XXXIII.—*On Lead Tetrachloride.*

By W. W. FISHER, M.A., Aldrichian Demonstrator of Chemistry,
Oxford.

THE existence of a tetrachloride of lead has been for many years generally assumed upon theoretical grounds, but direct experimental evidence has not hitherto been obtained to establish the composition of this interesting compound. It seemed to me possible that the method of analysis adopted to prove the existence of a tetrachloride of manganese would be suitable also for the analogous lead compound, and, as the result shows, this supposition was entirely verified by experiment. (See this Journal, 1878, xxxiii, 409.)

When lead dioxide is acted upon by moderately strong hydrochloric acid, a yellow solution is obtained smelling strongly of chlorine, which is decomposed by heat, with evolution of chlorine gas, while ordinary lead chloride is deposited in the crystalline form. This yellow solution gives a precipitate of brown hydrated peroxide of lead when treated with solutions of the fixed alkalis or alkaline carbonates, and also with oxides and carbonates not freely soluble in water, such as oxides of magnesium, zinc, mercury, and lead, and carbonates of barium, manganese, lead, and many other metals. Moreover, compounds of the alkalis with weak acids, such as acetic and boracic acids, similarly produce a precipitation of hydrated peroxide of lead. It is remarkable, too, that if excess of hydrochloric acid is avoided, and the liquid is carefully saturated with lead dioxide, the yellow solution, by simple dilution with pure water, is decomposed, and the same precipitation of lead dioxide observed, precisely as the solution of manganese tetrachloride is decomposed by the addition of water.

The method of experiment was the same as that followed in the analysis of the similar manganese compound, and the same apparatus was employed for performing the filtration with least possible loss of chlorine. But as the total chlorine could not conveniently be determined by means of the decomposition of potassium iodide, a solution of a ferrous salt of known strength was used in this case.

A quantity of lead dioxide was cautiously added to twice its weight of hydrochloric acid previously diluted with an equal volume of water. The yellow solution thus prepared was after a few minutes poured off from the precipitated protochloride of lead and treated as follows:—

A. 20 c.c. were withdrawn by a pipette and allowed to flow into a solution of acetate of soda, whereby a precipitate of peroxide of lead was obtained.

B. 20 c.c. were withdrawn by a pipette and added to a definite volume of ferrous sulphate of known strength in excess.

After a few minutes the sample A was filtered into a Woulffe's bottle by means of the apparatus already described in my former paper. The peroxide of lead upon the filter was washed, dried, and ignited, and the weight of lead calculated from the protoxide thus obtained. A small quantity of free chlorine present in the filtrate was estimated, after addition of potassium iodide, by standard sodium hyposulphite. The filtrate did not contain lead.

The sample B was titrated with a solution of potassium permanganate, and from the excess of ferrous salt left in the liquid the amount of chlorine used in oxidation could be calculated. Since, however, a small quantity of free chlorine invariably passed through the filter from the operation A, this amount had to be subtracted from the total chlorine deduced from operation B.

If we assume the reactions to take place as follows :—

it is evident that the lead obtained in the second equation (*i.e.*, operation A) stands to the chlorine obtained in the third equation (*i.e.*, operation B) in the ratio of 207 to 71, or 1 atom of lead to 2 atoms of chlorine.

The following numbers were obtained in the several experiments :—

Oxide of lead	·2947 gram
Chlorine	·0857 „

whence Pb : Cl = 1 : 1·97.

Oxide of lead	·5714 gram
Chlorine	·1679 „

whence Pb : Cl = 1 : 2·03.

Other experiments gave the ratios 1 : 1·98 and 1 : 1·96.

There is no doubt whatever that the yellow solution thus examined contains a compound of lead with chlorine in the proportion of 1 atom of lead to 4 of chlorine. And as the filtrate from the sodium acetate is free from lead, except in mere traces, such a solution is practically nothing else than the tetrachloride of lead in excess of hydrochloric acid.

Action of Hydrochloric Acid upon Red Lead.

When red lead is treated with a small quantity of hydrochloric acid, it darkens in colour and is converted into a mixture of lead protochloride

ride and lead dioxide. The further addition of hydrochloric acid dissolves the dioxide, and gives a yellow liquid identical in all respects with the solution described above. This fact is of considerable interest as being exactly comparable with the action of hydrochloric acid upon the so-called red oxide of manganese.

Action of Chlorine upon Lead Chloride.

Chloride of lead in the dry state is not acted upon by chlorine, but when suspended in dilute hydrochloric acid or solution of potassium or sodium chloride becomes converted into the perchloride by the passage of the gas through the solution. The solution so formed, in the case of hydrochloric acid, is identical in all respects with the yellow liquid already described. When, however, an alkaline chloride is used, the solution, from the absence of excess of acid, is more readily decomposed by water. Sulphuric acid and solution of alkaline sulphate give precipitates of lead sulphate only after some time, but with a warm saturated solution of sodium sulphate, a precipitate of *lead peroxide* is thrown down.

Sobrero and Selmi have investigated this subject (*Ann. Chim. Phys.* [3], **29**, 165) and obtained a compound $\text{PbCl}_4 \cdot 9\text{NaCl}$, while Nicklès (*ibid.* [4], **10**, 323), by the use of calcium chloride, obtained a compound $\text{PbCl}_4 \cdot 16\text{CaCl}_2$.

When a current of chlorine gas is passed into water containing lead chloride, there is at first no change apparent beyond a slight dissolution of chlorine. The liquid remains colourless, and yields with alkalis a precipitate of hydrated protoxide of lead almost white in colour. After some hours, however, if the passage of the gas be continued, a yellow solution of lead tetrachloride is obtained with simultaneous deposition of a coating of lead dioxide on the walls of the flask containing the liquid, which it should be noted has now become strongly acid. The chlorine gas used was carefully purified with anhydrous copper sulphate to remove all free hydrochloric acid, and some experiments were conducted in the dark; but as the result was in every case the same, it is evident that the acid is one of the products of the reaction,

It is probable that lead tetrachloride is first formed, and continually decomposed by the water present, until the acid liberated in the solution is sufficient to keep it in a stable condition. All the experimental evidence points to the conclusion that the higher chloride of lead is

unstable in the presence of water alone, but may exist as a double salt in the presence of other chlorides. Indeed the yellow liquids above described may be kept for several months in ordinary stoppered bottles. It is not possible to obtain any double salts by evaporation, but I think the solution contains lead as chloroplumbate, H_2PbCl_6 , or K_2PbCl_6 , and I am endeavouring to establish this point by further experiments.

Quantitative Estimation of Lead.

The conversion of lead-salts into peroxide by means of a current of chlorine, appears to afford in principle a useful analytical method. A solution of lead nitrate is but slightly acted on by chlorine (a perceptible quantity of peroxide is formed after some time), but in the presence of sodium acetate the precipitation appears complete. Lead acetate with chlorine is also converted into peroxide. As bromine water is a more convenient agent than chlorine gas for analytical purposes, I attempted to substitute one for the other, and, as the following experiments show, with entirely satisfactory results:—

A. 1.5395 grams of lead acetate, with excess of sodium acetate, were treated with bromine in cold water. After filtration the precipitated lead peroxide was ignited, and gave .9074 gram protoxide of lead. This equals 54.71 per cent. of lead.

B. .4320 gram acetate of lead, with acetate of soda and bromine water slightly warmed, gave .2538 gram of lead protoxide, which corresponds to 54.67 per cent. of lead.

C. 1.0615 grams acetate of lead, heated with sulphuric acid, gave .8495 gram of lead sulphate, indicating 54.79 per cent. of lead. The theoretical quantity of lead in the pure salt is 54.67 per cent.

This method, therefore, furnishes a satisfactory means for the quantitative estimation of lead in cases where the use of sulphuric acid may happen to be undesirable.

I wish to express my thanks to Mr. V. H. Velej, of University College, for the care with which he has performed most of the quantitative work connected with this investigation.