XVI.—*The Passivity of Metals. Part II. The Breakdown of the Protective Film and the Origin of Corrosion Currents.*

By ULICK R. EVANS.

ONE of the difficulties affecting quantitative work on corrosion is that the attack is not uniform, but commences at a number of isolated points, the progress of the corrosion depending on the distribution of the points of origin. It is therefore important to decide how and why corrosion begins at such points. Two general views are held : (1) The points may be mouths of invisible *cavities in the metal*, the interiors of which, being less accessible to dissolved oxygen, should be anodic towards the area outside. (2) They may be merely *breaks in a protective film*, where the exposed metal will be anodic towards the surrounding film-covered surface.

Tammann and Bredemeier (*Z. anorg. Chem.*, 1925, **142**, 54) have shown that cavities are often present in apparently sound metal, and the work of Seligman and Williams (*J. Inst. Metals*, 1920, **23**, 159) has indicated that certain types of local corrosion are connected with such cavities in aluminium, but this is probably an exceptional case. Callendar (*Proc. Roy. Soc.*, 1927, *A*, **115**, 349), who has studied the corrosion of aluminium in detail, considers that " the primary cathode and anode areas on a pure metal are determined largely by the distribution of oxide and other films." Similarly, for brass, Bengough and May (*J. Inst. Metals*, 1924, **32**, 155, 228) record certain cases of local attack connected with pre-existing cracks or pores ; but here again these examples are considered to be exceptional, and the investigators expressly

dissociate themselves from the views of Maass and Liebreich (*Z. Metallkunde*, 1923, **15**, 245), who consider that the grooves left on drawing brass are commonly responsible for serious corrosion. Bengough and his colleagues have long held the view that local failure of a protective " scale " is a frequent cause of localised attack (see, *e.g.*, Bengough and Hudson, *J. Inst. Metals*, 1919, **21**, 37).

On the other hand, the author and others have found some difficulty in regarding the sites of local corrosion simply as breaks in an otherwise continuous scale, since corrosion commences locally even on specimens carefully cleaned by abrasion. However, recent work has indicated that simple exposure to air causes a film to form over a metallic surface with astonishing rapidity (J., 1927, 1029), and thus the above objection has largely been removed.

The present work was designed to distinguish definitely between these two views and to apply the results to the study of the mechanism of corrosion.

EXPERIMENTAL.

Materials and Method.—Two samples of vacuum-melted electro· lytic iron foil (E 26 and E 28) and two of mild steel (H 26 and H 28) were prepared specially through the kindness of Dr. W. H. Hatfield. The analyses of these samples were :

	E 26.	E 28.	H 26.	H 28.
Carbon	0·04	0·03	0·18	0·26
Manganese	0·025	0·04	0·56	0·57
Silicon	0·010	Trace	0·04	0·15
Sulphur	0·013	0·005	0·047	0·014
Phosphorus	0·017	0·020	0·028	0·018
Nickel and Copper ...	0·09	Nil	0·10	0·09
Chromium	Nil	Nil	Nil	Nil
Heat-treatment after rolling	{ Annealed) above A_3 }	None	{ Annealed above A_3 }	None
Structure	{ Nearly equiaxial }	Lamellar	Normal	Lamellar
Thickness, mm.	0·09	0·21	0·11	0·21

In addition, some specimens of sand-blasted steel were kindly supplied by Mr. W. E. Ballard. Two kinds of zinc were employed, one a commercial sheet zinc containing 1·29% of lead, and the other rolled, through the kindness of Mr. H. C. Lancaster, from electro-lytic spelter of 99·97% purity. The copper was Kahlbaum's electrolytic foil ; and of the two specimens of aluminium employed, one was a hard-rolled sheet with 0·34% Si and 0·39% Fe and the other an annealed sheet with 0·33% Si and 0·40% Fe. Throughout this paper the terms " finely ground surface " refer to a surface ground with No. 1 (French) emery, and the description " rolled surface " denotes the surface as produced by the rolling-mill, the

specimens being washed with benzene and then with alcohol, but not abraded.

Anodic Corrosion under Anaerobic Conditions.—The " cavity theory " outlined above will account for local corrosion when dissolved oxygen is present. If the liquid contains no oxygen or oxidising agent, and the corrosion is produced by an externally applied *E.M.F.*, there is no reason why the interior of cavities, as such, should be corroded more readily than other places, provided that the conditions are such that the corrosion is favoured by increase of current density.

FIG. 1.
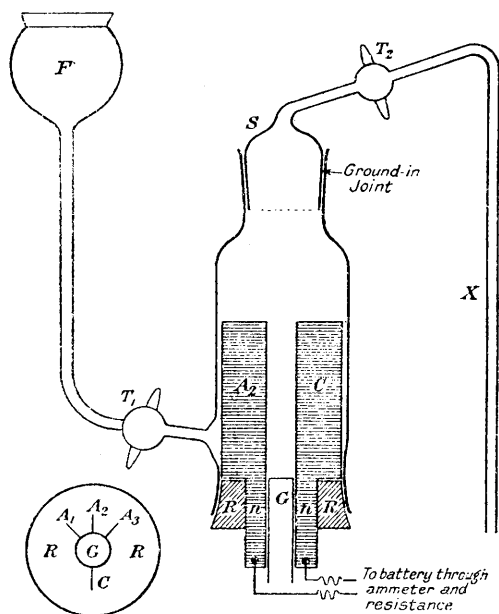
The electrolysis vessel (Fig. 1) could be completely filled with liquid without air space. Since it was essential to introduce the electrodes without heating, the following arrangement was adopted. The rubber stopper, R, was pierced by a central round hole, from which four slits extended radially. The narrow portion (n) of each electrode was introduced into the central hole, and pushed sideways into its proper slit, which was held open by suitable pressure upon the rubber in a vice; when all four electrodes were in their four slits, a closed glass tube G was pushed into the central hole, and the outside smeared with Durofix, making a water-tight joint. The rubber stopper was then put into its place in the vessel and

the ground-in stopper S with side tube X was introduced. $M/10$-Potassium chloride was admitted through funnel F and tap T_1, the vessel being tilted to ensure that air was expelled through tap T_2, none being entrapped at S. When electrolysis was proceeding, T_2 was closed and T_1 slightly open, so that the hydrogen collecting at S could expel a corresponding portion of liquid. Three of the electrodes served as anodes and one as cathode. The anodes were prepared at least 24 hours before the experiment and kept in a desiccator.

Electrolysis was first conducted between the cathode and the central anode, which was always of iron, but no account was taken of the results of the corrosion of that anode, since the liquid still contained a little oxygen during this preliminary electrolysis. The precipitate formed by interaction between the cathodic and anodic products was at first brown, then green, and finally white. As soon as a considerable quantity of the white product (ferrous hydroxide) had accumulated, showing that no free oxygen remained, the second anode was connected in place of the first. When this showed signs of corrosion, the connexions were transferred to the third anode, which received a rather longer treatment. The anodes were then taken out and studied under the microscope.

Anodes of electrolytic iron, steel, aluminium (two varieties), and zinc (two varieties) were thus studied under different surface conditions; the mean current density employed in most of the experiments was 0·03 amp./sq. cm. In every instance, corrosion commenced locally at isolated points. On electrolytic iron, it remained local, producing neat little undercut cavities of which the diameter increased only slowly as corrosion proceeded. On zinc the attack spread out rapidly from the points of origin, and aluminium showed an intermediate behaviour. On steel the attack remained less localised than on pure iron. The position of the points of local corrosion is significant. On ground specimens the points occurred arranged on the deeper grooves, whereas on rolled specimens they either fell on lines indicating the rolling direction or were connected with surface defects; in many cases there was a special tendency for the points of attack to lie near the edge of the specimen, where the metal had been stressed in cutting. In one sample of hard aluminium, rolled some years previously, pitting occurred along lines left by the rolling; some, at least, of the points of pitting represented the sites of tiny white dots which existed on the sheet when received; these dots apparently were due to incipient atmospheric corrosion which had failed to develop. Aluminium annealed after rolling showed numerous clean-cut pits, sporadically distributed and independent of the rolling marks; but there were also areas

showing general etching, and the boundaries of these areas tended to follow the rolling direction.

Now, those points which favour the initiation of corrosion when an external $E.M.F.$ is applied under anaerobic conditions are just those which favour corrosion in the presence of dissolved oxygen when no external $E.M.F.$ is applied. The cause must be the same in both cases. The first case cannot be explained by assuming a difference in oxygen concentration between the interior and the exterior of hypothetical cavities. Hence we are forced to conclude that the sites of local corrosion simply represent weak spots in the protective coating. They cannot, however, in all instances be actual *gaps* in the film such as would admit gaseous diffusion, since gaps of that character would have been healed through the exposure to air before the experiment—at least in some of the cases examined. But they may well represent weak spots where chlorine ions will pierce the skin in preference to other places under the directive influence of the externally applied $E.M.F.$ Such weak spots might, for instance, be places of great surface irregularity, or regions where intense internal stresses left in the metal keep the oxide skin in a distended condition. In some instances weak spots undoubtedly coincided with cavities in the metal itself ; but there appeared no reason to think that the existence of pores (as such) is a necessary condition for localised corrosion.

Corrosion (without Applied E.M.F.) *under Conditions of Differential Aeration.*—Strips of rolled steel or zinc were scratched with a file or diamond point and immediately partly immersed in $M/10$-potassium chloride or sulphate. Corrosion quickly set in along the scratch-lines, and extended downwards, this being the direction of lowest oxygen concentration. Possibly gravity also facilitated the downward spread of corrosion in some cases, notably that of zinc in a chloride solution, where the two primary products (zinc chloride and potassium hydroxide) can co-exist for a sensible time before producing a coherent precipitate ; but in most cases (*e.g.*, zinc in a sulphate solution) gravity appeared to play only a minor part, since even in specimens placed at an angle of only $20°$ to the horizontal, the spread of corrosion in the direction of low oxygen concentration was seen just as well on the lower side as on the upper side of the specimens. The uniform triangular groove left by the diamond point produced less marked corrosion than the irregular scratch made by a steel file. In the parts of the specimens near the water line, where the oxygen concentration was high, corrosion along the scratch lines frequently slowed down, or even ceased altogether, evidently because here the dissolved oxygen repaired the damage done to the skin.

All the observations made pointed to the fact that two mutually antagonistic changes were proceeding : (1) *direct combination* with oxygen, giving a protective oxide film ; and (2) *anodic attack* of the metal, yielding a *soluble* chloride or sulphate (which, however, soon produces a sparingly soluble hydroxide by interaction with the alkali formed simultaneously at the surrounding cathodic area).

Where oxygen is in excess, the first change, and where it is deficient, the second change, will usually prevail. The mere fact that anodic attack has commenced does not necessarily preclude subsequent repair by oxygen, if supplied in excess ; but if once sufficient loose corrosion product has been formed to prevent oxygen from diffusing to the metallic surface, the attack is not likely to be stopped at the points concerned.

In rolled unscratched specimens, local corrosion often set in at scattered " weak points " ; some of these may have been caused by unintentional bending in the laboratory, but in many cases, at least, they represented defects originating in the rolling mill, or even in the foundry. Even where intentional scratches had been made, corrosion sometimes occurred at the natural defects in preference to the artificial. The pure zinc, as received, had many breaks in the smooth surface, in some cases revealing under the microscope marked elongated cavities. Unscratched specimens partly immersed in $M/10$-potassium chloride developed within about 30 minutes rings or loops of membranous zinc hydroxide, and in practically every case the microscope revealed a defect of the kind mentioned at the centre of the ring or loop. No doubt at such places the original oxide film will tend to be weak, and the inaccessibility of the interior of the cavities to diffusing oxygen will appreciably reduce the chance of effective repair, so that corrosion continues apace at these places. This represents, therefore, a case where the " cavity theory " appears to be substantially correct.

Besides starting at scratches and depressions, corrosion frequently started from " weak points " on and very near the cut edges ; these appeared to result from the stresses produced by the slight bending which necessarily accompanies cutting ; corrosion also occurred wherever there were kinks or crumples of any sort.

Numerous experiments were carried out to study the effect of bending on the corrosion of electrolytic iron, steel, and zinc. Narrow strips of finely ground metal were exposed to dry air or $M/10$-potassium chromate solution, and then bent in the centre around a glass tube ; they were afterwards placed in porcelain dishes containing $M/10$-potassium sulphate or chloride ; in most experiments on steel or iron, potassium ferricyanide (2 g. per litre)

E

was also added as an indicator. Special corrosion was observed to set in at points situated on the bend; generally the convex side suffered more readily than the concave. Sometimes corrosion also set in at the ends where the specimen had been clinched with small pliers during the bending processes, but this was connected with the slight bending which the clinching involved; mere uniform pressure appeared to have very little effect. If the specimens were kept in air or potassium chromate solution for some hours between bending and immersion in the corrosive salt solution, the effect at the bend became less sharply defined, although corrosion still occurred at other places, notably over the " unaerated portion " where the bottom edge of the specimens rested upon the dish.

The results obtained with bent specimens are of interest in connexion with the author's observations on steel strips covered with thicker (visible) films of copper, nickel, and zinc (*Engineering*, 1928, **126**, 407). Here bending produced visible cracks, usually on the convex, sometimes on the concave, side; and corrosion commonly set in along these cracks. Mere pressure upon the film, however, even if intense, produced scarcely any damage to the film, and rarely led to corrosion. The close analogy with the new results suggests strongly that the corrosion produced by the bending of ordinary (unplated) iron, steel, or zinc is due to the cracking of an *invisible* skin of oxide or other compound. The residual stresses left in the metal itself, however, play an important part, because they tend to keep cracking or distending the films which are produced (after immersion) by the action of dissolved oxygen. Several examples of local corrosion set up by residual stresses have been seen during the present work, and the idea of film cracking may perhaps help to interpret the observations of others. Hatfield and Thirkell (*J. Inst. Metals*, 1919, **22**, 67) and Moore, Beckinsale, and Mallinson (*ibid.*, 1920, **23**, 225; 1921, **25**, 35; 1922, **27**, 149) have shown the effect of residual (internal) stresses on the corrosion of brass. Rawdon (*Ind. Eng. Chem.*, 1927, **19**, 613) has pointed out that the corrosion of several metals is facilitated by externally applied tensile stresses, and McAdam (*Proc. Amer. Soc. Test. Mat.*, 1926, **26**, ii, 224; 1927, **27**, ii, 102; 1928, advance proof) has studied the even more marked effect of alternating stresses on corrosion (see also Speller, McCorkle, and Mumma, *ibid.*, 1928, advance proof). Finally, Bengough, Stuart, and Lee (*Proc. Roy. Soc.*, 1927, *A*, **116**, 425) have found that different types of abrasion produce distinctly different values for the initial rate of the corrosion of zinc.

Apart from the intense *local* corrosion occurring at weak points, there occurs *general* corrosion on the lower parts of specimens

which are inaccessible to repairing oxygen. This regional attack commences at the bottom of the specimen and gradually advances upwards, the upper boundary remaining usually straight and hori·zontal. The phenomenon may possibly be due to the film substance being itself permeable to anions; but microscopic examination of specimens taken out at different stages of the process suggests that it is really due to the occurrence of a large number of minor weak points placed so close together as to constitute almost uniform leakage. This leakage occurs only at places inaccessible to dis-solved oxygen; where oxygen can penetrate, the minor weak points are kept in repair.

Experiments on Electrolytic Iron in Copper Salt Solutions.—It was shown in earlier work that iron exposed to dry air after grinding no longer reacts with copper nitrate solution, although it may still deposit copper from chloride or sulphate solution. No doubt the fact that copper nitrate is itself potentially an oxidising agent may account for this. Provided that stresses are not present which keep cracking the film too quickly, the nitrate may perhaps itself help to repair the film; if cracking is too persistent, copper will be deposited. The effects of different types of local abrasion on the deposition of copper have now been studied. Uniform grooves made on air-passive iron by a diamond cutter, a steel knife-point, or a smooth agate style were almost ineffective in producing depos-ition of copper, but where the iron surface had been abraded with jagged glass or with the edge of a carborundum wheel, rapid depos-ition of copper occurred. All types of abrasion will leave internal stresses in the metal, but the stresses left by the diamond, steel point, or agate style will not be likely to produce cracking in the skin; on the other hand, the forms of abrasion which tear the surface will leave tangential stresses likely to keep the film con-tinually in a cracked or distended condition. Moreover, the diamond, steel, or agate leaves a smooth surface, whereas the sharp glass or carborundum leaves a jagged surface, usually with micro-scropic undercut cavities, possibly containing fragments of the abrasive.

Electrolytic iron (E 28) exposed to dry air for 24 hours after fine abrasion, although hardly affected by $M/20$-copper nitrate (except to a small extent at the cut edges), became covered uniformly with copper when placed in $M/20$-cupric chloride or sulphate; the chloride gave a much less adherent deposit than the sulphate, and the copper colour (rather unexpectedly) appeared more slowly; the rapidity with which the copper colour appears in the sulphate bath may be the result of the good adhesion, since clearly the first traces of copper, if in good electrical contact with the iron, will serve as a

cathode upon which further copper can be deposited.   When iron
which had been scratched locally was dipped for about a second in
$M/20$-copper sulphate, washed quickly, and examined under the
microscope, copper deposition was seen to have already commenced
in the scratches, and sometimes the iron adjacent to the scratches
was also plated with copper ; the rest, however, was still bare.
Scratching with jagged glass or carborundum promoted copper
deposition most readily, but the diamond scratches also served as
places where copper deposition would commence preferentially ;
abrasion with the agate style, which leaves a smooth gently rounded
indent, seemed to have no effect in promoting deposition of copper.

   In more concentrated $(M/2)$ copper sulphate, the iron behaved
differently.   For a few seconds, no change occurred visible to the
unaided eye, although specimens immersed for one second only,
then quickly washed, dried, and examined under the microscope
showed the production of traces of metallic copper along the cut
edges.   Specimens immersed for longer periods underwent a rapid
alteration quite suddenly (often after about 10 seconds).   Depos-
ition of copper on the face commenced at certain points, usually
along the edges, but sometimes (in half-immersed specimens) on the
water line, or (in drop experiments) at the margins of drops.   Some-
times deposition of copper commenced at other weak spots where
the metal had been held with pliers or had otherwise suffered
pressure or bending.   Once commenced, the deposition of copper
spread out with great rapidity until the whole surface was plated
with copper.   In some specimens, however, the extension of the
copper deposit proceeded jerkily, being suddenly held up along
certain irregular lines, along which, presumably, the protective
film was specially adherent.

   The different behaviour of dilute and concentrated copper sulphate
solutions is easily understood.   Deposition of copper at the cut
edges involves anodic action upon the iron elsewhere.   Anodic
treatment of iron in a sulphate solution gives rise, as is well known,
to soluble iron sulphate at low current density, but at high current
densities other reactions become possible and the iron becomes
oxidised and passive.   Immersion of iron in dilute copper sulphate
is equivalent to anodic treatment at low current density, and
immersion in concentrated copper sulphate is equivalent to treat-
ment at high current density.   In this case the commencement of
the attack at the cut edges and the extension of the areas through
undermining of the skin are easily understood.

   Possibly the behaviour of the iron towards copper nitrate is to
be explained in a similar manner.   Where large breaks occur in the
oxide skin, replacement of iron by copper proceeds readily, the

necessary current density at the anodic portions being low.   If the cracks are very small, the anodic current density involved in the deposition of copper is high, and the iron becomes oxidised, healing the cracks, so that the action does not develop.   Of course, a smaller current density is needed to produce passivity in a nitrate than in a sulphate solution, and thus specimens of iron which fail to deposit copper from a nitrate solution may still react with a sulphate solution.

Experiments on Copper in Silver Nitrate Solution.—Finely ground copper, bent immediately after grinding and placed at once in $M/25$-silver nitrate, showed general blackening in a few seconds; there was no special phenomenon at the bend.   Finely ground copper, kept for 9 days in a desiccator, then bent and placed in the same solution, showed marked deposition of silver all round the bend, and practically none elsewhere, except at small isolated points; whereas if it was bent and then exposed to air for 9 days it showed no special deposition at the bend, the exposure having apparently " healed " the damage to the film.

These experiments are important, for they appear to exclude a possible alternative theory.   It might be argued that, since a distorted lattice is less stable than an undistorted one, strained metal should be anodic towards unstrained, quite apart from any question of film cracking.   This is probably true, but it does not seem to be the cause of the phenomena actually noted at the bends, which appear only when opportunity has been given for the cracking of a protective skin.

Origin of Corrosion Currents.—If the new results are considered in conjunction with those obtained in previous work on the corrosion produced by dissolved oxygen, it appears fairly certain that the sites of local attack are weak points in a protective film of oxide.   This is true of three important types of corrosion : (1) The corrosion produced by bending or stressing is due to the fact that the cracking of the film at the bends or stressed portion renders this part anodic to the rest.   (2) Corrosion in pits and parts of the surface screened from dissolved oxygen by foreign matter is due to the fact that here the film is kept in less good repair than elsewhere, and consequently the " unaerated " portions are anodic to the rest.   (3) Many instances of water-line attack are probably due to the fact that the protective skin adheres to the water–air instead of to the metal–water interface, thus exposing the metal.   In general, the junction of different phases represents a point of weakness on a protective film.   It is possible that the acceleration of corrosion by heterophase impurities may be due to the tendency of film failure to extend along the phase junctions.   It is a remarkable

fact that frequently non-conducting inclusions appear to be as potent in determining the sites of corrosion as conducting substances.

It must be recognised that there are many types of corrosion not determined by the distribution of films : these occur mainly in acid solution, where an oxide film would be dissolved.   Thus, in the corrosion of impure zinc by acids, the corrosion currents flow between zinc and its impurities.   Again, in the corrosion of copper, lead, and cadmium in acid solutions, electric currents may be set up by the unequal stirring of the liquid ; the parts over which water flows most rapidly become impoverished in metallic ions, and are thus kept anodic towards the rest, suffering intense local corrosion. It is noteworthy that the chief metal which shows this " stirring current " really well, even in *neutral* solution also, is copper, a metal of which the oxide film has only a very weakly protective character.   With zinc and iron in neutral solution, the points over which the water flows most rapidly usually become cathodic to the rest, owing to the increased supply of oxygen to these points.

It is fairly certain that in the types of corrosion mentioned above, the attack is connected with electric currents flowing between anodic and cathodic areas ; in general, the insoluble corrosion product is a secondary product formed by interaction between the materials formed on the anodic and the cathodic areas.   The currents set up by " differential aeration " have already been demonstrated and measured (*J. Inst. Metals*, 1923, **30**, 239) ; it is equally easy to demonstrate the current set up by bending one of a pair of similar electrodes ; the bent electrode functions as anode, but by bending the other, the current can be reduced to zero, or even reversed.

Donker and Dengg (*Korrosion und Metallschutz*, 1927, **3**, 217) consider that the maximum $E.M.F.$ available for the corrosion of iron is that of the cell iron|liquid|oxygen.   This $E.M.F.$ will theoretically fall between $1 \cdot 0$ and $1 \cdot 2$ volts according to the extent to which alkali is allowed to accumulate at the surface.   In the author's opinion, these theoretical values are only likely to be realised if the " aerated " (cathodic) area has a film which is perfectly free from weak points.   This is best seen if we consider the case of iron coated with a visible film of copper, instead of an invisible film of oxide.   Several potentiometric tests of steel which had been coated with a porous layer of copper by the Schoop process showed that the $E.M.F.$ of the cell steel|liquid|copper-covered steel is definitely less than that of the cell steel|liquid|solid copper, and the $E.M.F.$ of the former cell becomes smaller and smaller as the copper deposit is made thinner and more porous, as

is to be expected. It is not surprising, therefore, that the difference between the potentials of the anodic and the cathodic parts of ordinary (unplated) steel specimens corroded in $N/10$-sodium chloride solution under conditions of differential aeration has been found by McAulay and Bowden (J., 1925, **127**, 2605) to be only about 0·2 volt—far below the theoretical value. The question arises, however, whether a higher $E.M.F.$ might not be obtained under specially favourable conditions.

Some attempts were made to measure the $E.M.F.$ between aerated and unaerated steel under conditions such as to ensure a bountiful supply of repairing oxygen to all parts of the " aerated " area. The unaerated electrode consisted of a strip of finely ground steel fixed at the bottom of a glass vessel containing $M/10$-potassium chloride or sulphate, and for some days previous to the experiment kept joined by an external wire to a large piece of the same steel clamped above so as to pass through the water line. When the lower piece of steel was completely covered with rust, it was disconnected from the upper piece, and a narrow strip of steel was cautiously lowered until its lower edge just touched the surface of the liquid; regarding this as the aerated electrode, the $E.M.F.$ between it and the lower electrode was measured on the potentiometer. The values obtained varied with different strips, and also with the time, but usually fell between 0·22 and 0·26 volt; although slightly higher than those previously obtained, these voltages are still far below the theoretical values.

In the arrangement just described, it was the edge of the upper electrode which was presented to the liquid; $i.e.$, a typical weak place was employed. In order to avoid this, strips of filter-paper were pulled into two, so as to leave ragged ends terminating in fibres. One of these was hung over the edge of the containing vessel, and when it had sucked up liquid, a fresh piece of finely ground steel was clamped so that the damp fibres of the ragged end of the filter-paper strip just touched the metal; the $E.M.F.$ was then measured. In this way different points on the same piece of steel could be tested; as previously found by McAulay and Bowden, the readings varied considerably from spot to spot. Near the edges, the $E.M.F.$ was always low, and sometimes low values were also obtained at points in the centre, which could often be correlated with definite defects in the surface; but for most points in the centre the values ranged between 0·42 to 0·49 volt both in chloride and in sulphate solution. With electrolytic iron the range appeared to be almost the same (usually 0·41—0·45 volt), with much lower values near the edge. Although the value varied considerably according to the position chosen for the test on the

aerated electrode, experiments in which three separate *unaerated* electrodes were fixed in the apparatus—capable of independent connexion to the potentiometer—indicated that it made but little difference which one of the three was used.

It is surprising to find that an *E.M.F.* of nearly 0·5 volt can be set up simply by differences in oxygen accessibility. It is still far below the theoretical iron–oxygen value, but it seems probable that the *E.M.F.* between perfectly film-free iron and iron covered with an " ideal " film free from weak places might attain the theoretical value if balanced on the potentiometer. Such an *E.M.F.*, however, would not operate during the corrosion process, since it was found that the *E.M.F.* always dropped rapidly when it produced a current (*i.e.*, when it produced corrosion). It was noticed that after the two electrodes had been short-circuited even for a few seconds, low values were obtained, which slowly rose again with the time.

Experiments were also carried out with zinc, two varieties of the metal being used in both chloride and sulphate solution; as found by McAulay and Bowden, the *E.M.F.*'s were lower than in the case of steel, but varied considerably with the positions on a single specimen; values between 0·10 and 0·17 volt were obtained. The low values are naturally connected with the fact that the protective skin on zinc is much less perfect than that on iron. It does not follow that the corrosion currents set up by zinc under differential aeration conditions will be lower than those of iron. On the contrary, the low values of the *E.M.F.* measured with zinc are probably to be ascribed to the flow of local currents on the aerated electrode which, of course, cannot be prevented by balancing the system on a potentiometer.

The Extension of the Breakdown.—In order to follow the early stages of corrosion before any change became visible, a potentiometer method was employed similar in principle to that used by May (*Engineering*, 1928, **126**, 309), and by McAulay and Bastow (preceding paper). The potential of iron covered with a discontinuous layer of another material lies between the potential of uncoated iron and that of the coating material, but the value depends on the degree of discontinuity. For instance, iron sprayed with a porous coat of copper shows a potential close to that of compact copper if the porosity is slight, but close to that of iron if the coating is highly discontinuous. Similarly, iron covered with a discontinuous oxide film should give a potential on the positive side of the potential of film-free iron; if the breakdown extends, after immersion, the potential should move in a negative direction, whereas if healing predominates, it should move in a positive direction.

The metals to be tested were rubbed with French emery No. 1, cut into strips 1 cm. wide, washed with alcohol, ether, and benzene, and mounted in the usual manner by means of rubber in wide glass hoods; they were then kept for 24 hours in a vessel containing calcium chloride and soda–lime (certain iron specimens were treated in $M/10$-potassium chromate). Each separate specimen had a hood of its own, which, during the period before the test, served to protect it from accidental bending; during the experiment itself the hood served to exclude atmospheric disturbances, and formed a water seal which allowed the specimen to be lowered, almost instantaneously, into the liquid without danger of stresses to the metal (see Fig. 2). The liquid employed was $N/10$-potassium chloride

FIG. 2.
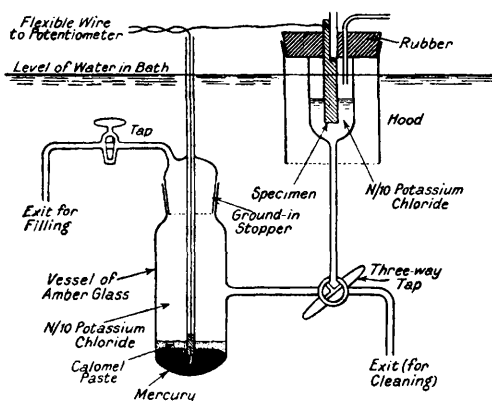
(previously shaken in a half-filled flask), and connexion was made through a three-way tap to a $N/10$-calomel electrode contained in a vessel of amber glass to prevent the disturbing influence of light on the potential; this vessel was completely full of liquid (no air space). Since the liquid was $N/10$-potassium chloride in both vessels, there was no appreciable error due to boundary potential. As the potential changed extremely rapidly, it was necessary to use a galvanometer detector, but the disturbance caused by passage of current was avoided by performing preliminary experiments which gave approximate readings for the potentials at different times, and these values enabled the potentiometer to be kept *nearly* in adjustment throughout the course of the actual experiments (with aluminium, this could not be done to the same extent, and the readings are probably less accurate). In these final experiments the values were obtained on a Weston voltmeter, checked against a Raake instrument. Preliminary experiments showed that the

E 2

shape of the electrode was not important; an immersed area of
1·0 × 1·5 cm. was found to be suitable. Altogether 49 specimens
were tested; a few of the results are shown in the curves of
Fig. 3, times being measured from the instant of immersion; the
temperature was 20°.

All these experiments were performed in duplicate. The iron,
steel, and zinc specimens showed sufficient agreement between
duplicates to be represented by a single curve, but the aluminium
specimens showed much greater individuality. The curves indicate
clearly that the breakdown extends less quickly on iron previously

Fig. 3.
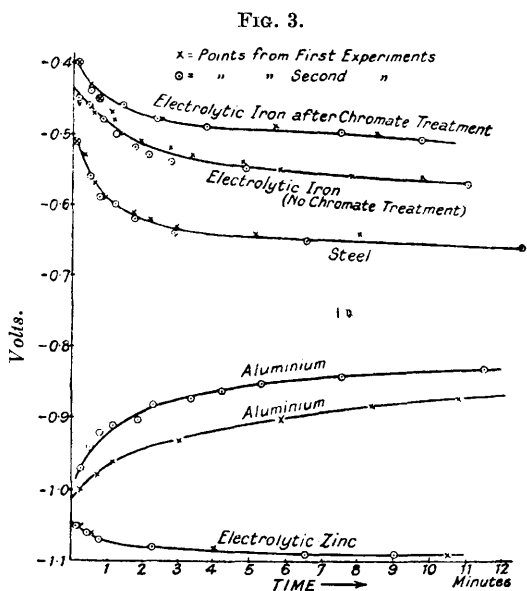
treated with potassium chromate than on iron merely exposed to
dry air for the same period—a conclusion previously reached by
McAulay and Bastow (preceding paper)—and also that the
breakdown on steel occurs more quickly than that on pure iron.
The final values of all three materials, reached after 22 hours, are,
however, approximately the same for steel, iron, and chromate-
treated iron. Zinc shows from the very first a value within 0·04
volt of the final value, indicating that the oxide film on this metal
has only a very small protective value; however, a small but
genuine drop was shown by all the zinc specimens tested.

Unlike iron, steel, or zinc, the aluminium specimens showed a
marked rise in potential with time. This appears to indicate that
on this metal the weak points tend to " heal," and the conclusion

is supported by the observations made later when the changes finally become visible; whereas the corroded areas on zinc, iron, and steel appear as patches which rapidly extend until they cover more than half the immersed surface, the corroding points on aluminium during the same period remain of microscopic dimensions. Although individual aluminium specimens showed different curves, all the specimens tested displayed this rise. Specimens of aluminium ground only 5 minutes before the experiment, however, showed a temporary fall in potential after immersion, followed by a much greater rise; no doubt, at first the stresses left by the recent abrasion permitted the breakdown to extend temporarily, but as soon as the stresses were relieved thereby, the healing influence began to predominate once more.

Another series of experiments was carried out in sulphate solutions; here the general form of the curves was the same, but the values have no absolute significance, owing to the error due to liquid boundary potentials.

Since this work was finished, French and Kahlenberg (*J. Amer. Electrochem. Soc.*, 1928, advance proof) have published a study of the effect of oxygen, hydrogen, and other gases on the potential of various metals. They consider that the alteration of the potential is " due both to absorbed gas and a condensed film of gas." The author agrees with many of the views put forward, but considers that the effect of oxygen on such metals as iron is much more satisfactorily explained by taking into account the effects of the discontinuous oxide film. In any case, the superior effect of potassium chromate over that of air, in elevating the potential, and the disturbing effect of surface weaknesses and residual stresses, can hardly be explained simply by considering absorbed and condensed gases.

Undermining and Flaking.—Closely allied to " passivity " is the phenomenon known as " flaking." Bengough, Jones, and Pirret (*J. Inst. Metals*, 1920, **23**, 80) found that when specimens of drawn brass were immersed in dilute ammonium nitrate solution the reagent penetrated below the surface, undermining the surface layers, which in the course of some weeks, could be peeled off; the thin films thus removed consisted of uncorroded brass and were about 0·01 mm. thick. A similar effect was afterwards obtained with rolled zinc by the author (*J. Soc. Chem. Ind.*, 1926, **45**, 42T).

The tendency for corrosion in rolled or drawn material to proceed parallel to the surface is readily explicable. Any type of attack which preferentially follows the crystal boundaries (whether it be attributed to intercrystalline impurities, intercrystalline cavities, or " amorphous " metal) will advance most quickly in this direction,

since in worked materials the crystals are elongated parallel to the surface; the arrangement of non-attackable inclusions in planes parallel to the surface will also form barriers tending to deflect the attack in the direction in question—an important matter in the corrosion of wrought iron (*ibid.*, 1928, **47**, 62T). But it is still necessary to explain why the surface layers of the metal should not be corroded away, leaving only an oxide skin, as was actually found to be the case with passive pure iron (J., 1927, 1020). We appear at first sight to be dealing with cases where the " protective film " consists, not of an oxide, but of the metal itself; and it is specially puzzling to meet this in a metal such as zinc, where, according to Russell (*Nature*, 1925, **115**, 455), two different electronic configurations of the metallic atom are not to be expected.

A series of microscopic observations has shown, however, that there is no sharp distinction between undermining of the surface in zinc and the stripping of the protective skin from passive iron. If pure iron is coarsely ground and coated with an oxide film either by heat-tinting in air or by treatment with potassium chromate solution, and the film is then undermined and removed by means of iodine, it is found to consist almost completely of oxide, with occasional specks of opaque metallic iron. If, however, the metal has been ground with a very fine abrasive before being rendered passive, treatment with iodine isolates flakes which show a framework of metal supporting " windows " of very thin oxide film. With aluminium, both the iodine method and the anodic method of isolating the surface film give flakes which are partly metallic, although in places the transparent oxide film, bearing the original marks of abrasion, can be seen free from any metallic support. It was found that the flaking which occurred when rolled zinc was immersed in $M/10$-potassium chloride or sulphate for some weeks was merely an extreme example of the same effect. To the naked eye the flakes appeared metallic and opaque; on treatment with dilute acid they dissolved quickly with effervescence; but a microscopic examination showed that some of the fragments were quite transparent in places, and in some cases it was possible with a wire point under the microscope to break the flakes into parallel layers. After considerable microscopic study, the opinion was formed that the flakes consisted of alternate layers of metallic zinc and zinc oxide.

The key to the phenomenon is provided by the work of Stead (*J. Iron and Steel Inst.*, 1921, **103**, 271), who found that iron heated to a high temperature in air suffered intergranular oxidation, the oxygen penetrating between the crystals, and separating them by a sheath of oxide. No doubt at lower temperatures the same

phenomenon can occur, but the oxide sheath will be thinner (invisible in sections) and will not penetrate so far. In rolled metal we may expect the debris of flattened grains composing the surface layers to have a certain amount of oxide between them; possibly the rolling may actually help to introduce oxide below the surface. Doubtless the subcutaneous oxide sheaths will not be continuous, but they will make the attack of the surface portion of the metal, either from above or below, a slow matter; the portion of the metal further from the surface will be corroded more quickly. Hence arises the undermining and loosening of flakes consisting partly of metal and partly of oxide, in proportions depending on the chemical and mechanical properties of the metal and on its previous treatment.

It remains, however, to consider why the film removed from iron which has been coarsely abraded before being rendered passive consists almost wholly of oxide. It would seem that here the violent abrasion produces a series of cracks through which the oxidising agent can pass, thus converting into oxide the portions of metal which would otherwise be isolated between oxide sheaths, and leaving only specks of metallic iron here and there. Such specks are actually seen in the microscopic examination of the separated film, and are arranged in an ordered manner connected with the abrasion directions. In metal which has been only gently abraded, less cracking occurs and the main function of the oxidising agent which produces the passivity is simply to repair any damage to the oxide film already present on the exterior surface.

Müller (*Z. Elektrochem.*, 1928, **34**, 583), in commenting on the author's previous work (J., 1927, 1020), accepts the view that the inertness shown towards copper salts after exposure to air or potassium chromate is due to a protective film, but considers that the passivity obtained by anodic treatment in acid solution cannot be ascribed to such a cause. He finds that iron rendered passive by exposure to air quickly deposits copper from an acidified copper salt solution, and that the time needed to produce passivity by anodic treatment of air-exposed iron electrodes is practically the same as that needed in the case of freshly polished electrodes. Moreover, iron which has been rendered passive by anodic treatment resists rusting under conditions which cause rusting of active iron. He concludes, therefore, that films play no part in causing anodic passivity, and that active and passive iron represent different states of the metal.

The facts brought forward by Müller accord well with the author's own experience. The film produced by the direct action of dry air or iron never survives such drastic conditions as Müller has

employed.   It breaks down, for instance, in the presence of chlorine ions (usually even sulphate ions), the attack setting in at any of the weak places which are not sufficiently supplied with the dissolved oxygen necessary for constant repair.   But if the iron itself is already supercharged with oxygen by previous anodic treatment, there is no reason for this breakdown to occur, whatever be the distribution of oxygen in the solution; as soon as the charge of oxygen is removed by suitable cathodic action (*e.g.*, by contact with zinc), the iron becomes capable of rusting, and this Müller has found.

The fact that the mild passivity produced by air-exposure is dispelled by acid-treatment does not mean that the anodic action may not in due course produce a new film.   As Müller has so neatly demonstrated, passivity does not set in during anodic treatment in sulphuric acid until the liquid layer next to the metal has become saturated with the metallic sulphate (or some other substance), which is seen separating out; when it is so saturated, the liquid has presumably lost its power to dissolve any oxide or other film which may be present on the metal.   On the whole, Müller's new experimental results appear to support the view of anodic passivity developed by Hedges (J., 1928, 976).

Summary.

Breakdown of the protective film on iron, steel, zinc, or aluminium tends to occur where the surface has been bent or cut, or where rolling or casting defects occur at the surface; at these points local corrosion sets in, and usually spreads out, although where dissolved oxygen is in excess the weak point often heals up again and the corrosion does not develop.   Pre-existing cavities may determine the sites of corrosion, as in zinc, their interiors being inaccessible to repairing oxygen; but this cannot be a common cause of localised attack, which can be obtained under anaerobic conditions if an external *E.M.F.* be applied.   Internal stresses are important in determining corrosion if they are of such a character as to keep the film in a state of weakness.   " Differential aeration currents " are due to the differences of potential existing between the places where the film is kept in repair by the presence of oxygen and those where it is not kept in repair; *E.M.F.*'s approaching 0·5 volt due to this cause have been measured, but the *E.M.F.* falls off when a current actually flows.   The extension of breakdown, or the repair of the film, can be followed by potential changes.