PAPERS ON ENGINEERING SUBJECTS.

CORROSION OF IRON AND STEEL, IN THEORY AND PRACTICE.

It has been estimated that 29,000,000 tons of iron are dissipated in the form of rust in the course of a year. This, representing as it does, one quarter of the world's normal output of iron per year, constitutes a formidable proportion of waste. The degradation of this amount of iron beyond recall, serious as it is, is, however, of less economic significance than the loss of that precious and irreplaceable commodity coal, seeing that every ton of iron requires from 4 to 5 tons of coal, or its equivalent, to produce it.

Yet another economic loss is the expenditure in effort and material in combating and attempting to prevent corrosion and, indirectly, from the use of alternative weaker materials of heavier scantlings. This is hardly calculable, but a consideration of the diversion of man power and material required to maintain the ferrous fittings of a single ship in an efficient condition will enable an idea to be formed of its significance in the industrial world to-day, from which it can only be concluded that the corrosion of iron is one of the most serious material problems of the age.

The corrosion problem is an exceedingly complicated one as a result of the many variables and inter reactions which can attend the practical cases, and it appears hardly feasible to produce any simple working theory capable of explaining the mechanism of corrosion of iron in its many phases. Of late years, however, the co-ordination of experimental observations and researches in new fields has led to a material advance in knowledge and to a crystallisation of ideas, and while the whole range of what may very well be called the phenomena has not perhaps been explained, many anomalies existing under the earliest theories have been cleared up. This fuller knowledge does not reveal a universal remedy, but it certainly indicates, if only indirectly, possibilities in improving our methods of combating the trouble and confining its influence.

It will be the object of these notes to present in convenient form and as briefly as may be possible the existing theories of corrosion of ferrous materials, together with some of the chemical and physical facts and other data which may have a bearing on the question, and to indicate on this basis the mechanism of the process as at present understood. Many of the points made are necessarily somewhat obscure and controversial, but by reference to his own particular experience the interested reader

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will be in a position to form some judgment as to the probability of the hypotheses given and the effect of the principal variables met with in practice.

Reference to the article in Papers No. 3 on the experiments dealing with the corrosion of boiler material will afford further practical evidence of the nature and extent of the corrosion in the presence of certain of the variables arising in practice.

By corrosion will be meant the surface deterioration of the metal when exposed to moisture and which would not arise if moisture were not present. This definition excludes the oxidisation of metal due to heat alone or erosion such as may arise when the metal is exposed to mechanical action.

Any acceptable theory of corrosion must be capable of explaining three fundamental facts, namely :---

(1) That iron will not corrode or rust in dry air.

(2) That iron will not rust in moist air provided the conditions of temperature are such that no liquid water can condense on its surface.

(3) That iron will not rust in pure liquid water if air is completely excluded.

Several theories have been advanced in attempts to explain the initiation and process of corrosion, and of these, two have survived the severe criticisms to which they have been subjected. They are the Acid theory and the Electrolytic theory.

It will be desirable, before proceeding to discuss them, to make brief reference to the more important of the physical and chemical aspects, upon a knowledge of which depends an understanding of the theories to be described.

Solution and Osmotic Pressures.

When a soluble material dissolves in water its molecules divide themselves throughout the mass of the liquid, and the force by which this is accomplished is known as the "solution pressure." The reaction to this force and which tends to prevent the solution (or equi-spatial distribution of the molecules of the dissolving body) is called the "osmotic pressure." When the "solution" and "osmotic pressures" balance, the substance exhibits its maximum solubility, and the water will be saturated with respect to that substance and to the physical conditions of temperature and pressure prevalent at that time. Any external factor which, acting on the system, tends to lower the osmotic pressure, will increase the extent of the solubility of the substance, and if the supply of the latter be maintained, the permanent presence of an osmotic pressure reducing influence will result in a continued solution of the substance.

As usually understood, the term solubility would make a sharp distinction between such materials as, for instance, soda and iron; actually the terms solubility and insolubility are relative only, since it is doubtful whether any substance exists upon which water has not some solvent action.

Electrolytic Dissociation.

One of two things may occur when a substance dissolves in water; either the solution becomes a conductor of electricity, *i.e.*, an electrolyte, or it retains its original non-conductive nature. A solution of sugar is illustrative of the latter. Acids, bases, and salts confer the former property on their solutions, and they effect this by splitting up or dissociating into atoms or groups of atoms which carry charges of static electricity. Such electrically charged atoms are known as "ions," and the dissociation whereby they are produced may be simply expressed in the following manner :—

	Hydrochloric Acid	==	Hydrogen Ions	+	Chlorine Ions.
(1)	HCl	=	H+	+	Cl-
1	Calcium Hydrate	-	Calcium Ions	+	Hydrate Ions.
(2)	$Ca(OH)_2$	==	Ca++	+	OH-OH-
	Sodium Sulphate	=	Sodium Ions	+	Sulphate Ions.
(3)	Na ₂ SO ₄	-	Na ⁺ Na ⁺	+	SO4

The nature of the electrical charge carried by an ion is indicated by the sign placed above the symbol and the relative magnitude by the number of these signs. The ions resulting from the solution of a compound are always of two kinds, "cations" carrying positive charges and "anions" carrying negative charges, and in solution the sum of the positive charges is always numerically equal to the sum of the negative charges. All acids in solution are characterised by the hydrogen cation, and all bases by the hydrate or hydroxyl anion. It must be remembered that the properties of an ion do not correspond with those of the uncharged atom; metallic or atomic sodium for example cannot exist in the presence of water, but the charged atom or ion can and does.

There are other ways in which ions may be produced, one of which is by the exchange of the charge from an already existing ion to an atom. The simplest example of this is the solution of zinc in an acid, which proceeds as follows:—

Zinc + Hydrochloric Acid = Zinc ions + chlorine ions + hydrogen.

(4)
$$\operatorname{Zn} + \frac{\mathrm{H}^{+}\mathrm{Cl}^{-}}{\mathrm{H}^{+}\mathrm{Cl}^{-}} = \operatorname{Zn}^{++} + \frac{\mathrm{Cl}^{-}}{\mathrm{Cl}^{-}} + \mathrm{H}_{2}$$
 (gas)

The hydrogen ions resulting from the ionic dissociation of the hydrochloric acid have transferred their charges to the metallic zinc, thereby becoming atomic and as such insoluble. They escape as gas bubbles from the surface of the zinc, the atoms of which, by acquiring charges, have entered solution as zinc cations. It is thus easy to visualise the solution of a relatively insoluble material, such as a metal, which may dissolve directly from the metallic condition, and this type of action should be borne in mind when considering the Acid and Electrolytic theories of corrosion.

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Electrolysis and Polarisation.

It was stated that when the solution of a substance in water resulted in its dissociation into ions, the system became a conductor. If a current is passed through such a solution by means of suitable electrodes a phenomenon known as electrolysis occurs, and it consists primarily in a mechanical movement or migration of the ions. The cations migrate to the negative electrode, or cathode, and the anions to the positive electrode, or anode. They surrender their respective charges to the electrodes and become atomic, and they may then leave the system by escaping as bubbles of gas, as in the case of the electrolysis of hydrochloric acid, or by plating out on the electrode in the metallic form, as for instance when a solution of copper sulphate is electrolysed.

Electrolysis may also take place without the aid of an externally applied current. If two dissimilar metals are partly immersed in the electrolyte, and electrically connected by means of a wire, a current will be generated at the expense of the more electro-positive metal; in other words, of the metal having the higher solution pressure. This metal expels positively charged ions from its surface into the liquid medium and becomes itself negatively charged, so that the dissolving metal appears as the negative pole of the external portion of the circuit. It is not necessary even that the two metals be externally in electrical contact; if they are placed in contact in the solution the same process will continue, the solution in this case taking the place of the wire.

When a metal dissolves in an acid the conversion of the metal to the ionic condition will occur by the exchange of charges between the hydrogen ions and the metal, as shown in equation (4), while in a neutral medium the metallic ions derive their charges from the metal itself, which becomes negatively charged. In an almost neutral medium a combination of these results takes place, and the evolution of the gas is too slow to be visible. Such a condition leads to polarisation. By an almost neutral medium is inferred a solution in which the concentration of hydrogen ions, characteristic of the acid, is relatively low. Polarisation is essentially the plating of the dissolving metal by a film of charged ions. If we consider the academic case of a strip of pure iron in pure water which will be assumed to be dissociated to a small degree into the hydrogen and hydroxyl ions, then the following sequence, analagous to the above, occurs :- By reason of its solution pressure, the iron shoots off from its surface a number of positively charged ferrous ions into the water, thus disturbing the electrical balance between the hydrogen and hydroxyl ions. As a result, the positive ion whose element has the lower solution pressure is displaced, and in this case the hydrogen ions surrender their charges to the iron strip and adhere to it in the form of a gaseous film, thereby restoring the balance between ionic changes. A galvanic current will thus flow from the iron strip via the ferrous ions in solution

and back again viâ the hydrogen ions to the undissolved metal. The gaseous film of hydrogen deposited is, however, a very poor conductor and offers a high resistance to this current, so that before long the circuit is effectively broken. Further solution of the iron is thus prevented by the polarising effect of this gaseous film and will not recommence until the latter is removed, that is, until some depolarising agent is brought into play.

Oxidation.

A further example of the production of ions is the case where the conversion of an atom to an ion is accompanied by the increase of the charge carried by an already existing ion. If chlorine gas is passed through a solution of ferrous chloride a re-action occurs in which the ferrous ion carrying two positive charges is converted into a ferric ion carrying three positive charges, while the chlorine changes from the atomic to the ionic condition.

Ferrous Chloride + Chlorine = Ferric Chloride. (5) $\operatorname{Fe}^{++} \operatorname{Cl}^{-} \operatorname{Cl}^{-} + \operatorname{Cl} = \operatorname{Fe}^{+++} \operatorname{Cl}^{-} \operatorname{Cl}^{-} \operatorname{Cl}^{-}$ (atomic)

The total amount of iron has not been increased; that of the chlorine or negative radicle of the compound has. This type of process is termed, "Oxidation," and it involves :---

(a) the increasing of the proportion of electro negative element of the compound, and

(b) the increasing of the magnitude of the charge carried by the electric positive radicle or iron.

The valency of the element is the number of hydrogen atoms that one atom of it can unite with or replace in a chemical compound. For most practical purposes the charges carried by an ion may be regarded as synonymous with valency; hence a ferrous iron carrying three positive charges is trivalent. The second change involved by oxidation may therefore be regarded alternately as increasing the valency of the electric positive radicle. Processes which result in a decrease in this valency are termed "reduction."

Hydrolysis.

The chemical definition of a salt implies a substance yielding a neutral solution.

It is generally known, however, that salts produced by the combination of a strong base with a weak acid impart basic re-actions to their solutions, while the solutions of salts resulting from the combination of a strong acid with a weak base are *acidic* in character. The solution of common soda in water affords a good illustration :—

Sodium Carbonate + Water = Sodium hydrate + Carbonic Acid. (6) Na₂ Co₃ + H₂O = 2Na HO + H₂CO₃

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The sodium hydrate produced has a very high solution pressure and is therefore very strongly ionised (or completely dissociated into sodium and hydrate ions). The hydrate ions confer a basic reaction to the solution, which the carbonic acid, because of its low degree of dissociation failing to produce a sufficiency of hydrogen ions, cannot neutralise.

The phenomenon whereby the characteristics of the stronger radicle are developed is that of Hydrolysis. It results from the fact that the radicle determining the reaction is more strongly ionised, or in other words, has a higher solution pressure than the other.

THEORY OF CORROSION.

Acid and Basic Theories.

While there is by no means academic agreement as to whether corrosion is initiated by the acid or the electrolytic process, there is general agreement from a practical point of view, that the phenomena of corrosion are with certain exceptions reasonably explained on an electro-chemical basis, and there is fairly complete evidence that the electro-chemical effect is an important factor in many cases of corrosion.

The formulation of the acid theory presumes that pure liquid water and pure oxygen are not alone sufficient to initiate the corrosion of pure iron, but that a third factor is necessary and this is the presence of an acid. It may be a feebly ionised acid like carbonic acid or it may be in the combined form, whence, by hydrolysis, the characteristic attacking hydrogen ion may be produced. In short then, the third factor implies the presence of hydrogen ions.

The electrolytic theory states that an acid as such is not essential in any form but that the solution pressure of pure iron in pure water results in the formation of ferrous ions and in the consequent discharge of an equivalent number of hydrogen ions which are assumed to exist in even the purest water.

Each theory, therefore, explains the initial attack upon the iron as the result of attack of hydrogen ions, and they differ merely in the fact that they presume the presence of these ions to originate from different sources.

Proceeding beyond the point of initiation, the compatability of these two theories is further demonstrated in that they both regard the presence of oxygen as essential to the continuation of the process.

The acid theory, viewing corrosion as a cyclic process in which a minute amount of acid may corrode an infinite quantity of metal, explains the process by the following sequence:— Firstly, the attack by the acid, for example carbonic acid, on the iron results in the production of a ferrous salt, in this case ferrous carbonate :—

(7) 2 Fe + 2 $H_2CO_3 = 2$ Fe $CO_3 + 2$ H_2

Secondly, the ferrous carbonate is acted upon by oxygen in the presence of water and is converted into the insoluble ferric hydroxide which is precipitated from the system. This is accompanied by the simultaneous regeneration of the original quantity of carbonic acid :—

(8) 4 FeCO₃ + O₂ + H₂O = 4 Fe (OH)₃ + 4 H₂CO₃

and the oxidisation of the hydrogen produced in equation (7) to water. The cycle is thus completed and corrosion will continue so long as the supply of oxygen required in equation (8) is maintained.

It will be noted in equation (7) that gaseous hydrogen is set free and this may be regarded as analagous to the liberation of hydrogen by the discharge of hydrogen ions in the following explanation offered by the electrolytic theory :—The first stage in the mechanism of the corrosion of pure iron in pure water and pure oxygen only is the transfer of charges from hydrogen ions to the metal. The latter enters solution and continues to do so until the polarisation, due to the film of gaseous hydrogen deposited on the metal surface, is sufficient to arrest the process. This stage may be represented by :—

(9)
$$\operatorname{Fe} + \frac{\mathrm{H}^{+}}{\mathrm{H}^{+}} \frac{\mathrm{OH}^{-}}{\mathrm{OH}^{-}} = \operatorname{Fe}^{++} \frac{\mathrm{OH}^{-}}{\mathrm{OH}^{-}} + \mathrm{H}_{2}$$
 (gas).

The liquid medium at this point is virtually a solution of ferrous hydroxide, Fe $(OH)_2$, and the second stage consists in the oxidisation and precipitation of the ferric hydroxide or rust :—

(10) 4 Fe $(OH)_2 + O_2 + H_2O = 4$ Fe $(OH)_3$.

This precipitation of ferric hydroxide disturbs the equilibrium of the system and in conjunction with the second effect of oxygen, which by combining with and removing the polarising film of hydrogen, depolarises the metal surface, results in the continued solution or corrosion of the metal.

On the basis of either theory, therefore, a continual supply of oxygen is necessary for the corrosion to proceed sensibly beyond its inception.

It will be of interest in connection with boiler work to include here a conclusion by Paul, which may be regarded as an amplification of the acid theory. As a result of his investigations he states that in the presence of an excess of carbonic acid, free or atmospheric oxygen is not essential to corrosion. For the corrosion to proceed by the complicated process described by him, which embraces organic reactions, it is necessary that the supply of carbonic acid should be maintained and its action is therefore not to be compared with the catalytic-like action of a trace of carbonic acid as explained by the Acid theory proper. There appears, however, little doubt that, when an excess of carbonic acid acts upon iron, organic compounds are produced, and it seems possible that the formation of these compounds may be accompanied by an evolution of oxygen. So the phenomenon noted by Paul may be the result of a combination of the two processes.

The Colloid Theory.

The electro-chemical theory is not applicable to the interpretation of all the phenomena connected with the various processes by which corrosion may occur or by which it may be accelerated or retarded. A consideration of these cases supported by experimental evidence has led Friend* to suggest a new theory which appears likely to stand as the essential mechanism of corrosion in the case of iron, although it is somewhat restricted in the case of some other metals. This theory does not repudiate the fundamental principles of the electro-chemical conceptions, but, by the application of a new hypothesis to certain stages of the corrosion of iron, permits a more comprehensive and satisfying explanation.

The following brief outline of some colloidal properties will assist an understanding of this theory :---

The modern application of the word "colloid" infers a particular physical condition and not, as originally, a definite class of materials. Thus, a colloidal solution is now understood to indicate, not necessarily a solution of gelatine or glue, as was the case at one time (colloid is the Greek word meaning glue) but any solution which possesses specific properties comparable with those of a gelatine solution. A solution of a colloid differs in many respects from that of a crystalloid or true solution : the osmotic pressure of the system is extremely small in comparison with the quantity of substance which may be present, and the colloid has little, if any, influence as regards depressing the freezing point or elevating the boiling point of the liquid medium. There exists very strong evidence that colloidal solutions, particularly those in which we are interested in this connection, are really suspensions in the liquid of extremely minute solid particles. The size of the particles we may here regard as intermediate between those in a mechanical suspension and those in a true or crystalloid solution, which latter are of course, of molecular dimensions. The fluid in which the colloid is suspended is known as the "dispersion" medium, and the colloid as the "dispersoid." The solution is called a "sol" and, when the fluid is water, a "hydrosol."

The two properties of colloids which have the most significance in regard to Friend's theory, are their behaviour in an electrical field and their precipitation from suspension by certain agents.

If a current is passed through a colloidal solution by means of two electrodes, a migration of the dispersoid occurs which may be looked upon as analagous to that of the ions in a true solution. In this case, however, the mechanical movement is in one direction only; either to the cathode or the anode, depending on the nature of the colloid. There is good reason

^{* &}quot;The Corrosion of Iron," Carnegie Scholarship Memoirs, Vol. XI, 1922.

to justify the assumption that the particles of a substance when in colloidal solution carry electrical charges, those colloids which migrate to the cathode carrying positive charges. Ferric hydroxide is one of the latter and is therefore considered to be an electro positive colloid.

Colloids may be precipitated from their solutions by the addition of compounds which undergo ionic dissociation in the dispersion medium, *i.e.*, acids and salts, and from their behaviour in the presence of such compounds it is possible to divide them into two groups, viz. :—" suspension " colloids and " emulsoid " colloids. The first group is the one with which we are particularly concerned here: they give non-viscous solutions and are precipitated by small quantities of electrolytes as compared with contrary properties in the case of the second group.

The precipitation by very small quantities of the electrolytes seems to occur by a neutralisation of the charges carried by the colloidal particles by those ions of the dissociated electrolyte having the opposite sign. Thus an electro-positive colloid will be precipitated by the electro-negative ion of a salt in solution, that is by the acid radicle (*vide* equation 3); on the other hand an electro-negative colloid will be precipitated by an electropositive ion. Further, colloids whose charges are presumably of opposite sign precipitate each other.

The concentration of electrolyte necessary to precipitate a colloid, small though it may be, has a minimum value, below which precipitation is not effected. This minimum value has been found to be of the same order for all electrolytes in which the precipitating radicles have the same valency. and the higher the valency the lower is its value.

Friend's colloid theory appears to have resulted from an examination of two apparent anomalies. When iron corrodes in moving water the rate of corrosion is influenced in an unexpected manner by the rate of flow. As the rate of flow is increased the corrosion is at first rapidly increased until it reaches a maximum. After this, however, further increase in the speed of flow is attended by a decrease in the rate of corrosion until, at and above a speed of flow of 3 to 4 feet per second, it appears to be almost entirely arrested, in so far as no visible sign of the corrosive action remains. In the case of similar experiments in an acid solution, the rate of corrosion was directly proportional to the speed of flow even at exceptionally high Also it was found that at a given velocity the rate velocities. of corrosion was almost constant, no matter what the concentration of the acid might be.

These contradictory observations are difficult if not impossible to reconcile by the theory of corrosion as hitherto described. Friend has, however, recently offered the following suggestions :---

(1) In contact with water and air, the iron is slowly oxidised to ferrous hydroxide which is produced in the colloidal condition, a condition in which it is usual for many substances to be particularly reactive chemically.

(2) This colloidal ferrous hydroxide is then oxidised by the presence of excess air to ferric hydroxide which is also produced in the colloidal form.

(3) The colloidal ferric hydroxide then acts as a catalyst and accelerates the oxidisation of more iron by itself undergoing reduction to the colloidal ferrous hydrate or hydroxide, but is immediately re-oxidised as in (2).

(4) The product of corrosion, rust, is ferric hydroxide precipitated out of solution.

Corrosion of iron in water would proceed by this theory in two ways, one being a simple process of solution and the other a catalytic process, the catalyst being a product of the corrosion of the iron. In water or neutral media, the catalytic process will predominate and the rate of formation of the catalyst colloid will largely determine the rate of corrosion. In an acid medium the process of simple solution will predominate.

The explanation of the different behaviours of iron in neutral and acid media is now clear. Rapid motion of a neutral medium will remove the catalysing colloid from the iron surface as rapidly as it is formed and consequently the corrosion is retarded. Rapid movement of an acid medium will, on the other hand, accelerate the rate of solution by increasing the number of hydrogen ions which are brought into contact with the iron in a given time.

Thus, on the basis of this theory, any agent, whether chemical, physical, or mechanical, which will destroy or remove electropositive colloids such as ferric hydroxide will tend to retard corrosion.

The second anomaly to which Friend applied his new theory is the influence of salt solutions of varying concentrations on corrosion. As a general rule the presence of a dissolved salt increases the rate of corrosion and the acceleration increases with increase in the concentration of the salt until a maximum rate is reached. Further increase in the concentration of the salt brings about a reduction in the corrosion rate.

The colloid theory offers a rational explanation of this anomaly, but it will be more convenient to defer dealing with this matter until a later stage.

Further support for the theory is derived from certain experiments on painted surfaces by reference to a consideration of the mutual action of the two types of colloids when present together.

The suspension colloids are in an unstable condition, which accounts for their great catalytic activity, while the emulsoid colloids are rather stable. When any of the latter are present they reduce the catalytic activity of the suspension colloids, and also tend to prevent their precipitation. Thus these emulsoid colloids are also called protective colloids, because they prevent the suspension colloids from precipitating and tend to stabilise them. Small amounts of protective colloids confer their own properties on other colloids due, as is generally believed, to the forming of a protective layer around them.

The foregoing provides an explanation of certain experiments of Friend in which he found that iron immersed in water for several months corrodes more seriously if protected by a thick layer of paint than with a thin one. The various paint mixtures used consisted of pure boiled oil with different amounts of deep Indian Red pigment (essentially iron oxide) ranging from 30 per cent. to 80 per cent. of pigment.

Paint is essentially colloidal in structure and the linoxyn or oxidized coat of linseed oil behaves as a protective colloid and thus *retards* the catalytic activity of the ferric hydroxide sols, reducing the rate of corrosion. But, as it is stated, a very thin film of the oil suffices to do that, and further thicknesses merely increase the quantity of protected colloid hydrosol and thus, by pure mass action, increase the rate of corrosion.

It should, perhaps, be pointed out here, that linseed oil films are appreciably porous and moisture and atmospheric gases can penetrate them to the underlying metal surface.

The property of the emulsoid colloid in surrounding and retarding the action of the suspension colloid also appears to explain the peculiar property of stainless steel cutlery in resisting the action of fruit juices, etc. As is generally known, stainless steel acquires its resistant properties to corrosion from the presence of some 11 per cent. to 14 per cent. of chromium. Stainless steels, made by suitably proportioning the constituents and proper heat treatment, will resist the action of vinegar, containing about 4 per cent. to 5 per cent. of acetic acid. A pure solution of acetic acid of the same strength, however, attacks the steel quite distinctly. The steel is similarly resistant to vinegar in the case of fruit juices. Citric acid, however, behaves in the same way as acetic acid; thus lemon juice does not attack stainless steel while pure citric acid of the same strength exerts a distinct though slow corrosive action.

The fact that vinegar and lemon juice have a much less pronounced corrosive action than pure solutions of acetic and citric acid of the same strengths may be explained by the presence in the natural products of organic colloids (emulsoids), the retarding effect of which has been dealt with above.

Another anomaly explained by the colloid theory is the curious effect of the rise of temperature upon the relative corrosive properties of distilled water and sea water on iron. Sea water is more corrosive than distilled water at ordinary temperatures, but as the temperature is increased, the difference between the effect of sea water and distilled water does not become nearly so marked. This anomaly cannot be explained on the basis of oxygen solubility. The colloidal theory, however, affords the following explanation. Ferrous hydroxide sols are sufficiently stable to withstand precipitation upon boiling of the liquid under favourable conditions. But the addition of small quantities of electrolytes readily causes their precipitation upon rise of temperature. While, therefore, the normal tendency of sea water would be to increase corrosion with rise of temperature, this tendency is in part counteracted by the retarding action due to the increased precipitation of the catalytic sol. The result is that, relatively to distilled water at similar temperature, the rate of corrosion falls.

Yet another property of colloids is their precipitation by dehydration of the sol in which the absorbed water is driven out. Thus ferric hydroxide hydrosol may be precipitated by alcohol, due to dehydration.

Iron will not corrode in pure ethyl alcohol and alcohol does not ionise in water—in other words, it is not an electrolyte. Consequently, it would not be expected that the corrosion of a piece of iron would be influenced in any chemical way by the addition of alcohol. Some effect might be expected from any variation in the oxygen content attending the presence of alcohol in the water, and it might be supposed that the corrosion effect would follow the oxygen content.

Experiment, however, shows that there is not the slightest relation between the rate of corrosion and the oxygen solubility variation due to variation in the alcohol content, and that the presence of alcohol reduces corrosion to a much greater extent than the lower oxygen content alone would do. This is explained on the basis of the colloidal theory by the fact that alcohol tends to precipitate the ferric hydroxide hydrosols due to dehydration.

Other theories no longer tenable may be briefly referred to.

The peroxide theory concluded that water and oxygen alone were necessary for corrosion to commence and proceed. An intermediate product, hydrogen peroxide, was supposed to be produced during the formation of rust and to accelerate corrosion by oxidising and precipitating the ferrous hydroxide first produced and also by itself attracting the metallic iron.

The oxide theory regarded the process as one of simple oxidisation, similar to that which results if iron is heated to a sufficiently high temperature in dry air, but by occurring in an aqueous medium the products of the oxidisation were hydrated. It is probably the oldest and original theory and was at once discarded when the fact that liquid water was necessary was discovered. It however, paved the way for the acid theory.

Biologists have drawn attention to organisms which decompose ferrous salts, both mineral and organic, and cause the precipitation of rust. It is not surprising therefore, that a theory should have been brought forward suggesting that such organisms may be a direct cause of corrosion. There are no grounds whatever, for such a theory.

It is interesting, however, to note that recent bio-chemical investigations have shown that sea water frequently contains in solution much more than its due proportion of oxygen. The surplus over the equilibrium limit in experiments carried out in the Thames estuary was found to vary with the time of the year, and in the summer months was found to be more than 60 per cent. more than sea water in equilibrium with the air would retain under similar conditions of temperature and pressure.

The presence of this excess oxygen is due to the dissociation of the CO_2 taken up from the carbonates in sea water by the chlorophyllous organisms present in the sea, and it is said that, by the absorption in this very gradual way, the sea water may actually attain a concentration as much as five times the amount of dissolved oxygen that it would ordinarily absorb.

This high concentration may, in fact be attained, given favourable conditions as regards temperature and sunlight (both accelerate the growth of the organism) and the necessary abundance of the organisms. The effect of combination with oxidisable matter and the escape into the air at the free surface, following the upward diffusion in solution, however, is to reduce the quantity of oxygen present. Moreover, the solution is necessarily highly unstable and any agitation of the water or increase of temperature would lead to the release of much of the excess.

This phenomenon may possibly have a considerable bearing on the corrosive action of natural sea water, and account for anomalies met with in comparing results obtained under laboratory and service conditions respectively.

FORMS OF CORROSION.

If the Ionic or Electro Chemical theory of corrosion be accepted, it is easy to divide up most of the cases of corrosion met with in practice, into three types :---

- (1) Auto corrosion.
- (2) Contact corrosion.
- (3) Externally induced corrosion.

Dealing first with the last named, this type is due to the passage of a current generated from some external source, through the metal, while the latter is in connection with an electrolyte. If the current flows in that direction which necessitates the metal acting as an anode, then corrosion results. This type is not so common as the other cases, but it may arise in various items of ship's equipment from the presence of stray currents and leakages.

The most commonly occurring types, however, are Auto and Contact Corrosion. Auto Corrosion is that which occurs when a

metal is in contact with an electrolyte, but is not at the same time in contact with any other electrical conductor, either metallic or non-metallic. In the academic case of pure iron, corrosion would proceed simply by the exertion of the solution pressure of the metal in conjunction with the presence of hydrogen ions and the oxygen dissolved in the electrolyte which both depolarises the metal surface and oxidises and precipitates the primary products of solution as ferric hydrate or rust. In practical cases, auto corrosion proceeds by the galvanic action which is set up as a result of heterogeneous structure of the metal or No commercial metal exists in which there is perfect alloy. homogeneity: there is always some characteristic of structure, some slight degree of segregation or the presence of embedded impurities which is sufficient to impart varying potentials or solution pressures to adjacent areas of the metal surface. For this reason auto electrolysis is set up by which the more electropositive areas dissolve and, in the case of ferrous material, are eventually precipitated as rust.

Contact corrosion occurs when the metal is in contact with some other conducting material which is also immersed wholly or partly in the electrolyte. If this other conductor is a metal, then the corrosion of the first metal will be either accelerated or retarded, according to whether it is or is not electro-positive to the other conductor. Other conditions being the same the rate of contact corrosion of a metal is usually greater than its rate of auto corrosion. If the second conductor is non-metallic in character (e.g., iron oxide, iron carbide, etc.) it may generally be assumed to be electro-negative to the metal and contact between them will result in accelerated corrosion of the metal.

In both types, auto and contact corrosion, galvanic action is the primary cause of corrosion and each process is one of electrolysis.

The local action entailed by non-homogeneity or non-metallic inclusions usually causes pitting. Considering, for example, the corrosion of a bar which is quite uniform, both chemically and physically, except for a small spot which will be assumed to be electro-positive to the bar as a whole. As corrosion of the bar proceeds, the material at this spot will be preferentially dissolved, since it has a higher potential than the rest of the metal. ferrous ions resulting from the solution here will exist as colloidal ferrous hydroxide and, as positive colloids, will migrate to the negative pole of the galvanic circuit of metal surrounding the spot. In the presence of oxygen, they will be here precipitated as ferric hydroxide and as corrosion proceeds, a wall of this material will be built up around the electro-positive area. This wall may continue to grow inward until a dome or cone is formed in the familar form. A similar process goes on if a particle of an electro-negative body occupies the spot, and in this case the surrounding metal is dissolved and the ferric hydroxide deposited in the centre.

If the products of corrosion are regularly removed the action will ultimately cease when sufficient of the irregular material has been removed and the equality in potential thereby restored.

It is to be specially noted that rust particles are electronegative to iron and their transportation by moving water from any particular corrosion spot to hitherto unattacked iron surface may consequently initiate pitting.

From what has been said, there will be no difficulty in differentiating between galvanic and electric action, since the latter always implies an externally generated current. The actions are alike in principle, but their results differ greatly in degree and character. Electrical action usually tends to induce a more or less uniform corrosion over the entire surface of the metal which comes within its sphere of influence, but galvanic action, by reason of the low E.M.F. of the local currents which are generated and also because of the fact that it may result from the potential differences between adjacent areas (as in auto corrosion) on the same surface, more frequently results in a selective or preferential corrosion of certain portions of the metal.

Tables are usually given in the text books showing the positions of the various metals arranged in order of their solution pressures or electric potentials. For the large majority of cases, this may be accepted, but it must be remembered that the relation between the solution pressures of two metals may be influenced by other factors such as the concentration, composition and temperature of the electrolyte. It does not follow that because under one set of conditions a metal exhibits a higher solution pressure than a second, this will always be the case. The relationship may be reversed, so that the metal which was originally electro-positive is now electro-negative or the magnitude of the difference between the solution pressures may be increased or reduced.

This offers some explanation for many curious anomalies, which contact with corrosion troubles is sure to present sooner or later.

Beside the effects mentioned of segregation, impurities, etc., in promoting galvanic action, it is known that physical heterogeneity has a like effect. This can be proved experimentally by taking two samples from the same bar and straining one piece in some way or other. If the two pieces be placed in an electrolyte and connected externally by a wire through a galvanometer, a current will be seen to flow, thus demonstrating that the two pieces of metal originally alike now have different solution pressures, although of very small magnitude. There is no general rule by which it may be predicted whether the strained metal will be electro-positive or electro-negative to the unstrained metal, but in practical work it would appear that in general, the strained metal is the more electro-positive, as will be recalled by a consideration of the internal corrosion of boilers. This difference in physical condition may lead to pitting or grooving by the process already described for material lacking in homogeneity and in the case of grooving the effects may become serious.

A particularly ingenious and convincing method of demonstrating the galvanic mechanism of auto corrosion is that perfected by Cushman and Walker (J. Iron and Steel Institute, 1909).

EFFECT OF OXYGEN.

For all practical purposes the action of pure water alone on iron may be regarded as nil, for even though the metal be soluble in it to a slight extent the water would soon be saturated with ferrous ions, and in the absence of air or oxygen the state of equilibrium would not be disturbed. The same argument holds equally good in the case of natural water containing dissolved atmospheric gases. The oxygen present can only combine with a limited quantity of iron, and once it has done this equilibrium will obtain. It is clear, therefore, that for corrosion to proceed a continual supply of oxygen is necessary, and it follows also, that the rate at which the gas can replace that which has already entered into chemical action with the iron will determine the rate at which the metal corrodes.

In short, with pure water, oxygen may be regarded as the prime factor in corrosion.

The gas is also equally essential in cases where iron corrodes in slightly acid electrolytes. Under these conditions the metal goes into solution as a ferrous salt, and the acidity will soon be neutralised. The action of the oxygen is to decompose these ferrous salts, thereby precipitating ferric hydroxide or rust and liberating the acid, which can now proceed to attack more iron.

INFLUENCE OF IMPURITIES, ETC., IN THE WATER.

Since the corrosion of iron is due primarily to attack by hydrogen ions, it may be anticipated that acid media will have a pronounced stimulative action on corrosion, and conversely that alkaline media will inhibit or arrest corrosion. The influence of saline media is not so readily predicted, though they might be expected to accelerate corrosion, if only because their presence is conducive to ionic activity.

As a general rule each of these anticipations is verified in practice; electrolytes which give acid solutions accelerate corrosion, and those which give alkaline solutions (*i.e.*, produce hydroxyl ions) inhibit corrosion, and may, *if the concentration of* hydroxyl ions be high enough, entirely prevent corrosion. Exceptions to these generalities are numerous however, and result in anomalies whose consideration is of particular importance.

The action of acid solutions on iron is invariably a solvent one. The first products of acid attack are a ferrous salt and gaseous hydrogen. In most cases, the latter escapes as a gas, but if the acid be also what is termed an oxidising agent—for instance nitric acid—the hydrogen may be oxidised to form water as quickly as it is evolved. This oxidisation of the hydrogen evolved in the case of non-oxidising acids, such as hydrochloric acid, is dependent upon the presence of oxygen, and the nature of the final product is here determined by the quantity of acid present relative to the amount of metal. If the acid is in excess, the soluble ferric chloride will result, but if on the other hand the quantity of acid is small, then the action of oxygen will be to precipitate the ferric chloride as rust and to liberate the free acid.

The action of carbonic acid on iron is analogous to that of hydrochloric acid in dilute solution; the ferric carbonate first produced is precipitated as rust in the presence of oxygen. Carbonic acid is seldom if ever absent in the case of water, and although it is generally considered a weak acid, its effect may be very considerable, and where the supply of oxygen is not restricted, corrosion can proceed at a very rapid rate.

Chromic acid, like nitric acid, is also an oxidiser, but its behaviour towards corrosion processes offers a striking contrast to that of other acids. It does not stimulate corrosion, but inhibits the process, and the same property is exhibited by its salts, the chromates and bichromates.

Iron will not corrode in alkaline media unless the concentration of alkali be very low. The influence of alkalies is inhibitive, and corrosion may be entirely prevented by suitable concentrations. Several explanations have been advanced to account for this. According to the acid theory of corrosion, the inhibitive action is due to their absorption and consequent fixation of carbonic dioxide. This is of course indisputable, and is no doubt one of the factors which adds to the nett inhibitive effect.

The electro-chemical explanation is more comprehensive; it points out that hydrogen ions and hydroxyl ions cannot exist in the same solution at the same time if the latter are in excess, nor can hydrogen ions be found in such a solution. Corrosion cannot, therefore, proceed on iron immersed in it. If the concentration of hydroxyl ions is not sufficiently in excess, then potential differences may segregate the hydrogen ions from the hydroxyl ions, and corrosion can occur locally. This offers some explanation why very dilute solutions of alkalies do not prevent corrosion, and also why the corrosion which occurs under such conditions frequently takes the form of pitting.

The precipitating action of the electro-negative hydroxyl ion on the catalysing and electro-positive ferric hydroxide, referred to under the colloid theory, however, offers the most satisfactory explanation. The precipitation of a positive colloid requires a definite minimum concentration of an electro-negative ion. Hence, until the concentration of the alkali is sufficient to give this minimum, no precipitation occurs and corrosion proceeds. For this reason, very dilute alkaline solutions do not prevent corrosion, but have actually a stimulative effect.

Friend has also put forward on the above lines a rational explanation of the influence of neutral salts on corrosion, a matter which has hitherto been incompletely understood.

The action of salts in chiefly dependent on their concentration. If this is sufficiently high, then corrosion may be retarded or even completely arrested, while low concentrations almost invariably cause an increase in the rate of corrosion as compared with that obtaining in pure water. This behaviour of neutral salts has been recognised for some time, and their inhibiting influence was considered to be due to the decreasing solubility of oxygen, which occurs in saline solutions as the concentration of the salt increases. The preliminary increase in the corrosion rate was not understood. It has been shown, however, that excepting for sodium chloride (on which presumably the general conclusion was based many years ago) the reduction in the rate of corrosion is not proportional to the reduction in the solubility of oxygen in the salt solution, being in fact much more rapid. Thus the rate of corrosion may be reduced to a value approaching nil by a salt concentration which reduces the oxygen solubility by only 40 to 50 per cent. of that in pure water.

The values of the limiting concentrations at which corrosion ceases have been shown to decrease with increase in the valency of their electro-negative ions, so that whereas comparatively high concentrations of monovalent ions are necessary to prevent corrosion, relatively low concentrations of divalent ions suffice.

Friend explains the foregoing behaviour of different salts and of different concentrations of the same salt as follows :---Until the critical concentration is reached, corrosion is stimulated in a manner similar to that already described for alkalies. When the concentration corresponding to maximum corrosion is reached, the precipitating action of the electro-negative radicles of the salt comes into play and a retardisation of corrosion results, the effect increasing with the concentration of the salt.

The differences exhibited by various salts whose precipitating ions differ in valency are shown by Friend to be in agreement with the figures given by Linder and Picton, who investigated the relative precipitating powers of various negative ions, and found them to have the following ratio :—

Chromates	and]	Bichron	nates	-	-	-	1,000
Sulphates	-	-	-	-	-	-	670
Chlorides a	and N	itrates	-	-	-	-	3

He points out that, by considering the problem in this way, it is easily understood why very small concentrations of chromates have such extraordinary inhibitive powers and why the concentrations of common salt and other chlorides, etc., necessary to produce an appreciable retardation of corrosion are relatively so high.

When two or more salts are present at the same time, the problem becomes still further involved. There may be, for instance, one salt whose concentration is below the critical point and another whose action is inhibitive. Interaction may take place between the salts and result in one case in the production of an acid solution and in another case in the production of an alkaline solution. For example, when potassium bichromate and common salt are present together, a condition of equilibrium is established in which hydrochloric acid is produced. Two contending factors thus result, the stimulating acid and the inhibiting chromates, and since the removal of the acid by its attack on the iron would lead to a continuation of its production, it would seem that a nett stimulative effect might occur.

The effect of increasing temperature reduces the value of the critical concentration and tends, therefore, to reduce the rate of corrosion from the foregoing cause.

The behaviour of magnesium salts is of particular interest for This, of the soluble salts, has the worst reputation boiler work. from the corrosion point of view. It is a constituent of sea water and may, therefore, enter the boiler if impure feed is used. Even if it enters in very small quantities its concentration is constantly increasing. Carbonate of lime, which is usually present, tends to hold the corrosive properties of the magnesium in check all the while it is in solution, but as it is ultimately deposited as sludge, this safeguard fails. Under boiler conditions, the magnesium chloride is dissociated in contact with the plates and tubes into its constituents, the nett result being the production of hydrochloric acid and magnesium hydroxide. The hydrochloric acid liberated in contact with the iron immediately attacks the latter to produce ferric chloride, which is then acted on by the magnesium hydroxide to yield ferrous oxide and to regenerate the original quantity of magnesium chloride. A corrosive cycle is thus established. The action, in common with many chemical processes, probably increases with the temperature and requires a certain temperature to initiate it.

Corrosion can occur in this way without the help of any free dissolved oxygen, so that the presence of black ferrous oxide in boiler tubes does not necessarily imply that overheating has occurred, as is sometimes supposed. If present, however, oxygen will complete the oxidation of the metal commenced by the corrosive salt, by oxidising the black ferrous oxide to ferric oxide or rust. In doing this it will undoubtedly have an accelerating effect on the rate of corrosion.

Calcium chloride behaves in a similar manner. It may be formed in a boiler if the water contains calcium carbonate and magnesium chloride. Other salts which may possibly be met with in various branches of boiler practice and which have corrosive effects are magnesium sulphate, the nitrates of lime and magnesium, the sulphates of iron, aluminium and manganese and all ammonium salts. Sodium salts are generally considered innocuous, but the chloride may be considered potentially corrosive when salts of magnesia are present, *e.g.*, magnesium sulphate would be converted to magnesium chloride. Sodium carbonate, if present in quantity in boilers, causes the corrosion of the non-ferrous boiler fittings, and, incidentally, induces priming. The direct action of pure oils on iron may be regarded as nil. but as is generally known, the free organic acid produced under the temperature conditions obtaining in boilers by the hydrolysis of animal and vegetable oil, can attack iron in a similar manner to carbonic acid, the action being cyclic and regenerative. It is probably not so generally known, however, that hydrocarbon or mineral oils, which consist simply of hydrogen and carbon, can develop acidity, although by a different process from that which results in acidity in fatty oils. This process is one of oxidation resulting from prolonged exposure at high temperature to the air. The acid products so produced can attack iron and copper.

INFLUENCE OF THE COMPOSITION AND STRUCTURE OF THE METAL.

Composition.

That variations in the composition have appreciable influence on the rate at which corrosion proceeds has long been recognised. It is here proposed only to give the influences of the principal constituents always present in ordinary steels used industrially.

The effect of carbon on the rate of corrosion will be determined by its quantity and condition. Carbon may be present in iron in several forms. As graphite, which may occur as clearly defined flakes of appreciable size or in a very finely divided condition. In these cases the carbon is free or uncombined. Combined, or carbide carbon, occurs as pearlite, troosite, martensite, etc.

Each variety has its influence on the corrodibility of the metal, but the information available is scanty, and to some extent contradictory. It is to be pointed out that the influence of carbon is considerably modified by the treatment accorded to the metal, e.g., heat treatment and tempering, etc. It would seem that the corrodibility of annealed steel increases with the carbon content up to about 0.89 per cent. and then decreases. In quenched and tempered steels, however, no variation in the corrodibility has been noticed up to 0.96 per cent. of carbon.

Free carbon in the form of graphitic flakes may readily be conceived to accelerate corrosion by providing points of lower potential than the metal and thereby stimulating galvanic action. It appears that white cast-iron, which contains its carbon in a finely divided condition and is close grained is much less susceptible of attack in acid media than are those irons in which the carbon is in the graphite form.

Graphitisation is a form of corrosion peculiar to cast-iron and as a result of which the corroding metal becomes covered with a layer of graphite, which preserves the appearance and shape of the original metal. The mass is soft enough to be cut with a knife, and the metal being oxidised to ferrous oxide, fills the interspaces of the residual mass of graphite. This form of corrosion is typical of that occurring on cast-iron condenser doors, for example, but is not confined to sea-water, being also noted on cast-iron pipe-lines and sometimes on cast-iron economiser tubes, etc., and cast-iron circulating pump casings dealing with fresh water.

This type of corrosion does not occur with the purer forms of iron, and under parallel conditions steel or wrought iron would usually suffer alternatively from pitting.

Silicon in amounts exceeding 3.0 per cent. has a marked effect in increasing the resistivity of the iron or steel containing it, mainly against acid attack. The presence of silicon in quantities sufficient to have any reasonably inhibitive influence renders, however, the metal brittle and difficult to work, and so restricts its scope for practical work.

It is generally agreed that sulphur has a stimulating influence on corrosion processes, and that this effect is directly proportional to the amount of sulphur present. In good quality steel any sulphur is contained as manganese sulphide and if this compound is uniformly distributed, its influence becomes considerably modified. Inferior steels may be deficient in manganese and in these the excess sulphur is combined with iron as ferrous sulphide. It is difficult to avoid the segregation of these sulphides during the manufacture of the steel and the heterogeneity so produced is an aid to galvanic action. Further, once corrosion has commenced, the sulphur becomes oxidised to sulphuric acid, which of course greatly accelerates the subsequent corrosion. The corrosion on materials in which the sulphides are segregated frequently takes the form of pitting. In the case of sulphur then the influence on corrosion is two-fold, but most significance attaches to the fact that one of the products of the corrosion is itself a particularly active initiator and accelerator of corrosion.

The phosphorus content of steel affects the mechanical properties to so great an extent that the permissible or specified amount is low. Its effect on corrosion would appear to be beneficial rather than otherwise, and the greater amount of phosphorous present in common iron has been considered to be responsible for the somewhat increased resistivity of this class of material in comparison with the more refined grades of iron and steel.

Manganese has had a bad reputation as regards corrosion, but it is now generally considered that this is due to the product which it forms with sulphur rather than the manganese itself, whose influence is negligible.

Surface Impurities.

Millscale is probably the most important of this group of stimulative factors. It might be expected that millscale, owing to its lower degree of oxidisation and consequent less pronounced electro-negativeness towards iron, would be a less powerful stimulative than rust. There is, however, abundant evidence to prove that this is not the case, and that millscale is a particularly powerful accelerator. This may be explained from a consideration of the physical characteristics of the two substances. Rust is usually an open and porous structure and is comparatively loosely attached. On the other hand, millscale is extremely hard and dense and adheres strongly to the metal. It is moreover an excellent conductor of electricity in comparison with rust.

A perfectly continuous coating of millscale acts as a good protective coating, but if its continuity is broken, as is almost invariably the case in manufactured material, then it promotes electrolytic action and gives rise to rapid corrosion. Pitting and grooving are very frequently attributed to millscale. The necessity for its removal in all classes of work is now generally appreciated.

Other impurities, such as cinder and slag inclusions, whose occurrence in commercial products is not uncommon, have a similar influence to millscale in stimulating galvanic action. Also, during the process of rolling, particles of scale and other impurities become embedded in the metal surface, and the corrosion of such material sometimes occurs in parallel lines as a result.

Structural Heterogeneity.

The influence of segregation has already been mentioned in connection with the sulphur content. The process of corrosion is initially one of solution and is dependent on electrolytic conditions which are established on the surface of the metal. If the metal is perfectly homogeneous and free from impurities, there can be no segregation and the formation of electrolytic couples on its surface cannot result from such a cause. Iron must go into solution before it can be converted into rust, and in so doing a current must necessarily flow from the point at which the iron is dissolving to some other point on the metal surface. Any influence which facilitates the flow of this current will accelerate corrosion and segregation, therefore, by providing points of lower potential, tends to induce an increased rate of solubility.

It is interesting to note in connection with the effect of homogeneity and purity that a highly polished iron or steel surface, especially the latter, offers remarkable resistance to corrosion as compared with an ordinary smooth surface, and particularly with a rough or cast surface. It is supposed that the effect of polishing is to spread a film of pure iron over the surface, covering the impurities and segregations, and thereby imparting an enhanced resistivity to the metal. Another explanation is that polishing removes the greater portion of surface impurities and consolidates the surface, rendering it less porous. Still another explanation, which anticipates the conclusions reached in the next section, is that it removes the distorted skin due to machining operations.

In any case, whatever may be the true explanation, an attendant retarding factor would accrue from the fact that the surface does not retain water to the same extent or in the same way as a rough surface.

The lowered rate of corrosion, however, applies almost wholly to the rate of initiation. Once the corrosion has established a hold on the metal surface, the effect of polishing ceases to operate.

Physical Heterogeneity—Localised Strains.

The fact that the strained portion exhibits a different potential to the remainder has already been mentioned. Localised internal strains may be produced in the metal in several ways—during the processes of manufacture, or by conditions to which it is exposed on service. The strains due to manufacturing conditions may of course be removed by careful annealing, but local variations in strain cannot be eliminated on service.

Modern methods of cold working greatly accelerate the corrodibility of the metal. The immediate vicinity of a punched hole in a steel plate, for instance, is usually the point at which corrosion commences. The grooving of sharp bends on plates and pipes and the pitting of rivet heads and tube ends which occurs in boilers are again due to the same cause.

Cold working a metal or working it at temperatures below which re-crystallisation cannot proceed, results in the production of a film of amorphous material between the crystal grains and this material is electro-positive to the crystallised portion. The first stages of the corrosion of such material is, therefore, sometimes more pronounced along certain more or less well-defined lines as the metal, in addition to being strained, has also been given a heterogeneous structure.

Stainless steel is no exception to this, and when severely distorted it rusts comparatively readily: for example, a coil of severely cold drawn wire will rust into a solid mass if left exposed to the atmosphere for a few months.

It is well known that surface wounds on a metal, such as indentations, scratches, abrasions, etc., and also fractured surfaces, become centres of corrosion. This is readily understood in the light of the foregoing remarks, since the metal must have been locally strained when the wounds were inflicted. Such defects exhibit an electro-positive character to the adjacent metal and it would appear to be the rule that strained portions of a metal always assume this character.

Influence of Heat Treatment.

This aspect has naturally received considerable attention in the case of stainless steel and iron, to which the following remarks particularly apply.

Whatever theory be held as to the cause of corrosion of iron, there can, as already mentioned, be no doubt that commercially pure iron is soluble in water of ordinary purity. By the presence of sufficient chromium in solid solution in the iron, this solubility is reduced to an infinitesimally small amount.

It has also been mentioned that heterogeneity in a metal tends to increase corrosion owing to galvanic effects. This is particularly evident in the case of steels; the carbide present is electro-negative to the iron and, other things being equal, steel will corrode faster than pure iron, as is generally known. The same effect is obtained in stainless steels. With any given stainless steel, the greatest resistance to corrosion is obtained after quenching in such a manner as to give a homogeneous martensite (that is a condition in which the carbide is in solid solution), while the least resistant form is obtained on annealing the steel so as to produce a complete separation of carbide and ferrite. The separation of the carbide not only tends to decrease the resistance to corrosion owing to galvanic effects, but in addition it lowers the concentration of the chromium in solution in the iron (since the carbide which separates out contains a certain amount of chromium) and hence the ground mass of iron is not so insoluble as when it contained the whole of the chromium in solution.

The ordinary steels do not of course contain chromium, but the effect of heat treatment follows the same trend. Hardened and tempered materials are more resistant to corrosion than the annealed material, this following from the pearlite structure, *i.e.*, the dissociation of the carbide from the ferrite, in the latter case.

CORROSION OF IRON AND STEEL IN PRACTICE.

A number of the examples of typical corrosion in Naval practice, particularly as regards the boilers, will now be discussed in the light of the foregoing theories, together with the question of protective measures.

In a modern three-drum boiler, with the feed-water entering the top drum, any corrosion below the water-line usually takes the form of pitting of the tubes, generally at the ends and to a relatively small extent. Occasional pitting and grooving may be noticed elsewhere but not to a marked extent, unless the parts have been subjected to heavy work during construction or are exposed to concentration of stress due to pressure or temperature. For example, rivet heads, sharp plate bends and seams, may suffer more markedly than other parts.

In the vicinity of the feed inlet to the boiler, pronounced pitting is usually experienced, and this becomes evident if the feed-water is permitted, by accident or design, to impinge on any pressure parts; otherwise with the usual design of internal feed-pipe, the external surface of this readily renewable fitting is usually severely attacked. Above the water line the corrosion takes the form of pitting or chains of pitting, extending in some cases almost to grooving at the highest parts, running vertically down in the case of chain pitting or grooving from the source of origin. As in the case of the lower parts of the boiler, the worked or more highly stressed parts may be subject to selective action. As a rule, the pitting above the water line is more severe than elsewhere and tends to persist longer.

Experience shews that the corrosion in the form of pitting is more active in the early life of the boiler and its effects tend to decrease. This might be expected from the fact that the inequality of potential tends to be reduced as the "high" spots are removed by corrosion and in addition the usual treatment of pitted surfaces in boiler maintenance would tend to the same end.

The material of boiler plates has, from the nature of the work done during construction and the stresses to which they are exposed on service, to be of a ductile nature. These required properties entail a pearlite structure of the steel, that is a structure in which the hard carbide is distributed uniformly in the softer ferrite : in other words, segregation. So, apart from the other constituents necessarily present, the material is unfavourably situated in respect to the tendency of local galvanic action to occur. Some parts are more likely to be exposed to a free supply of oxygen and there the tendency to pit will be accentuated.

Under the high temperature conditions obtaining in a boiler gas cannot remain *in solution* in the water, and the bulk of the gases entering with the feed will probably be released soon after the entering feed mixes with the hotter water in the boiler and be carried up with the generated steam to the steam space and thence onward. The remainder will circulate through the boiler tube system. The concentration of oxygen is consequently a maximum in the steam drum and for this reason the more severe action should occur there, particularly in the uppermost parts where there is but little circulation. The products of corrosion there formed may ultimately gradually trickle down with the condensed steam and initiate or accelerate corrosive action in its path.

In the tube system itself, the concentration of oxygen is relatively low for the reasons given, and the velocity of flow of the water or mixture of steam is probably sufficiently high to give rise to what is termed turbulent flow and remove the corrosion products, thus retarding any corrosion. At entry to the tubes, eddies and back waters are formed, and in the latter the conditions are favourable to corrosion proceeding, observing moreover that the tube ends are severely worked by the expanding and belling processes.

Similarly at positions in the boiler where the circulation is sluggish and a regular supply of gas is possible or where gas may be trapped, *e.g.*, the landing of a plate, the corrosion can proceed and very rapidly if the plate is severely stressed—either by working during manufacture or by temperature difference or alteration of form. This appears to account for the defects experienced in the flanged corners of boiler and plates and in the seams of water-pocket wrapper plates. In the latter case, even when the action has been detected, it is impossible to remove entirely the corrosion products and the action is thereby accelerated.

In the earlier designs, where the feed entered at the bottom drums into a separate space isolating the outer tube rows, the corrosion in the water drum was generally more severe than is now the case, but the corrosion of the tubes was not markedly different. It would be expected that as the water passing through these tubes had not been de-aërated in any way, that the corrosion would have been more severe, but on the other hand, the corrosion may have been retarded by the speed of flow through the tubes being relatively higher in view of the small number of tubes employed in connection with the feed heater space. That the speed of flow has an effect on the corrosion appears to derive support from the fact that in certain designs of boilers with a separate feed-heater element and drum, as fitted in some T.B.Ds., the corrosion was very severe and the life of the tubes but a short one. Here the tube nest was relatively wide and the speed of water flow consequently low.

The fitting of contact feed-heaters has exercised a marked effect in reducing the corrosion of boilers. The solubility of gas in water is, of course, rapidly reduced as the temperature is increased. In earlier days, however, the full effect of any gas present had to be taken by the boilers, as will be recalled by the severe deterioration of the economiser tubes and steam collector fittings of the Belleville boilers. The generator tubes also suffered, although in a lesser degree, more particularly at the *vena contracta* of the first generator tubes, where, presumably, the remaining gas would be released as a result of the agitation and increase of temperature at entry, and remain, as this part would not be exposed to the scouring effect of the steam and water stream.

In the Babcock boilers for installations without feed heaters, the corrosion was frequently severe, although the results varied considerably from vessel to vessel. Generally, the trend of the corrosion followed the course described above, *i.e.*, it was more pronounced in those places where the water velocity would be expected to be lowest and where the concentration of gas was a maximum.

The effect of CO_2 in practice, as distinct from oxygen, is doubtful. It will be seen from the earlier remarks that this, as a weak acid, reacts simply on the iron and in the presence of a supply of oxygen the action is regenerative; a small quantity of acid is thereby capable of attacking a large quantity of iron. Alternatively, the reaction may possibly be a very complicated one and proceed without the presence of a supply of oxygen, but in this case a continuous supply of CO_2 is necessary.

There is very little precise data, but under the conditions obtaining in Naval practice, the quantity of CO_2 in the boiler feed-water would appear likely to be small in comparison with the oxygen and the general use of lime in moderate quantities would tend to counteract its influence in provoking an acid attack on the boilers. It is to be noted that, with the other gases, the solubility of CO_2 in water decreases as the temperature of the water increases and accordingly the bulk of any CO_2 entering with the feed would probably pass upward with the steam. This gas may possibly, therefore, contribute to corrosion in the upper parts of the steam collector, in view of the fact that the water there is largely condensed steam from which the lime necessary to neutralise the action is missing. Also the same tendency would exist in the vicinity of the entering feed, seeing that the solution of lime is there a minimum.

It has been mentioned that iron dissolves more rapidly in a dilute alkali than in a neutral solution and to this extent the use of lime may be actually harmful. On the whole, and while it is probably not equally effective in neutralising the acidity due to CO_2 at all parts of the boiler, a strictly moderate use of lime appears to be recommended by general experience. To be effective for the purpose in view, however, it is essential that the supply of lime used for this purpose should be kept in air tight containers. Otherwise its useful properties in combining with the CO_2 in the boiler will be anticipated.

The forms of corrosion in boilers referred to hitherto are those accelerated by and requiring a continuous supply of oxygen or carbonic acid gas. A more serious form is that due to the formation of acid by the dissociation of the constituents of sea water; the steps by which magnesium chloride may be converted into hydrochloric acid have been given. In practice, in small tube boilers, the use of impure feed has in many cases led, particularly in vessels of the T.B.D. type, to very rapid corrosion of the boiler tubes, the severity of this attack being in a decreasing order from the fire rows outward, i.e., the tubes which attained the highest temperature were more severly attacked. The course of this attack appears to be as follows: -The concentration of the sea water solution gives rise at first to a deposit of the insoluble salts, which in turn leads to an increase in the temperature of the metal of the tube and to exposure of the bare metal in places by the cracking or upheaval of the scale due to temperature changes. The soluble salts, particularly magnesium chloride, react in the presence of hot iron to form hydrochloric acid which attacks the iron in a regenerative way. The fact that the action proceeds more rapidly in the fire rows points to the fact that a high temperature is required. In fact, the milder action on the wing tubes is more likely to be due to the circulation of surplus hydrochloric acid generated in the hotter The fact that other parts of the boiler are not so tubes. severely attacked may possibly be explained by the observation of Friend that the rate of corrosion of iron by acids depends upon the speed of flow of the acid over the surface of the iron. Also the parts not exposed to rapid flow may be protected by a lime deposit.

The excess hydrochloric acid generated in this way may also be vapourised and pass on to other parts of the machinery Priming, which is likely to system and cause corrosion there. occur when salty feed is used, may have a like result. Thus. it sometimes happens that the severe corrosion of boiler tubes occasioned in this manner is attended also by corrosion of the steel parts of the turbines. Ordinarily, with adequate provision for drainage, the turbines may be maintained in a practically dry condition so that, notwithstanding the presence of any gases coming over with the steam, there need be very little corrosion with ordinary maintenance precautions, as experience shows. Once, however, corrosion is commenced by an acid action, the hygroscopity of the corrosion products may lead to moist surfaces and so to continuous corrosion in the presence of a supply of gas and moisture, even when the initiatory cause of the corrosion has been eliminated. The choking of the drains by the products of corrosion also tends to retain moisture at positions within the turbine and so to accelerate the action.

The evaporator is also a possible source for the generation of HCl. Actually the concentration of sea water with the densities and temperatures usually obtaining there is not sufficiently high to dissociate the magnesium chloride by the method already described. The presence of HCl has, however, been traced on occasion and has been attributed to the maintenance of a low working level leaving the scaled surface of the upper coils exposed. There is evidence that HCl may be vaporised to a small extent at moderate temperatures from a solution of magnesium chloride and the presence of HCl in the vapour from evaporators may possibly be explained in an action of this type proceeding in the concentrated sea water.

In any case the vapour carries forward with it any gases in the sea water and may therefore, unless arrangements are made to afford the gases an opportunity of escaping, convey a proportion into the feed system. It is very desirable of course, that the aërating arrangements fitted in connection with the test tanks for drinking water should not be used for the boiler make up.

Superheater tubes in the Naval Service have been fairly free from corrosion troubles. In general, the superheater tubes are protected to a certain extent by an oxide scale due to the passage of steam over the heated tube, and any corrosion is usually found at the inlet ends of the tubes where moisture is present. In the event of priming occurring, however, as for example, from the entrance of salty feed to the boiler, there is a possibility of HCl being carried over and attacking the tubes. Further, in sensibly vertical dispositions of U bend tubes, the upper parts may be attacked by trapped gases in the presence of water, *e.g.*, when the superheater is nominally at W.W.

Although not closely concerning Naval practice, it will be of interest to record that with the advent, with higher boiler pressures in shore practice, of steel economiser tubes instead of the cast iron fittings formerly employed, serious external corrosion has been experienced. This arises from the acid attack due to condensation on the relatively cold tube of steam from the furnace gases in association with sulphur dioxide from the same source. It may be noted that this may very well occur in Naval practices when airing stoves are employed and that in any case the funnels are liable to the same attack in a mild degree. The entrance of rain water is, however, generally the principal cause of any corrosion of the latter fittings and to any external attack on boiler tubes, observing that due to the sulphur content, damp soot is an accelerating influence.

Protective Measures.

It is very doubtful whether the convential galvanic action sensibly enters at any stage into the mechanism of the corrosion of zinc protectors as fitted in boilers and indeed there is every reason to suppose that the metallic connection between the zinc and the boiler does not endure for more than a few hours' steaming, Also, experimental evidence indicates that zinc oxide is electronegative to steel, and when this product is formed, the galvanic action, supposing such to exist, would exercise a contrary effect from that intended and lead to local corrosion of the steel in the vicinity of the zinc.

The zinc protectors fitted in the economiser tubes of Belleville boilers were always attacked, although the metallic connec-Further, the zinc tion was necessarily an imperfect one. protectors in the steam spaces of boilers are usually attacked in no less a degree than the zincs in the water spaces, although the boiler may have never been filled to W.W. during their period of service. It appears therefore, that the attack is due mainly to the zinc dissolving in the electrolyte in the presence of The zincs in the steam space, in common with the oxygen. other surfaces there, are certainly wet when the boiler is under steam, and consequently the metal will dissolve in the same way as iron, but, on account of its higher potential, at a more rapid rate, and the process proceeds by virtue of the presence of a The oxide is hygroscopic and continuous supply of oxygen. porous, and once the process has started, the action proceeds no less rapidly than that on the immersed zincs in the lower part of These upper zincs are, in some respects, more the boiler. favourably situated in view of the greater concentration of oxygen obtaining there and possibly a somewhat higher temperature.

The main function of the zincs then appears to be to divert to themselves the effects of the gas which could otherwise be available for furthering the corrosion of the standing parts of the boiler. From a consideration of the temperatures and the amount of oxygen present under standing and steaming conditions respectively, it appears that the bulk of the action occurs under the latter conditions.

If, therefore, no gases were present, the necessity for zinc protectors would not arise.

A photograph (unfortunately unfit for reproduction here) is on record which illustrates very clearly the effect of zinc protectors in this connection. It illustrates the corrosion which occurred in the economiser tubes of the Belleville boilers of one of the older cruisers, when for some reason, not on record, zinc protectors somewhat shorter than the length of the tube were fitted. In this case, the portions of the tube not covered by the zinc protectors had suffered very heavy pitting while the other part of the tube was in good condition.

The steel plate protectors fitted in condensers, etc., also appear to fulfil a similar duty to the zinc slabs in the boiler in diverting by their own corrosion a certain amount of the gas that might otherwise accelerate corrosion at other parts. In short, they are de-gassing agents, and notwithstanding the remarks already made as to galvanic action, if the metallic connection could be maintained in a greater degree than at present obtains, it seems likely that the acceleration of their oxidisation induced thereby would tend to enhance their usefulness in this particular application.

A great deal of controversy has arisen in recent years as to the merits of the electrolytic systems for the protection of boilers, etc., and in the face of the amazing diversity of experience with such systems it is not possible to express an opinion. In common with other corrosion problems, the diversity arises no doubt from the wide range of variables and inter-reactions in practical work, rather than from the merits and demerits of the system. The process has an advantage in combating the tendency of any stray external electrical influences to exercise a general corrosive effect on the boilers or other fittings, but experience and the local nature of the corrosion generally experienced indicates that such influences are exceedingly rare. In practice, therefore, its function seems to be confined to the generation of hydrogen in the expectation that its dissemination over the pressure parts may neutralise the effect of the oxygen entering with the feed in accelerating corrosion. In effect, the function appears identical with that of the zinc or steel protectors, and if the hydrogen could be disseminated over and be maintained on the parts to be protected, it would be greatly superior to the zinc protectors which cannot prevent the access of oxygen to those parts but only divert a portion of the oxygen supply from them.

While it is improbable with the designs fitted that the dissemination of hydrogen is achieved below the water line in boilers, it seems likely that its use may lead to benefit in combating corrosion above the water line under steaming conditions, and to benefit throughout under standing conditions.

Both processes are, however, but palliatives and the object in view can be better and more certainly achieved by eliminating the underlying cause, *i.e.*, by preventing the admission of gas into the boiler feed-water.

Boiler compounds are used in some services either solely as an anti-corrosive measure when distilled water is used or both as an anti-corrosive and anti-scaling agent when impure feed may be used. Such compounds vary greatly in their composition and also in their effects, but even the best are bad when used without discrimination and an understanding of their action. As regards anti-corrosive compounds, the composition of the more successful types appears to be based upon the properties of alkalies, when used in sufficiently high concentration, in inhibiting corrosion for many of the conditions under which boilers may work. For their successful application, therefore, it is necessary that the required minimum degree of alkalinity of the boiler water should be maintained and, moreover, that the tests made for this purpose should be of a definite nature, e.g., the titrating of a sample of the water with acid. The ordinarily practised rough tests such as the litmus reaction are not sufficiently definite, particularly if sea water may be present, even in small quantities.

An alkali that has been frequently employed in boiler compounds is sodium carbonate. An objection to its use rests in the possible embrittleing effect on the boiler parts due to its decomposition to caustic soda. Sodium carbonate in any case tends to cause foaming or priming when used in more than very small quantities and particularly so if the feed-water be impure, and also to form precipitates with some of the impurities which are then deposited to form scale on the heating surfaces. Certain chemicals, such as sodium phosphate, tannic acid and dextrine reduce this tendency to prime or to form scale and substances of this type are accordingly usually found incorporated in the boiler compounds with the inhibiting alkali.

Another system for preventing corrosion and scaling when using impure feed, which has been lately brought to notice, appears of particular interest in view of the earlier discussion on the colloidal theory. In this system, known as the "Infiltrator," a steam supply from the boiler is passed into and through a small vessel containing linseed (the ordinary uncrushed seeds) and then back to the water in the boiler. One can hardly fail to connect the surrounding of the catalytic ferric colloid by the emulsoid colloid digested by the steam from the linseed as being a possible explanation of the success which has said to have attended its use in France in combating corrosion in Belleville boilers using salt feed. Further, as regards the prevention both of scale forming and priming which is also claimed in this application, a similar mechanism may be in force whereby the impurities are surrounded and precipitated as a sludge.

In respect to priming, the commoner causes in modern practice are the sudden dissemination in the boiler of unduly large quantities of finely suspended matter. These particles form the nuclei for the generation of steam and if present in large quantities lead to the sudden formation of an increased quantity of steam within the water whose passage onward leads to this undesirable state of affairs. Magnesium salts in particular are of a very light and flocculent nature, and are believed to be the main cause of priming. If, as appears possible, these small particles are surrounded and precipitated by the larger particles of the emulsoid, their effect in inducing priming would be minimised. This explanation is of course quite conjectural, but it may be remarked that starch or dextrine, which forms in water an emulsoid colloid in particles of very large size (as colloids go) enters into the composition of many boiler compounds, while potato peelings have been known as a specific for priming since very early days. It is not on record, however, that this homely remedy was considered also an anti-corrosive as, from a consideration of the colloidal theory, it would appear likely to be.