XVII.—*The Mechanism of Corrosion.*

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THE present paper describes a study of the corrosion of partly immersed specimens of zinc, iron, steel, aluminium, and copper in potassium chloride and sulphate solutions, with special reference to the thin films which give rise to interference colours in certain parts of the specimens. Hitherto these colours have been regarded as the result of direct oxidation of metal where the original film has been rendered pervious by cathodic or incipient anodic action; but the fact that the second-order colours are far brighter than the second-order " temper colours " produced by heating in air, suggests that they are really due to precipitated hydroxide, not anhydrous oxide. The films commonly found on the glass surface of vessels in which iron specimens have been corroded—although showing the ordinary rusty yellow colour of ferric hydroxide by scattered light—show similar bright high-order colours by regularly reflected light; these films on glass must be produced by precipitation or hydrolysis, and it appears probable that the colours formed on the metal itself are due to soluble iron salts diffusing through the original protective skin into a liquid containing excess of alkali, which precipitates the iron as a uniform film of hydroxide as it emerges. This view is supported by observations on copper and aluminium, where similar colours pass continuously into thicker, less uniform, deposits which are undoubtedly formed by interaction of soluble copper or aluminium salts with the cathodically formed alkali. The idea that the tints on iron are due to hydroxide was first suggested to the author by Professor Fearnsides.

The colour sequence is always essentially the same as that observed in the case of silver iodide films on silver. The colours belonging to different " orders " may be distinguished by Roman numerals, thus: yellowish-brown I, reddish-mauve I, deep blue I, greenish-blue I, steely silver, (hiatus), yellow II, red II, blue II, green II, yellow III, red III, green III, red IV, green IV, red V. On zinc and aluminium, partly owing to the transparent character of the film substance, the early colours are weak, for reasons given elsewhere (*Chem. Ind.*, 1926, **45**, 213). In general, the colours cannot be seen when the specimens are in the liquid, and a new procedure was therefore adopted. Numerous identical specimens, which had been simultaneously submitted to corrosion, were successively withdrawn, washed, dried, and examined microscopically. The series thus produced provided a narrative of the various changes, which revealed many facts previously overlooked.

Eight materials have been examined—electrolytic zinc, commercial zinc, electrolytic iron (two varieties), steel (two varieties), aluminium, and copper—the analyses being given in the preceding paper. These were studied under numerous different surface conditions; the description " rolled surface " denotes the original rolled metal, washed with benzene and alcohol but not abraded, and the terms " coarsely ground," " finely ground," and " very finely ground " imply abrasion with emery paper No. 2 (Oakey), No. 1 (French), and No. 000 (French), respectively. Two liquids were employed, *viz.*, $M/10$-potassium chloride and $M/10$-potassium sulphate.

Qualitative Results.

In the description of the qualitative work, the term " partly immersed strips " is used to denote strips about 6 cms. long and 2 cms. wide, placed in glass vessels at an angle of 70° and immersed to a depth of 4 cms., the four corners resting against the glass. Only a bare summary of the results obtained from several hundreds of specimens can be given.

Zinc.—Finely ground, very finely ground, or rolled specimens in $M/10$-potassium sulphate soon develop tiny white spots at " weak points " distributed in the manner indicated in a former paper, and from these spots descend narrow ribbons of adherent white matter; the whiteness (seen by scattered light) is most intense at the point of origin, indicating that the deposit is here thickest (the sequence of interference tints, when visible, confirms this).

During the first 40 minutes after immersion, all this white matter is *adherent* ; no cloudiness is produced in the liquid. The cause is clear. Over an area of weakness, the film is virtually porous, and at each pore the exposed zinc is anodic towards the oxidised neighbouring metal; the anodic and cathodic products, zinc sulphate and potassium hydroxide, thus appear side by side and interact so close to the metallic surface that the zinc hydroxide adheres to it. The deposit of zinc hydroxide will clearly not at first be of uniform thickness, and at low thicknesses, interference tints are not conspicuous, but as the deposit develops, the thickness naturally becomes more equal and the later tints can usually be seen, provided that the surface conditions be suitable; on very finely ground zinc, the earliest colours from yellowish-brown I upwards have been detected. The deposit of precipitated hydroxide shields the metal below from the repairing action of oxygen, thus assisting the corrosive action to spread, particularly in the direction of low oxygen concentration. Hence the whitened area extends downwards. But, clearly, when the adherent zinc hydroxide covers any considerable area, it will prevent any cathodic reaction on that

area, since such a reaction requires oxygen; it is evident that the alkali must now come from the uncovered zinc outside the whitened area. Consequently there is produced along the borders of the white streak a membranous wall of zinc hydroxide, growing *outwards at right angles to the metallic surface* and enclosing the white streak like the finger of a glove; simultaneously, the liquid begins to be cloudy, and finally a precipitate, formed by interaction of zinc sulphate and potassium hydroxide which have met far away from the metallic surface, begins to settle to the bottom of the containing vessel.

Outside the membranous wall of zinc hydroxide, alkali is now in excess. Any leakage of zinc sulphate through imperfections of the skin will here produce an adherent film accurately parallel to the metallic surface, which will therefore be less white by scattered light, but will show better interference tints by reflected light than the adherent deposit produced within the membranous wall. Thus we get a series of coloured bands running parallel to the membranous wall and just outside it, the colours indicating that the film is thickest next to the wall, and especially at the parts nearest to the original area of weakness.

We must, therefore, distinguish four different types of zinc hydroxide, all produced by precipitation where zinc sulphate and potassium hydroxide meet :

Type A, produced when zinc sulphate and potassium hydroxide are formed at numerous points side by side on the metallic surface; this is closely adherent, not removed by rubbing, very white (by scattered light), but showing only poor interference tints or none at all.

Type B, produced when zinc sulphate and potassium hydroxide are formed over two separate areas; it constitutes a membranous wall at right angles to the metallic surface, following the junction of these areas; it adheres weakly to the metal, being easily rubbed off, and leaving simply a whitish line to show where the wall has been.

Type C, produced when zinc sulphate and potassium hydroxide meet far from the metallic surface; it is a flocculent precipitate, and sinks to the bottom of the vessel, or rests as a loose non-adherent blanket on the lower part of the specimen.

Type D, produced when zinc sulphate oozes through a defective oxide skin into liquid containing potassium hydroxide in excess; it constitutes a very regular film, with good interference tints, and only showing whiteness when it reaches considerable thickness.

The corrosion which commences simultaneously at numerous weak spots (especially on or near the cut edges) doubtless uses up

much dissolved oxygen at the cathodic areas; the repairing power is thus impaired, and so streaks of zinc hydroxide commence to descend from fresh points higher up; these streaks usually broaden as they descend. Also at the bottom of the specimen, where oxygen becomes completely exhausted, a continuous whitened region appears bounded by a horizontal upper boundary, which advances steadily upwards with the time. Within a day from the start, nearly the whole surface has become covered with zinc hydroxide, with the exception of a narrow area near the water line; this is separated from the corroded area below by the sinuous " mantle " formed by the union of the membranous fingers mentioned above; frequently the tops (domes) of the mantle touch the water level. In general, the greater part of the area below the mantle suffers corrosion in the later stages, being covered with a blanket of precipitated zinc hydroxide which shuts off the supply of repairing oxygen. Samples of the pure zinc with a very finely ground surface show in the later stages microscopic grey points arranged along the abrasion lines; these are points where the zinc has been so much corroded that the original whitened surface has disappeared, and they become more and more frequent as the original areas of weakness are approached, becoming there practically continuous.

The portion above the mantle constitutes the cathodic zone in the final stages, and suffers comparatively little corrosion. A series of little white points appears along the water line itself—a place where a protective film usually breaks down—but, doubtless owing to the good supply of repairing oxygen and of alkali, the amount of corrosion here is trivial. A small amount of adherent hydroxide is produced, the white points uniting in the later stages to form a continuous line along the water level, whilst colours spread downwards from the water line as roughly horizontal bands, the sequence indicating that the film is thickest near the top, where blue I or even red II is commonly reached. A thin scum of membranous zinc hydroxide is often seen floating on the water surface.

In the later stages, the alkali produced plentifully over the main cathodic zone causes the liquid to creep up the surface above the water level, and at the top boundary of the area wetted by creepage further small quantities of zinc hydroxide are formed; between this and the water line the surface displays second- or third-order interference tints.

Whilst on rolled zinc and even on finely ground zinc, corrosion commences at well-defined points, on coarsely ground zinc the production of zinc hydroxide is less severely localised, evidently owing to the larger number of weak points. Likewise, in $M/10$-potassium chloride solution, the corrosion product has a rather more diffuse

aspect than in sulphate solution; thus, finely ground specimens of the commercial zinc in chloride solution somewhat resemble coarsely ground zinc in sulphate solution.   The corrosion extends less quickly than in a sulphate solution under the same conditions of surface, but seems to commence at a greater number of points.   On finely-ground pure zinc, the final line of the mantle is invariably more sinuous in chloride than in sulphate liquids; the appearance suggests that many weak points which can become effective centres of corrosion in chloride solutions do not function as centres of attack if the larger (SO_4'') anions alone are present.   Pure zinc gives more sharply defined white points than commercial zinc—possibly another sign that impurities aid the extension of the areas affected by the breakdown.

The difference observed between the effect of chloride and sulphate solution is in part due to the different flocculating powers of the two species of anions.   A series of experiments was conducted in which $M/10$-potassium sulphate containing small quantities of alkali ($M/200$) was added in varying amounts to $M/10$-potassium sulphate containing small quantities of zinc sulphate ($M/200$); parallel experiments were carried out with $M/10$-potassium chloride solution.   It was found that, for corresponding proportions, precipitation of zinc hydroxide occurred far more quickly in the sulphate than in the chloride liquid; in order to obtain the same rate of precipitation a smaller amount of alkali was needed in sulphate than in chloride—this is no doubt due to the fact that SO_4'' and OH' ions have a far greater flocculating power than Cl' ions.   Evidently in a sulphate solution we may expect to find zinc hydroxide produced close to the seat of corrosion, whilst in chloride solution the soluble zinc chloride will have to wander further into the alkaline region before yielding a precipitate.   Thus even in the early stages, the corrosion product formed in the chloride solution is largely non-adherent; at a weak point, instead of a dense adherent white spot, we get a somewhat gelatinous " blob " or (in the case of the pure zinc) a loop-shaped membranous wall of zinc hydroxide extending out at right angles to the metallic surface, and enclosing the point of attack on three sides.

Aluminium.—The commencement of corrosion on aluminium is not unlike that on zinc, but since the oxide film is of a protective, self-healing character, the corrosion remains localised at points for a long time instead of becoming general.   The attack develops more quickly in chloride than in sulphate solutions, although in both solutions it is very slow.   In rolled specimens the corrosion product appears as an adherent white deposit at points along blemish-marks, and also at the edges and along the water line; on

abraded specimens there are numerous microscopic white points arranged on the groove-lines. The water-line attack is relatively more important on aluminium than on zinc; the fact that the corrosion over the lower part of the specimen is very slow must mean that the oxygen consumption is low; consequently there is not likely to be an appreciably higher oxygen concentration at the water line than elsewhere, and the special factor militating against water-line attack on zinc is therefore inoperative in the case of aluminium.

The corrosion product (aluminium hydroxide) remains adherent for much longer than in the case of zinc. In sulphate solution, practically the whole is still adherent after 4 days, the liquid being only very slightly cloudy; in chloride solution there is more cloudiness, and near the edges of coarsely abraded specimens, there is some fluffy aluminium hydroxide; after 15 days, there is much settled flocculent precipitate in chloride solutions, and some in sulphate solutions.

On rolled specimens, the adherent corrosion product formed in the early stages constitutes such a uniform layer as to produce interference tints; these commence from the weak points as circles, usually somewhat elongated downwards, the most advanced tints being in the centre; above the first-order tints, the rings show distinct white cloudiness, which is very intense in the centre; when held at the proper angle, the scattered light from the cloudy inner rings shows colours complementary to those seen by regularly reflected light (a common optical phenomenon). One specimen taken out after 4 days in the sulphate solution displayed first-order yellow over the main part of its surface, although the yellow was so faint that it might have escaped notice but for the fact that it passed gradually into the higher colours. The second- and third-order colours visible under the microscope around the points of breakdown are very clear and beautiful; one specimen taken out after 7 days showed the entire sequence from yellowish-brown I to red V around one centre of breakdown. Near the water level the colour rings are very numerous and somewhat elongated in a horizontal direction, sometimes uniting to form bands of colour roughly parallel to the water line.

It is interesting to correlate the results with those observed on zinc. On aluminium, hydroxide of flocculent type C is only produced at a late stage, whilst the membranous type B is usually absent; this allows the two adherent types A and D to pass gradually into one another, instead of being sharply divided at the mantle line as in zinc.

Iron.—The attack on iron commences in a similar manner to

that on zinc. Green points appear near the edges, also on rolling defects, and sometimes on abrasion marks, and spread downwards and to some extent sideways, producing arch-shaped green areas; at first the green deposit is adherent, as on zinc, but after a time a membranous wall (brown on the outside, green within) appears round the edge of each green area, and about the same time cloudiness appears in the solution, a green or brown precipitate finally settling to the bottom. Later, above the membranous wall, bright interference tints appear. Thus four types of corrosion products are obtained, analogous to the types A, B, C, and D obtained with zinc, but the question is complicated by the fact that the product varies from ferroso-ferric hydroxide (green) to ferric oxide (brown) (compare Scholten, *Korrosion u. Metallschutz*, 1928, 4, 73).

The behaviour in chloride and sulphate solutions is much the same, but on steel H 28 there is a greater tendency for streaming to occur from central weak points in chloride solution, whilst in sulphate solution central streaming is seldom observed; the etched areas usually descend in graceful curves from points on the cut edges, whilst at the bottom regional corrosion commences with horizontal boundaries gradually moving upwards. The differences between chloride and sulphate solutions are no doubt due to the greater penetrating power of chlorine ions. On the whole, electrolytic iron behaves like steel, but specimen E 28 shows a greater tendency to the production of central points of streaming than steel H 28, which has a similar thickness; probably this is simply because the steel contains fewer rolling defects. On the other hand, *ceteris paribus*, there is a greater tendency for " healing " to occur when impurities are absent. Thus within an hour of introduction into either sulphate or chloride solution, one series of strips of thin electrolytic iron (E 26) showed streaming from certain surface defects; but corrosion from these points soon ceased to develop, and after 21 hours it was confined to a region at the bottom bounded by a straight horizontal line.

Specimens when taken out always show the corrosion near the water line to be very slight; indeed it is usually impossible to detect the place at which the water level has been. As explained in discussing aluminium, water-line attack only occurs where the corrosion is slow enough to leave the oxygen concentration almost uniform. This may occur, with iron, if corrosion is retarded by the presence of a film-repairer, such as potassium chromate, in the solution, or of chromium in the metal.

Specimens of sand-blasted steel behaved somewhat differently from abraded steel. The sand blasting evidently produces a systematic distribution of weak points, and each becomes marked

by a little tuft of rust. A true mantle is always formed, separating a highly corroded area below from a very slightly corroded area above. The number of tufts of rust per unit area above the mantle is roughly the same as that below, but whereas those below the mantle almost join to form a continuous blanket, those above are of microscopic dimensions. The case is interesting, since it displays superimposition of two effects—those of (1) the original mechanical treatment, and (2) the distribution of oxygen in the liquid.

Copper.—The oxide film on copper is less protective than that present on most other metals; when this is remembered, the observations made on the corrosion of copper in chloride and sulphate solutions fall into line with those on zinc, iron, and aluminium. The behaviour varies greatly with the abrasive treatment used, as was shown by parallel experiments with abrasives of six different degrees of coarseness.

Very finely ground samples of copper placed in potassium chloride solution soon develop sharply-defined brown points, situated mainly near the edges and bottom; those situated in the centre spread out in all directions, but most rapidly downwards, producing little oval areas; the dark matter on these areas is adherent, and specimens taken out at intervals reveal a series of rich but dark interference tints, the colours indicating that the film is thickest near the point of origin; corrosion from weak spots near the edge extends inwards as horizontal streaks following the principal grinding direction, and these also pass through colour changes in the usual sequence. The colours gradually spread until they cover the greater part of the submerged surface; there is no membranous corrosion product, and, as in aluminium, there is a gradual transition from deposits of type A into type D. On the more coarsely ground specimens, dark matter appears as larger irregular patches, with boundaries related to the grinding direction, but rather vaguely defined; this material is somewhat more loosely adherent and discontinuous; the dark patches are surrounded by a paler zone of brownish deposit which exhibits variations of tint probably produced by interference; presumably this corresponds to the type D deposit on zinc, whilst the dark material corresponds to the type A deposit. The pale brown zones spread rapidly over the whole surface, followed by the darker areas, which, in the more coarsely ground specimens in potassium chloride solution, often cover the whole immersed area after 21 hours, apart from a narrow band at the water line. Examination of specimens taken out from chloride solutions has shown that two constituents are present in the adherent deposit, one black and quickly dissolved by very dilute hydrochloric acid, the other red and less quickly dissolved. Presumably these

are respectively cupric and cuprous oxide. Probably the immediate products of corrosion are cuprous chloride and potassium hydroxide, and the former, being sparingly soluble, is acted on by the alkali *in situ*, yielding cuprous oxide, or where oxygen is present in excess, cupric oxide. A certain amount of white cuprous chloride can still be seen in the deposit.

After 3 days a new phenomenon sets in. The dark areas covered with the " Type A " deposit begin to develop a greenish substance upon the dark oxide layer, whilst the liquid becomes cloudy, and finally greenish-grey matter settles to the bottom of the vessel. The green matter appears to be mainly basic cupric chloride, and is probably produced by the action of dissolved oxygen on the cuprous chloride according to the reactions suggested by Bengough and May (*J. Inst. Metals*, 1924, **32**, 115). About the same time, breakdown of the protective film occurs along the water level, where a green line of corrosion product gradually develops, which easily rubs off, revealing bright copper sensibly corroded. The water-line corrosion is most serious on the coarsely ground specimens, but the formation of green matter on the lower part of the surface, and on the bottom of the vessel, is most rapid on finely abraded specimens.

In potassium sulphate solution, the early phenomena are somewhat similar, but the dark deposit extends less quickly over the surface, and in general shows less brilliant colours. In the later stages the deposit appears to contain a greater proportion of the black and less of the red constituent than the deposits formed in chloride solution. Probably the primary products are cuprous sulphate and potassium hydroxide, but the former no doubt begins to decompose before interacting with the alkali, thus accounting for the usually rather " dirty " character of the deposit, and the higher ratio of cupric to cuprous oxide ; the deposit has a whitish appearance when held in certain lights, and this may conceivably be due to small amounts of surviving cuprous sulphate. In contrast with chloride solution, there is even after 30 days no appreciable cloudiness or settled deposit in the vessel, but slight waterline corrosion occurs on the coarsely abraded specimens.

Quantitative Results.

In the quantitative work, the strips were clamped at the dry part above the water line so that they stood vertically and in a central position in beakers 9 cms. high and 4 cms. in diameter ; the metal did not touch the glass (or any solid) anywhere on the immersed area, and except in series B, the specimens were abraded 24 hours before the experiment with No. 1 (French) emery, and

were washed with alcohol, ether, and benzene before being weighed. The glass beakers were themselves placed in a closed copper box sunk in a thermostat bath, and fed continuously with a stream of purified air (or oxygen in sub-series A1). To prevent the otherwise serious loss of heat by radiation from the copper lid, this was covered with asbestos (separated from the copper by a narrow air space), and the whole thermostat, which was electrically stirred, controlled, and heated, was placed in a cupboard with asbestos lining. The last of the 9 vessels comprising the purification train was also placed in the cupboard (the temperature of which differed by only a few degrees from the bath itself), and from this the air passed through a metal coil placed in the bath before it entered the box; it emerged from the box through a water trap.

Every experiment was carried out in duplicate. Each point on the curves shown in Fig. 1 depends on a different pair of specimens, and thus the curves are fairly representative of the whole material, and not of a single piece. (In the oxygen-absorption method, where the complete curve is derived from a single specimen, the points necessarily fall better on a single curve, but it does not follow that the same curve would be given by other specimens.) The agreement between duplicates is often rather poor in the early stages, better in the middle, and extremely poor in the final stages; in the middle stages the variation from the mean is similar to that obtained by Bengough, Stuart, and Lee (*Proc. Roy. Soc.*, 1927, *A*, **116**, 425), who measured the oxygen absorption during the corrosion of horizontal specimens, but in the later stages the reproducibility is very much worse than that obtained by these authors, whose method is greatly to be preferred for obtaining equations connecting corrosion and time. Specimens cut from certain portions of the steel sheet were found to corrode perceptibly more quickly than those taken from other regions. For that reason, specimens to be compared within a single series were taken, as far as possible, from contiguous portions. In this respect Series A and B are not strictly comparable to Series C.

In spite of the valid objections to the partial-immersion method, there are several reasons why the corrosion of partly immersed specimens is specially worthy of quantitative study. (1) Nearly all the conditions which cause serious corrosion in practice are water-line conditions (the margin of drops may be included within the term " water line "). (2) The method ensures a free supply of oxygen to the metal at the water line, and thus it is possible to avoid the unsatisfactory conditions (met with in much of the early work on completely immersed metallic specimens) where several materials, capable of corroding at different rates under conditions

of excess of free oxygen, actually have been found to corrode with the same velocity, this velocity being imposed by the limited rate of supply of dissolved oxygen. (3) If the specimens are clamped above the water line, the disturbing influence of differential aeration around the point of support is avoided. (4) In vertical specimens, the corrosion—although starting locally—usually soon spreads and becomes fairly general; with horizontal specimens, the same spreading occurs, but more gradually. (5) The insoluble corrosion product in vertical specimens is largely precipitated in a non-adherent form, easily removed by wiping; there are no pits to retain the product; in the case of iron and steel, the error caused by the small amount of corrosion product not removable by wiping is probably less than the weighing error.

In the case of zinc, however, the error due to closely adherent matter is still appreciable, for specimens which had been corroded for 24 hours, if rubbed with very fine emery paper until the adherent white matter was removed, lost additional weight; undoubtedly this loss was partly due to the grinding away of metallic zinc, as well as of corrosion product, but the results suggested that the true corrosion loss was distinctly higher (by about 10%) than the loss of weight would suggest. In the 70-hour experiments, the creepage of the cathodically formed alkali above the water line caused the presence of a very large amount of closely adherent corrosion product, so that here the figures for the decrease in weight are valueless as a measure of corrosion. It is likely that the 48-hours results with zinc were slightly vitiated by the same cause. It may be added that experiments extending over several weeks again show a reduction in the error due to adherent product; only a limited amount of corrosion product can adhere, and this becomes continuously less important as the total corrosion increases; the agreement between duplicates also becomes better again, as shown in previous work.

When aluminium was investigated, the error due to adherent matter became so serious that in the early stages the change in weight entirely failed to represent the corrosion. Both in sulphate and chloride solution the alteration in weight was small : in all experiments up to 48 hours, it was less than 1 mg. The corrosion product formed on specimens exposed for short periods (4—14 hours) was such that it was nearly entirely removed on wiping, and consequently the specimens lost weight; but on longer exposure to the corrosive medium (48 hours), the product underwent a change (probably the well-known " ageing " of hydroxides) and became tightly adherent, so that the specimens even after wiping were found to have gained weight. Experiments (not carried out

in a thermostat) extending over several weeks indicated that on long immersion a large amount of loose precipitate of type C was formed, and consequently specimens lost weight again. It is evident that here no conclusions can be drawn from the alterations in weight. The qualitative inspection of specimens, however, makes it quite certain that the corrosion of aluminium is very slow compared to that of zinc and iron. In considering the change in aluminium hydroxide, it is interesting to recall that a change in the physical properties of iron rust occurs on storage (Aston, *Trans. Amer. Electrochem. Soc.*, 1916, **29**, 449), whilst the oxide film produced on aluminium by exposure to air at high temperature also undergoes a spontaneous change very suddenly, becoming impervious to oxygen (Pilling and Bedworth, *J. Inst. Metals*, 1923, **29**, 573).

The results of the quantitative experiments are given in the tables below; the data of Series C are plotted as curves in Fig. 1; the 70-hour experiments are omitted for reason given above.

Series A.

Effects of shape of electrode in (1) oxygen and (2) air.

(All electrodes were cut from steel H 28 and finely abraded. Experiments were conducted for 22 hours at 25·0°.)

Breadth of specimen, cms.	Depth of immersed portion, cms.	Solution.	Loss of weight, mg.	
			(1).	(2).
1·2	3·0	$M/10$-KCl.	9·3 9·7 } 9·5	3·8 4·0 } 3·9
2·4	2·0	,,	14·7 15·5 } 15·1	5·6 5·8 } 5·7
2·4	3·0	,,	16·5 16·6 } 16·5	6·4 7·4 } 6·9
2·4	4·0	,,	16·6 17·4 } 17·0	7·2 7·2 } 7·2
2·4	3·0	$M/20$-KCl.	15·3 16·8 } 16·0	6·6 5·7 } 6·1

Series B.

Effect of abrasive treatment.

(All specimens were cut from electrolytic iron, E 28, ground with different grades of French emery, and corroded for 8 hours at 25·5°. Immersed area = 2·5 × 2·5 cms. in each case. Liquid, $M/10$-K_2SO_4.)

Grade.	Loss of weight, mg.	Grade.	Loss of weight, mg.	Grade.	Loss of weight, mg.
000	3·0 3·0 } 3·0	0	3·1 2·7 } 2·9	2	2·4 2·8 } 2·6
00	2·8 3·1 } 2·9	1	2·5 2·7 } 2·6	3	2·5 2·9 } 2·7

Series C.

Effect of time of immersion.

(Immersed area, 2·5 × 2·5 cms.   Temp. 25·0° ± 0·1°.)

	Electrolytic iron, E 28.		Electrolytic zinc.	
Time, hrs.	$M/10$-KCl.	$M/10$-K$_2$SO$_4$.	$M/10$-KCl.	$M/10$-K$_2$SO$_4$.
1·5	0·4 } 0·7 } 0·5	0·9 } 0·6 } 0·7	1·6 } 1·3 } 1·4	1·2 } 2·1 } 1·6
4	1·1 } 1·1 } 1·1	0·9 } 1·1 } 1·0	3·1 } 3·2 } 3·1	2·5 } 2·8 } 2·6
7	1·9 } 2·2 } 2·0	1·5 } 2·1 } 1·8	6·5 } 6·6 } 6·5	6·7 } 5·5 } 6·1
14	3·6 } 3·1 } 3·3	3·1 } 3·2 } 3·1	9·8 } 9·8 } 9·8	9·7 } 9·0 } 9·3
24	4·8 } 4·9 } 4·8	4·8 } 4·9 } 4·8	15·0 } 16·4 } 15·7	15·2 } 15·8 } 15·5
48	9·1 } 8·2 } 8·6	9·4 } 10·3 } 9·8	29·2 } 26·5 } 27·8	23·3 } 27·9 } 25·6
70	13·0 } 14·1 } 13·5	14·1 } 13·1 } 13·6	34·6 *	16·6 *
			35·0 *	21·0 *

Steel, H 28.

Time, hrs.	$M/10$-KCl.	$M/10$-NaCl.	$M/10$-K$_2$SO$_4$.	$M/10$-MgSO$_4$.
1·5	0·7 } 0·6 } 0·6	0·7 } 0·8 } 0·7	1·2 } 0·6 } 0·9	0·4 } 0·4 } 0·4
4	1·1 } 1·0 } 1·0	—	1·2 } 1·2 } 1·2	—
7	1·9 } 2·2 } 2·0	2·0 } 2·0 } 2·0	2·2 } 2·8 } 2·5	0·6 } 0·6 } 0·6
14	3·6 } 3·6 } 3·6	—	3·5 } 3·6 } 3·5	—
24	5·4 } 5·5 } 5·4	4·4 } 4·9 } 4·6	5·3 } 6·1 } 5·7	1·0 } 1·3 } 1·1
48	9·9 } 11·1 } 10·5	12·2 } 11·3 } 11·7	9·2 } 9·9 } 9·5	3·0 } 3·0 } 3·0
70	18·4 } 16·8 } 17·6	14·4 } 16·6 } 15·5	18·4 } 16·8 } 17·6	—

* Results valueless owing to adherent matter (see p. 121).

Discussion of Quantitative Results.

The experiments of Series A show that corrosion occurs more than twice as rapidly in oxygen as in air; since, however, the specimens of sub-series (1) were necessarily exposed to air while being placed in position, the ratio found for the two velocities cannot be regarded as exact.   The initial disturbance of the oxygen-exposed specimens lasted for not more than 5% of the total time, but it was decided to adopt air as the gaseous medium for the Series B and C.   The effect of replacing air by oxygen is not only to increase the rate of corrosion, but also to restrict the corroded area to strips running along the bottom portion and the two edges. This is an additional proof that the direct result of oxygen is the formation of a protective film, and attack only occurs at places where the oxygen concentration is so low that it fails to keep the protective film in repair.   The replacement of air by oxygen

multiplied the total corrosion by an amount varying from 2·4 to 2·6 in the different experiments; but owing to the greater localisation of attack, the *intensity* of corrosion (the corrosion per unit area of the part affected) was in several cases increased as much as 7 times.

The experiments of Series A also show that the effect of doubling the *breadth* of the specimens is nearly to double the corrosion, but the alternative method of increasing the immersed area, *viz.*, by prolonging the *depth* of the immersed portion, has much less effect. The effect of halving the concentration of potassium chloride is only slight.

The experiments of Series B were suggested by the qualitative observation that corrosion became visible earlier on finely ground than on coarsely ground specimens; these observations made it seem probable that whilst *local* abrasion of a violent character increases corrosion of the part affected, violent abrasion of the *whole* surface somewhat retards attack by providing an undue number of weak points. The results of Series B showed, however, that even after only 8 hours the effect of the character of abrasion

FIG. 1.
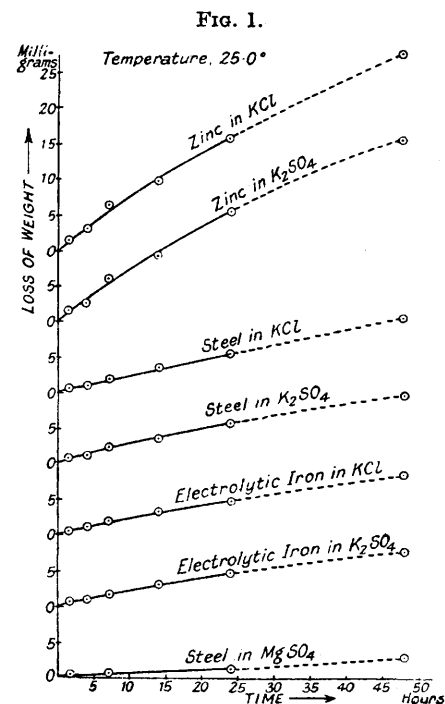
had become trivial, although there appears to be a slight decrease of attack on passing from extremely fine to coarse abrasive.

Series C represents the main group of experiments, where the time of immersion was altered, the immersed area being kept constant. The data, plotted in Fig. 1, show that zinc is corroded much more rapidly than iron. On the other hand, steel gives curves almost parallel, in the early part, to those obtained with electrolytic iron. With zinc, steel, and electrolytic iron, potassium chloride yields curves nearly parallel to those obtained with potassium sulphate; sodium chloride—in spite of rather irregular results in the later stages—appears to cause an initial velocity of corrosion

similar to potassium chloride, but magnesium sulphate produces very much slower attack than potassium sulphate.

The interpretation of the experimental results is simple. The maximum available *E.M.F.* is that of the cells iron|oxygen or zinc|oxygen, but this will be in practice reduced by (*a*) *anodic polarisation*, (*b*) *cathodic polarisation*, and (*c*) *fall of potential across the liquid*. Where the conductivity of the liquid is very low, the factor (*c*) may be important, and here the conductivity may be the main factor in determining the rate of corrosion, as was found by Bengough, Stuart, and Lee for very dilute solutions in exceedingly pure water. For concentrated solutions, however, the fall of potential due to the resistance must certainly be very small, and the conductivity of the liquid, as such, will hardly affect the corrosion velocity ; thus it is not surprising to find that the corrosion velocity is scarcely altered on passing from $M/20$- to $M/10$-potassium chloride. Probably on aluminium, where, owing to the self-healing character of the oxide skin, the anodic areas remain very small, the rate of corrosion is controlled mainly by factor (*a*) ; but on iron and zinc, where the anodic areas spread out over nearly the whole surface with great rapidity, it will be factor (*b*) which will determine the current passing between anodic and cathodic portions, *i.e.*, the rate of attack. The cathodic polarisation largely depends on the supply of oxygen (the " depolariser ") to the portions bordering the water line. Thus pure oxygen causes more rapid corrosion than air, and the effect of doubling the *breadth* of the specimen is nearly to double the attack (it is not quite doubled, since there are exceptional opportunities for diffusion at the two ends of the water line). On the other hand, an increase of the vertical dimensions of the immersed area will not greatly affect the supply of oxygen, although it will increase the potential anodic area ; thus the effect on the corrosion velocity is much less important. There is no reason why changing from potassium chloride to sodium chloride or to potassium sulphate should seriously affect the cathodic polarisation, and these changes hardly affect the corrosion velocity in the early stages, but the use of magnesium sulphate involves the deposition of a layer of sparingly soluble magnesium hydroxide over the cathodic region (clearly visible when the specimens are withdrawn), and this interferes with the diffusion of oxygen to the metallic surface, thus greatly retarding the attack.

There is no special reason why the presence of carbide in the metal should seriously affect the cathodic polarisation, and thus, in the early stages, steel corrodes with nearly the same velocity as iron. On the other hand, zinc corrodes with an entirely different velocity from iron, since here the *basic* value of the (unpolarised)

E.M.F. is different, and consequently, given the same facilities for oxygen supply, the value of the current under polarisation conditions will be different for the two metals. Thus the partial-immersion method is capable of demonstrating differences between the corrosion resistance of different materials where such a difference exists, thus differing entirely from the total-immersion method, where—at great depths—the oxygen-supply rate might impress the same velocity of corrosion on different metals.

In stating that steel corrodes at approximately the same rate as electrolytic iron, it must be added that this applies only to conditions of *differential* aeration, where an *E.M.F.* may be developed quite independently of the existence of a second phase in the metal. Under conditions of *uniform* aeration, the state of affairs is different. It was shown by the author (" Corrosion of Metals," 1926, p. 108) that, when discs of electrolytic iron were whirled in ordinary distilled water containing oxygen, practically no rusting occurred, although discs of steel whirled in the same water rapidly became rusty; where differential aeration currents are excluded, the *E.M.F.* between iron and carbide particles probably becomes important.

The fact that on ordinary iron and steel, chlorides and sulphates produce in the early stages approximately the same rate of corrosion, agrees with the results of former work with the drop method (*J. Soc. Chem. Ind.*, 1924, **43**, 315T). It is, of course, in contrast with the state of affairs met with in those materials where—owing to the highly protective quality of the oxide skin—the anodic areas remain small and the velocity is controlled by the anodic polarisation. Such an example is afforded by aluminium, where the penetrating chlorine ions produce much more rapid corrosion than sulphate ions, as is indicated by the long-period tests of Jablonski (*Korrosion u. Metallschutz*, 1926, **2**, 218).

In the later stages of corrosion, various complicating factors enter. The anodic area creeps up close to the water line, and the corrosion product begins to interfere perceptibly with access of oxygen to the metallic surface. Again, in some cases physical changes in the corrosion product may set in, increasing the error due to the matter which continues to adhere after wiping. Both these factors will tend to diminish the loss in weight. At the same time, other factors arise which tend to increase the rate of attack; for instance, alkali creeps up the surface above the water line, enlarging the potential cathodic area, at the expense, however, of increased circuit resistance. It would appear that the first set of factors predominates in the case of zinc, whilst in steel the second set is important, although the last part of the curve cannot be said to be definitely known, owing to lack of reproducibility. In any

case the change of weight measured in the later stages, although of technical importance, ceases to have any simple scientific significance.

It is to be noticed that in the early stages, where the anodic areas are small and anodic polarisation must be of perceptible influence, complete agreement between duplicates is not to be expected, since the number and distribution of weak points will vary from one specimen to another; actually at this early stage the divergence between the values given by duplicates often exceeds the balance error. Later, when the anodic areas grow, and cathodic polarisation controls the velocity, the agreement between duplicates in most cases becomes quite good. Moreover, almost the same results are given by different salts (potassium chloride and sulphate) and by different materials (electrolytic iron and steel); this fact is the more remarkable when we recall that the shapes, distribution, and aggregate areas of the anodic regions are utterly different in the various cases mentioned (for instance, the boundary of the anodic area is far more sinuous in chloride than in sulphate solutions). But when corrosion begins to develop from points close to the water line, the shutting off of oxygen may be different for the duplicate specimens, according to the chance disposition of the weak points relatively to the water line. Thus the agreement between duplicates becomes exceedingly poor.

Considering the question of reproducibility generally, it would seem that good agreement between duplicates may only be expected in certain circumstances, *viz.*, when the determining factor is *some external condition which can be controlled* ; for instance, where it is determined by the supply of oxygen to an area which is clear of corrosion product, or where—as in Bengough's work on very dilute chloride solutions—it is determined by the concentration of chlorine ions. Reproducibility is definitely not to be expected, however, when the velocity is controlled by the chance distribution and sizes of a limited number of small anodic areas (weak spots). That the variation is not due to experimental error is proved by Bengough's work; here, in spite of extreme precautions, in a typical case the variation from the mean in two parallel experiments ranged from 1·7 to 6·7%. The difference of reproducibility under different conditions is also illustrated by the author's early work with the drop method (*J. Soc. Chem. Ind.*, 1924, **43**, 315T) : four drops of N/10-potassium chloride, at 29·2°, gave practically the same amount of corrosion in 5·5 hours (*viz.*, 0·65, 0·65, 0·66, and 0·66 mg.), but in 48·7 hours the reproducibility had become poor (3·50, 2·57, 3·25, and 5·12 mg.), although clearly the effect of analytical error and initial disturbances (and indeed all *experimental* errors) must be

less serious in the longer experiments. Drops of potassium sulphate and nitrate gave similar results, but salts which can only succeed in penetrating exceptionally " weak " points showed far greater divergence between duplicates. Thus one drop of $M/30$-sodium phosphate produced 0·65 mg. of corrosion in 24 hours at 29·2°, whilst another drop of the same solution under identical conditions produced only 0·005 mg.; evidently the first drop happened to develop a weak spot, whilst the other did not. Many authorities appear to think that the study of " unreproducible phenomena " is unworthy of scientific attention. Where the divergence between duplicates is due to experimental error or lack of proper control this view is correct; but where the divergence is due to other causes, such an attitude is untenable. Clearly, however, it will be necessary, in studying cases (like corrosion by sodium phosphate) where results show variations over a wide range, to perform perhaps 10 or 20 repetitions of each experiment, and to use larger areas than are permitted by the drop method. The method described in this paper allows 15 experiments, each on an immersed area of 2·5 × 2·5 cms., to be performed simultaneously in a thermostat of ordinary laboratory size, and may prove useful for extending the work to such cases.

Summary.

The corrosion of half-immersed specimens of zinc, aluminium, iron, steel, and copper commences at certain weak points, mainly along the bottom and cut edges, but frequently in the centre also; in those cases where the rate of corrosion is very slow, it may occur along the water line. In zinc, iron, and steel in chloride or sulphate solutions, the attack spreads out from these points very rapidly, the greater part of the immersed area being finally attacked; the insoluble corrosion product is of four different types, which appear according to the manner in which the anodic and the cathodic products come together; in copper and aluminium one of these types is usually absent, but otherwise there is general correlation between the results with zinc, iron, and steel.

Quantitative experiments show that under conditions of differential aeration, electrolytic iron is attacked nearly as rapidly as steel, and potassium sulphate and potassium chloride cause similar rates of corrosion, notwithstanding that the shapes of the corroded area are quite different; magnesium sulphate causes much slower attack. Zinc is attacked more quickly than iron, and aluminium much more slowly. Oxygen produces quicker attack on steel than air, but the attack is restricted to a smaller portion of the specimens; doubling the breadth of half-immersed specimens nearly doubles the rate of attack, but increase of the length of the immersed area

has much less effect. All these results are understood if it is remembered that the corrosion current flowing between the cathodic and the anodic areas will depend on the *E.M.F.* of the cell metal|oxygen greatly reduced by polarisation. With aluminium, where the film repairs itself readily and the anodic areas remain small, the anodic polarisation will be most important, but with zinc, iron, and steel, the cathodic polarisation, which depends on the supply of oxygen, will determine the rate of attack; iron is corroded less quickly by magnesium sulphate than by potassium sulphate, since the cathodic product, magnesium hydroxide, interferes with the access of oxygen to the metal; zinc is corroded more quickly than iron—even with the same facilities of oxygen supply—because here the value of the unpolarised *E.M.F.* is higher.

<div align="right">[*Received, November 3rd,* 1928.]</div>