharp decrease. Friend[16] obtained similar results in his experiments, although the critical velocity which he found was fifty times as great as that of Heyn and Bauer. Speller[17] on the other hand, finds a regular increase of corrosion with velocity, with no indication of a critical point of maximum activity over the ranges studied by Heyn and Bauer and by Friend.

It is difficult to explain these apparent contradictions. Unquestionably the difference in experimental methods is responsible for the difference in results. Heyn and Bauer and Friend used clean metal specimens, flowed the water past them, and determined corrosion rates from the losses in weight. Speller passed water through steel pipe, calculating his corrosion results from the amount of dissolved oxygen removed from the water by its passage through the pipe. Probably the most important difference is the complete absence of corrosion products at the start of the experiment in the first cases as compared to their presence in Speller's work.

Evans,[18] commenting on Friend's work, states: "It seems more likely that the falling off in the rate of corrosion at high water speeds is due to the fact that the more rapid stream insures uniform oxygen concentration over all parts of the surface." This implies the formation of a somewhat protective film of corrosion products over the whole surface—a film which reduces corrosion primarily because it does not break down locally to give strongly anodic spots of corroding metal. Evans' experiments to prove this theory are not conclusive and considerable experimental work is necessary to confirm the observations of a "critical" velocity

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[15] Mitt. pgl. Materialprüfungsamt, **28**, 62 (1910).

[16] J. Chem. Soc., **119**, 932 (1921).

[17] J. I. E. C., **15**, 134, (1923).

[18] J. I. E. C., **17**, 363, (1925).

under a wide variety of conditions before any one explanation can be accepted.

Attempts to check Friend's results over the same velocity range have been made by rotating a vertical cylindrical test piece in distilled water.[19] The method of preparing the surface for testing was found to be a variable of greater importance than the speed of rotation. In a series of about six runs at varying velocities and with a uniform method of preparation by grinding with coarse emery, corrosion was found to increase with velocity with only one exception (which, incidentally, could not be duplicated in a later run). Speller's results definitely indicate that under practical conditions in the corrosion of pipe, corrosion increases continuously with velocity—a result which would be expected from the theory of oxygen diffusion if complications such as surface conditions and character of rust film are not superimposed and determinant.

In acid corrosion the effects of velocity are somewhat more definite. Friend's experiments in whirling a horizontal steel disc in sulfuric acid led him to conclude that the corrosion rate was directly proportional to the velocity and that different concentrations of acid give the same corrosion rates at the same velocity.

A more comprehensive study[20] of this problem has been made by rotating a vertical steel cylinder, thereby avoiding differences in velocities at different points on the surface. In general the corrosion rate at rest was higher than that at low velocity, but further increase in velocity raised the corrosion. Experiments with sulfuric acid varying from 0.004 to 5.0 normal showed that, while corrosion at rest varied nine-fold over this range of concentration, at high velocity the rate was practically the same for all strengths and therefore independent of concentration. Further experiments in which atmospheres of oxygen or of nitrogen were maintained over the acid showed that the corrosion at high velocity was due primarily to the action of oxygen dissolved in the acid, whereas the corrosion at rest was due chiefly to the action of the acid in liberating hydrogen gas. Increase in velocity reduced the amount

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[19] Otto Rickers, M.S. Thesis M. I. T., 1922.

[20] Whitman, Russell, Welling, Cochrane, J. I. E. C., **15**, 672 (1923).

of hydrogen gas evolved, possibly because the bubbles were smaller in size and therefore required more work for their formation. Conversely, increase in velocity allowed faster oxygen reaction by speeding up diffusion processes.

The effect of velocity on protective films is unquestionably an important factor in certain cases. It is now generally admitted that many examples of so-called "erosion" are really corrosion phenomena in which the protective film of corrosion products is removed by the high velocity. Whitney,[21] in studying the corrosion on steam turbine buckets by testing samples in a water-splashing device, found that the substitution of hydrogen for air in the system eliminated all traces of the corrosive or "erosive" action. He states, "Between the extreme case of eroded propellers" (which Whitney admits is mechanical action) "and simple chemical corrosion there is a large field of destruction of metals in which the action commonly spoken of as mechanical erosion is more probably chemical corrosion, with subsequent removal of the new compound by erosion."

A striking example of this effect is shown in the corrosion of steel by concentrated sulfuric acid.[22] At rest, the steel samples were practically unattacked by 100 per cent acid, but when they were rotated at a velocity of 60 cm. per second the corrosion was severe, particularly where the sample rubbed against its glass supporting rod. At such points the penetration was as great as 0.3 cm. in 72 hours. Samples which had been previously treated by quiet immersion in the same acid (thereby building up a protective film) showing an initial resistance to attack at high velocity and corroded only half as much as did the untreated samples. The authors conclude that: "This phenomenon further confirms the concept that the low corrosion at rest is due to film protection and that the acceleration with velocity is largely the result of removing the film. The presence of solid corrosion products suspended in the acid probably has a further effect of the same general nature."

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[21] J. I. E. C., **17,** 385 (1925).

[22] Whitman and Russell, J. I. E. C., **17,** 348 (1925).

EFFECT OF DISSOLVED SALTS

Friend [23] has reported an extensive series of beaker tests on iron in neutral salt solutions, using the results to support his theory of catalytic acceleration of corrosion by the colloidal corrosion products. In these tests, however, other factors besides the specific action of the salt on corrosion are involved. Thus Friend himself points out in a later paper that the presence of the salt not only changes the solubility of oxygen in the solution, but that it also changes the specific rate of oxygen absorption. For authority on this latter point he refers to the excellent work of Adeney and Becker on the rate of solution of atmospheric gases by water.

The results of beaker tests are therefore inconclusive since the changes in gas absorption and solubility may have a much greater influence on the result than the specific effect of the salt itself.

Evans attempts to avoid the complications of variable rate of gas absorption in a beaker test by studying the action of drops of salt solution placed on a clean metal surface. It would seem, however, that the results of such tests would also be of limited applicability, since the degree of convection within the drop would certainly vary with the nature and concentration of the salt.

A few tests[24] on the corrosiveness of salt solutions flowing through steel pipe have been made by the oxygen drop method. In these tests the effects of rate of oxygen solution and of variable convection velocities as a function of the solution are presumably eliminated. While the conditions do not parallel those existing during water-line or spray corrosion they represent the many cases where metal is completely submerged in salt solution.

In this same work the solubility of ferrous hydroxide in distilled water and in the various salt solution was determined. The authors emphasize the parallel effect of the salt in reducing corrosion and in reducing the solubility of ferrous hydroxide, ad-

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[23] Carnegie Scholarship Mem., **11**, (1922).

[24] Whitman, Russell and Davis, J. A. C. S., **47**, 70 (1925).

vancing the theory that the specific effect of the salt on corrosion is to change the solubility of the initial product of corrosion. If this is rendered less soluble it precipitates closer to the metal surface and forms a more adherent and protective film. Conversely, a salt which increases the solubility makes the film less protective and increases the rate of corrosion.

The effect of salts in localizing corrosion may be evidenced in two directions. In the first place, by greatly increasing the conductivity of the solution, they lengthen the distance over which an electrochemical cell can operate. This makes it possible for a large cathode area to concentrate its corrosive activity upon a small unprotected anode area and cause rapid pitting.

In the second place those salts which cause the formation of protective films may accentuate pitting to a marked degree under certain circumstances. It seems to be generally true that a tendency towards greater film protection increases the tendency toward localization of corrosion. Thus the pitting of iron in dilute solutions of sodium carbonate has been noted by Lyon[25] and others. The addition of excess lime to calcium brines and of cautic soda to sodium brines, while it reduces corrosion, actually increases pitting to a marked degree.[26] Evidently the major part of the surface is protected but certain localized spots are left exposed to concentrated attack, just as the iron exposed by a pinholen in tin plate suffers rapid corrosion because of the large active area of cathodic tin surrounding it.

The close relationship between passivity and the formation of protective films is becoming more evident as the result of these studies. The action of alkalies on iron has been termed "passivifying"—it is now known to be the result of protective film formation due to decreased solubility of the corrosion product.[27] Chromates have been shown to render iron hydroxides practically insoluble in water. Steel in concentrated sulfuric acid is still another instance of passivity where the evidence for the action of

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[25] Lyon, J. Am. Soc. Nav. Eng., **24,** 845 (1912).

[26] Whitman, Chappell and Roberts, Refrig. Eng., **12,** 158 (1925).

[27] Speller and Texter, loc. cit.
Whitman, Russell and Altieri, loc. cit.

protective film is reasonably convincing. While there are still many cases which have not been subjected to critical examination in the light of the film theory, the concept may be accepted as a practical working basis for further investigation of such problems. In particular, its application to the development of alloys resistant to strongly oxidizing conditions may indicate the answer to many problems which are as yet unsolved.

SUMMARY

The electrochemical theory is now generally accepted as most adequately explaining corrosion phenomena at ordinary temperatures.

The presence of dissolved oxygen is necessary for appreciable corrosion in so many cases that the nature and character of its reaction are matters of primary importance. The rate of diffusion of oxygen to an effective cathode surface frequently determines the rate of corrosion. Variations in oxygen concentration between different points on the surface, if maintained for a considerable time, lead to effects which result in localized corrosion and pitting.

The usual effect of velocity is to increase corrosion due to dissolved oxygen, both by increasing diffusion and by breaking down protective films. Certain results which indicate a maximum in the plot of corrosion against velocity in natural waters have not been satisfactorily explained.

The effect of dissolved salts on the rate of corrosion may be intimately related to the manner in which they affect the solubility of the corrosion product. The presence of dissolved salts often increases the pitting tendency. This is due both to the increased conductivity of the solution, and, in the case of salts which reduce corrosion, to the tendency for large portions of the surface to become protected themselves and to concentrate their activity upon small unprotected anodic areas. Certain "passivity" phenomena are evidently due to protective film formation and it seems possible that the concept of protective films may be adapted to all cases of passivity.