XXXIX.—*Anomalous Behaviour of the Hydrogen-Electrode in Solutions of Lead Salts, and the Existence of Univalent Lead Ions in Aqueous Solutions.*

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AN attempt was made to measure the hydrolysis of lead salts by the electrometric method described by one of us (Trans., 1908, 93, 41). Solutions of lead chloride, sulphate, and acetate were experimented with, but in every case it was noticed that the electrode did not attain a steady value in the usual time (ten minutes), and even after some hours it had not reached a value such as would be expected from Ley's measurements on the hydrolysis of lead chloride by the inversion method (*Zeitsch. physikal. Chem.*, 1899, 30, 193). For instance, a solution of lead acetate, which reacted alkaline to litmus, gave after two hours a hydrogen-ion concentration of the order 10^{-4} , whereas one would expect a value not greater than 10^{-9} . In fact, the value found for the hydrolysis was in all cases far higher than was expected.

Two possible explanations suggested themselves, firstly, the separation from the solution of a metal more "noble" than hydrogen, and, secondly, the possibility that lead itself might be precipitated on the electrode when the current passed in such a way that the hydrogen-electrode was acting as a cathode.

The first possibility was disproved by using a solution of very pure lead chloride, previously boiled with lead clippings, to remove silver or any other metals more "noble" than lead. This solution behaved in exactly the same manner as the others.

The possibility of deposited metallic lead causing the phenomenon was disposed of by two experiments. A few milligrams of metallic lead were deposited on a hydrogen-electrode, which was then tested in 0.001*N*-hydrochloric acid; the potential registered showed that the lead had in no way altered the character of the electrode, which behaved exactly as an ordinary hydrogen-electrode. Lastly, an experiment was carried out in which the hydrogen-electrode always acted as anode, but precisely similar results were obtained.

Although the above experiments conclusively prove that lead itself cannot cause the phenomenon, there yet remains the possibility that lead-platinum alloys may be formed, in which the lead, on the analogy of the osmotic pressure of mixed crystals, has a lower solution pressure than that of pure lead, and, perhaps, of hydrogen itself, and

hence may be precipitated as alloy by the latter. But it was noticed that the potential obtained depended on the velocity with which the hydrogen bubbled through the solution; the quicker the stream the lower the hydrogen potential, and vice versa. Now each bubble of gas rose from directly beneath the electrode, consequently the faster the stream of gas the more would the surface film of the electrode be disturbed. This suggested that the action $\text{Pb}^{++} + \text{H} \rightleftharpoons \text{Pb}^+ + \text{H}^+$ was occurring in the surface film; the faster the stream of gas the more quickly would the free acid, produced through the reduction of bivalent to univalent lead ions, be carried into the main bulk of the liquid, and, hence, the lower would be the hydrogen potential. This consequence was tested by shaking the electrode, when the same effect was observed as on increasing the velocity of the gas, and also by arranging in the same solution two electrodes differently situated as regards the incoming gas. There was a marked difference in the potentials recorded by these electrodes, that directly above the place where the gas entered giving a decidedly lower value than was given by the electrode which was further removed from the disturbing influence of the hydrogen. These facts are sufficient evidence to disprove the formation of such an alloy as already described.

Thus the anomalous behaviour of the hydrogen-electrode in solutions of lead chloride, sulphate, and acetate seems best explained on the assumption that the hydrogen-electrode reduces the bivalent to a univalent lead ion with the production of free acid, and the potential registered is that of the surface film, rich in the hydrogen ion.

The existence of Pb^+ -ion in solution has not previously been noticed, but the existence of lead sub-oxide (Pb_2O) has been rendered tolerably certain by the experiments of Tanatar (*Zeitsch. anorg. Chem.*, 1901, **27**, 304), recently confirmed by Brislee (*Trans.*, 1908, **93**, 154).

The discrepancy observed in the use of the copper voltameter has been definitely proved to be attributable to the formation of cuprous salts in solution. The silver voltameter shows a similar behaviour, and Bose (*Zeitsch. Elektrochem.*, 1907, **13**, 477) has shown that a sub-valent silver ion can exist in solution. To test the possibility of a univalent lead ion, the method described by Richards, Collins, and Heimrod (*Zeitsch. physikal. Chem.*, 1900, **32**, 321) for copper, and by Bose (*loc. cit.*) for silver, has been used. This is based on the fact that the formation of the sub-salts of copper and silver is attended by the absorption of heat. On heating the metal in contact with a solution of its salt, the equilibrium shifts towards the sub-salt, whilst, on cooling, the process reverses and metal is precipitated.

The apparatus used is shown in the figure. The right limb contained a column of pure granulated lead surrounded by a steam-jacket, whilst the left spiral limb was kept cool by a stream of cold water. In this

way, a constant circulation of the solution contained in the apparatus is kept up by the differences of density occasioned through the difference in temperature between the two limbs. The apparatus contained a 1.3 molar-normal solution of lead acetate slightly acidified with acetic acid. After a few days, distinct crystals of lead began to appear on the glass at the bottom of the hot limb, and these grew steadily, forming quite a network of shining crystals. Nothing, however, appeared in the cold limb, where crystallisation was expected, but, on introducing a piece of lead into the top of the spiral condenser, well-defined crystals soon made their appearance on it, and these steadily increased in size. This proves that the solution in the cold limb was supersaturated with the univalent ion, for, unless crystallisation is started by introducing a piece of lead, no crystals appear until the solution reaches the cold end of the column of lead.

Although the crystals obtained in the cold limb can only be due to the reaction $\text{Pb}^{++} + \text{Pb} \rightarrow 2\text{Pb}^+$ having taken place in the hot limb, and being reversed in the cold, still it is possible that the crystals at the bottom of the lead column were due to a weak thermo-current flowing from the hot solution above to the comparatively cold solution at the bottom of the limb, for it is evident that the solution would not immediately attain the temperature of the jacket.

This possibility was tested in two ways. In the first case, an experiment was devised in which there were present all the conditions for such a thermo-electric current, but the cumulative effect due to the circulation was dispensed with. The apparatus consisted of a glass tube sealed at one end. It contained a rod of lead and a molar-normal solution of lead acetate, acidified with acetic acid. The upper part of the tube was enclosed by a steam-jacket, the lower was at the ordinary temperature. All the conditions for a thermo-current present in the former experiment are satisfied here, but, owing to the want of circulation, there is little chance of univalent lead ions formed in the upper and hot portion diffusing to the cold end in sufficient quantity to cause any marked crystallisation.

At the end of a week, the experiment was stopped, and the rod of

lead examined. At the junction of the hot and cold parts of the lead, a very little spongy lead had been deposited. The quantity so obtained was far less than that in the former experiment, and totally different in appearance. Thus it is definitely proved that a slight thermo-current from the hot solution above to the colder beneath does exist, but the lead deposited is not only much too small in quantity to explain that deposited at the bottom of the lead column in the "circulation" experiment, but is also of the spongy nature with which we are familiar in the electrolysis of solutions of many lead salts.

Moreover, the thermo-electric theory was again disproved by repeating the "circulation" experiment with one altered condition; the lead column was broken by glass beads into a number of short sections, between the ends of which there could be no appreciable difference. Yet, after two days, crystals of lead began to appear, and in a short time formed a network round the whole of the bottom section. Rapid crystallisation also took place on a piece of lead introduced into the top of the cold condenser.

We are therefore justified in concluding that in the "circulation" experiments the whole of the crystalline lead deposited is due to the reaction $\text{Pb}^{++} + \text{Pb} \longrightarrow 2\text{Pb}^{\cdot}$ taking place in the hot, but reversing in the cold, and, moreover, the presence of a univalent lead ion in aqueous solution has for the first time been proved.

Summary.

1. The hydrogen-electrode cannot be used to determine the hydrolysis of lead salts, owing to the reduction of the bivalent to the univalent lead ion.
2. A solution of lead acetate, heated with lead, forms a sub-acetate, and this is attended with the absorption of heat.
3. A piece of lead in a solution of lead acetate, which is maintained at two different temperatures, forms a thermo-cell, the current flowing from the hot solution to the cold, and causing the deposition of traces of spongy lead at the cold end of the column of lead.

In conclusion, we wish to take this opportunity of thanking Prof. F. G. Donnan for the interest he has displayed in these experiments.

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