109. *The Electrochemistry of the Rusting Process along a Scratch-line on Iron.*

By R. S. THORNHILL and U. R. EVANS.

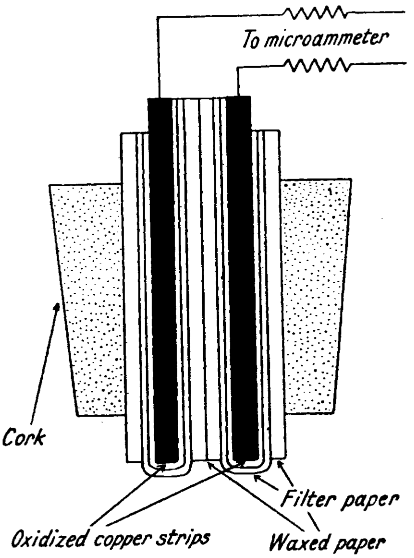
An apparatus is described which permits the measurement of electric currents passing around a scratch-line on iron covered with filter-paper soaked in bicarbonate solution; a fraction of the current is diverted through two nearly non-polarising electrodes to a galvanometer, and calibration on a second paper through which known currents are passed gives the relation between the galvanometer readings and the true current flowing through the first paper. The relation between the current and the corrosion produced suggests that the corrosion is mainly or wholly electrochemical. Ferrous ions are formed in the early stages, in amount corresponding approximately to the current passing; later, electrochemical oxidation of ferrous to ferric iron appears to set in, increasing the current in relation to the corrosion velocity.

IN previous papers (Evans, Bannister, and Britton, *Proc. Roy. Soc.*, 1931, *A*, **131**, 355; Evans and Hoar, *ibid.*, 1932, *A*, **137**, 343), the electric currents flowing between different regions of rusting iron were found to account quantitatively for the corrosion produced; but hitherto such tests have depended, directly or indirectly, on the cutting of the metal along the boundary of the anodic region. It would seem important to make a comparison between current and corrosion during natural corrosion *without cutting the specimen*, and an improved form of the apparatus introduced for detecting currents flowing around a scratch-line (Evans, *Nature*, 1935, **136**, 792) has made this possible.

When a single scratch-line is engraved on the surface of iron (previously exposed to air after abrasion), and a piece of filter-paper soaked in sodium bicarbonate solution of suitable concentration is laid on to the surface, rusting will take place along the scratch-line, whilst the region around will remain free from corrosion. This simple distribution of attack requires the correct concentration of bicarbonate and a suitable form of iron. Concentrated solutions render the whole surface passive, probably because ferrous bicarbonate is sparingly soluble in concentrated sodium bicarbonate, and very dilute solutions produce attack at numerous other points; but at intermediate concentrations (usually 0·1—0·06N) the corrosion is confined to the most susceptible region, which, on iron of uniform quality, will usually be the scratch-line. The exact concentration needed to produce attack along the scratch-line depends on the previous history of the iron; the probability of corrosion diminishes with the length of pre-exposure of the scratch to air (Mears and Evans, *Trans. Faraday Soc.*, 1935, **31**, 532), and consequently a more dilute solution is needed to produce attack along a scratch-line which is not freshly engraved, increasing the danger of undesired corrosion elsewhere. A long period of storage between the abrasion of the whole surface and the production of the scratch-line is also found to necessitate an increased dilution, probably because the engraving of a scratch, whilst removing much of the air-formed oxide film, pushes down a portion into the groove—for which there is other evidence (Evans, Iron and Steel Institute Corrosion Committee, 5th Report, 1938).

The proper choice of iron is equally important if corrosion is to occur along the whole length of the scratch-line and not elsewhere. Carbonyl iron sheet, despite its purity, was found to be unsatisfactory, on account of either its softness or its slight porosity. The material chosen for the present experiments was the iron forming the basis of the "ferro-type" sheets used in photography, which contained C, 0·115; Mn, 0·35; Si, 0·045; S, 0·020; P, 0·072; Cr, 0·050%. This iron gave the desired distribution of attack, although the exact concentration required to confine attack to the scratch-line varied from sheet to sheet; the corrosion rate also varied, but this did not affect the object of the research, since the current generated by a given specimen was always compared with the corrosion produced on the *same* specimen. The sheets were abraded with French emery Hubert No. 3, and cut into squares 2·5 × 2·5 cm., which were kept in a desiccator for at least a week before being used. Even on this material, rust sometimes appeared at or near the cut edges of the squares; this could only be avoided by using concentrations so high that parts of the scratch-line failed to be attacked. The outlying regions of attack did not interfere with the measurement of the electric currents around the scratch-line, but they prevented the estimation of corrosion based on determination of the weight loss of the specimen, and it was necessary to estimate the attack by igniting the filter-paper after trimming off the rusty patches at the edges, and weighing the ferric oxide. This method of estimating corrosion was checked with the loss of weight of the specimen by means of separate experiments in which the outlying rusted areas were *not* cut off, agreement being obtained to within the balance error; the greatest difference in seven experiments was ± 5%.

FIG. 1.

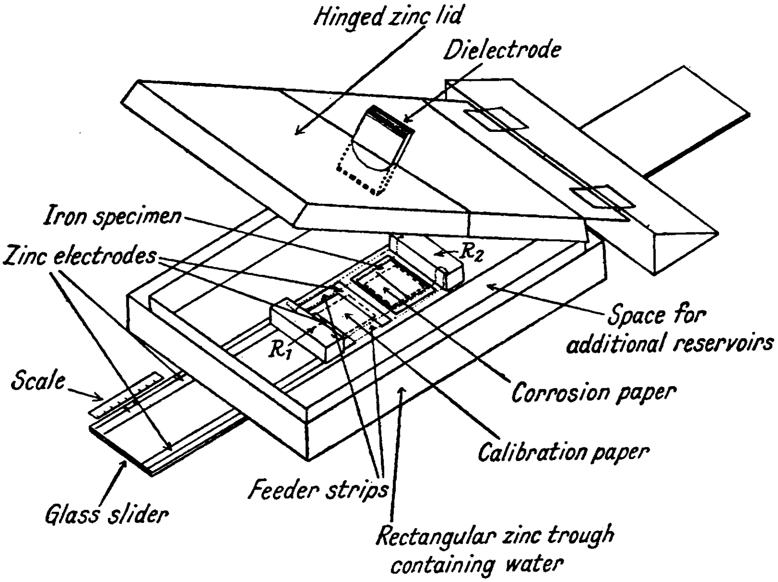


EXPERIMENTAL.

Apparatus.—The electrical measurements depend on diverting through a galvanometer a *small fraction* of the current flowing along the wetted filter-paper, by way of a pair of copper–copper oxide electrodes (sufficiently free from polarisation for the purpose), so as to tap and return the current along two lines 2 mm. apart, the device being known as a "dielectrode." In constructing a dielectrode (Fig. 1), two strips measuring 6 × 2 cm. are cut from copper sheet previously abraded with Hubert No. 3. French emery, wiped with cotton-wool, and heated uniformly in a mildly oxidising gas flame until the last of the interference colours disappears. When cool, each is wrapped twice with a strip of filter-paper 2 cm. wide, a piece of waxed paper (2 × 6 cm.) is placed on each face, and the whole assemblage is joined together by applying wax along the longer edges. Two of the packs thus formed, placed face to face with the lower ends level, and fixed in position between two halves of a longitudinally cut cork, constitute a dielectrode. The current picked up by the dielectrode is measured by means of a Weston galvanometer Model 440 of 154 ohms resistance (1 divison = $0{\cdot}25 \times 10^{-6}$ amp.).

Since the fraction of current diverted by a dielectrode tends to vary with time, it is necessary to provide for continuous calibration against known currents. An essential condition for accuracy is that the paper along which the calibration currents are passed must be identical in " wetness " and concentration with the paper over which the natural corrosion currents are flowing. The calibration current is made to pass through a square of wet filter-paper, the electrodes being two L-shaped strips of zinc cemented to the waxed glass slider shown in Fig. 2. This filter paper (known as the " calibration paper ") must rest on a smooth wax surface, level with the zinc electrodes. The calibration current is provided by an accumulator, joined to the two ends of a 140-ohm sliding resistance, so as to provide any *E.M.F.* between 0 and 2·0 volts; it is measured with a Ferranti microammeter (250—0—250 microamps.), itself calibrated against other instruments. The iron square carrying the scratch-line is sealed into a depression in the wax, so that the filter paper covering it (known as the " corrosion paper ") is in the plane of the calibration paper. Both corrosion paper and calibration paper consist of Swedish filter-paper 2 cm. square. Two waxed celluloid boxes R_1 and R_2 are attached to the slider by wax and contain cotton-wool soaked in sodium bicarbonate solution. These serve as reservoirs, for both the calibration paper and the corrosion paper. To prevent evaporation, the specimen and reservoirs are enclosed in a flat zinc box; the " lid " of the box, which carries the dielectrode, is fixed to a hinged frame and fits into a rectangular zinc trough forming a water-seal, so that the raising and lowering of the dielectrode through 3 mm. does not give access to the atmosphere. The humidity inside the box is maintained by two additional reservoirs containing moist cotton-wool; these are not shown in the diagram.

Fig. 2.



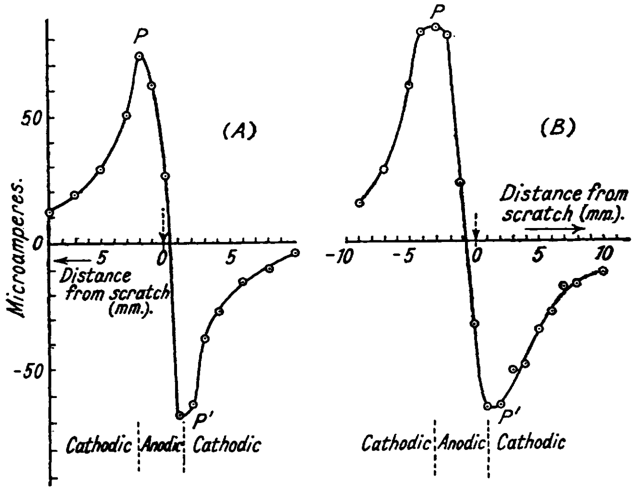
The two boxes R_1 and R_2, filled with sodium bicarbonate solution, are connected together by two feeder-strips of filter-paper running along the edges of the slider. The feeders are joined, when the specimen is in position, to the calibration and the corrosion paper by narrow fibres of filter-paper. When the dielectrode is not in use, it rests on a waxed celluloid bridge over which passes another strip of filter paper in contact with the feeder strips. This arrangement ensures (1) that the essential parts of the apparatus remain at the same degree of wetness throughout the experiment, and (2) that the soluble corrosion product, *i.e.*, ferrous bicarbonate, is not swept away from the scratch by liquid flowing between R_1 and R_2. (Such sweeping—which gave trouble in early experiments—can be practically eliminated by allowing an hour for the two reservoirs to come into hydrostatic equilibrium before an experiment is started.)

Procedure.—For each experiment, a square of iron is engraved with a single central scratch-line (parallel to the abrasion marks), with the Mears–Ward Machine (*J. Soc. Chem. Ind.*, **1934**, **53**, 382T) under a load of 500 g. The specimen is next fixed on the slider with wax, the calibration and corrosion papers, previously soaked in solution, are placed in position, and at least 5 minutes are allowed for the rust line to develop, before any readings are taken.

The dielectrode is first calibrated. A current of 20 microamps. is passed through the calibration paper, the dielectrode is brought down momentarily, and the deflexion of the galvanometer noted. The current is reversed, and the deflexion again noted. This is repeated in turn at + 40, — 40, + 60, — 60, + 40, — 40, + 20, — 20 microamps. In plotting a calibration curve, each galvanometer reading is corrected by deducting the mean of the two " zero readings " obtained with the dielectrode raised before and after the reading in question.

The variation of corrosion current with distance from the scratch is then measured by moving the slider forward 1 mm. at a time, the dielectrode being brought down in each position for just sufficient time to read the galvanometer; the mean of the two zero readings is deducted, as described above. In this way the whole specimen is traversed, first in one direction and then in the other. The dielectrode is re-calibrated after each traverse. Some typical curves showing the distribution of current around the scratch-line are reproduced in Fig. 3; areas where the curve slopes downwards to the right are anodic, whilst those sloping upwards to the right are cathodic; the asymmetry, displayed in the curves published earlier (Evans, *Nature*, **1935**, **136**, 732), is found on some specimens, but not on all. Fig. 3*B* refers to the same square as 3*A*, but to a later stage of the corrosion; it will be noted that the anodic area tends to extend with time—a fact also indicated by the spread of the etched area on the metal.

FIG. 3.



During an experiment lasting one hour, three determinations are made of the current at the points (*P* and *P'*) between the anodic and the cathodic areas; in longer experiments, six determinations are made. By plotting these currents against time, an estimate of the total coulombs furnished is obtained.

After each experiment, the filter paper carrying the rust formed along the scratch-line is removed from the specimen and any subsidiary rust spots are cut off and rejected. Any loose or soluble product on the metal is wiped off with a second (smaller) piece of filter-paper. The two fragments of paper are left overnight in air containing ammonia vapour to precipitate any soluble iron compounds and are then washed free from sodium salts (colorimetric estimation of the iron in the wash-water with thiocyanate showed it to be about 0·00001 g., which can be neglected). The papers are then ignited in a silica crucible, cooled, and weighed on a balance sensitive to 10^{-5} g., Gauss's method being employed.

Influence of Material chosen as Support for the Calibration Paper.—Since at least part of the current flows along the layer of liquid shut in *below* the calibration paper, it was feared that the material chosen as support might affect the thickness of this layer and consequently the relation between the galvanometer reading and the true current strength; this would vitiate the accuracy of calibration, since the calibration and corrosion papers *cannot* rest on the same material (the former *must* rest on a non-conductor, and the latter on iron). Accordingly, comparative experiments were carried out with calibration papers resting on four different bases, *viz.*, celluloid, wax, glass, and mica. The relation between the current flowing through the paper and that tapped through the galvanometer was found to be independent of the basis material (Fig. 4).

FIG. 4.

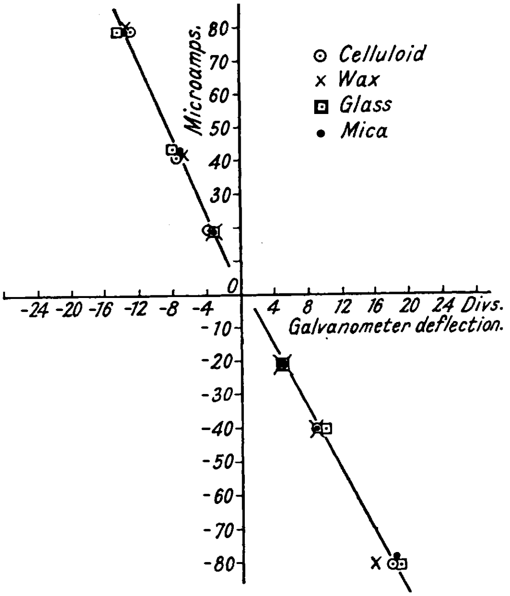
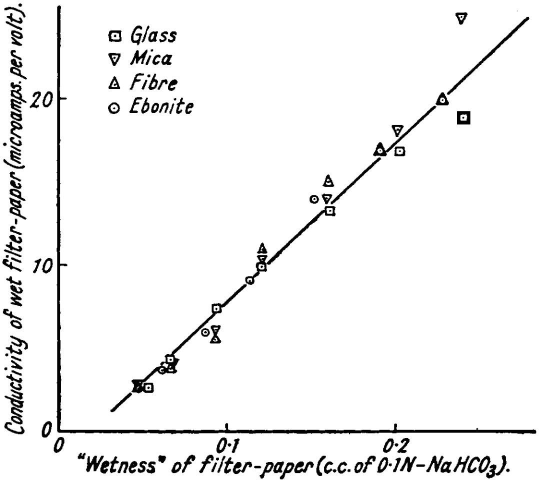


FIG. 5.



In other experiments the applied voltage E was plotted against the current i for various degrees of wetness of the strip as measured by the number of c.c. of bicarbonate solution dropped on it. When i/E was plotted against wetness, the points for all the bases tested (fibre, ebonite, glass, and mica) followed the same straight line (Fig. 5). It was concluded that the basis material makes no serious difference to the measurements, and that the choice is one of convenience; in the actual experiments, wax was used.

Influence of the Fraction of Current shunted through Measuring Circuit.—The method of measurement involves the diversion of a certain fraction of the current which would otherwise flow through the corrosion paper; clearly, if this fraction is excessive the estimate of current obtained will differ from that which would be flowing had no diversion taken place. To ascertain whether the proportion shunted was too great, three sets of comparative experiments were conducted, each for 12 hours with 0·06N-sodium bicarbonate (*a*) with about 8% of the current shunted, and (*b*) with only about 4% shunted (this was obtained by introducing a resistance of 5000 ohms into the galvanometer circuit); the calibration curve of (*a*) was, of course, about half as steep as that of (*b*). The numbers obtained for the current (see Table) were, within the limits of accuracy, the same, suggesting that the shunting of current, up to 8%, does not greatly disturb the situation. It was, however, found inadvisable to keep the dielectrode in contact with the corrosion paper for longer than was absolutely necessary to obtain a reading; otherwise polarisation occurs.

Comparison between the number of coulombs calculated when different fractions of the current were diverted.

Added resistance of galvanometer circuit, ohms	Nil	5000
Fraction of current diverted, %	8	4
Experiment 1	1·08	1·13
„ 2	1·26	1·25
„ 3	1·13	1·12

Time Limits of Accuracy of Experiment.—As the amount of iron corroded by a scratch 2 cm. long is of the order of 0·1 mg. per hour, experiments lasting less than an hour will be inaccurate owing to the balance error. An upper time limit is fixed by the fact that in lengthy experiments the accumulation of rust will render the resistance of the corrosion paper slightly higher than that of the calibration paper, destroying the conditions requisite for accuracy. To ascertain when this error becomes serious, pieces of soaked filter-paper were placed for different times on squares of iron each bearing a scratch-line, and were then removed to a wax support and used as calibration papers. If the period of rusting was less than 40 hours, the same reading was obtained (for a given current) whether the dielectrode was brought down on the rust-line or elsewhere; but after longer periods, a slightly higher reading was obtained on the rust-line, because the increased resistance deflected an undue proportion of current through the measuring circuit. In actual experiments, the error would probably become perceptible somewhat earlier, because the test just described neglects the obstruction due to membranous rust extending across the liquid layer between filter-paper and metal, which is left behind when the filter-paper is transferred to the wax. It is believed, however, that for experiments not exceeding 12 hours, this particular error will be imperceptible.

A more serious error affecting long-continued experiments is caused by redeposition of iron as hydrated magnetite on the cathodic areas when the iron salts from the anodic areas reach these regions. Although paper soaked in bicarbonate on iron for periods up to 24 hours *without measurement of current* left no visible matter on the metallic surface, those in which the current had been measured often left a black or green stain on the cathodic region which cannot easily be removed by the ordinary cleaning methods, *e.g.*, cathodic treatment in citric acid (Evans and Hoar, *loc. cit.*, p. 346). Probably the slight pumping action produced when the dielectrode is brought down on to the filter-paper and raised again, helps the iron salts from the anodic scratch-line to reach the cathodic portions, and thus promotes partial redeposition. A similar dark mark is produced if a crystal of ferrous sulphate is placed on a piece of iron carrying a filter-paper soaked in sodium bicarbonate, whilst a black or dark green deposit is formed at the water-line on strips of iron partly immersed vertically in sodium bicarbonate. These deposits are almost certainly magnetite, partly hydrated, and their formation is easily understood. In the absence of iron salts, the only possible cathodic reaction is the deposition of hydrogen ions (or perhaps sodium ions), with immediate oxidation by atmospheric oxygen to water (and perhaps hydrogen peroxide) along with alkali. But when once iron ions have reached the cathodic area, they can also take part in the cathodic reaction, being similarly depolarised by oxygen to form oxides of iron. Once this has occurred in an experiment on iron engraved with a scratch-line, a deficiency of corrosion product in the filter-paper is to be expected. It is believed that this error is not appreciable in experiments that last less than 6 hours, certainly not in experiments lasting 3 hours.

RESULTS AND INTERPRETATION.

Fifty experiments were carried out in the three main series, the results being plotted in Figs. 6, 7, and 8; each point represents a separate experiment and is based on 20—40 different readings, involving the plotting of 6—12 calibration curves.

The experiments of Series A (Fig. 6) were conducted in the open laboratory. Correspondence between current and corrosion should not be affected by fluctuation of temperature in point of *time*, but inconstancy in point of *space* might possibly lead to " distillation " of liquid from one point to another, and thus disturb accuracy of calibration. Series B and C (Figs. 7 and 8) were therefore carried out in an air thermostat at 25°, and in Series C steps were taken to prevent the external air current from passing over the water in the water-seal, which might cause slight local cooling through evaporation. This final series was confined to experiments lasting for periods up to 3 hours, since it was desired to avoid the risk of the errors mentioned above, which affect long-period experiments; the experiments of series A and B included periods up to 12 hours.

Faraday's law indicates that one coulomb should correspond to 0·29 mg. of iron, if the anodic attack yields only *ferrous* salts, but only 0·19 mg. if *ferric* salts alone are produced, or if the *subsequent oxidation* of ferrous to ferric iron occurs as an electrochemical process. Most of the numbers lie between these limits (indicated by the oblique lines of Figs. 6, 7, and 8) or just outside them; the shorter experiments correspond to higher ratios of milligrams to coulombs than the longer ones. It is concluded that ferrous salts are formed in the early stages in amount corresponding almost quantitatively to the current passing, but as the ferrous salts accumulate in the scratch-line, they become oxidised electrochemically to ferric salts, producing extra current so that the corrosion per coulomb diminishes.

FIG. 6.

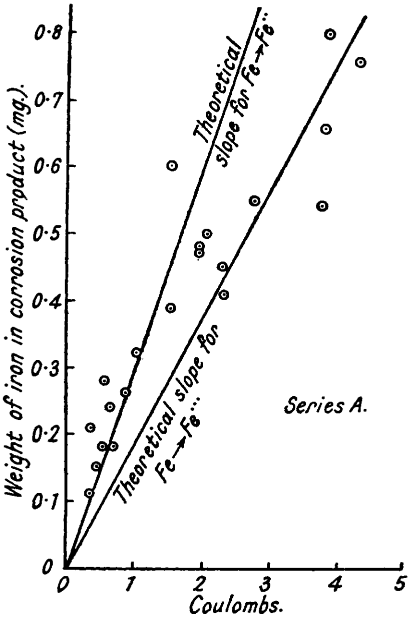


FIG. 7.

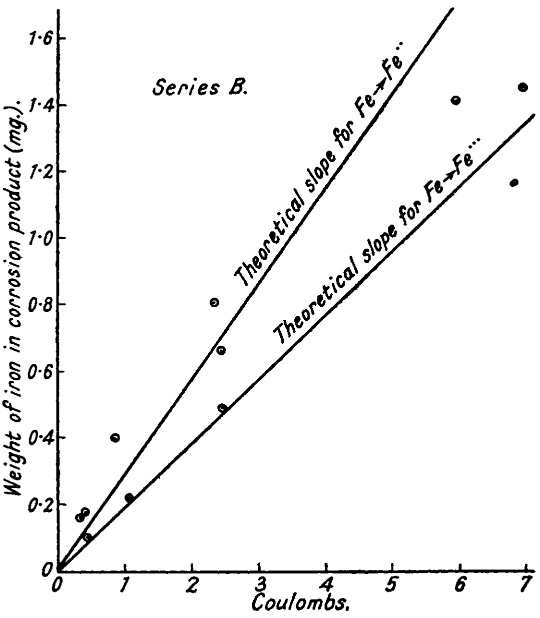
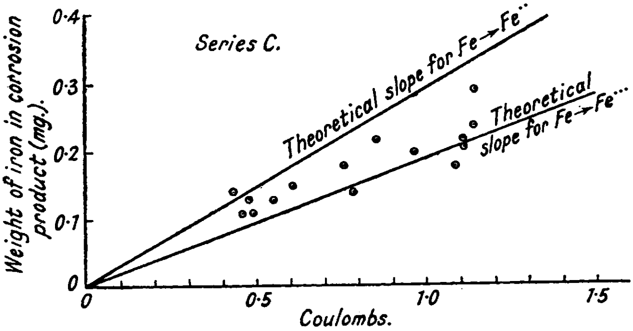


FIG. 8.



That current can be generated by the oxidation of ferrous compounds (at the anode) through atmospheric oxygen (taken up at the cathode) is proved by experiments on the cell

Ag | $NaHCO_3$ (N/16); $FeSO_4$ (N/100) (air excluded) | $NaHCO_3$ (N/16); Na_2SO_4 (N/100) (air admitted) | Ag.

Three such cells furnished a current of 26—29 microamps. (falling gradually to 10—14 microamps. in 10·5 hours). This current must be produced by oxidation of the ferrous compound, since three "blank" cells,

Ag | $NaHCO_3$ (N/16); Na_2SO_4 (N/100) (air excluded) | $NaHCO_3$ (N/16); Na_2SO_4 (N/100) (air admitted) | Ag,

gave no measurable current during the same period. The anodic production of ferric iron was confirmed by the fact that the silver anodes removed from the three cells containing ferrous sulphate were found to be covered with a golden varnish-like film of ferric hydroxide (the oxidation of 3 molecules of ferrous sulphate should give 2 molecules of ferric sulphate and one of ferric hydroxide).

The electrochemical formation of *ferric* compounds at a dissolving iron anode under conditions when the accumulating ferrous compounds were prevented from being swept away from the electrode was shown by W. J. Müller and Löw (*Z. Elektrochem.*, 1934, **40**, 575) to occur when the potential exceeded a certain value. Their experiments were made in cells fed with *current from an external source.* It has hitherto been assumed that in the cells present on *naturally corroding* iron (which *generate their own currents*), ferrous compounds are formed *electrochemically* and are then oxidised *chemically* by atmospheric oxygen to give rust. Doubtless this normally occurs, but, in the corrosion produced by soaked filter-paper on iron, the accumulation of ferrous products at the anode will be favourable for their electrochemical oxidation, and, by providing a surplus current, may lead to lower values for the ratio of milligrams to coulombs.

The measurements do not absolutely exclude the possibility of direct chemical attack on the metal in the early stages. If, for instance, it were assumed that ferric compounds were produced electrochemically from the outset, then the current would account for little more than half the total corrosion in the earliest stages. The fact that a rust-line appears in a few minutes actually shows that ferric compounds are formed in the early stages, but this is almost certainly due to the oxidation of ferrous compounds by the air. If it were to be assumed that ferric iron is exclusively produced by electrochemical action from the outset, it must also be assumed that there is less direct chemical attack on the metal in the later stages than in the early stages—which is extremely unlikely, since, as already stated, the attacked area extends with time. The rational explanation is that from the commencement the greater part of the attack is electrochemical, with the formation of ferrous compounds in the early stages and ferric compounds later. The high values for the shorter experiments in Series A and B were probably due to errors, since they were not obtained for corresponding periods in the more accurate experiments of Series C.

CONCLUSION.

The corrosion occurring around a scratch-line on iron covered with bicarbonate-soaked paper appears to be *mainly or wholly electrochemical in character,* ferrous compounds being formed in the early stages, in amount roughly corresponding to the current passing; as these accumulate, they are oxidised electrochemically to ferric salts, increasing the amount of current in relation to the corrosion-rate.

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THE METALLURGICAL LABORATORIES, CAMBRIDGE UNIVERSITY. [*Received, January 28th,* 1938.]