THE ELECTROLYTIC THEORY OF THE CORROSION OF IRON.—I.*

THE REAL CAUSE OF IRON RUST.

BY DR. ALLERTON S. CUSHMAN.

FROM the standpoint of the modern theory of solutions, all reactions which take place in the wet way are attended with certain readjustments of the electrical states of the reacting ions. The electrolytic theory of rusting assumes that before iron can oxidize in the wet way it must first pass into solution as a ferrous ion. The subject has been interestingly treated by Whitney, who discussed it from the standpoint of Nernst's conception of the source of electromotive force between a metal and a solution. When a strip of metallic iron is placed in a solution of copper sulphate, iron passes into solution and copper is deposited, this change being of course accompanied by a transfer of electrical charge from the ions of copper to those of iron. Hydrogen acts as a metal and is electrolytically classed with copper in relation to iron. If, therefore, we immerse a strip of iron in a solution containing hydrogen ions, an exactly similar reaction will take place, iron will go into solution, and hydrogen will pass from the electrically charged or ionic to the atomic or gaseous condition. In such a system the solution of the iron and, therefore, its subsequent oxidation must be accompanied by a "precipitation" or setting free of hydrogen. It is very well known that solutions of ferrous salts as well as freshly precipitated ferrous hydroxide are rapidly oxidized by the free oxygen of the air to the ferric condition, so that if the electrolytic theory can account for the original solution of the iron the explanation of rusting becomes an exceedingly simple one.

As iron has been shown by Whitney, Dunstan, and the writer to rust in the presence of pure water and oxygen alone, the electrolytic theory as a fundamental cause of the wet oxidation of iron must stand or fall on the determination of one crucial question, viz.: Does iron pass into solution, even to the slightest extent, in pure water? If iron does dissolve, the electrolytic theory is so far satisfactory; if it does not dissolve, we must conclude that the oxygen finds some way of directly attacking the metal.

Almost everyone will admit that in the case of impure iron, with its unhomogeneous physical and chemical constitution, electrolysis will supervene, but it must be remembered that we are now concerned with the underlying cause of the wet oxidation or hydroxylation of iron, regardless of its state of chemical purity.

According to the dissociation theory, even the purest water contains free hydrogen ions to the extent of about 1 gramme in 10,000,000 liters. If iron dissolves in the purest water it should be by interchange with hydrogen, and as Whitney has pointed out, pure water is to this extent an acid. In order to get experimental evidence on this crucial point, Whitney describes the following experiment:

"A clean bottle was steamed out for a time to remove soluble alkali from the glass and was then filled with pure distilled water, which was kept boiling by passing steam through it for fifteen minutes. While still boiling, a bright piece of iron was placed in the bottle. A stopper (in some cases rubber and in others cork) carrying a tube open in a capillary several inches above the stopper was inserted into the bottle and firmly fastened in place, the water being kept boiling. Finally, the glass capillary was heated hot by means of a blowpipe and sealed by squeezing the walls together. The bottle was then allowed to cool to a temperature of about 80 deg. C., and the neck of the bottle was finally covered with paraffin to prevent leaking. It was thought that in this way the oxygen, carbonic acid, and other gases in the water were completely removed. Bottles containing iron and sealed in this manner have stood without any visible change for weeks. In some cases a little air was subsequently admitted to bottles which had stood in this way with the iron apparently unaffected, and within a few minutes the water became cloudy and assumed a yellow color. Ordinary rust rapidly deposited upon the glass and in spots upon the metal. In fifteen or twenty minutes the production of rust throughout the bottle was perfectly evident. It seemed plain from the rapidity of formation of oxide and its precipitation on the glass that the iron had dissolved in the water before the addition of the air, and that the latter simply permitted the formation of the insoluble oxide." This conclusion has been attacked, but it appears to the writer to be demonstrated that Whitney was right in his assertion that iron goes into solution up to a certain maximum

concentration in pure water, without the aid of oxygen, carbonic acid, or other reacting substances.

This point established, it becomes apparent that the rusting of iron is primarily due, *not to attack by oxygen, but by hydrogen ions*. Absolute confirmation of this view will be given later on.

All substances in solution which contain hydrogen ions, such as acids, stimulate the corrosion of iron. This is also true of salts of strong acids and weak bases, which, though perfectly stable in a dry condition, hydrolyze in solution to an acid reaction; or which, though neutral in fresh solutions, undergo slow decomposition under the action of light, with the formation of acid salts or free acid. With certain exceptions, salts which are perfectly neutral in solution do not prevent oxidation but appear to aid it by increasing the electrolytic action. All substances which develop hydroxyl ions in solution, such as the alkalis or salts of strong bases with weak acids, to a certain extent inhibit, and, if the concentration is high enough, absolutely prohibit the rusting of iron.

Under the electrolytic theory the explanation of the protection afforded by hydroxyl ions is a simple one. Owing to the small dissociation of water, hydrogen ions can not exist in a solution in which the hydroxyl ions are in excess. As hydrogen ions can not exist or be locally formed in sufficiently strong alkaline solutions, no attack is made upon the iron, which remains permanently unaltered. If, however, the concentration of the hydroxyl ions is not sufficiently great, electrolysis can go on with an apparent stimulation of the pitting effects similar to that produced by perfectly neutral electrolytes, such as sodium chloride.

It is known that solutions of chromic acid and potassium bichromate inhibit the rusting of iron. In order to determine the concentration necessary to produce complete protection, a number of polished strips of two different samples of steel were immersed in bichromate solutions of increasing concentration, contained in tubes which were left quite open to the air. There were twelve tubes in each series, ranging by regular dilutions from tenth-normal down to ten-thousandth normal. At the end of two months the last four tubes showed graded rusting with accumulation of ferric hydroxide. No rusting had occurred in any of the solutions above tube No. 8, which contained six-hundred-and-fortieth normal bichromate, a strength corresponding to about 8 parts of the salt in 100,000 parts of water, or about 2 pounds to 3,000 gallons. Since solutions of bichromate do not hydrolyze with an alkaline reaction, but on the contrary are usually slightly acid, some other explanation must be found for this remarkable phenomenon. On first thought it would seem a paradox that a strong oxidizing agent should have the effect of preventing the oxidation of iron, and yet this is precisely the case. If, however, the initial cause of rusting is the hydrogen ion, it is possible to believe that under certain conditions oxygen would prove the most effective of all inhibitors. Dunstan, Jowett, and Goulding have claimed that this peculiar action of chromic acid and its salts is due to the fact that they destroy hydrogen peroxide. This explanation is not satisfactory, and it is fair to inquire whether the electrolytic theory is capable of furnishing a solution of the problem. Furthermore, it will be shown that additional evidence can be brought forward which can not be made to apply to any other theory.

The writer has observed that if a rod or strip of bright iron or steel is immersed for a few hours in a strong (5 to 10 per cent) solution of potassium bichromate, and is then removed and thoroughly washed, a certain change has been produced on the surface of the metal. The surface may be thoroughly washed and wiped with a clean cloth without disturbing this new surface condition. No visible change has been effected, for the polished surfaces examined under the microscope appear to be untouched. If, however, the polished strips are immersed in water it will be found that rusting is inhibited. An ordinary untreated polished specimen of steel will show rusting in a few minutes when immersed in the ordinary distilled water of the laboratory. Chromated specimens will stand immersion for varying lengths of time before rust appears. In some cases it is a matter of hours, in others of days or even weeks before the inhibiting effect is overcome.

The passivity which iron has acquired can be much more strikingly shown, however, than by the

rusting effect produced by air and water. If a piece of polished steel is dipped into a 1 per cent solution of copper sulphate, a 10-second immersion is sufficient to plate it with a distinctly visible coating of copper which can not be wiped off. A similar polished strip of steel which has been soaked over night in a concentrated solution of bichromate and subsequently well washed and wiped will stand from six to ten 10-second immersions in 1 per cent copper sulphate before a permanent coating of copper is deposited. Even a momentary plunging of the metal into the bichromate will induce a certain passivity, but the maximum effect appears to require a more prolonged contact with the solution.

The first explanation of this phenomenon which naturally presents itself is that a thin film of either oxide or chromate has been formed on the surface of the metal. It is almost inconceivable, however, if such a film is formed, that it can not be seen with the aid of a microscope. There is evidence which appears to indicate that no such film of oxide is formed. It is easy to cover polished iron with a visible film of oxide by simply flaming it gently in a Bunsen burner. Such films do not succeed in protecting the iron either from the rusting or the copper sulphate test. Still more convincing than this is the fact that if a polished surface which has been rendered passive by immersion in bichromate is heated to 100 degrees C. (212 degrees F.) for some hours, its passivity disappears and it again behaves in a normal manner. None of the oxides or chromates of iron are in any sense volatile compounds, so that if a solid but invisible film is really formed, it is in some manner dissipated by heat. Further than this, a chromated strip of iron which is kept in a vacuum soon loses its passivity, whereas a similar strip kept under ordinary conditions remains passive for long periods.

The passivity of iron was discovered by Keir in 1790. Since the phenomenon is produced only by strong oxidizing agents or by galvanic contact when oxygen can separate on the iron, it was explained by Faraday, Wiederman, and others as due to a thin oxide film. From the evidence given above, however, it seems that the passivity of iron is better explained as a polarization effect produced by the separation and retention of oxygen on the surface of the metal. If the rusting of iron is due primarily to the action of hydrogen ions, iron in the condition of an oxygen electrode should be more or less well protected from electrolytic attack.

Keir observed that polished iron which had been immersed in red fuming nitric acid was altered in some manner so that its power of precipitating silver and copper from their solutions was inhibited, and this occurred, in the discoverer's own words, "without the least diminution of metallic splendor or change of color." In the writer's experience red fuming nitric acid does not produce the passive condition as successfully as solutions of chromic acid and its salts. Mugdan discussed the passivity acquired by iron which was immersed in fuming nitric or sulphuric acid and concluded that it was not due to the formation of an oxide film, but was a true passivity in the sense of an *ennobling* (*Veredlung*) of the metal, accompanied by a low electrical potential.

Moody asserts that potassium bichromate prevents the formation of rust, owing to the fact that it slowly dissolves iron and its hydroxides. He observed that the addition of ammonia to solutions of chromic acid and its salts which had been allowed to act on iron produced precipitates of hydroxide. This point has been carefully investigated by the writer, with the following results: Iron which is free from manganese is not attacked by solutions of bichromate, even if boiled for days in a flask fitted with return condenser. Manganese is, however, readily soluble in bichromate solutions, and therefore iron rich in manganese yields a sufficient amount to the solvent action to produce a small amount of brownish manganese hydroxide when the bichromate solution is poured off, made slightly ammoniacal, and allowed to stand. If metallic manganese is boiled in bichromate solutions it dissolves readily, and subsequent addition of ammonia produces an abundant precipitate of brown manganese hydroxide.

If polished iron is allowed to stand for some time in standard tenth-normal potassium bichromate solution, the oxidizing strength of the latter as measured by its titration value is slightly reduced without the

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solution of the iron or the production of any visible effect. Under the same conditions a standard solution of neutral potassium chromate is slightly reduced with the appearance of a small amount of chromic hydroxide. In fact, all the evidence obtainable points to the abstraction by the iron of some of the available oxygen of chromic acid and its salts without the formation or solution of iron oxide films.

In order to show beyond doubt that an oxygen electrode is formed by immersing iron in a strong solution of bichromate the following experiment was made: Two polished steel electrodes were prepared and chromated by immersion for a number of hours in a strong solution of potassium bichromate. The prepared electrodes were then thrust tightly through a rubber stopper, closing a Jena flask, which was then filled with pure freshly boiled distilled water. The electrodes were then attached to the poles of a primary battery at about 2 volts potential. At the end of half an hour, although the potential was not sufficient to disengage bubbles of gas and no visible change had occurred, the electrode which was connected to the zinc pole of the battery had lost its passivity, the other retaining it.

It might still be objected that if a film of oxide had been formed it might suffer reduction at the negative pole. It is, however, very easily shown that electrodes which have been oxidized by gentle heating are not reduced under the conditions of this experiment.

Wood in 1895 commented on the power of paints and pigments containing certain oxidizing agents,

notably potassium bichromate and lead chromate, to form on iron and steel surfaces a thin coating of oxide which so effectually protects the metallic surfaces from corrosion that after the removal of the paint the metal still resists atmospheric effects for a long time, as well as the stronger effect of immersion in sea water or acidulated waters and sulphurous and other vapors. This action, Wood adds, is very obscure and not thoroughly understood; but the fact remains, and extended experiments in this field only demonstrate its presence and usefulness.

The oxide film theory has been held for many years to account for the passivity of iron, but in the writer's opinion the protection afforded by certain oxidizing agents is electro-chemical and not mechanical. Perhaps the most conclusive proof that electrolytic action must take place before rusting can occur is given by an experiment of Moody's, which has been repeated and confirmed by the writer. Dunstan and his co-workers claimed that when iron is placed in hydrogen peroxide the metal is rapidly oxidized, with formation of ferric hydroxide. As Moody has pointed out, commercial hydrogen peroxide is invariably acid and contains impurities. In perfectly pure hydrogen peroxide bright iron will catalytically disengage oxygen and retain its polished surface unacted upon. It is not an easy matter to prepare a perfectly neutral pure solution of hydrogen peroxide, but it can be accomplished by two fractional distillations at 85 degrees C. (185 degrees F.) under reduced pressure (700 millimeters) of commercial dioxygen. Before distilling the second time the solution should be

made barely alkaline with a few drops of one-hundredth normal potassium hydroxide. In a pure neutral one per cent solution of hydrogen peroxide thus prepared, Moody's observation was confirmed. Iron immersed in the solution remained bright for a protracted period. Hydrogen ions do not exist in a pure neutral solution of peroxide; therefore neither solution of iron nor electrolysis can take place. If the flask containing the specimens covered by pure hydrogen peroxide solution is connected to a vacuum pump, oxygen is disengaged freely and boils off the metal without the slightest appearance of rust.

Reduced to its simplest terms, the following explanation of the rusting and corrosion of iron seems to the writer the only one that is tenable. In order that rust should be formed iron must go into solution and hydrogen must be given off in the presence of oxygen or certain oxidizing agents. This presumes electrolytic action, as every iron ion that appears at a certain spot demands the disappearance of a hydrogen ion at another, with a consequent formation of gaseous hydrogen. The gaseous hydrogen is rarely visible in the process of rusting, owing to the rather high solubility and great diffusive power of this element. Substances which increase the concentration of hydrogen ions, such as acids and acid salts, stimulate corrosion, while substances which increase the concentration of hydroxyl ions inhibit it. Chromic acid and its salts inhibit corrosion by producing a polarizing or dampening effect which prevents the solution of iron and the separation of hydrogen.

(To be continued.)

INCANDESCENT ILLUMINANTS.*

PROGRESS IN MANTLES.

BY JAMES SWINBURNE, F.R.S., ETC.

A LITTLE more than twenty years ago, Auer von Welsbach, who was engaged on researches on the rare earths, invented the modern incandescent mantle. His first mantles were made of zirconia and yttrite earth, in the proportion to make a normal zirconate. Shortly afterward, he found that the best material has a basis of thoria. Pure thoria, which requires care in its preparation, gives very little light, but if a small percentage of a colored and permanent oxide, such as ceria, is added, it gives good illumination.

There has been much discussion about the theory of the incandescent mantle. It has been generally assumed that the temperature of a Bunsen burner is too low for a mantle to give the light it does by simple radiation, unless it is much hotter than the flame. Unfortunately, the temperature of the flame is generally taken with a thermo-couple, and this gives far too low a reading, as the thermo-couple never reaches the real temperature of the flame. But, admitting that the temperature of the flame is high, it is still urged that the light given by the thoria with a small percentage of ceria is so great that there is something else than mere thermal radiation. It is said that the ceria acts as a catalytic agent, and that it oscillates between two states of oxidation. Ceria does act in somewhat the same way as platinum; for instance, if a ceria mantle is put on a lighted burner, and the burner turned out, and the gas turned on again, the ceria mantle will glow and will finally light the gas. It is odd that this is not brought forward by the advocates of the catalysis theory; but the opponents might urge that zirconia will do the same thing, and the zirconia mantle gives very little light. This does not really dispose of the catalytic theory.

According to the simple radiation theory, the light depends only on the emissivity, or blackness of the mantle, and its temperature. Its temperature must be lower than the flame, as it must be robbing the flame of the heat it radiates. In order to give the flame every chance of supplying the heat, the threads of the mantle have to be made very fine, so that the flame can rush through the meshes, and the hot gas should be in brisk movement through the interstices of the mantle. By using a special draft arrangement, known as the intensive system, about twice the light per cubic foot of gas can be obtained. In order to get the highest temperature the emissivity should be low, that is to say, the mantle should be very white; but then, though it would get to a high temperature, it would give very little light. On increasing the emissivity the light will first increase, but this means a lower temperature, so that as the emissivity is increased from white to black, the total radiation increases, but as that means a greater abstraction of heat from the flame, the mantle is cooler, and therefore radiates a larger proportion of the energy as heat and a smaller proportion as light, so the mantle gets redder and gives less light. This is just what happens in practice, whether ceria or any other colored oxide is used.

It has been urged that as pure ceria is white, adding it cannot make the mantle blacker; but ceria is white only when cold. A mantle may look quite white cold, and be darker in color when hot. Rubens has devised an experiment to show this. The mantle is strongly illuminated by an arc and condenser, and its image is thrown on the screen. It looks quite white, of course. On lighting the gas, the mantle, instead of becoming still brighter, at once becomes dull. Again, alumina, which is white, gives little light. Chromium oxide is so dark that it gives only a dull red glow. But on adding a little chromium oxide to the alumina, a dark red light is first given, because the chromium oxide is too dark; but as soon as it combines with the alumina to make a light pink mantle, a good light is obtained.

The incandescent mantle is now applied not only to the ordinary Bunsen burner, but to an inverted form, which lends itself to decoration, and to the petroleum lamp. It is now also applied to air carrying a little hydrocarbon gas, and this application is said to provide an extraordinarily cheap light, which is especially useful for country houses.

One of the drawbacks of gas, compared with electric lighting, is that merely turning on does not light gas. This difficulty has been largely overcome by the use of the by-pass, but further advances have been made. Welsbach has discovered that an alloy of cerium and iron gives off sparks on being scraped or filed, and a burner has been designed in which the act of turning on the gas scrapes a little wheel of this alloy, causing a spark, which lights the gas. This overcomes the drawback of having a little jet always burning. Another invention allows the gas to be lighted from a main tap. Each burner has an attachment, which lets the gas straight through to the burner when the pressure is on; but on turning the main supply off, and allowing a little gas to pass at the controlling tap, the attachment to each burner turns off the burner and lights a little pilot jet, which keeps alight until the light is wanted again. On turning on the main tap, the pilot jets light the various burners and go out themselves. By this means burners can be fully lighted up by turning one tap at the door of the room.

The electric incandescent light is undergoing a great change. Carbon is being replaced by metal wires. It has been found possible to make wires of high enough resistance of tungsten, osmium, tantalum, and a few other metals and compounds. The osmium lamp was the first of these, but there was difficulty in making it of high enough resistance. The tantalum lamp is now in great demand. It is made for 100 to 130 volts, and is much more efficient than the carbon lamp. It will not last long on alternating currents, however. The wires of a lamp that have been run for some time on a direct current show a curious notched or crinkled appearance under the microscope. But a wire that has been run on an alternating circuit looks as if the metal had been melted into short cylinders with round ends, and these cylinders had stuck together end to end without their centers being in a

line. Sometimes the little cylinders are nearly separated, merely touching at a corner. This action is very extraordinary, and has never been explained. In addition to this, when a lamp breaks down on an alternating circuit, the wire sometimes goes at one point, and sometimes it breaks in several places, and tangles itself up in an extraordinary way; at other times it breaks up into numerous little pieces, which will be found lying on the inside of the globe. Some of the other lamps show a change under the action of the current, but it is not so marked as in the case of tantalum.

One of the most interesting of the new lamps is the zircon. It is said to be made of zirconium and tungsten, and lamps of this material have been made for 200 volts, a matter of the greatest importance from a distribution point of view. It is possible that the conductor is really a zirconide of tungsten, and this opens up a new series of compounds. A zircon lamp for 100 volts has really six separate loops of wire mounted in series inside a bulb. A recent improvement is to provide an extremely light spring for each loop, so as to keep it taut. The lamp can then be used in any position.

Tungsten seems to be the favorite metal, as it gives a very high efficiency. It is probable the lamp of the future will have an efficiency of nearly a candle per watt, and this is promised by the use of tungsten. At the same time it must be admitted that to make a wire with a resistance of 500 ohms small enough to give 20 candles with 20 watts is a triumph of inventive skill.

The adaptations of plants growing in arid regions, for accumulating and holding a reserve supply of water, have been described by Dr. MacDougal, in the "Fifth Year Book of the Carnegie Institution of Washington." Special storage organs and storage plants are most abundant in regions in which the scanty rainfall occurs during a brief period only, while during the remainder of the year precipitation is comparatively lacking. The development of tissues for storage purposes is varied, and shows some important morphological features. *Ibervillea sonora*, one of the cucumber family, produces a storage organ the size of a squash, at the base of the stem, which is covered with a skin highly resistant to evaporation. During the dry season these structures lie unchanged on the hot sand. At the commencement of the rainy season, roots and shoots are quickly formed, and the fruit and seed matured, when the thin stems die down and the organ rests for another season. Some of these storage organs were collected and placed on a dry shelf in a museum, in 1902, where they have since remained. Every year since, at a period corresponding to the rainy season in its native habitat, thin stems are produced, which eventually die back. Five years' growth has already been made at the expense of water stored up in 1901, and the storage organs are still sound and will probably furnish supplies for the annual production of stems and leaves for some years to come.

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