Recent Work on Corrosion and Oxidation.

A LECTURE DELIVERED BEFORE THE CHEMICAL SOCIETY IN LONDON ON OCTOBER 4TH, 1945.

By U. R. EVANS.

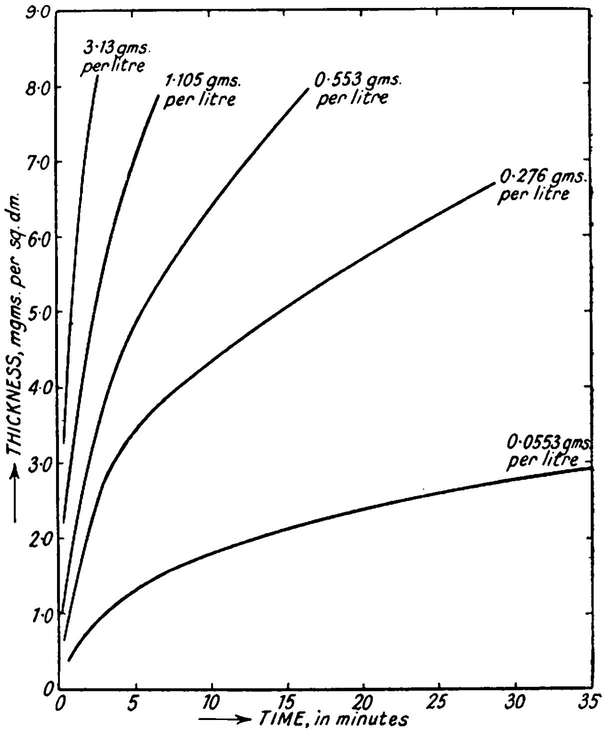
Significance of the Subject to the Pure Scientist.—In view of the large amount of study devoted to combination between non-metal and non-metal, or between metal and metal, it may seem strange that so little notice is paid by pure scientists to combination between metal and non-metal. Certainly, the products of such combination, the metallic salts and compounds, receive some attention—mainly from the elementary student—but the kinetics of the combination processes are almost completely ignored both in the textbook and in the lecture room, although such processes often obey simple, well-defined laws and principles, susceptible of reasonable interpretation. The cause of this apparent unpopularity may perhaps be found in the name. Many of these reactions are, for convenience, described as " Corrosion Processes," a term which implies an unwholesome change leading to something unclean and ugly. Consequently—although the great economic and industrial importance of corrosion, which is responsible for costly damage and sometimes disastrous breakdowns, frequently forces the applied chemist and engineer to subject the phenomena to *ad hoc* research, often empirical and not always profitable—yet the pure chemist takes little or no part in this work; indeed he often remains unaware of its existence, since the results are printed in industrial journals and abstracted in the " B " series of *British Chemical Abstracts.*

Actually, the belief that products of combination of metals and non-metals are invariably ugly is hardly justified. Where the processes lead to films which display interference colours, rather beautiful effects are often met with. Oxide films on nickel show four orders of attractive interference colours (red appears four times), and when transferred from the metal to transparent plastic they still show bright tints, which are now complementary to those shown on the metal (Evans, *5th Report of Iron and Steel Institute Corrosion Committee,* **1938**, p. 225). Even rust, deposited on glass or plastic, often displays bright colours by reflected light, whilst exhibiting its typical dirty yellow appearance by transmitted light.

But in any case, the neglect of one of the natural divisions of Chemistry for no good scientific reason must necessarily lead to a mistaken picture of the whole, especially when the neglected reactions obey laws and principles which appear—at least at first sight—very different from those governing the familiar part of Chemistry. We cannot individually study everything, but we can at least make our collective studies a representative sample of the whole. It is hoped that, in planning instruction or research for the post-war period, chemists will bear in mind that the neglect of one division of their subject in the past affords no convincing justification for its continued neglect in the future.

FIG. 1.

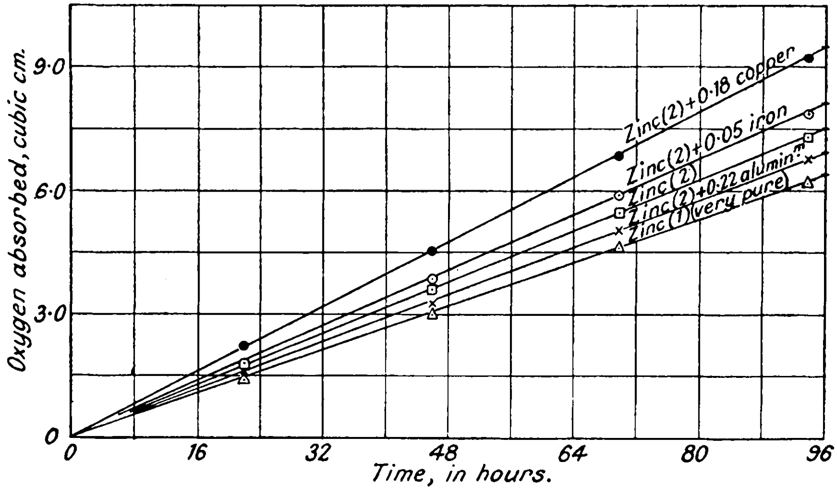
Growth of iodide on silver.



Classification of Reactions.—It is not unusual to distinguish between " dry " and " wet " processes—the first being exemplified by the appearance of compact oxide scale on iron heated in air, and the second by the formation of hydrated rust on iron immersed in a salt solution containing oxygen. Such a classification is unsatisfactory; it is not logical, for instance, to separate the formation of iodide films on silver by exposure to iodine vapour (a dry process) from their formation by immersion in a solution of iodine (a wet process). Another scheme of classification distinguishes between " direct chemical combination " and " electrochemical action "; but the high-temperature oxidation of copper, formerly regarded as a typical case of direct combination, is now believed to involve migration of ions through the scale under an E.M.F.

A more satisfactory classification is a division into (*a*) film-forming reactions and (*b*) others. If a reaction converts the surface of the metal into a solid film, which isolates metal from reagent, it is likely to die away with time. If the products pass into solution, this cause of retardation is absent, although other causes (*e.g.*, exhaustion of reagent) may operate. The formation of solid silver iodide on silver immersed in a chloroform solution of iodine (Evans and Bannister, *Proc. Roy. Soc.*, 1925, *A*, **125**, **370**) is a good example of a film-forming reaction; the rate of thickening dies away with time, being over the greater part of each curve (Fig. 1) inversely proportional to the thickness attained. The corrosion of zinc or its alloys partially immersed in potassium chloride solution (Borgmann and Evans, *Trans. Electrochem. Soc.*, 1934, **65**, 249) is an electrochemical reaction with soluble cathodic and anodic products (potassium hydroxide and zinc chloride), where there is no falling off of reaction with time, the curves (Fig. 2) being remarkably straight. But such processes do not invariably give straight lines; the corrosion of magnesium in sodium chloride solution (Lewis and Evans, *J. Inst. Metals*, 1935, **57**, 231) is represented by nearly straight lines at intermediate concentrations, but not at high or low ones (Fig. 3).

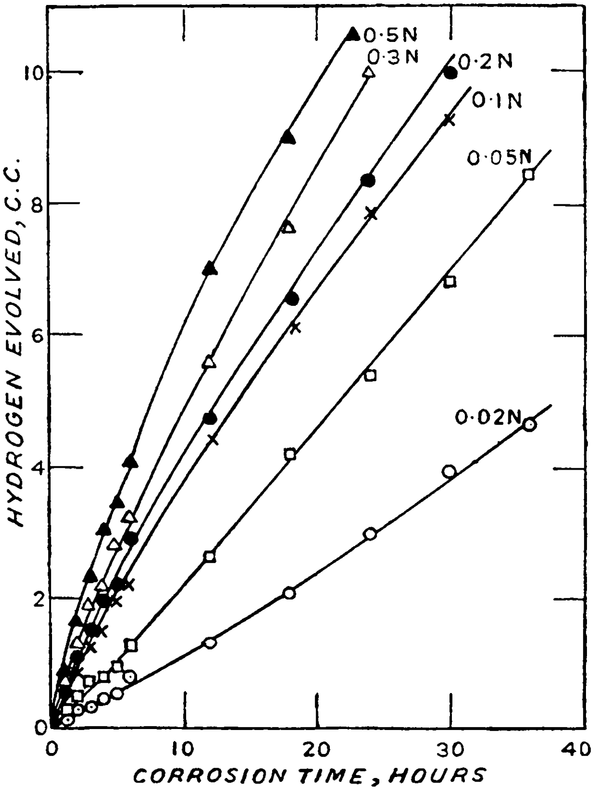
Fig. 2.



From the *Transactions of the Electrochemical Society*, 1934, **65**, 259, and printed here with the Society's permission.

Fig. 3.

Effect of concentration of sodium chloride solution on corrosion.



Filming Reactions.

Gravimetric Study of Oxidation.—The obstructive character of oxide films is shown by the fact that most metals can be kept in fairly dry, pure air without visible change; yet change does proceed—as demonstrated gravimetrically by Vernon. The curves for the oxidation of zinc in air at ordinary temperatures (Vernon, Akeroyd, and Stroud, *J. Inst. Metals*, 1939, **65**, 301) show rather rapid change at first, falling off as the film thickens.

Electrometric Study of Oxidation.—For short exposures to air, it is convenient to ascertain the thickness by measuring the millicoulombs needed for the cathodic reduction of the film in ammonium chloride solution (*e.g.*, cuprous oxide to metallic copper, or ferric oxide to the ferrous condition so that it passes into solution). If the current is obtained from a high E.M.F. applied to a very high resistance (Fig. 4), its strength remains constant despite changes of resistance or back E.M.F. in the cell, and only the time need be measured to obtain the coulombage. A voltmeter or potentiometer gives the end-point, since the potential drop needed to force this constant current through the cell will increase when reduction of oxide gives place to liberation of hvdrogen.

Fig. 4.

Electrometric estimation of oxide films.

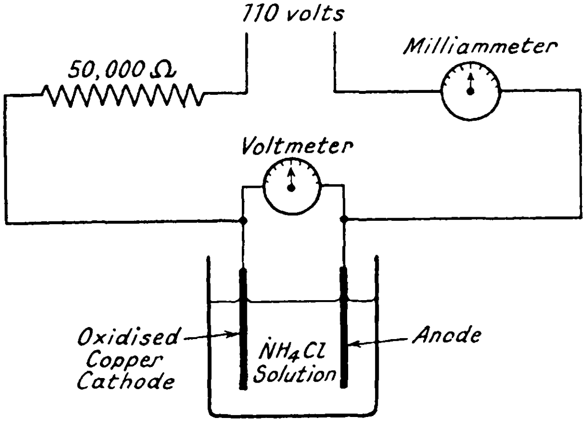
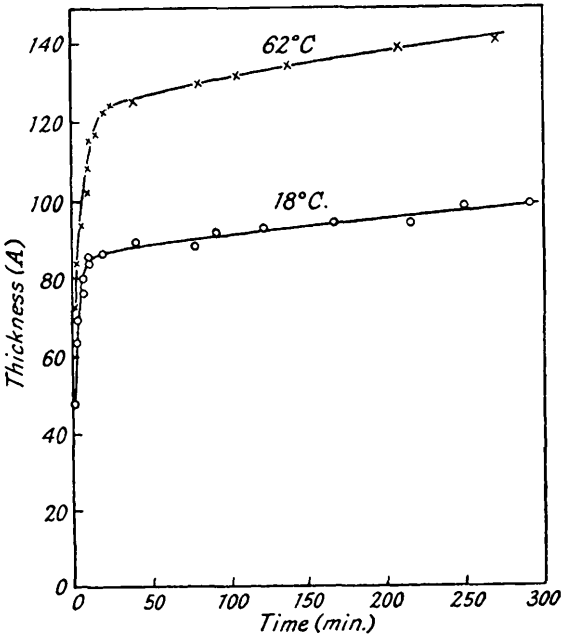


Fig. 5.

Oxidation of copper in air.



By exposure of copper or iron to oxygen for different times, and measurement of the coulombage needed for reduction, oxidation–time curves have been obtained (Evans and Miley, *Nature*, 1937, **139**, 283; *J.*, 1937, 1295). Even at ordinary temperatures, copper (Fig. 5) and iron (Fig. 6) begin to oxidise quickly, but the rate of attack soon slows down and the metal suffers no visible change; on iron, rough surfaces develop more oxide than smooth ones. At high temperatures (Fig. 7), the oxidation is more rapid and the films soon reach thicknesses sufficient for interference colours, but there is still a marked tendency for the rate to fall off with time.

FIG. 6.

Oxidation of iron in a desiccator at 18° *after different abrasions.*

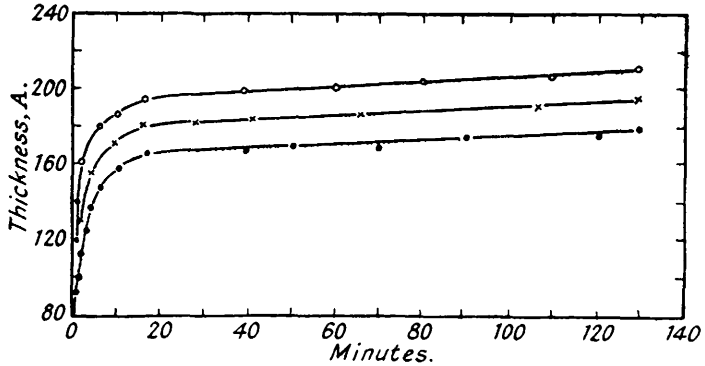
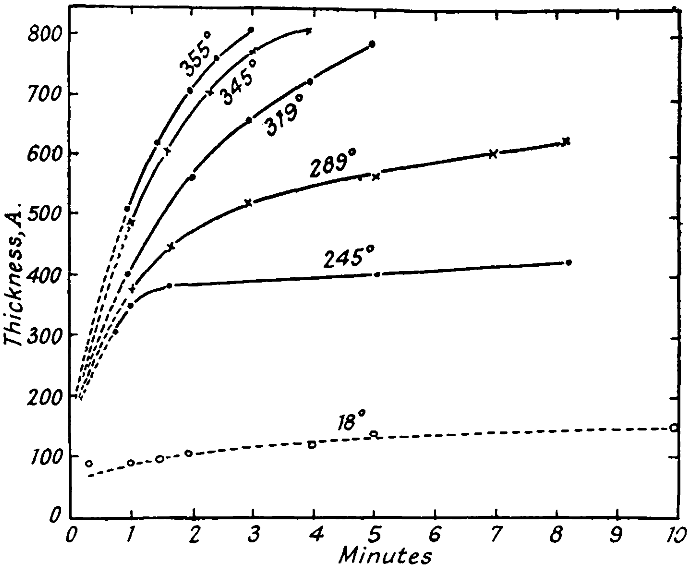


FIG. 7.

Oxidation of iron in an electric furnace after standard abrasion (broken curve from data of Fig. 6).



Oxidation of Light Metals.—This falling off with time is not invariably met with. Pilling and Bedworth (*J. Inst. Metals*, **1923**, **29**, 529) calculated from specific gravities that when the ultra-light metals, potassium, sodium, calcium or magnesium, are oxidised, the oxide produced would occupy a smaller volume than the metal destroyed, and the oxide coat is likely to be porous and non-protective. Such metals burn in air, and the oxidation curve recorded by Pilling and Bedworth for calcium at 500° is a straight line. Recently Gulbransen (*Trans. Electrochem. Soc.*, 1945, **87**) has stated that magnesium gives a straight line only at high temperatures, where the metal is volatile; at lower temperatures there is an appreciable falling off of oxidation with time.

Oxidation of Heavy Metals.—The heavier metals do not readily burn in air, and yield oxidation curves which definitely fall off with time; this is not surprising, since the oxide, if unconstrained, would occupy a larger volume than the metal destroyed in producing it and is thus likely to be obstructive. Iron obeys a logarithmic equation at low temperatures (Vernon, Akeroyd, and Stroud, *J. Inst. Metals*, **1939**, **65**, 321), which can be written

$$y = k_1 \log (k_2 t + k_3),$$

where y is the mean thickness at time t. At high temperatures it obeys (Portevin, Prétét, and Jolivet, *Rév. Met.*, **1934**, **31**, 101, 186, 219) the well-known parabolic equation

$$y^2 = k_4 t + k_5$$

In both these equations the *k*'s are constants independent of time but varying with temperature. Zinc, which has a low melting point, was found by Vernon and his colleagues to conform to the logarithmic law throughout the solid range..

The lecturer believes that the logarithmic equation is due to discrete mechanical breakdowns of the film due to the compressional stresses arising from the volume relation mentioned above. The wrinkling of the film observed when it is freed from constraint by the anodic undermining of the metal to which it is attached (Evans and Stockdale, J., 1929, 2651) testifies to the real existence of these compressional stresses, and it has been shown that such discrete breakdowns can lead to the logarithmic relationship (Evans, *Trans. Electrochem. Soc.*, 1943, **83**, 335).

The parabolic law is generally regarded as due to lattice imperfections in the oxide films, which at high temperatures become semi-conductors; the existence of these defects provides a means for the passage of metal cations outwards, accompanied by electrons, to meet the oxygen. Experimental evidence of the passage of metal outwards through the film in such cases has been furnished by Pfeil (*J. Iron Steel Inst.*, 1929, **119**, 520) and by Wagner (*Z. physikal. Chem.*, 1933, *B*, **21**, 37). Sulphide films, where the defects are more numerous, allow appreciable transport to take place at lower temperatures than oxide films; copper exposed to air containing hydrogen sulphide develops the same sequence of colours at ordinary temperatures as is developed at high temperatures in pure air. The presence of imperfections is shown by the fact that cuprous sulphide and ferrous sulphide contain less metal than the formulæ Cu_2S and FeS would indicate; the mineral, pyrrhotite, has been assigned the formula $Fe_{11}S_{12}$ in some mineralogical textbooks, but is best regarded as FeS with about 1/12 of the cation sites vacant, and with about $\frac{1}{6}$ of the cations in the ferric state, so as to maintain electrical neutrality.

The Electrical Basis of the Oxidation Constant.—The constant of the parabolic equation should, according to the conception of transport by lattice defects, be represented by Wagner's expressions, of which the simplest form (which neglects variation of conductivity with pressure) is

$$k_4 = [2Jn_e(n_c + n_a)\kappa E]/D\mathbf{F}$$

where κ is the specific conductivity, n_e, n_c and n_a the three transport numbers representing the share taken by electrons, cations and anions in transporting electricity, $\mathbf{F}$ Faraday's number, J the equivalent weight of the film substance (whether oxide, sulphide, iodide or other compound), D its density, and E the E.M.F. of the cell metal/non-metal. An instructive derivation of these expressions has been provided by Hoar and Price (*Trans. Faraday Soc.*, 1938, **34**, 876), and a simple exposition of the mechanism of film growth by Price (*Chem. and Ind.*, 1937, 769).

Only in three cases of film growth are the transport numbers known. Here, the observed and calculated values of the velocity constant show good agreement (see table), although the values of *k* in different cases are of different orders of magnitude. The velocity constant *k* used in the table is equal to $k_4D/2J$.

Calculated and experimental values of the constant k, as defined by the equation $d\dot{\eta}/dt = k/y$, *where* η *is the amount of oxide, sulphide or iodide in g.-equivs. per sq. cm.*

(Tabulated by L. E. Price from papers by C. Wagner.)

Reaction.	Temp.	Calc.	Exptl.
$2Cu + I_2 = 2CuI$	195°	$3{\cdot}8 \times 10^{-10}$	$3{\cdot}4 \times 10^{-10}$
$4Cu + O_2 = 2Cu_2O$	1000	6×10^{-9}	7×10^{-9}
$2Ag + S = \alpha Ag_2S$	220	$2\text{–}4 \times 10^{-6}$	$1{\cdot}6 \times 10^{-6}$

Improvement of Oxidation Resistance by Selective Oxidation Treatment.—Price and Thomas (*J. Inst. Metals*, 1938, **63**, 21), studying the numbers for the oxidation resistance of copper alloys obtained by Fröhlich (*Z. Metallk.*, 1936, **28**, 368), noted that qualitatively the results fitted the electrical theory of oxidation, since the addition of metals like aluminium and beryllium, whose oxides had high electrical resistance, enhanced the oxidation resistance of copper, whereas metals with oxides of low resistance conferred little benefit. Quantitatively, however, theory and observation seemed to clash. If the protective film on copper–aluminium alloys were pure alumina, the improvement should be at least 80,000 times (transport numbers being in doubt, an exact prediction was impossible); Fröhlich's measurements, however, showed an improvement of only 36.

Price and Thomas attributed this discrepancy to the presence of copper oxide in solid solution, which would diminish the resistance of the alumina, and expressed the view that pure alumina films—if obtained—would afford the theoretical improvement. They heated a copper alloy containing 5% of aluminium in hydrogen containing a trace of water vapour (corresponding to 0·1 mm. mercury pressure)—a treatment designed to oxidise aluminium, a metal with extremely high affinity for oxygen, but not copper. This treatment left the alloy unchanged in appearance, but evidently a protective film had been produced, since on being heated for 4 hours at 800° in oxygen, the specimen still remained unchanged in appearance, although an untreated specimen of alloy, heated in oxygen (for the same time and at the same temperature) became greatly blackened. Quantitative experiments showed that the treatment gave an improvement of 200,000 times, which compares reasonably with the prediction of theory (at least 80,000).

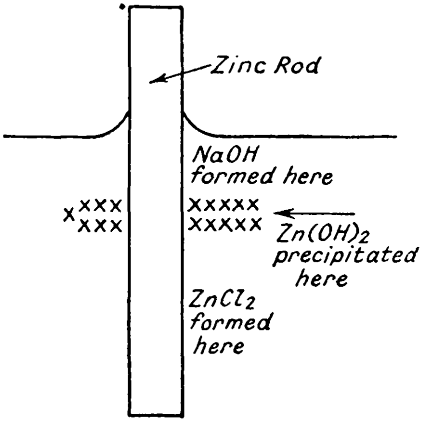
This process, known as " selective oxidation," not only provides a means of greatly improving the resistance of copper alloys to high-temperature oxidation in unpolluted air, but also the resistance of silver towards tarnishing in air containing sulphur compounds—a change which, for reasons given above, occurs at ordinary temperatures.

Non-Filming Reactions.

Action of Salt Solutions on Heavy Metals in Presence of Oxygen.—A solution of oxygen in pure water is likely to produce a layer of sparingly soluble oxide or hydroxide on the metal, and the attack will usually be unimportant—although exceptions could be cited. If, however, a salt is present in the water, electrochemical changes—often leading to freely soluble anodic and cathodic products—become possible, provided that the surface is not equipotential. In practice, some factor is usually present to produce a flow of currents between different parts of the metal. Clearly, if the specimen consists of two metals in contact, relatively strong currents may be expected. However, a single metal, if locally deformed, may generate currents, the deformed portion being usually anodic to the rest. Alternatively, if the oxide film or scale covering the surface is locally discontinuous, the bare metal will be anodic. Even an ideally uniform metallic specimen partly immersed in solution with air above will generate a current, the part near the water-line being usually the cathode, since oxygen, a cathodic stimulator, can here be replenished most readily. A few typical cases of electrochemical corrosion are discussed below.

FIG. 8.

Effect of vertical zinc plate or rod partially immersed vertically in sodium chloride solution.

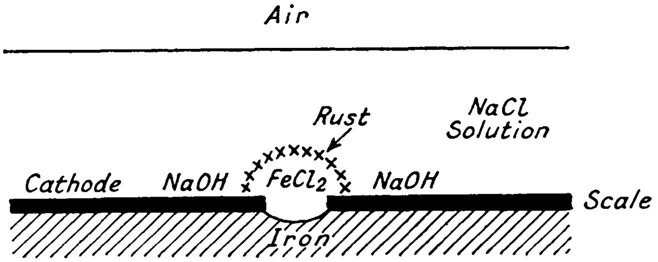


Zinc Rod Partially Immersed in a Salt Solution (Fig. 8).—If zinc is partially immersed in a solution of sodium chloride, oxygen at the water-line zone will be converted by the cathodic reaction into OH' ions, whilst, a little lower down, zinc will suffer anodic attack providing $Zn^{\cdot\cdot}$ ions. The cathodic and anodic products can be regarded as sodium hydroxide and zinc chloride respectively, and will give zinc hydroxide, often in a membranous form, at the level where they meet. The reaction is thus the combination of zinc, oxygen and water to form zinc hydroxide, but it will be noticed that zinc is destroyed at *one* point, oxygen taken up at a *second*, and zinc hydroxide precipitated at a *third*. Clearly, although the zinc hydroxide is sparingly soluble, it will not, for geometrical reasons, give protection to the metal, and attack will continue without stifling itself (cf. Fig. 8). This is the main danger of electrochemical attack; it often leads to freely soluble substances as the primary products, and the secondary product, although sparingly soluble, appears out of physical contact with the seat of attack. Where one of the primary products is sparingly soluble, even electrochemical action is retarded or prevented, as shown later.

Iron Covered with Discontinuous Mill-scale in Salt Solution below Air (Fig. 9).—Steel leaves the rolling mill covered with a thick oxide scale, usually discontinuous. If placed in sodium chloride solution, the metal exposed at a hole in the scale will be anodic to the scale, the current being usually controlled by the rate of supply of oxygen to the mill-scale around the hole, which forms the cathode. Since the cathode is relatively large, the rate of arrival of oxygen and consequently the current strength will be considerable, but its whole effect will be concentrated on the small anode (the iron exposed), so that the intensity of attack (the corrosion per unit area of the part affected) will be serious, and " pits " may be quickly produced at holes in the scale. A membrane of rust (Fe_2O_3, H_2O) is usually formed over each pit, where anodic and cathodic products meet. The removal of mill-scale usually diminishes the rate of penetration into a steel plate or pipe and consequently the risk of perforation, although the total attack may sometimes be increased.

FIG. 9.

Corrosion at breaks in oxide scale on iron immersed in sodium chloride solution.



Iron Covered with a Discontinuous Coating of Copper.—A continuous coating of copper will largely protect steel against attack, but if the copper is scraped away locally, exposing the steel, the dangerous combination of large cathode (the copper) and small anode (the exposed steel) arises, and intense local attack develops; electrochemical considerations indicate that under some, but not all, conditions, the attack will be more intense than if no copper were present; this intensification has been realized in the laboratory (for instance, Evans, *J. Inst. Metals*, 1928, **40**, 99).

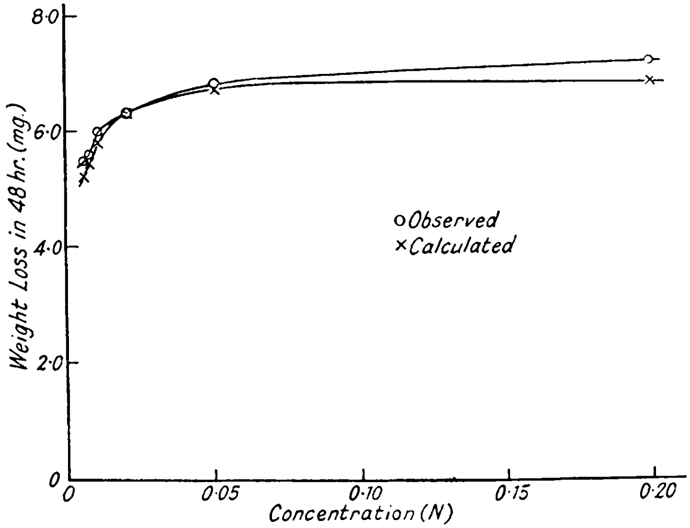
Iron Covered with a Discontinuous Coating of Zinc.—If the coating is of zinc, a metal anodic to iron, the iron exposed at a gap may receive cathodic protection, provided that the gap is not too wide. The protection of iron is achieved at the expense of the zinc, but it is better for the attack to proceed sideways instead of downwards, especially as this will reduce the chance of a fatigue crack developing. Zinc is often applied by dipping steel into the molten metal, or by electro-plating, or again by spraying (" metallization "). Lately it has become a practical proposition to apply it as paint, and experiments at Cambridge show that paint coats containing 95% of metallic zinc held together with polystyrene can be obtained, and give good protection against sea-water, even when applied to a rusty surface, since the zinc reduces the rust, and builds a conducting bridge to the iron below it. Rusty iron, coated with zinc-rich paint, and pierced with a scratch-line exposing the bright metal, has been kept in sea-water for two years without the development of fresh rust (Mayne and Evans, *Chem. and Ind.*, 1944, 109; Evans, *Met. Ind., London*, 1945, **67**, 114).

Quantitative Demonstration of the Electrochemical Character of Corrosion.—The currents flowing between anodic and cathodic areas on naturally corroding specimens have a real existence. They have been detected and measured by four independent methods, and were found strong enough to account for the amount of corrosion actually observed. The four methods are severally described in the following papers : Evans and Hoar, *Proc. Roy Soc.*, 1932, *A*, **137**, **343**; Thornhill and Evans, J., 1938, 614; Brown and Mears, *Trans. Electrochem. Soc.*, 1938, **74**, 495; 1942, **81**, 455; Agar, reported by Evans, *J. Iron Steel Inst.*, 1940, **141**, 221P.

Only the first and last of these will be considered. The method developed by Hoar depended on the availability, through the kindness of the late Dr. W. H. Hatfield, of a steel so uniform as to give reproducible distribution of anodic and cathodic areas on partial immersion in salt solutions. Specimens were cut along the dividing line, and the two halves mounted in their correct position partially immersed in salt solution and joined to an external source of current. The cathode potential drop was measured and plotted against the current passing. Having obtained this relation, Hoar took uncut specimens, and, by measuring the cathode potential drop, was able to ascertain the current flowing and thus, on division by Faraday's number, to calculate the corrosion; this was found to agree well with the corrosion experimentally determined by loss of weight (Fig. 10).

FIG. 10.

Corrosion of iron in potassium chloride solution (a) *observed by weight loss*, (b) *calculated from purely electrical data* (T. P. Hoar).



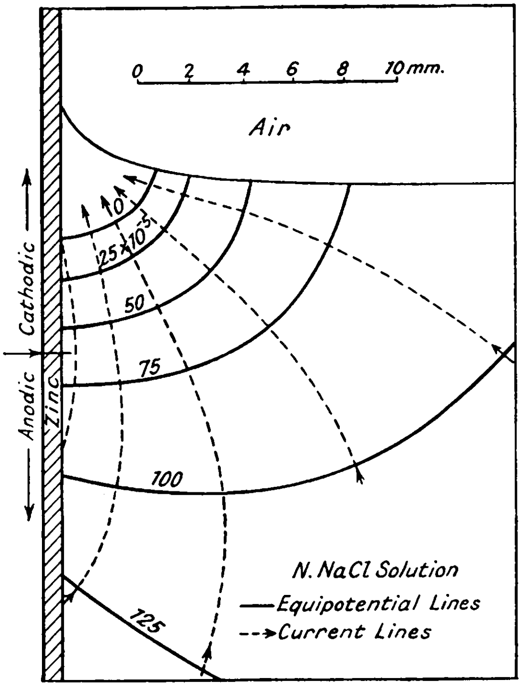
The most recent method, used by Agar just before the war in his study of zinc partially immersed in salt solution, depends on the plotting of equipotential lines (Fig. 11); if the specific conductivity of the liquid is known, the distance between the equipotentials provides, on application of Ohm's law, a means of estimating the current. Calculation from the electrochemical data accounted for the whole of the corrosion below the water-line; a small amount of corrosion on the zone wetted by creepage above the water-line may have had a different origin, but the outbreak of hostilities interrupted the research before this matter had been fully investigated.

Soluble Inhibitors.—If a water contains a sufficient quantity of a substance yielding a sparingly soluble substance either as cathodic or anodic product, even electrochemical corrosion will stifle itself. Thus we have two classes of soluble inhibitors, known as cathodic and anodic inhibitors respectively.

An important example of a cathodic inhibitor is calcium bicarbonate, which is present in most hard natural waters. It is the presence of this compound which makes it possible to carry these waters through steel pipes without their emerging red with rust, and without the objectionable property of producing red stains on white articles washed in it—as would happen if ferrous salts were present. As soon as these waters begin to act on iron, the rise of pH value at the cathodic surface causes the precipitation of calcium carbonate, which coats the cathodic areas and smothers the cathodic reaction. Although subsequently the calcium carbonate interacts with iron salts formed in the incipient anodic reaction to give a clinging form of rust, this rust has considerable protective action, and keeps the rate of corrosion far below that produced by soft waters. A water containing carbonic acid in excess of the amount needed to hold the calcium carbonate in solution will not at once throw down a film, and will therefore produce serious attack on steel pipes, emerging either rusty or (worse still) containing ferrous salts. If passed through a bed of limestone or calcined dolomite—to convert the excess carbonic acid into calcium bicarbonate—such waters often become suitable for pumping through steel pipes. Nevertheless, these inhibitors are not entirely efficacious, and will produce rust on bright, freshly abraded steel.

FIG. 11.

Potential distribution and current flow around zinc with sodium chloride (J. N. Agar).



Anodic inhibitors are more efficient. An example is potassium chromate, which serves to precipitate any trace of ferrous salts, formed at a discontinuity in an invisible oxide film, in physical contact with the metal, thus healing the " leakage " (Hoar and Evans, J., 1932, 2476). A piece of bright, abraded steel, placed in water containing chromate, remains bright and unrusted, but the concentration of chromates needed for complete inhibition increases with the chloride concentration; if the chromate added be insufficient, the area suffering attack will be diminished more than the total of corrosion, so that the corrosion per unit area of the part affected will be increased, and the attack intensified. It can be shown from electrochemical principles that this is to be expected (Evans, *Trans. Electrochem. Soc.*, 1936, **69**, 213); it is really another example of the combination of large cathode and small anode. These anodic inhibitors are, therefore, dangerous, since if added in insufficient amount, they intensify attack.

We have, therefore, to choose between two classes of inhibitor, one relatively safe but inefficient, the other relatively efficient but dangerous. Attempts are being made at Cambridge by Palmer to work out an inhibitive system which will be both safe and efficient, and some encouraging progress has been made.

Inhibitive Pigments.—Inhibitors are also used in anti-corrosive paints. Obviously potassium chromate is too soluble to be incorporated in a paint, but zinc chromate, which is sufficiently soluble to confer inhibitive properties on moisture soaking in through a paint, but not so soluble as to be rapidly washed away, is a common component of priming paints—often in conjunction with ferric oxide. The best known inhibitive pigments are, however, lead compounds, and the mechanism of their action is now under study at Cambridge by Mayne, who has found that generally the true inhibitor is not the pigment itself, but an organic compound, such as lead linoleate.