LXXVI.—*The Existence in Aqueous Solutions of a Univalent Cadmium Ion, a Subvalent Thallium Ion, and a Bivalent Bismuth Ion.*

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IN a recent paper by Denham and Allmand (this vol., p. 424), certain anomalous results were obtained in attempting to measure the hydrolysis of lead salts by the use of the hydrogen electrode, and these could be satisfactorily explained only by the assumption that the bivalent lead ion is reduced to the univalent state in the surface film of the electrode. This conclusion was further tested by carrying out a "circulation" experiment, wherein a hot solution of lead acetate has been circulated over granulated lead for some days in order to obtain a cumulative effect; for a description of the apparatus, the original paper must be consulted. After a few days, definite metallic crystals were observed, separating out at the bottom of the column of lead. An analysis of these has since been carried out, and the percentage of lead was found to be 99·8. The low value is undoubtedly due to superficial oxidation of the crystals after their removal from the apparatus. It may be mentioned that the percentage of lead in the lowest oxide of lead (Pb_2O) is 96·3.

The separation of these crystals might conceivably be due to the formation in the hot limb of a complex anion, with a reversal of the reaction in the cold, but this view cannot be reconciled with the results obtained with the hydrogen-electrode, wherein it was proved that a reduction takes place with the consequent production of acid. The fact that both series of experiments were carried out in the absence of oxygen, excludes the possibility of such an ion as Pb^{IV} causing the phenomenon. Thus, the only explanation which appears to satisfy the results of both sets of experiments is that, under certain conditions, the bivalent lead ion may be reduced to a univalent state.

Precisely similar remarks apply to the metals, cadmium and thallium, the experiments with which will shortly be described, but in the case of bismuth the hydrogen-electrode was not used to test the reduction. However, the absence of air in the "circulation" experiment at least excludes the view that such an ion as Bi^{V} causes the separation of crystals.

A ready method for demonstrating the separation of lead crystals from solutions of lead salts lies in the use of reduced lead. If a hot solution of lead chloride be poured on a quantity of this finely-divided powder and allowed to cool, many bright crystalline faces of metallic lead may be seen scattered over the surface of the heavy powder. The effect is even better when a few pieces of granulated lead project above the bulk of the reduced metal. Crystal spikes grow from the corners of the massive metal, and, in conjunction with the experiments described previously, demonstrate the equilibria:

This experiment is extremely suitable as a lecture experiment to show the presence of a univalent lead ion.

If a hot solution of lead nitrate is used, exactly similar crystals appear, but it is advisable not to heat the solution too strongly or the presence of insoluble salts may mask the effect.

Univalent Cadmium Ion.

Nothing is known of any solid sub-salt of cadmium with the exception of the suboxide, the existence of which was first established by Tanatar and Levin (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 495) and recently confirmed by Brislee (*Trans.*, 1908, **93**, 154).

The formation of a univalent ion of cadmium has been tested by carrying out a "circulation" experiment of the type described.

In this experiment, as well as in all succeeding ones, the column of metal in the hot limb was always broken into short sections in order

to prevent any possible thermo-currents that might cause the deposition of metal. The metal was granulated, whilst the acid solution used was 4-molar-normal with respect to cadmium sulphate.

After forty hours, the lowest section of the column was found to be thickly coated on the glass with a large number of beautiful fern-like crystals. On introducing a piece of cadmium into the top of the cold condenser, crystals soon began to grow from its corners. The same peculiar case of supersaturation therefore occurs as was noticed in the case of lead. The reduction of the bivalent to the univalent ion takes place in the hot limb with absorption of heat, and one would expect the action to reverse spontaneously in the cold limb with the deposition of metallic cadmium. But this only occurs in contact with the metal, and at the ordinary temperature a solution may contain far more univalent ion than corresponds with an equilibrium condition unless crystallisation is induced by the introduction of a nucleus. Bose (*Zeitsch. Elektrochem.*, 1908, **14**, 85) has recently commented on a similar phenomenon in the $\text{Au}^{+++} \rightleftharpoons \text{Au}^+$ equilibrium.

The crystalline cadmium was easily removed from the granulated metal which it enclosed, and, after washing and drying, was found to weigh 4.5 grams. This represents the yield from a five days' experiment. It is evident that if the experiment is begun with sufficiently pure materials the resulting crystalline metal must be of very great purity, for the two main factors in securing a good yield are a large metallic surface and a high ionic concentration. Thus it is extremely unlikely that any impurity would be present both in the ionic and metallic states in sufficient quantity to display any tendency to form an ion of lower electrovalency. The method therefore appears applicable for securing very pure specimens of certain metals for atomic weight determinations.

An analysis of some of the deposited crystals gave the following result: 0.6303 gram of the metal was converted into the sulphate, and weighed as such. The cadmium contained in this salt amounted to 0.6306 gram

Subvalent Thallium Ion

The apparatus contained granulated thallium, and a tenth-normal solution of thallic sulphate. After two days, small, but definite, crystals began to grow on the surface of the metal in the bottom section, and these crystals increased steadily in size. As in the previous cases of lead and cadmium, this result is best explained by assuming the reaction :

Previously nothing has been known of any ion of thallium lower

than the univalent, but this experiment shows that in all probability a subvalent ion (Ti_2^+) exists in solution, and it is probable that in this we must look for an explanation of the action of light on the haloid salts of thallium. It has long been known that these salts darken under the action of light (compare Kuhlmann, *Bull. Soc. chim.*, 1864, [ii], 1, 330; Buchner, *Sitzungsber. K. Akad. Wien*, 1865, [ii], 52, 644, and Hebbeling, *Annalen*, 1865, 134, 11). Now Luther (*Zeitsch. physikal. Chem.*, 1899, 30, 628) has brought forward strong evidence that the colour change of silver halides under the action of light is due to the formation of coloured sub-salts, and Bose has continued the work by demonstrating the existence of a subvalent silver ion in aqueous solution.

The existence of such a salt as Ti_4SO_4 in solution renders it probable that the action of light produces a similar effect on the thalious halides as it does on silver halides; the darkening on exposure to light would, on this assumption, be due to the formation of coloured sub-halides of thallium (Ti_2Cl , &c.).

Bivalent Bismuth Ion.

Numerous workers, among whom may be mentioned Schneider (*Pogg. Ann.*, 1855, 96, 130), Weber (*ibid.*, 1859, 107, 596), Heinz (*ibid.*, 1844, 63, 55), and Berthelot (*J. Pharm.*, 1828, 14, 616) claim to have prepared compounds of bivalent bismuth, but in no case has the resulting product been proved to be the pure substance. Some years ago Tanatar (*Zeitsch. anorg. Chem.*, 1901, 27, 437) brought forward strong evidence in favour of the existence of bismuth sub-oxide, whilst Brislee (*loc. cit.*) has recently confirmed his conclusions.

In order to investigate the possibility of an ion of lower valency than Bi^{+++} , a "circulation" experiment has been carried out. The metal was, as usual, granulated, and the solution was a saturated solution of bismuth oxychloride in hydrochloric acid. After four days, tiny crystals were noticed a short distance from the bottom of the column of metal. Moreover, a piece of metal which projected at least an inch above the top of the steam jacket also showed distinct signs of adhering crystals. The temperature of the solution in the neighbourhood of these crystals was found to be 94° , that is, a drop of six degrees was sufficient to cause a marked reversal of the ionic reaction. But as this fall in temperature might give rise to a weak thermo-current with the consequent deposition of metal, the projecting piece of metal was removed, glass beads introduced, and on these a piece of bismuth placed. In twelve hours, this piece had assumed a bright crystalline appearance, due to the large number of small adhering crystals.

It is of interest that the crystals do not first appear quite at the bottom of the column, where crystallisation from the cold saturated solution might be expected. In the lead experiments, it was noticed, but not recorded, that a nucleus of metal does not induce crystallisation when the temperature is below 50° ; here, as well as in the above case of bismuth, the phenomenon is probably due to the velocity of crystallisation being extremely small below that temperature.

The deposition of crystals in the above experiment is in all probability due to the reduction of the trivalent ion to one of lower electrovalency, and, in conformity with what is known concerning the sub-salts of bismuth, BiCl_2 and BiO , we must regard that ion as the bivalent one.

Sub-salts of Nickel, Antimony, and Arsenic.

Although a suboxide of nickel has been described, no signs of crystallisation were obtained in a "circulation" experiment with nickel and nickel sulphate solution. As it must be less difficult to obtain an aqueous solution of a sub-salt than to prepare the solid substance, this result seems to throw doubt on the existence of the suboxide.

In the case of arsenic and antimony, no sign of crystal growth had occurred when the metal was heated for ten days in contact with an acid solution of the chloride, although this is probably due to the low concentration of the metallic ion.

Summary.

1. Evidence has been brought forward for the existence of lead sub-chloride and sub-nitrate in aqueous solution.
2. The existence of cadmium sub-sulphate and of a univalent cadmium ion in aqueous solution has been rendered tolerably certain.
3. The presence of a subvalent ion of thallium has been similarly investigated, and it is probable that the darkening of thallos haloids in light is due to the formation of sub-haloids.
4. The trivalent bismuth ion has been reduced to the bivalent state in aqueous solution.
5. A negative result has been obtained for nickel, arsenic, and antimony.

In conclusion, I wish to thank Professor F. G. Donnan for the facilities and advice which he has placed at my disposal during the course of these experiments.

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