XXII.—*The Wet Oxidation of Metals. Part III.* *The Corrosion of Lead.*

By BERTRAM LAMBERT and HERBERT EDWIN CULLIS.

THE numerous researches which have been published on the action of water and oxygen on metallic lead have all been carried out with metal covered with a surface film of oxide.

It is well known that metallic lead, on exposure to the air, undergoes surface oxidation with the production of a dark-coloured oxide, which is generally described as a suboxide. Even the most highly purified lead undergoes this surface oxidation on exposure to the air, although in the case of lead which has been distilled in a vacuum and kept for a long time before exposure to the air, the brilliant metallic lustre is not appreciably dimmed for many days (see later).

The aim of the authors in the present investigation was to study the action of (a) water alone, (b) water and oxygen together, on metallic lead, first pure water and then pure oxygen being brought into contact with pure metallic lead, under such conditions that the lead, previous to the contact of the water, was entirely free from any trace of oxide.

This object was attained by distilling lead (previously made by Stas' method and fractionated in a vacuum) in a quartz apparatus, in a high vacuum, then distilling pure water on to the metal, and finally allowing pure oxygen to come in contact with the lead and water.

The apparatus used for preparing and storing the oxygen, for preparing the water, and for bringing each of them into contact with the metal was identical in every respect with that used in similar experiments on the corrosion of iron (Lambert, T., 1912, 101, 2058 *et seq.*)*.

* In a criticism of these experiments, Armstrong (*Science Progress*, 1913, 8, 73) insists that, in spite of the elaborate precautions taken, it is impossible, in an apparatus of this kind, to get rid of the gases (especially carbon dioxide) condensed on the surface of the glass. He takes exception to the statement that the whole of the glass surfaces was strongly heated for long periods (during the frequent successive operations of exhaustion which followed the washing out of the apparatus with pure oxygen), and states, in particular, that the large Schmidt stopcocks used in the apparatus could not, in his opinion, have been heated.

The barrels of these stopcocks are made of Jena normal glass and are hollow, the bore consisting of a tube fused across the hollow barrel. Thus the mercury-seal, which covers the top and bottom of the barrel, fills the hollow space in the barrel itself and circulates round the tube, forming the bore of the stopcock. The difference between the coefficients of expansion of the Jena glass of the barrel and

The only difference was in the type of vessel used for the reaction. This was constructed as follows: The vessel *A*, of about 150 c.c. capacity, was made of ordinary soft glass; the side-tubes *M* and *N* were drawn out to capillaries, and were sealed at *X* and *Y* to the oxygen and water supplies respectively. At *C* junction was made between this glass part and the quartz part of the apparatus *BCDEFG* by means of a ground joint. This ground joint was about 4 cm. long, and was ground very accurately. It was lubricated with glacial phosphoric acid, and was protected by a mercury cup *H* (represented in the figure by a dotted line). The quartz part of the apparatus (drawn in fine line in the figure in order to distinguish it from the glass part, which is drawn in thicker line) was of

the shape shown, and was made from transparent quartz tubing. It projected at *B* into the interior of the vessel *A*, so that when water was distilled into it the water which collected there must have condensed on a quartz surface, and could not have been in contact with a glass surface after condensation.

Metallic lead, which had been prepared as described below, was placed in the quartz tube at *F*; it was introduced through the open end *G*, which was then sealed off in the oxy-coal-gas flame.

The whole apparatus between the oxygen storage vessel and the

the ordinary soft glass of the outside makes it possible to heat these stopcocks to 200° without any risk of fracture if the operation is carried out with care. In the experiments the stopcocks were strongly heated to a temperature above 200° by surrounding them with boxes made of asbestos sheeting—so as to give, in effect, a hot air-bath—and then heating the boxes with a Bunsen burner.

water storage vessel (see Fig. 1, T., 1912, 101, 2058) was then very thoroughly exhausted by means of a mercury pump, and all the glass and quartz surfaces were strongly heated until the Plücker tube attached to the apparatus would not allow any discharge to pass from a large induction coil. The apparatus was then washed out with pure oxygen and exhausted many times, being strongly heated during each process of exhaustion. The residual gases at the end of several of the later operations were frozen out in tubes surrounded with liquid air and examined spectroscopically, but no trace of the carbon dioxide spectrum was ever detected.

The lead was then distilled in the high vacuum thus obtained by surrounding the quartz part of the apparatus *GFE* from *G* almost to *E* with an electrical resistance furnace and raising the temperature to about 1200°. The lead distilled, the oxide on the surface combining with the quartz, and being left behind as a lead silicate together with some metal at *F*. A large globule of metal collected at *E* and smaller globules along the lower part of the tube *EF*. These globules were of very brilliant lustre, and resembled silver or mercury globules in appearance. They had no trace of the bluish colour which is usually associated with metallic lead. Some of the lead vapour condensed as a grey, finely-divided, mirror-like deposit in the neighbourhood of the globules.

After the distillation the quartz tube was allowed to cool, and then water was distilled into the apparatus from a solution of barium hydroxide in a vacuum; the water was caused to collect in *DE* by cooling this part with ice. Oxygen was then allowed to enter the vessel, and afterwards the capillaries at *M* and *N* were sealed off.

It was possible in this way to bring pure water and pure oxygen into contact with pure lead without the previous contamination of the metal with a film of oxide.

For details of the methods of preparing, storing, and testing the purity of the water and oxygen, and for fuller details of the methods employed for bringing them in the highest state of purity into the reaction vessel, see T., 1912, 101, 2058 *et seq.*

Preparation of the Lead.

Many methods were employed to prepare lead in a high state of purity previous to its distillation in the manner described above, but it was found very difficult to remove all traces of iron. Finally, lead was prepared by the method described by Stas (*Bull. Acad. roy. Belg.*, 1860, 10, 295). It was cut into small chips by means

of a pure iridium spatula on to which a cutting-edge had been ground.*

The lead was then distilled in clear quartz tubes, which were about 7—8 mm. bore and 25 cm. long, and were divided into three compartments by narrowing the tube down to capillaries. The tubes were exhausted while the metal was kept in the molten state, and finally the lead was distilled at about 1200° . The first fraction was collected in the first compartment, which was then sealed off. The middle fraction was collected in the second compartment, whilst the residue was left behind in the third compartment. It is worthy of note that the globules of lead obtained in this way adhered very closely on the under side to the quartz, producing a very fine reflecting surface. It was found that if the distilled lead was exposed to air a short time after distillation, but when quite cold, the brilliant surface was quickly dimmed by a film of oxide. If, however, the metal was kept in the vacuous tube for several months, exposure to the air did not then cause any appreciable decrease in its brilliant lustre for several days.

It was only the middle fraction of lead that was used in the experiments described above.

Results of Experiments and Discussion.

In all the earlier experiments the water and oxygen were brought into contact with the lead within a few days of the distillation, and the results were the same. Very rapid oxidation took place. In the case of the metal, which was under the surface of the water, this resulted in the formation of crystals of white lead hydroxide, together with a brown-coloured oxide or hydrated oxide. The white crystals were detached from the metal, and at first caused a kind of opalescence in the water; the brown-coloured oxide adhered to the surface of the metal. The opalescence was visible within a few hours of the admission of the oxygen. The small globules of metal which were out of contact with the liquid water behaved similarly; the metallic lustre disappeared quickly, and a dark brown (almost black) coating of oxide appeared on the surface of the lead.

In the case of the grey films of metal which were not under the surface of the water the result was very striking; within half an hour after the admission of oxygen the grey films turned bright yellow throughout, and then after a few days the yellow colour began to change to a dull red. This latter change was slow, and

* Pure iridium is so hard that it is possible to grind a sharp cutting-edge on to a plate of the metal.

requires many months for completion. It is accelerated by light.*

The yellow substance is undoubtedly the unstable, yellow form of lead oxide, which is then gradually converted into the more stable red modification. It affords an interesting example of Ostwald's law of successive reactions.

It would appear from these experiments that metallic lead, even when very pure, undergoes very rapid oxidation in contact with pure water and pure oxygen.

It seemed possible, however, that lead which was freshly distilled in this way, in spite of its chemical purity, might not be physically homogeneous. In all probability metallic lead can exist in more than one physically different form, and in the change from the vapour phase (through the liquid) to the solid phase, the most unstable form would be produced at first. Judging from analogy to similar cases, one would expect that the change (or changes) from the unstable form (or forms) to the stable form would be slow, and so a globule of lead prepared by distillation would, soon after its preparation, contain more than one modification of the metal.

According to the electrolytic theory of corrosion, as interpreted by one of us (*Trans., Faraday Soc.*, 1913, **9**, 108), the lead, being physically heterogeneous, would tend to pass into solution in the electrolyte water because the different modifications of the metal, having different electrical potentials (or solution pressures), would tend to produce an electric current, with the consequent passing into solution of the metal at the relatively electropositive parts.

Now pure metallic lead is insoluble in water, in a vacuum, so far as chemical tests show. This was proved by experiments carried out in a similar manner to the above, in which freshly distilled lead was brought into contact with pure water in a vacuum, and left for many months; the water was then removed, evaporated down to a small bulk, and subjected to careful tests, but no positive evidence was ever obtained of the presence of lead in solution. This can only be taken to show, however, that the rate at which chemically pure, but physically heterogeneous, lead passes into solution in pure water is infinitesimally small, or so small that insufficient lead passes into solution, even after long periods of time, to be detected by chemical tests.

Corrosion is, however, undoubtedly preceded by, and takes place

* Ordinary litharge, which consists of a mixture of these two forms of lead oxide and, when freshly obtained, is yellowish, turns darker in colour when exposed to the action of light.

through, a process of solution of the metal, so that the rate at which lead passes into solution in water must be enormously increased by the presence of oxygen. It seems probable that the case is parallel with that of iron; oxygen probably accelerates the passing of the lead into solution by destroying the polarisation, which, in the absence of oxygen, is sufficient to reduce to an infinitesimal value the electric current which can pass between the electrically different parts of the metal.

If these considerations are valid, then pure metallic lead, if it be kept in a vacuum a sufficiently long time for the unstable forms to change into the stable form—for the metal to become physically as well as chemically homogeneous—might be expected to withstand the action of water and oxygen without undergoing corrosion.

In order to test this possibility, two exactly parallel experiments were carried out, side by side, in two vessels of the type described above. The lead used in each case was from the same fraction, and the temperature at which the lead was subsequently distilled, in the two vessels, was the same. Within twenty-four hours after the distillation of the lead, water was distilled into the two vessels, and then one of the vessels, containing pure lead and pure water only, in a vacuum, was sealed off and set aside for twelve months. Oxygen was admitted into the other vessel before it was sealed off, and the result in this case was the same as that described above.

After the lead in the first vessel had remained in contact with water in a vacuum for twelve months the metallic lustre of the metal was quite unaffected. The point of one of the capillaries was then broken off in an atmosphere of pure oxygen, and the gas thus allowed to come into contact with the lead and water. For more than a week there was no visible tarnishing of the brilliant metallic surface of the large globule of lead which was under the surface of the water, but after that time the metallic lustre was gradually dimmed by the formation of a dark-coloured coating of oxide on its surface. The rate of corrosion was, however, so slow that after more than six months' exposure to the combined action of water and oxygen the layer of oxide was thin enough to display interference colours. After exposure for nearly a year the globule of lead is covered with a layer of a dark brown oxide, and minute crystals of hydrated lead oxide can be seen in the water.

The surface of the smaller globules of lead along the portion of the tube *EF* and out of contact with liquid water was oxidised very slowly but, perhaps most striking of all, the grey films of finely-divided lead which underwent such rapid oxidation in the parallel experiment showed no similar change; for many months there was no apparent change in their appearance, but now, after

nearly a year, a small patch of the yellow form of the oxide has appeared.

The differences between the behaviour of the lead in these two parallel experiments is very striking and significant. Although keeping the pure lead for a period of one year in water in a vacuum does not result in entirely preventing corrosion when oxygen is brought into contact with the metal, yet the rate of the oxidation is enormously decreased.

The differences between the two specimens of lead, prepared in precisely the same manner—differences brought out by “ageing” the metal—are probably only differences of a physical character. If, as seems probable, lead can exist in different modifications, the more unstable forms will predominate in the freshly distilled metal, and thus give it a heterogeneous character, which is, moreover, gradually changing. When the metal is kept for a long time in a vacuum it would become more homogeneous as far as its physical character is concerned, and consequently the rate at which it would pass into solution in water in the presence of oxygen would be greatly decreased.

The results of these experiments thus afford very strong evidence of the validity of the electrolytic theory of corrosion.

In the corrosion of lead, the metal probably passes into solution as lead ions, owing to the electrolytic action between the electrically different parts of the metal. In the absence of oxygen, the velocity of this action is infinitely small, because the hydrogen separating out at the relatively electronegative parts introduces an enormous resistance to the passage of the current. Oxygen greatly accelerates the action by oxidising the film of hydrogen—destroying the polarisation—producing water and, probably, hydrogen peroxide (see later).

The lead ions then combine with the hydroxyl ions of the water to form an undissociated lead hydroxide, since lead is a very weakly basic element.

If, as seems probable, the dark-coloured oxide first formed on the metal is a hydrated, plumbous oxide, $\text{Pb}_2\text{O} \cdot 2\text{H}_2\text{O}$, the lead will pass into solution as plumbous ions and produce, with the hydroxyl ions, an undissociated plumbous hydroxide. In that case, the oxygen will play a second part, in oxidising the plumbous to plumbic hydroxide—the ordinary white, crystalline hydroxide of lead.

It has been shown by Traube (*Zeitsch. physikal. Chem.*, 1900, **32**, 137), Dunstan (T., 1911, **100**, 1835) and others, that hydrogen peroxide is formed when lead, water, and oxygen are brought together. The hydrogen peroxide theory of the corrosion of metals

was first put forward by Traube, and, according to this theory, the reactions involved in the wet oxidation of lead were represented thus:

Now, Traube has shown that hydrogen peroxide is formed when oxygen is passed through the cathodic chamber of an electrolytic cell in which dilute sulphuric acid is being electrolysed between platinum electrodes. The hydrogen peroxide must be formed by the action of ordinary molecular oxygen on electrolytically-formed hydrogen, probably at the moment of its formation, and while it is in the nascent state.

Since lead passes into solution in water, by a process of electrolysis involving the formation of hydrogen, one would expect some hydrogen peroxide to be formed as well as water, but the formation of this substance is not directly concerned with the wet oxidation of lead or any other metal.

It might be expected, however, that the hydrogen peroxide would have a further oxidising action on the lead oxide produced, and this proves to be the case. It was stated above that the film of finely divided lead, produced by distilling the metal, underwent very rapid and complete oxidation, with the production, first, of the yellow modification of lead monoxide, and then of the more stable red form. This oxide film (both the yellow and red forms) is very readily soluble in cold dilute nitric acid if treated with the acid within a few days of its production. If the action is allowed to go on, as it was in some cases, for many months, then the oxide film is not completely soluble in dilute nitric acid, but leaves behind a brown deposit of lead peroxide, PbO_2 . The examination of some specimens of lead that had been in contact with water and oxygen for many years showed quite appreciable amounts of higher oxides, which gave the brown peroxide when treated with dilute nitric acid.

Either or both of the oxides, Pb_2O_3 , Pb_3O_4 , might be present (a quantitative analysis was not possible), and they are probably formed by the action of hydrogen peroxide on the lower oxide.

Summary of Conclusions.

(1) Pure lead which has been distilled in a vacuum undergoes very rapid corrosion when subjected to the action of pure water and pure oxygen within a short time of the distillation of the metal. Chemical tests fail to show the presence of lead in solution before the addition of oxygen.

(2) If the lead prepared in this way is kept for long periods in water, in a vacuum, before the oxygen is added, the rate of corrosion is enormously decreased.

(3) Pure lead which has been distilled in a vacuum, and kept for some months, can be exposed to ordinary air for many days without any appreciable diminution of its brilliant metallic lustre, but more prolonged exposure causes the gradual formation of a dark-coloured oxide on the surface of the metal. The pure, distilled lead resembles silver or mercury in appearance, and shows none of the blue or bluish-grey colour usually associated with metallic lead.

(4) The electrolytic theory of corrosion is applicable to lead. The passing of the metal into solution, which precedes corrosion, is due to electrolytic action between the electrically different parts of the mass of lead. In the case of chemically pure lead, the physical heterogeneity (due to the presence of different allotropic modifications of lead in the mass of metal) causes parts of the mass to be electrically different from other parts, and these electrical differences persist for a long time after the preparation of the metal.

(5) Hydrogen peroxide, which is produced in the wet oxidation of lead, is the product of a subsidiary action, and has no direct bearing on the process of corrosion. It plays a part, however, in oxidising the monoxide to higher oxides.

THE UNIVERSITY CHEMICAL LABORATORIES,
OXFORD.

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