LXXVII.—*The Rusting of Iron.*

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IN a recent number of this Journal (Trans., 1905, **87**, 1548) appears a paper by Dunstan, Jowett and Goulding, in which these authors contend that the rusting of iron is a change mainly depending on the direct interaction of iron, water and oxygen, and that the part played by carbonic acid in the atmospheric corrosion of the metal is merely subsidiary. The conclusions at which they arrived were based mainly on the assumption that they had succeeded in eliminating carbonic acid in an experiment in which they allowed iron, water and oxygen to remain in contact, and in which rusting occurred. From their observations they infer that the formation of hydrogen peroxide is a necessary part of the chemical process of atmospheric rusting. In further support of this explanation they submit analyses of rust which they regard as being fairly represented by the formula $Fe_2O_2(OH)_2$ and as having a composition identical with the red substance formed on immersing iron in commercial hydrogen peroxide solution. Dunstan and his co-workers do not appear to have been aware of the extreme difficulty of completely excluding carbonic acid. That they in their most important experiment did not take adequate precautions to ensure the absence of carbonic acid is clearly shown, for in their description of it they make the significant admission that on allowing oxygen to pass into the vessel containing water and iron "action immediately commenced, a substance of a green colour being produced, which rapidly changed to the red colour characteristic of rust." No more conclusive evidence that carbonic acid was present in the materials used could be afforded than the formation of this green colour, which invariably accompanies the early stage of attack of carbonic acid on iron in presence of air or oxygen.

Action of Oxygen and Water on Iron.

The crucial question as to whether or not direct interaction takes place between oxygen, water and iron has engaged my attention for several years and the experimental inquiry pursued has led to definite results which are hereinunder recorded and which are in direct conflict with the evidence put forward by Dunstan.* After several partial failures due to the difficulty of constructing an apparatus capable of excluding the merest traces of carbonic acid, an arrangement has been devised by means of which it has been found possible to leave iron, oxygen and water in contact for many weeks without even a speck of rust appearing on the surface of the metal.

The apparatus consists of a distilling flask, *A*, having a capacity of about one and a half litres, the side tube from which passes through the long condenser case, *B*, forming a bend at *C* in which the metal under experiment is placed. The other end of the bend is attached to a flask, *D*, which acts as a receiver. The second flask is connected in series with a large aspirator, *G*, by means of a U-tube, *E*, tightly packed with soda-lime and a caustic potash tower, *F*. On the posterior side of the distilling flask, *A*, is a second U-tube, *H*, also packed with soda-lime, which communicates with a caustic potash tower, *K*, itself in connection with an air-reservoir, *L*, containing moistened sticks of caustic potash. When the aspirator, *G*, is working, air enters the apparatus through a minute orifice at the upper part of the tube *M*, which is filled with soda-lime. From and including the stopcock *N* to the side of the tube joining *E* and *F* all parts of the apparatus are fused together, so that when reasonable precautions are taken leakage of carbonic acid from the air into the bend *C* is entirely prevented. The other parts of the apparatus are securely joined together by pressure india-rubber tubing wired in place and having its surface covered with vaseline.

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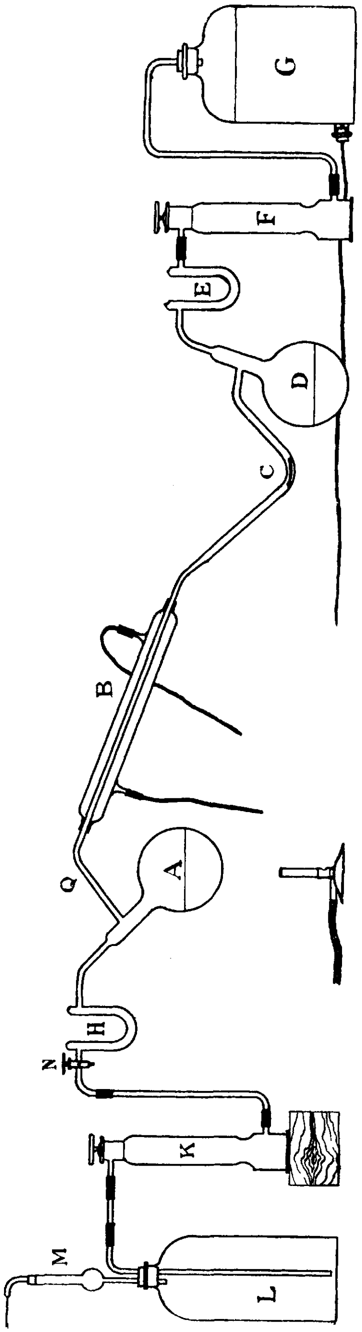
* *Loc. cit.* See also *Proceedings of the Royal Artillery Institution*, 1899, No 5, 26 ; and *Report on Atmospheric Corrosion*, Steel Rails Committee, 1900.



The metal used in the experiments was a soft Swedish iron which was cut from a thick bar into cylindrical pieces about 40 mm. in length and 2 mm. in diameter. These were highly polished and slightly curved so as to lie evenly in the bent tube. The metal contained 99·8 per cent. of iron, and each cylindrical piece weighed a little less than 1 gram.

The experiment consisted in placing one of the pieces of iron in a bent piece of clean, dry glass tube which was as quickly as possible sealed into position at *C*. A slow current of air was drawn through the apparatus for about three weeks so as to remove all traces of carbonic acid from contact with the iron. Water was distilled from the flask *A*, which contained a one per cent. solution of barium hydroxide, until more than half a litre had passed over. The cock *N* was turned off during distillation and, with the object of preventing carbonic acid finding its way into the apparatus through a sudden inrush of air, care was taken to cool the apparatus very slowly after distillation. A current of air was again drawn steadily through the apparatus and the metal kept under observation. The bent tube was of such a size and shape that each bubble of air on passing through the water in it exposed the upper surface of the iron to oxygen, whilst the lower surface remained immersed in water.

When an experiment was made under the conditions described it was found that no general rusting occurred, but that, however carefully the operator worked, after an interval varying between a few days and several weeks the ends of the iron which rested on the glass became discoloured, and in some cases a few brown specks formed on the surface of the metal not in contact with the glass. It appeared probable that this discoloration was due to carbonic acid and moisture shut in the apparatus during the process of fusing the bent tube in its place, and accordingly a different mode of procedure was adopted. Before the bent tube was fused into position, it was partly filled with a one per cent. solution of chromium trioxide which just covered the iron. When the apparatus had been swept with air free from carbonic acid for three weeks, water was distilled through the bend until all the chromic acid was washed into the receiver, *D*. After the liquid in the bent tube became colourless, the distillation was continued until a volume of water exceeding that already distilled had passed over. Air was again drawn through the apparatus, and at the end of six weeks the iron was perfectly bright with the exception of those parts which rested on the glass and which showed a slight discoloration. As interaction between glass and iron appeared to take place, a means was devised whereby in subsequent experiments the contact between these two substances might be avoided. This was effected by covering the ends of the iron cylinders with paraffin wax. Commercial paraffin wax was purified by repeatedly shaking it, in the molten state, with hot water. The wax was allowed to cool until the temperature fell to just above the melting point, when each end of the piece of metal was dipped in and quickly drawn out two or three times. By this means a blob of wax, covering some 3 mm. of the cylinder, was fixed at each end. These blobs allowed the metal to lie in the bent tube without touching the glass. Several experiments were made with iron protected in this manner, and it was found in every case that, even after the long-continued passage of air through the water containing the iron, the metal remained perfectly bright. In one experiment, after distillation, the current of air was continued for five weeks. During this time, approximately 56 litres of air passed over the iron. Since the iron weighed 0·9 gram, the total weight of oxygen in the air to which it was exposed exceeded by thirty times the amount required the convert the whole of the metal into ferric oxide, but not even one speck of rust appeared. In another experiment, after passing air having a total volume of 32 litres through the apparatus for three weeks, during which time the metal remained perfectly bright, the glass tube was cut at the point *Q* immediately above the distilling flask. Air containing carbonic acid, but cleaned by its passage through a tower containing pumice-stone moistened with distilled water, was then drawn through the apparatus.

In the course of six hours, the surface of the metal was distinctly tarnished. After seventy-two hours, during which time approximately 16 litres of air were drawn through, the whole of the surface of the metal was corroded and a considerable quantity of red rust had collected in the bend of the tube.

It must therefore be accepted that when carbonic acid is entirely excluded, no interaction takes place between oxygen and iron in presence of water. Under such conditions, oxygen alone is unable to induce oxidation of the metal, but as soon as air containing its normal quantity of carbonic acid is admitted vigorous rusting results.

Influence of Carbonic Acid on the Absorption of Atmospheric Oxygen by Iron.

Having regard to the remarkable sensitiveness of iron to carbonic acid, to which reference is made later, it appeared of interest to determine the influence of carbonic acid on the absorption of atmospheric oxygen by iron. The apparatus used consisted of a dropping funnel having a globe of 110 c.c. capacity. This funnel was attached by its stem and by a length of pressure india-rubber tubing to a second similar but smaller funnel. The upper opening of the larger funnel could be closed by a caoutchouc stopper into which was fixed a piece of capillary tube bent at a right angle, through which air could be admitted and connection made with a Hempel bulb so as to enable the necessary absorption to be carried out.

In those experiments in which it was desired to exclude carbonic acid, the apparatus and measuring vessels were rinsed and filled with water prepared by distilling one per cent. barium hydroxide solution in an atmosphere which had been exposed to caustic potash and soda-lime.

In estimating the absorption, the dropping funnels were first filled with water, 10 grams of clean, fine iron wire in the form of a spiral were introduced into the globe of the larger funnel, and then 100 c.c. of air admitted and the globe tightly stoppered. After the desired period had been allowed for interaction, the volume of oxygen remaining was directly measured by absorption with pyrogallate.

In the first set of experiments, ordinary air and distilled water which had been exposed to air were used, whilst in the second set these were replaced by air which had been in contact with soda lime for twenty-four hours and water distilled from barium hydroxide solution.

The experiments were made in pairs and the following measurements were recorded :

	Percentage of total oxygen in 100 c.c. of air absorbed by 10 grams of iron.	
	Ordinary air and distilled water.	Air and water almost entirely freed from carbonic acid.
After 6 hours' exposure	5·7	none
,, 24 ,, ,, ...	29·1	none
,, 72 ,, ,, ...	61·3	0·9
,, 168 ,, ,, ...	94·3	3·8

In those experiments in which ordinary air and distilled water were used, the iron after six hours' exposure was covered with a coating in part green and in part brown, and the water was slightly turbid. After twenty-four hours, the iron was completely covered with brown rust and the water was very turbid. Precisely similar conditions were observed to prevail in the experiments in which the materials remained together for seventy-two hours and one hundred and sixty-eight hours respectively. In the series of experiments in which air and water almost entirely freed from carbonic acid were used, the iron remained perfectly bright and the water clear after six hours' exposure. In the second experiment, after twenty-four hours' exposure, the surface of the iron was still perfectly bright, but a few small, brown specks were observed in some places where the iron touched the glass. After seventy-two hours' exposure, the iron still remained bright, but the number of brown spots had increased. Specks of rust were to be seen not only where the iron touched the glass, but also in some places where the iron in crossing touched itself. After one hundred and sixty-eight hours' exposure, the appearance of the iron was very much the same as after seventy-two hours' exposure, but the water showed a slight opalescence. The slight attack on the iron and the small absorption of oxygen which took place in this series of experiments were no doubt due to the minute but inevitable leakage of carbonic acid into the apparatus at the time the iron was introduced. The experiments, however, show clearly that the absorption of oxygen by iron when exposed to air and water is almost entirely stopped if the minute quantity of carbonic acid which air and water usually contain is almost entirely removed.

Composition of Iron Rust.

Various analyses of iron rust have been published from time to time, but there is no record that specimens representative of the material in course of comparatively rapid formation have been examined. With the object of obtaining further evidence concerning the composition of rust, samples were obtained from the unpainted interiors of iron flushing tanks in constant use. In such tanks the iron is under conditions specially favourable to rusting, the metal being alternately and in rapid succession exposed to air and water. Several of the tanks from which material was obtained had remained unscraped for years, and the sides were blistered with masses of rust, brown on the exterior, but quite black inside. Every sample of this rust when placed in hydrochloric acid effervesced briskly, yielding a gas which was completely absorbed by potassium hydroxide. The samples contained an inappreciable quantity of calcium carbonate, and the condition of the iron present in each is given in the following table:

Number of sample	1.	2.	3.	4.	5.	6.
Percentage of iron as ferric oxide.........	55·73	51·12	64·60	65·13	68·89	67·46
,, ,, ferrous oxide	32·86	36·57	25·74	25·66	23·18	24·40
,, ,, ,, carbonate .	11·40	12·31	9·66	9·21	7·93	8·14

In order to determine the effect of leaving recently-formed rust fully exposed to air, a portion of one of the samples was roughly powdered and spread on a porcelain dish. After remaining for eight days, when the whole of the surface of the material had changed to a rich brown colour, it was again submitted to analysis. The percentage of iron present as ferrous oxide was found to have been reduced from 32·86 per cent. to 14·11 per cent. and the percentage of ferrous carbonate from 11·4 per cent. to 5·62 per cent., or in each case by slightly more than 50 per cent. The readiness with which ferrous oxide and ferrous carbonate on exposure to air undergo oxidation forming ferric oxide accounts for the low percentages of ferrous iron found in most samples of rust by previous observers.

It is clear that rust kept moist, that is, in contact with what is really a very dilute solution of carbonic acid, and still adhering to iron, contains a large proportion of its iron in the ferrous state and much carbonate. The persistence of ferrous iron under such conditions is easily understood, for the material is partly surrounded by a reducing atmosphere of hydrogen, which is constantly being liberated at the surface of the metal.

The composition of rust in course of formation is altogether out of harmony with the view that hydrogen peroxide is an effective agent in its production. In this connection attention must be directed to the fact that Dunstan and his co-workers assume that by the interaction of iron, oxygen and water twice as much hydrogen peroxide is liberated as is necessary to oxidise the ferrous oxide simultaneously formed. If hydrogen peroxide were actually produced in the ratio stated, ferrous oxide and ferrous carbonate would not be found in rust, since both these substances undergo immediate oxidation in presence of hydrogen peroxide. The only rational interpretation of the presence of a large percentage of ferrous compounds in rust is that the first stage in the atmospheric corrosion of iron involves the interaction of carbonic acid and metal, resulting in the formation of ferrous carbonate which gradually becomes basic in character through loss of carbonic acid.

Interaction of Iron and Carbonic Acid.

The remarkable ease with which iron is dissolved by carbonic acid is not generally recognised. The following experiment serves as an illustration of the sensitiveness of the metal to attack. Distilled water which has been shaken with or left in contact with air is poured on a perfectly clean, polished surface of iron. At the end of forty seconds, when the water is seen to be clear and the metal perfectly bright, the water is allowed to run into a porcelain basin containing a drop of a dilute solution of potassium ferricyanide. A marked blue coloration immediately results. If a similar experiment be made with rain water instead of distilled water, the iron is found to be even more readily attacked, ferrous salt in solution being detected after thirty seconds' contact. The ferrous iron found in solution in these experiments is obviously formed by the interaction of a very dilute solution of carbonic acid and iron, for recently-boiled distilled water does not dissolve the metal.

An estimation of the amount of iron dissolved by carbonic acid was made by placing clean iron borings in water kept saturated with carbonic acid at atmospheric temperature and pressure. In these experiments, hydrogen was steadily evolved from the surface of the metal, but, provided air was excluded, the solution remained clear and colourless. In a series of experiments in which 250 c.c. of liquid and 500 grams of clean iron borings were used, the solution found to contain:

After 20 hours' contact	....	0·2546 gram	of FeO	per litre
,, 30 ,, ,,	....	0·3771	,,	,,
,, 56 ,, ,,	....	0·5245	,,	,,
,, 96 ,, ,,	....	0·8172	,,	,,
,, 26 days' ,,	....	2·139	,,	,,

Measurements of hydrogen evolved were also made. In one experiment, 500 grams of clean, fine iron borings were placed in a flask of 2400 c.c. capacity, and the flask and leading tube were subsequently filled with a solution of carbonic acid saturated at 18°. At the end of seven days, 635 c.c. of hydrogen had been collected, and the gas was still being slowly evolved when the experiment was stopped at the end of three weeks. In the absence of air, the solution remained perfectly clear and colourless, but on boiling a green precipitate was formed. This precipitate effervesced with acids, turned red on exposure to air, and gave all the reactions of ferrous carbonate, so that the iron when in solution must have existed as ferrous bicarbonate. The solution was readily decomposed by atmospheric oxygen, yielding a mixture of ferrous carbonate and ferrous and ferric hydroxides, part of the carbonic acid being simultaneously regenerated. On account of the ease with which this change takes place it follows that, in presence of air, a definite weight of carbonic acid will exert a greater corrosive influence on iron than will an equivalent quantity of hydrochloric or sulphuric acid.

Influence of Substances on the Rusting of Iron.

It is not necessary to attribute the inhibiting effects on rusting of such compounds as the alkalis, sodium nitrite, and potassium ferrocyanide to the power they possess of decomposing hydrogen peroxide, for it has been shown that these compounds interact with carbonic acid (*Proc.*, 1903, **19**, 157, 239). Moreover, some substances, such as potassium iodide, which destroy hydrogen peroxide, do not inhibit but actually accelerate rusting. Whilst it is true that a small mass of iron remains bright in a large volume of one per cent. chromium trioxide, nevertheless, iron slowly passes into solution and may be precipitated by the addition of ammonia. If the ratio of iron to chromium trioxide is great, brown ferric hydroxide separates from the solution in the course of a few weeks. Chromic acid, which does not attack iron, appears all the more to exert a protecting influence on the metal because of the ease with which it dissolves ferrous carbonate and ferrous and ferric hydroxides. In solutions exposed to air and containing not more than 0·1 per cent. of chromium trioxide, iron rusts very rapidly, although such solutions react strongly with hydrogen peroxide.

It is assumed by Dunstan that chromic acid and potassium dichromate prevent the rusting of iron because they decompose and therefore interfere with the existence of hydrogen peroxide, which he regards as an intermediate product of rusting. If this form of argument were valid, the inhibiting power of the substances named might equally well be ascribed to their power of decomposing and, therefore, interfering with the existence of ferrous carbonate which, as has been shown, is immediately formed by the interaction of iron and water containing carbonic acid. Like chromic acid, nitric acid may be said to prevent rusting, for a sheet of iron half exposed to air and half immersed in the strong acid remains perfectly bright. A solution of hydrogen peroxide, free from acid, behaves similarly, and it might not unreasonably be suggested that the inhibiting effect results from the power of each of these substances to destroy ferrous carbonate.

Action of Hydrogen Peroxide on Iron.

According to Dunstan, when iron is placed in hydrogen peroxide solution the metal is rapidly oxidised with formation of a substance identical with natural rust, and which, when dried, has the formula $Fe_2O_2(OH)_2$. In his experiments, Dunstan used commercial hydrogen peroxide, but he appears to have been unaware that commercial preparations of hydrogen peroxide are highly impure. I have examined a large number of specimens from various sources and find that every one contains free hydrochloric acid. Many samples also contain phosphoric acid and other impurities. In presence of hydrochloric acid, which energetically attacks iron, and of the powerful oxidising agent, hydrogen peroxide, there is nothing remarkable in the formation of hydrated ferric oxide, but it appeared of interest to compare the behaviour of iron towards hydrogen peroxide solution containing no free acid. Distilled hydrogen peroxide was therefore diluted with unboiled distilled water to 20-volume strength, and a small cylinder of polished iron was introduced. The surface of the metal immediately became covered with bubbles of gas and a slow but steady stream of oxygen escaped from the solution, but no formation of brown oxide could be observed. The experiment was repeated in glass tubes, the open ends of which were drawn out to capillaries bent twice at right angles and terminating under mercury seals. In every case the evolution of oxygen from the surface of the metal continued for from nine to fourteen weeks, at the end of which time the solution failed to decolorise an acid solution of potassium permanganate. During these periods the surface of the metal was exposed to hydrogen peroxide, and was also surface-swept by oxygen in presence of water without the least sign of rust appearing or of the iron undergoing any change in weight or in appearance, thus affording conclusive evidence as to the indifference of iron not only towards hydrogen peroxide, but also towards oxygen in presence of water.

The experiments recorded in this paper conclusively show that oxygen is unable to oxidise iron directly in presence of water, but that when a minute quantity of carbonic acid, such as is contained in air, is present, absorption of oxygen takes place. The explanation of rusting as a process involving the production of hydrogen peroxide, as advanced by Dunstan, is refuted, not only by the complete indifference of iron towards oxygen in presence of water, but also by the composition of rust in actual formation and by the fact that hydrogen peroxide, when free from acid, does not oxidise iron.

On the other hand, the ready interaction of iron and carbonic acid —which exists in all natural waters—resulting in the formation of hydrogen and ferrous salt, affords a satisfactory explanation of the first stage of rusting, which is followed by a more or less complete oxidation of ferrous salt by atmospheric oxygen leading to the production of rust, the composition of which is variable and dependent on the extent to which oxidation of ferrous salt has taken place.

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