XXIV.-Note on a Reaction of the Acetates upon Lead Salts, with Remarks upon the Solubility of Lead Chloride.

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WHEN sodium chloride is added to either acetate or nitrate of lead, if the solutions be sufficiently concentrated, it is well known that a white precipitate is formed, and this is regarded as lead chloride. But chemists are perhaps not generally aware of the fact that if acetic acid be immediately added to the precipitate produced in the acetate solution, the whole is entirely dissolved for the moment, but crystals of lead chloride speedily begin to form; the precipitate in the lead nitrate solution remains unchanged on the addition of acetic acid. And further, if to the clear solution, after the precipitation of lead nitrate by sodium chloride, any acetate be added, even in the cold, a cloudiness is immediately formed which gradually becomes a precipitate. This is particularly the case with copper acetate, which, if agitated with the solution above referred to, yields in a few hours a copious deposit, perfectly soluble in acetic acid. It was thought at first that this might prove a characteristic test for the acetates, but experience showed that the formates and probably other members of that group yielded the same reaction. It occurred to me subsequently that it might be the insolubility of the acetates in sodium chloride that produced these somewhat singular results, and although experiments did not show that this was entirely the case, it sufficiently proved that sodium chloride took an important part in the reaction, as copper acetate gives a precipitate in strong solution of sodium chloride. This does not happen with ammonium, sodium, or potassium acetate, yet if one drop of a lead salt be added, a precipitate is produced which is immediately soluble in acetic acid. Formates and acetates can thus be easily distinguished from malates, tartrates, citrates, phosphates, &c., the soluble salts of which yield precipitates with lead solutions, but are insoluble in acetic acid. But by far the most sensitive test for the presence of acetates and formates is the employment of a copper salt. When copper acetate is largely diluted with water and boiled, the greater part is decomposed; free acetic acid is evolved, and black copper oxide precipitated, but even long-continued ebullition fails to effect entire decomposition. When, however, one-thousandth part of copper acetate is merely heated with sodium chloride, an immediate precipitate is produced, with formation of oxychloride of copper, which does not blacken or change colour after prolonged boiling. It is, of course, unnecessary to use this copper acetate. If a drop of any acetate be added to copper nitrate or chloride, and gently warmed,

especially in the presence of sodium chloride, the reaction is very evident. Although it has been stated that formates and acetates behave similarly, an experienced eye can detect the difference. Formic acid gives a blackish-grey deposit, evidently containing free oxide of copper, whilst acetic acid yields a bright grass-green precipitate unchanged by any duration of ebullition.

Mr. Carter Bell, in an elaborate and interesting paper (Chem. Soc. Journal, xxi, 350) on the Solubility of Lead Chloride, states the remarkable fact that this salt becomes less soluble when hydrochloric is added to a certain point, and increases in solubility when more of the acid is added. Pure water dissolves 0.946 or 1 in 120; with the addition of 1 per cent. hydrochloric acid, only 0.347, while with 14 p.c. of the acid 0.090 is dissolved, which is the maximum quantity. After the liquid becomes more acidified, the solubility of the salt increases, so that at 72 per cent. of acid it is more soluble than in water, and in the pure acid (sp. gr. 1.162) as much as 2.900 is dissolved. The reaction is rather different when sodium chloride is used as a solvent. My own experiments proved that the solubility of lead chloride in pure water was 1 part in 120, agreeing exactly with the result obtained by Mr. Bell. On the addition of sodium chloride to the extent of 5 per cent., its solubility decreased very considerably, and only 1 in 437 remained in solution. When, however, the lead salt was digested with a concentrated solution of sodium chloride, it was found to be rather less soluble than in water, viz., 1 in 129. This fact can be exemplified in an interesting manner by the addition of solution of sodium chloride to an aqueous solution of lead chloride, when crystals of the latter are deposited, and vice versa, when water is added to a solution of lead chloride in concentrated sodium chloride.

Although chemists are aware that when lead sulphate is treated with hydrochloric acid, lead chloride is formed and free sulphuric acid remains in solution, it may probably not be known how immediately even a cold saturated solution of sodium chloride decomposes lead sulphate. And it almost appears that at first there is not only an actual decomposition, but a solution, as 1 gram of lead sulphate dissolves perfectly in 100 grams of solution of sodium chloride, and after some hours deposits crystals of lead chloride. Sulphuric acid, or a soluble sulphate gives no precipitate with lead chloride dissolved in sodium chloride. Mr. Bell has also remarked upon the different forms of crystals of lead chloride, some being in fine needles and others in feathery plates. Both varieties can be obtained most beautifully by the following method. A solution of aniline hydrochloride forms lead chloride with difficulty; indeed both solutions must be rather concentrated before any reaction is perceptible. On leaving the liquid to stand some time, fine needle-shaped crystals are deposited, and if to the

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mother-liquor a few drops of sodium chloride be added, a beautiful mass of iridescent scales is produced, differing entirely in physical structure from the former. An observation of no great importance may also be mentioned. When potassium iodide is added to a solution of lead chloride in sodium chloride, the precipitate is not amorphous, but has the brilliant spangly appearance which it presents when deposited from its solution in hot water.

It may be mentioned in conclusion that the most sensitive test for the presence of an acetate or formate is a solution of copper chloride in sodium chloride. When this is gently warmed and remains perfectly bright a very minute amount of either a formate or acetate yields a precipitate; but it may be advisable to add a trace of lead salt and boil, as the phosphates, &c., of copper are more soluble in acetic acid than the corresponding lead salts.