THE MECHANISM OF THE SO-CALLED "DRY CORROSION" OF METALS.

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GENERAL.

Types of Corrosion.—It is generally recognised that the ordinary corrosion of most common metals requires the presence both of water and oxygen, but that the phenomena vary considerably according to whether the water or the oxygen is present in excess. For convenience we may distinguish:—

(*a*) "*Wet Corrosion.*"—When a metal is completely immersed in water, the rate of corrosion (except in the case of those metals which can displace hydrogen as a gas from water) is controlled by the rate of diffusion of dissolved oxygen to the metallic surface, and is usually slow, owing to the small solubility of oxygen.

(*b*) "*Wet-and-dry Corrosion.*"—When a metal is periodically wetted (*e.g.* by rain) and then allowed to dry, the rate of corrosion is usually much quicker, because water and oxygen obtain almost simultaneous access to the metal. Likewise, when a stream of water containing *entangled* air-bubbles impinges on a metallic surface, corrosion is usually comparatively rapid.

(*c*) "*Apparently-dry Corrosion.*"—Where a metal protected from rain is exposed to the air, corrosion is slow owing to the deficiency of water. If moisture is absent altogether, metals are unaffected by air; but if an invisible film of water is present on the metal, a perceptible oxidation of the latter takes place in some cases; it is usually greatly accelerated if volatile electrolytes such as hydrogen chloride, sulphur dioxide or ammonia are present.

This "apparently dry" type of corrosion is the subject of the present paper. The information available in chemical literature is somewhat scattered and fragmentary, and it was thought best to establish the important facts afresh by experiment. Researches will be described dealing with the influence of

I. the presence of *volatile electrolytes*,
II. contact with a *dissimilar metal* and
III. *humidity*

upon the corrosion of an "apparently dry" metal; the results are then used in discussing

IV. the *mechanism* of the process.

Materials.—In the main experiments, the metals tested were in the form of thin sheet or foil, although in some of the subsidiary experiments, other forms of the metal were introduced for comparison. Different samples of the same metal from different sources, varying greatly in purity, were used, but it may be stated at once that except in a few instances the general character of the corrosion did not appear to be affected greatly by the degree of purity. The greater number of experiments were carried out with "electrolytic copper," "pure zinc,"[1] "pure lead," and 70/30 brass obtained from Messrs. Griffin, and with Kahlbaum's "pure iron foil." Mr. C. T. Heycock very kindly provided various samples of aluminium, copper, brass, nickel, and tin. Numerous commercial or domestic forms of metals, mostly obtained locally, were used in some of the tests; these included commercial lead sheeting, bronze and silver coins, tin plate, knitting needles, safety razor blades, spring steel, iron bolts and nuts.

Preparation.—It is important to note that all the results recorded below refer (unless otherwise stated) to specimens *cleaned and roughened by rubbing with coarse emery-cloth*, although in some of the subsidiary experiments samples carrying their natural "scale," were introduced for comparison. The roughened specimens had the advantage of presenting a large surface to the corrosive agency, and the interpretion of their behaviour was not rendered difficult by any doubts regarding the nature of the "Beilby film" which exists on the surface of polished metals. Acid pickling was not used except in the case of some of the iron samples. The size of specimens employed varied according to the question to be investigated; in the main experiments described in Part I. the copper, zinc, lead, and iron specimens were 2-inch square, but this proved to be unnecessarily large for the purpose; the specimens of the more valuable metals were smaller.

"*Reproducibility.*"—Many workers on corrosion have noticed that different samples of the same material, exposed under apparently similar conditions, do not behave, even qualitatively, in the same way. In the experiments described below, whenever any appreciable corrosion-phenomenon was noticed in a specimen of a metal exposed to any particular corrosive agency, a second specimen of the metal was exposed to the same agency in a separate vessel, to ascertain whether the behaviour could be reproduced; in all important cases, a large number of different specimens of the same metal (from different sources) were subjected to the same agency. In only a very few cases (*e.g.* copper, aluminium, and iron in the presence of hydrogen chloride) was a lack of "reproducibility"—real or apparent—met with; in each of these cases, special experiments were undertaken to investigate the factors involved. Altogether 320 specimens were exposed during the research.

PART I.—INVESTIGATION OF THE INFLUENCE OF VOLATILE ELECTROLYTES.

Experimental Method.—The main experiments were carried out in glass "desiccator-vessels" of the usual pattern, having a diameter of 6 inches; the zinc grid supplied with the vessels was replaced by a glass plate supported on glass beads and covered with filter-paper. The solution containing the volatile electrolyte was placed in a small vessel at the bottom of the desiccator, whilst the specimens were laid flat on the filter-paper or leaned against the walls of the upper part of the desiccator, the lower edge resting against the glass plate which prevented the specimens from slipping

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[1] The zinc was clearly of thermal, not electrolytic, origin, and contained some lead and a trace of iron; cadmium was absent.

forwards. The numerous subsidiary experiments needed for repetition and investigation of special points were carried out in an apparatus formed by placing a small glass tumbler inside a large glass tumbler. The inner tumbler contained the solution, and on its upper edge rested loosely a glass plate covered with filter-paper, on which the specimens were laid; the outer tumbler was covered with a large plate luted round the edge with vaseline.

In the main experiments, conducted in November and December, 1922, the vessels were kept in a fume cupboard, the temperature of which never rose above 16° C.; a smaller series of experiments had been conducted in June, 1921, and a comparison of the results showed that the phenomena at summer temperatures were similar to those at winter temperatures, although naturally the corrosion was rather more rapid. The main experiments conducted over sulphuric acid and water were continued for 27 days; those over hydrogen chloride, sulphur dioxide, ammonia, hydrogen sulphide and carbon dioxide for 15 days; the duration of the numerous subsidiary experiments varied according to the point to be investigated. When the vessels were opened, a considerable decrease of pressure was noticed in the vessels containing ammonia and sulphur dioxide, due no doubt to absorption of oxygen, whilst an increased pressure was noticed in the vessel containing hydrochloric acid, which was ascribed to the liberation of hydrogen.

Exposure over Concentrated Sulphuric Acid.

Specimens of copper, zinc, lead, tin, nickel, aluminium, and iron remained perfectly bright and unaffected after one month's exposure in a vessel containing sulphuric acid; a steel razor-blade retained its edge unblunted.

Exposure over Water.

One month's exposure in a vessel containing water produced no serious change on any metal. The iron, however, showed tiny dots of brown rust on the surface. Several metals became slightly duller, the lead darkening considerably, whilst zinc acquired a yellowish grey or greenish grey colour; the change was only superficial. Copper scarcely altered, although it became slightly dull in places; tin, aluminium, and α-brass remained bright and unchanged.

Exposure over Water Saturated with Carbon Dioxide.

The phenomena were practically the same as over water, but the changes appeared more quickly. Iron developed tiny dots of rust within a few days, and some of these grew to small but conspicuous spots in two weeks.

Exposure over Water Saturated with Hydrogen Sulphide.

Hydrogen sulphide caused a conspicuous alteration in the appearance of several metals, but the change did not penetrate below the surface. The Kahlbaum iron was most affected, becoming covered within two weeks with a very thin coating of rather loose dark-brown rust. Copper began to darken within a few minutes of its introduction, and in half an hour developed beautiful interference colours, being rose-purple, blue or steely-silver in different places. After a day it had turned greyish or bluish-black; even after two weeks the change was only superficial. Lead became dulled to a bluish-grey colour, but even after two weeks it retained something of a metallic lustre. Brass showed discoloration in places, a bluish-grey iridescence being produced; at other points the original yellow, slightly dulled, remained. Tin and aluminium were practically unchanged.

In all the experiments so far described, the metals remained "dry" in the ordinary sense of the word. In the work described below, certain cases occur in which (no doubt owing to the fact that the corrosion product was a deliquescent body) the metal, although dry when introduced, quickly became wet.

Exposure over Concentrated Ammonia (·880).

Copper began to darken after a few hours; after a day the colour was black, and drops of deep violet-blue liquid had appeared on the surface. The production of this liquid increased as corrosion proceeded, and it soon began to flow off the copper into the lower part of the vessel. The blue liquid showed the tests for nitrites; this was not unexpected, since Bassett and Durrant[1] have shown that the main product of the corrosion of copper by aqueous ammonia in presence of air is the nitrite $[Cu(NH_3)_4](NO_2)_2$. After two weeks, the deposit on copper was greenish-black, but was quite thin; the metal below was unchanged and not brittle. Alloys containing copper, like coinage bronze and brass, also turned black and shed the violet-blue liquid. Brass was changed in mechanical properties also, some samples becoming so brittle after two weeks as to crumble in the fingers; this is probably a case of intergranular penetration,[2] since the fracture shows the yellow colour of unchanged brass in the interior.

The changes shown by the other metals were quite superficial even after two weeks. *Zinc* developed some dark grey patches, but remained dry and practically unattacked. *Lead* turned a dull bluish-grey, with yellow or brown patches. *Tin* remained bright, dry and unchanged, and the same was true of *aluminium*, apart from a slightly frosted appearance on the surface. *Iron* and *steel* seemed to be unaffected by exposure to ammonia; a razor-blade retained its edge unblunted after 8 days. This fact is of some interest since it is commonly believed that the rapid rusting of steel-work kept near stables is due to the ammonia from the manure; it is more probably due to carbon dioxide. Many samples of *nickel* were almost unaffected by ammonia; some samples darkened considerably, and even shed a blue liquid, which was found, however, to contain copper; copper, of course, is a common impurity in commercial nickel.

Exposure over Water Saturated with Sulphur Dioxide.

All the specimens of *iron* and *steel* became dark within a few hours; after a day, they were nearly black, and were sufficiently moist to have produced a distinct brown "rust-stain" upon the filter-paper on which the specimens rested. After two weeks the articles were covered with a brown or black deposit, about 0·1 mm. thick, with local excrescences of wet yellow-brown ferric hydroxide; the deposit, which gave a cloudy solution in water but a clear solution in dilute acid, showed the reactions of sulphate and contained more ferrous iron than ferric. The corrosion was most serious; the metal composing the "edge" of a razor-blade was removed altogether.

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[1] H. Bassett and R. G. Durrant, *Trans. Chem. Soc.*, **121**, (1922), 2630.

[2] Compare H. Moore, S. Beckinsale, and C. E. Mallinson, *J. Inst. Met.*, **23** (1920), 223; **25** (1921), 35; **27** (1922), 149.

Nickel also became black, and after two days began to shed copiously a pale green liquid. After two weeks, the deposit on the nickel was about 0·5 mm. thick; it was of a greenish-black colour, loosely adherent, and nearly completely soluble in hot water, leaving a small dark insoluble residue; the solution contained more sulphite than sulphate.

Zinc became dull after a few hours, but continued to look "dry" (in the ordinary sense of the word) for some days. After six days it was patchy, being bluish-grey in some parts and white in others; the appearance gradually became damp and warty. After two weeks it was found to be covered with a moist pasty white deposit, about 0·2 mm. thick, below which the zinc was unchanged. The "paste" dissolved in cold water yielding a solution which was only slightly cloudy; a few dark specks (probably foreign metals) remained undissolved; the solution contained much sulphate and some sulphite.

The attack upon the other metals was of a much more superficial character; the metals remained "dry" in the common sense of the word. *Copper* quickly lost its lustre and after two weeks was dull reddish-brown on the surface, but the altered film was extremely thin; brass also suffered discoloration, becoming dull yellow, grey or purplish in different places. *Lead* became a little darker; *tin* turned slightly yellowish-grey, but remained lustrous; *aluminium* remained bright and apparently quite unchanged.

Exposure over Concentrated Hydrochloric Acid.

Zinc placed in a vessel containing hydrochloric acid became visibly damp within an hour, no doubt owing to the hygroscopic character of zinc chloride; the metal soon became very wet, and a thick colourless liquid ran off the metal as corrosion proceeded. Corrosion was very rapid; half the area of a zinc sheet originally 2-inch square was completely eaten away in two weeks. In the last stages of corrosion, minute hydrogen bubbles were seen to be produced upon the wet metal, showing that when once the corrosion is fairly started it does not need the presence of oxygen.

Lead began to show iridescent interference colours (bronze, blue or pinkish in different places) within twenty minutes; afterwards the colour became dark grey. The attack was only superficial even after two weeks. *Tin* likewise suffered a superficial attack only; the surface became greyish, but remained dry.

Aluminium proved rather variable, and special experiments were performed. Of ten different commercial samples, including sheet, wire and turnings, exposed with their "natural surfaces," nine became covered within one day with a feathery growth of aluminium chloride; one sample of foil remained bright except in a few spots, whilst in another experiment a specimen of foil (surface roughened with emery) remained apparently unchanged—apart from a slightly frosty appearance—for two weeks. The thickness of the feathery chloride deposit was in some cases considerable; a wire of diameter less than 1 mm. became covered in 8 days with a growth extending outwards to a distance of 1 cm.

Copper also showed a rather variable behaviour. Most specimens, whether bright or covered with oxide by preliminary heating over a flame, became only superficially attacked, the colour appearing dull red, brown or even black; scraping usually revealed a thin whitish layer, possibly cuprous chloride, and below this unchanged copper. Some specimens, however, became covered locally with a comparatively thick green deposit, mainly cupric chloride.

α-Brass, of which six different samples were tested, differed from copper in becoming extremely "wet," no doubt owing to the deliquescent character of zinc chloride; the liquid shed by the brasses was of a dirty green-yellow colour and deposited green needles of cupric chloride. In addition, some samples became covered in places with a thick pale green deposit consisting of the so-called "basic chlorides" of copper and zinc (possibly hydroxides with adsorbed chloride); below the deposit, the brass was superficially blackened, possibly with redeposited copper. The observations on brass and copper recalled to mind many of the observations upon the "wet corrosion" of the same materials made by Bengough[1] and by Wurstemberger.[2]

Iron behaved in a very interesting manner in the presence of hydrogen chloride, and numerous subsidiary experiments were performed with different kinds of iron and steel. Whenever the specimens studied were freshly rubbed with emery and free from rust or scale, they remained dry, but lost their lustre, acquiring a whitish-grey frosted appearance; when they were taken out and exposed to ordinary damp air (free from hydrogen chloride) water was absorbed, and the surface became covered with damp brownish rust, caused by the oxidation of ferrous chloride to ferric hydroxide. If, on the other hand, the articles had rusty patches when they were introduced, the rust quickly combined with hydrogen chloride, and the ferric chloride—being deliquescent—absorbed moisture; a damp patch thus appeared on the metal, which was yellow at first, but quickly lost its yellow colour owing to the reduction to ferrous chloride. The damp patch—which appeared dark in contrast with the frosted dry surface around—gradually extended in area, but after some days it became less conspicuous, and the specimens gradually came to have a "dry" appearance. Where the liquid which collected on an originally rusty specimen passed on to filter-paper, it became brown owing to oxidation; but the liquid found on the metallic specimens themselves immediately after removal from the vessel contained only ferrous iron. If the moist specimens of iron were exposed to air free from hydrogen chloride, no brown colour appeared for a time; the adherent liquid was strongly acid, and minute bubbles of hydrogen could be seen coming off from the iron surface; after some hours, the acid became used up, and the specimens became covered over with brown or red rust, whilst the filter-paper on which they rested was covered with a brownish-yellow stain.

Some types of scale can act in a similar manner to rust, causing the condensation of a visible amount of moisture, evidently through the formation of ferric chloride. But although the effect of rust or scale causes a striking visible modification in the initial behaviour of iron, yet experiments with weighed specimens show that the presence of rust or scale has only a comparatively small influence on the final amount of corrosion after some days. In one comparative experiment, three razor-blades were exposed to hydrogen chloride for two days, then washed, dried, and reweighed. The rust-free blade had lost 18·7 mgs., the blade carrying 0·8 mg. of scale had lost 33·7 mgs., whilst that carrying 1·2 mg. of rust had lost 19·4 mgs. Experiments with low-carbon steel gave similar results.

PART II.—INVESTIGATION OF THE INFLUENCE OF CONTACT BETWEEN DISSIMILAR METALS.

Experimental Method.—Two forms of "compound pieces" were employed, containing the four metals, zinc, copper, lead and iron, disposed so

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[1] G. D. Bengough, R. M. Jones, and R. Pirret, *J. Inst. Met.*, **23** (1920) 65.

[2] F. von Wurstemberger, *Zeitsch. Metallkunde*, **14** (1922), 23, 59.

as to show the effect of contact between each pair of metals. In the *first form*, three strips of copper, zinc and lead sheet (each measuring about 8 × 2 cms.) were placed so as to form a triangle, being bound together at the corners by iron bolts and nuts; the compound piece thus resembled a "tripod," the iron bolts forming the legs; the metals were pressed together with "parellel pliers" at the points of contact. In the *second form*, strips of the four metals were crossed at right angles by four similar strips, which passed alternately below and above the first four strips, the two sets of strips being like the warp and woof of a fabric; the strips were turned over at the end, and pressed with pliers. This second form is very compact and convenient for short-period tests; it is unsuited for long-period tests, since the contact deteriorates as the metals lose their springiness through corrosion.

"Compound pieces" were exposed over different liquids in the vessels described in Part I., and the following results were observed:—

Over *concentrated sulphuric acid*, no change could be seen.

Over *water*, the lead was distinctly less darkened in the area around the iron bolt than elsewhere; this was apparently a case of electrochemical protection, although the metals were "dry" in the ordinary sense of the word. An apparently similar phenomenon of protection of "dry" lead by iron was observed some time ago by the author at a point on a domestic water-system.

Over *hydrochloric acid*, much more marked protection occurred, although the effect was less surprising, since the metals became damp. The lead as a whole quickly darkened, but the portion in contact with zinc remained light and bright indefinitely; in fact the bright marginal portion extended as the corrosion proceeded. Special experiments were conducted to see whether this was merely a "pickling action" due to the acid liquid which collected on the zinc; but it was proved that actual contact between the metals was necessary in order to obtain the effect.

Over *sulphur dioxide solution*, the *copper* turned a dull brownish-red at points remote from other metals, but had a pink colour near the contact with zinc; curiously enough, still closer to the line of contact with zinc, there was a thin very dark brown rim, probably due to the re-deposition of copper; similar phenomena were noticed in one specimen near the contact with lead. The *lead* assumed a slight brownish tinge, possibly due to traces of sulphide, at points remote from other metals; but near the contact with zinc or copper, the brown tinge ceased, and the lead was bluish-grey; the absence of the brownish colour was, however, not due to electrochemical contact action, because in this case it was shown that the brown colour could be removed by treatment with the acid corrosion-product from the zinc without actual contact between the metals.

Over *ammonia*, zinc showed near the junction with copper a most remarkable yellowish-white excrescent growth of oxide, having a flower-like form; the zinc was eaten right through where it touched the copper, although elsewhere it had suffered comparatively little corrosion. Lead also became covered with yellowish oxide at the junction with copper. These looked like cases of electrochemical contact-action; but, since subsidiary experiments showed that both lead and zinc are to some extent oxidised by the blue liquid flowing from off the copper even in cases where the copper was not in contact, it is impossible to be definite on this point.

PART III.—INVESTIGATION OF THE INFLUENCE OF HUMIDITY.

The Adsorbed Film and the Dew Film.—It is generally agreed that if a substance is placed in air that is not absolutely dry, a certain number of water molecules become attached to the surface; if the air is distinctly unsaturated, the adsorbed film produced is probably of molecular thickness, but the surface concentration of adsorbed water increases as the pressure of aqueous vapour in the air is increased. On a *bright smooth* metal, the gradual increase of the amount of the adherent water with the water-content of the air must suffer a break near to the place where the air becomes saturated; about this point the adherent film of water becomes so thick that it gathers itself into small droplets, and thus becomes visible as a "dew film." On bright metals, therefore, we can distinguish between the *invisible adsorbed film* formed in *unsaturated* air and the *visible dew film* formed in *supersaturated* air. On the other hand, on a *rough* metal, it seems likely that the passage from unsaturated to saturated air will not be accompanied by any sharp change. A rough surface can be regarded as a series of valleys and ridges, and clearly the condensation of water in quite large amounts can occur in the "valleys," even whilst the air is still "unsaturated" with respect to a level surface of water; as the vapour-pressure of the air is increased, deposition will occur at points where the concave curvature is less—that is to say, the moisture-film will gradually extend up the sides of the "valleys." This preferential deposition of water in the "valleys" is probably the reason why the deposition of small amounts of water from distinctly supersaturated air on roughened metals does not usually produce any *visible* dew-film. In the experiments described in Part I. of this paper, in which the temperature of the vessels varied with the temperature of the laboratory, much visible moisture was deposited in drops on the interior of the glass; yet except in those cases where a deliquescent corrosion-product was formed, the roughened specimens continued to "look dry," in the ordinary sense of the words.

Special experiments were carried out to investigate this point further. Roughened specimens of metal were placed in a glass vessel in which stood a smaller open vessel containing water at 12° C. After fifty minutes the vessel containing water was removed, and the whole vessel was cooled to 2° C. in a freezing bath; much moisture was seen to condense on the glass and undoubtedly much must have been deposited on the metals also, but they still appeared quite "dry," and left no mark of moisture when pressed on to filter-paper. Other experiments with weighed specimens showed that the uptake of water could be detected by the increase of weight.

It is probable that in practice, even indoors, the air becomes supersaturated with moisture much more often than is realised. If water is exposed in an open vessel in an ordinary room, the air above the water will become charged with moisture by day; at night when the temperature falls, water will be deposited on any metal article in the neighbourhood, although unless the article has a polished surface the deposition will usually escape notice. On the sea-coast of hot countries where (owing to a large difference between the "day" and "night" temperatures) there is a phenomenal deposit of dew, the corrosion of metals is usually exceptionally rapid. Nevertheless, although most of the corrosion in practice is caused by the deposition of moisture from supersaturated air, it is of some importance—both from the practical and theoretical standpoint—to determine whether corrosion can occur in presence of air unsaturated with water, and experiments were started to decide this question.

Experiments in Unsaturated Air Containing Volatile Electrolytes.—If a metal is enclosed in a vessel containing, say, hydrochloric acid, and the vessel is kept at a constant temperature in a thermostat, the distillation of moisture from the acid on to the metallic surface should be avoided. Special precautions must, however, be taken in commencing the experiment, to ensure (1) that the metal is always warmer than the acid, until both come to the temperature of the thermostat and (2) that the "fume" (consisting of tiny drops of liquid acid) which hydrogen chloride invariably produces when it mingles with damp air does not come in contact with the metallic surface.

Two methods were adopted. In the *first method*, the metal specimens were placed in a small tumbler covered with filter-paper, and provided with a wire handle, like that of a bucket; this was placed in a larger tumbler, containing also a vessel with calcium chloride; the whole was covered with a glass plate luted with vaseline, and placed in a thermostat at 25·0° C. for two hours. Then the large tumbler was removed from the thermostat, and the smaller tumbler was lifted out of it and placed in a second large tumbler containing concentrated hydrochloric acid (or ammonia) at 13° C; this second large tumbler was then covered, and placed in the thermostat at 25·0° C. During the transfer the metal was 12° warmer than the acid; any tiny drops of acid that might be formed by contact with moist air would be prevented from entering the inner tumbler by the filter-paper cover; such droplets cannot have been formed within the inner tumbler owing to the fact that the air within was relatively warm and dry.

The *second method* had the advantage that the vessel could be completely immersed in the thermostat bath; the metal specimens were placed in a wide-mouthed stoppered bottle, previously dried with calcium chloride; a tap-funnel was fitted, the stem of which passed through the stopper, and coming nearly to the bottom of the bottle led into a small open tube, shaped like a short test-tube, which served to prevent splashing when liquid was run in through the tap-funnel. The bottle was placed in the thermostat at 25·0° C. for 23 hours, and then concentrated hydrochloric acid at 19·3° C. was run in gently from the tap-funnel into the test tube; after this the vessel was kept in the bath at 25·0° C. for some days.

Both the methods gave the same results, and showed that *corrosion could be initiated in unsaturated air.* Zinc in hydrogen chloride was corroded actually more quickly at a constant temperature of 25° C. than in an exactly parallel experiment conducted at a fluctuating temperature (below 15° C.). Even in the experiments conducted in the thermostat, the zinc became covered with liquid; but this is not surprising since if once a trace of zinc chloride is formed, it will absorb water even from unsaturated air. Lead in hydrogen chloride quickly darkened; in a "compound piece," the lead remained bright along the line of contact with zinc, although dark elsewhere, thus showing electrochemical protection. Copper blackened in the presence of ammonia, but (in contrast with its behaviour in saturated air) did not shed any blue liquid.

Experiments in Dried Air Containing Volatile Electrolytes.—It seemed important to ascertain whether such substances as hydrogen chloride, hydrogen sulphide and sulphur dioxide could cause corrosion to metals in air dried by means of a dehydrating agent. Three cases were selected for investigation, namely, lead in hydrogen chloride, copper in hydrogen sulphide, iron in sulphur dioxide; the colour-change produced in these three cases is (in the presence of moisture) especially sensitive and rapid.

An apparatus was set up in which a current of hydrogen chloride, prepared by the action of sulphuric acid on ammonium chloride, and dried by bubbling through sulphuric acid, could be made to pass in turn through two stoppered "test-tubes," the first containing a small quantity of sulphuric acid, and the second a small quantity of water; the delivery tube in each case passed two-thirds of the way down the test-tube, and did not dip into the liquid. Two strips of emery-ground lead had been introduced into the upper parts of the two test-tubes overnight. In the morning a slow passage of gas was passed through the two tubes; the lead which was over water commenced to darken perceptibly at the bottom in two minutes; in ten minutes a marked blue interference tint had appeared, although the specimen kept over sulphuric acid was bright and unchanged. In seventeen minutes the blue interference colour at the bottom of the specimen over water had given place to a dull grey; the specimen over sulphuric acid at this stage began to show faint interference tints in places. Thus although tarnish is not prevented entirely by drying over sulphuric acid, the velocity is greatly reduced.

A more striking difference was observed in the action of hydrogen sulphide on copper. The specimen over water had lost its bright metallic lustre, and had become first a fine rose, then purple, then steely grey, before the specimen placed over sulphuric acid showed any change at all. After an hour, the specimen over water was dark grey, whilst the specimen held over sulphuric acid had arrived at the stage reached by the specimen over water in about a minute.

It was shown that various specimens of iron could be kept in sulphur dioxide dried with sulphuric acid for four days without suffering any change at all; in the presence of moisture this gas causes darkening in two hours, whilst within four days a thick crust of corrosion product appears.

The experiments show that the presence of water is a vital factor in determining corrosion even when volatile acidic substances are present, but that slow superficial corrosion can occur in many cases when the moisture-content is very far below the saturation-value.

PART IV.—DISCUSSION OF RESULTS—THE MECHANISM OF CORROSION.

It has generally been assumed that the corrosion of "dry" metals is essentially different from that of metals immersed with water; it is commonly believed that in the first case there is a direct (chemical) oxidation of the metal, whilst in the second case electrochemical action (corrosion couples) comes into play. Since, however, corrosion does not take place unless a film of moisture is present, it is at least worth considering whether the second explanation would not serve for both types.

It has been pointed out elsewhere that a maximum rate is in general fixed for the corrosion of a metal *immersed* in a neutral liquid by the rate of diffusion of dissolved oxygen over the layer next to the metal;[1] (sometimes the production of a protective oxide film may reduce the rate still further,[2] but we may leave this out of account for the present purpose). If the anodic and cathodic areas are close together, even a very poorly conducting liquid like distilled water will suffice to carry the current corresponding to this maximum rate of attack; and since a highly conducting liquid will not in general allow a higher rate of diffusion of oxygen, the rate of corrosion (in cases where oxygen is needed for the reaction) will be largely independent of the conductivity of the liquid. But if the metal is *not immersed* in the liquid, but is only *covered with a film* of moisture of ultramicroscopic thickness, and exposed to air, the case is very different; here we have almost unlimited access of oxygen, but the thinness of the film will certainly restrict the flow of current between anodic and cathodic areas if the film consists

[1] U. R. Evans, *J. Inst. Met.*, **28** (1922), 119.
[2] U. R. Evans, *Trans. Faraday Soc.*, **18** (1922), 1.

of a poorly conducting body like pure water. If, therefore, the corrosion of an "apparently dry" metal is of the electrochemical type, we may expect the rate of corrosion to be increased by the presence of electrolytes. This is found to be the case; hydrogen chloride, sulphur dioxide, hydrogen sulphide and carbon dioxide all increase the rate of corrosion, and the same is true of ammonia; it is difficult to see why acid and alkaline substances should act in the same way, except on the supposition that they both serve to *increase the conductivity* of the film.

If the main corrosion product is a *deliquescent* substance, the actual thickness of the moisture-film should notably increase as corrosion proceeds, and according to the view suggested above, corrosion should be accelerated. This is borne out by the experimental facts. In cases where the metal becomes visibly wet, and sheds quantities of liquid containing a deliquescent corrosion product (as does zinc in hydrogen chloride, nickel in sulphur dioxide, and copper in ammonia), corrosion is serious and deep-seated. In other cases of serious corrosion, such as iron in sulphur dioxide, the amount of liquid shed is very small, but the fact that a stain appears on the filter-paper on which the metal is laid shows that the metal does become moist. On the other hand in hydrogen sulphide and carbon dioxide, the metals continue to "look dry," and corrosion is (except perhaps in iron) merely superficial; nor is this surprising seeing that the sulphides and carbonates are insoluble substances having no affinity for water.

The possibility of the formation of a hygroscopic corrosion-product is the most important factor in determining the rate of corrosion. But there are clearly other influences involved. The presence of ammonia is well known to shift the electrode potential of copper from the "noble" towards the "reactive" end of the potential series, and this shifting will raise the E.M.F. of the corrosion couples and will thus be favourable to corrosion. The presence of acidic substances in the moisture film will raise the hydrion concentration, which will likewise raise the E.M.F. of the corrosion couples; iron and zinc in the final stages of corrosion in hydrogen chloride actually expel hydrogen as a gas—and presumably the presence of oxygen becomes unnecessary. Furthermore, the presence of hydrogen chloride or sulphur dioxide in most cases will prevent the formation of a protective film of insoluble substance, whereas in the presence of carbon dioxide, hydrogen sulphide, or water alone, a protective film of carbonate, sulphide, oxide, or hydroxide will tend to appear; this would explain the comparatively slow corrosion in such cases.

Thus the experimentally observed facts of the "apparently dry" type of corrosion are best explained on the hypothesis that it is due to electrochemical action in the film of adherent moisture. The existence of what appear to be cases of electrochemical protection and contact-attack at the junction of dissimilar metals affords additional support to this view, whilst the diminution of corrosion as the moisture-film is removed by the action of dehydrating substances is most easily understood if we adopt the electrochemical theory of corrosion.

The fact that iron is not attacked in the presence of ammonia is not surprising when we remember that alkalis always tend to prevent the anodic corrosion of iron, inducing passivity. The immunity of aluminium from corrosion by most volatile electrolytes is also to be expected, since aluminium is a substance which cannot function as an anode in most solutions; but an aluminium valve becomes leaky in the presence of chlorides, and it is not surprising to find that aluminium is considerably attacked by an atmosphere containing hydrogen chloride.

It was noticed repeatedly in the corrosion of lead by hydrogen chloride or copper by hydrogen sulphide that the interference colours appeared first at certain points, and gradually spread out in regular sequence from them. It may be suggested tentatively that minute cathodic areas may be present at the centres from which the colours spread out, the rest of the metal functioning as anode. The current density would thus be high in the parts of the surface close to the centres, and a given tint would quickly be produced there; but at points remote from the centres the current density would be low, and a longer time would be needed to reach the same tint.

It is important to note that the remarks just made are intended to refer only to the production of interference colours at low temperatures; preliminary experiments which have been made on the production of temper-colours on iron exposed to air above 220° C. appear to show that here we have to deal with a different kind of phenomenon. This is confirmed by the independent work of Pilling and Bedworth,[1] who find that the oxidation of copper at 800° C. does not require the presence of moisture.

SUMMARY.

Experiments on the behaviour of "apparently dry" metals, roughened with emery, show that no corrosion occurs when they are kept over sulphuric acid, and only slow, superficial corrosion when they are kept over water. The rate of attack is greatly increased by the presence of volatile electrolytes in the air, sulphur dioxide being most dangerous to iron and nickel, ammonia to copper and its alloys, and hydrogen chloride to zinc and aluminium; hydrogen sulphide and carbon dioxide somewhat increase the rate of rusting of iron, but produce only superficial changes on other metals. Contrary to popular belief, the corrosion of iron is not caused by the presence of ammonia. Corrosion of metals by volatile electrolytes appears to require the presence of some moisture, but proceeds in air which is distinctly unsaturated. Special phenomena occur at the contact of dissimilar metals, apparent electrochemical protection being observed in some cases.

The phenomena are best explained if we consider that electrochemical action occurs in the adherent (usually invisible) film of moisture. Volatile electrolytes increase the *conductivity* of the film and thus accelerate corrosion. Where they tend to produce hygroscopic corrosion-products, they bring about the absorption of further moisture and thus increase the *thickness* of the film; in several cases (zinc in hydrogen chloride, copper in ammonia, nickel in sulphur dioxide) the metal, originally dry, soon begins to shed liquid copiously, and in such cases corrosion is very serious.

The greater part of the experiments were carried out in the Goldsmith Laboratory of Metallurgy, Cambridge, and I wish to thank Mr. C. T. Heycock F.R.S., both for his kindness in allowing me the facilities for carrying on the work, as well as for the provision of a variety of materials. The thermostat experiments were carried out in the Physical Chemical Laboratory, by kind permission of Professor T. M. Lowry, F.R.S.; I wish also to thank Mr. L. L. Bircumshaw for his help in connection with that portion of the work.

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[1] N. B. Pilling and R. E. Bedworth, *J. Inst. Met.*, **29** (1923).