

CXIII.—*Liquid-line Corrosion.*

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THERE are many instances of enhanced corrosion occurring at the liquid line, when a solid is partly immersed in a liquid which has a chemical action on it, or which simply dissolves it. The phenomenon was first described by Spring (*Z. physikal. Chem.*, 1889, **4**, 658) for calcite dissolving in hydrochloric acid and for sucrose and sodium carbonate dissolving in water. He concluded that the extra dissolution was due to an enhanced reactivity of the solvent at the surface. This explanation was denied by Klobukow (*ibid.*, 1890, **5**, 180), who suggested that the greater portion of the solid was protected by the downward streaming of the product, whilst fresh solvent was always being drawn in at the liquid surface. Ganguly and Banerji (*Z. anorg. Chem.*, 1922, **124**, 140) believe that the phenomenon is related to the surface tension of the liquid, since the effect was diminished in the cases they investigated by covering with a layer of oil.

The water-line corrosion of metals offers a special case of great practical importance. Here it is generally held that atmospheric oxygen assists in the corrosion near the surface of the liquid. Evans (compare "Corrosion of Metals," Arnold, 1924, p. 106) takes a more definite point of view and ascribes the effect to the automatic removal of ions from the metal in the vicinity of the water line, through the relatively cathodic nature of the portion above. Watson and Watts (*Trans. Amer. Electrochem. Soc.*, 1923, **44**, 1) investigated many cases of slow corrosion of metals in aqueous solution and concluded that the effect was due to protection of the rest of the metal through the downward flow of the reaction products.

EXPERIMENTAL.

During the course of several years' work on the dissolution of metals in various reagents the author has been continually confronted with this phenomenon, and has had opportunities of studying

it, where the reaction velocity is fairly rapid. These seem to be more suitable and trustworthy conditions than the slow corrosion over periods of several weeks previously investigated.

Strips of zinc and magnesium were partially immersed in *N*-hydrochloric acid. The strips were eaten through along a line about 0.5 mm. above the water line some considerable time before the rest of the metal dissolved. Owing to the vigorous evolution of hydrogen, the reaction products were washed in an upward direction instead of downward, and the effect cannot be due in this case to protection of the metal thereby. Watson and Watts (*loc. cit.*) state that water-line corrosion does not take place when zinc dissolves in hydrochloric acid with disengagement of hydrogen. This statement, however, must be due to error of observation.

The effect has also been repeatedly obtained in the dissolution of magnesium in ammonium chloride solution, dilute sulphuric acid and dilute nitric acid, with zinc in dilute sulphuric acid and dilute nitric acid, and with aluminium in solutions of caustic soda and hydrochloric acid. Scarcely any effect was observed in the dissolution of iron in hydrochloric acid.

In all these cases the rate of gassing was sufficient to prevent any downward streaming of the reaction products. It seemed possible, however, that the depolarising action of oxygen contained in the surface of the solution could account for the increased velocity of corrosion. The experiments were therefore repeated in an atmosphere of hydrogen. Identical results were obtained, and thus it is established that the water-line corrosion of metals occurs in absence of the two causes which have been discussed.

Further evidence against the necessity for oxygen is furnished by the strong preferential liquid-line corrosion when strips of copper or iron are partly immersed in strong solutions of nitric acid. Here, the solution itself is a much more active depolariser than atmospheric oxygen. Again, although iron was not observed to undergo appreciable extra corrosion at the water line in hydrochloric acid, the effect is very marked when a mixture of hydrochloric and nitric acids is used. An idea of the magnitude of the effect is gained from an experiment in which copper sheet 0.022 inch in thickness dissolved in a mixture of 25 c.c. of nitric acid, 10 c.c. of hydrochloric acid, and 65 c.c. of water. When the water line was completely cut through, the thickness of the undissolved metal was 0.010 inch.

The excessive corrosion takes place just above the water line, at the place where a film of liquid creeps up the metal, and it seems that the increased velocity of reaction is a property of this film. Further evidence supporting this suggestion is gained from some observations on the dissolution of magnesium and zinc in dilute

acids. At suitable rates of reaction the ascending bubbles of hydrogen coalesce near the end of their course, forming a large bubble on either side of the metal sheet just under the water line. The bubble bursts in a short time, but is immediately formed again. Thus, during the greater part of the reaction, there exists just below the water line a thin film of solution in contact with the metal and bounded by the large bubble of hydrogen. Subsequent examination of the metal showed in every case a roughly circular patch indicative of strong preferential corrosion in the region adjacent to the bubble.

This explanation appears to account for the observation by McCulloch (*J. Amer. Chem. Soc.*, 1925, **47**, 1940) that when a rubber band is wrapped tightly round a piece of iron which is then immersed in dilute hydrochloric acid, the iron is strongly corroded under the rubber band.

The author has also repeated Spring's experiment, dissolving sticks of marble in 0.5*N*-hydrochloric acid and in *N*-nitric acid. Under these conditions, the upward wash of carbon dioxide bubbles causes a visible upward streaming of the soluble product, which can be observed to fall subsequently down the sides of the vessel. Excessive corrosion at the water line occurred in both cases. Here the oxygen theory or the electrolytic theory cannot enter. Gurwitsch also (*Z. physikal. Chem.*, 1924, **109**, 375) has performed experiments where the product of solution is specifically lighter than the solvent and yet found increased activity at the surface of the solution.

In experiments where little or no gas evolution occurred and the reaction products were allowed to flow down the metal, the effect was quite different when the metal broke off at the water line. The piece of metal was found to be progressively thinned from the bottom to the water line, resembling a fine wedge. In the other cases, where downward streaming was prevented, the fallen metal was of uniform thickness as though it had been sawn.

Whilst it may be admitted that the downward streaming of reaction products and depolarisation by oxygen may assist in preferential corrosion at the liquid line in suitable circumstances, these experiments indicate that the phenomenon takes place in absence of these causes, thus supporting the original hypothesis of Spring.

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