ART. XXVI.—*On some Double Salts of Lead Tetrachloride*;
by H. L. WELLS.

THE existence of lead tetrachloride has long been surmised from the fact that the corresponding oxide, when dissolved in cold hydrochloric acid, gives a yellow solution in which sulphuric acid does not give an immediate precipitate. Lead tetrachloride itself, however, has never been isolated, nor has any double salt which it forms been satisfactorily described.

Sobrero and Selmi† found that when chlorine is passed into a solution containing sodium chloride and lead chloride, the liquid becomes yellow. They found it impossible to isolate the compound either by evaporation or cooling, so that they determined the lead, sodium and chlorine in such a solution, and found it to contain these constituents in the ratio corresponding to $\text{PbCl}_4 + 9\text{NaCl}$. Sobrero and Selmi say that per-

* R. D. Irving and C. R. Van Hise: l. c., p. 389-393.

† Ann. Chim. Phys., III, xxix, 161.

haps this is the formula of the compound, but they put a question-mark after it. Their analysis indicates the existence of PbCl_4 in combination with NaCl , but if the solution had contained a compound of that composition, which was stable with water, it probably could have been isolated by evaporation. The fact is that the double salts of lead tetrachloride are not stable with water, as will be shown in the present article. Therefore, since a large excess of sodium chloride must have been present in the solution of Sobrero and Selmi, their analysis could not have determined the composition of the double salt that it contained.

Nicklès* saturated a strong solution of calcium chloride with lead chloride and chlorine and analyzed the solution. He found it to contain lead, calcium and chlorine in the proportions represented by $\text{PbCl}_4 + 16\text{CaCl}_2$. In conclusion Nicklès does not claim that any such double salt exists, but merely claims to have indicated the existence of PbCl_4 .

In view of the fact that the formulæ $\text{PbCl}_4 + 9\text{NaCl}$ and $\text{PbCl}_4 + 16\text{CaCl}_2$ merely represented the composition of solutions, it is remarkable that they are given in some handbooks of chemistry as real chemical compounds. It may be mentioned that Carnegie† has used the formula $\text{PbCl}_4 \cdot 9\text{NaCl}$ in support of a theory on double halides.

O. Seidel‡ mentions unsuccessful attempts to isolate PbCl_4 and its double salts with the chlorides of other metals.

Fisher§ dissolved lead peroxide in hydrochloric acid and found that all the lead in the solution was precipitated again as peroxide by the addition of sodium acetate. He was evidently not aware of the fact that Rivot, Bendant and Daguin|| had shown, long before, that lead is completely precipitated as peroxide by the addition of sodium acetate and chlorine to its solutions. Fisher found that two atoms of chlorine were used (as would be expected) in precipitating one atom of lead as peroxide. His conclusion that his experiments showed the existence of lead tetrachloride has, apparently, little foundation.

More recently, Ditte¶ has made some experiments on the solubility of lead chloride in solutions containing hydrochloric acid and chlorine. He apparently does not believe in the existence of lead tetrachloride, for he does not mention the compound, while he explains the precipitation of lead peroxide, when such solutions are diluted, by saying that lead chloride is partly dissociated by the act of solution, that the solution then contains oxide of lead, and that this is peroxidized by the

* Ann. Chim. Phys., IV, x, 323.

† Jour. pr. Ch., II, xx, 205, 1879.

|| Ann. Mines, V, iv, 239, 1853.

‡ Am. Chem. Jour., xv, 10, 1893.

§ Jour. Chem. Soc., xxxv, 282, 1879.

¶ Ann. Chim. Phys., V, xxii, 566, 1881.

oxides of chlorine formed when chlorine is passed into the solution.

Nikolukine has succeeded in isolating double salts of lead tetrachloride with ammonium and potassium chlorides. He showed that these compounds contain lead and extra chlorine in the proportion required for PbCl_4 , but there is no evidence in the abstracts of his article* that he determined the composition of the double salts. His original article in Russian is not accessible to me. Nikolukine prepared the compounds by dissolving lead dioxide in concentrated hydrochloric acid in sealed tubes, and adding the alkaline chlorides to the solutions thus produced. He describes the double salts as having a lemon-yellow color, and states that they are pretty stable, the ammonium chloride compound being decomposed at 120° .

The present investigation has been undertaken with the view of determining the composition of the salts which Nikolukine discovered, and especially in order to investigate the corresponding rubidium and caesium compounds, which, from analogy, were expected to be more insoluble and stable than the potassium salt. As a result, it has been found possible to prepare the whole series in a state of purity, and the expectations in regard to the easy preparation of the rubidium and caesium salts have been fully realized. The following salts are to be described:

These salts are all yellow, and they all crystallize in the isometric system with an octahedral habit.

These salts show a new relation between lead and other metals of Mendeléeff's group IV, with which this type is very common, especially among the double fluorides. It is to be noticed also that this type is almost invariable among the double salts which tetrahalides form, for platinum, iridium, osmium and palladium give analogous, isomorphous compounds, while, as has been recently shown by Dr. H. L. Wheeler of this laboratory, tellurium gives an extensive series of octahedral salts of this type. The octahedral form of the anhydrous salts of this type is very characteristic, and it seems to be universal, except among the fluorides.

All of the lead salts to be described are decomposed by water with the formation of lead peroxide. Chlorine is usually set free at the same time. It may be assumed that two successive reactions take place, which may be represented by the following equations:

* *Berichte*, xviii, 370, 1885; *Jour. Chem. Soc.*, I. 123.

The extent to which the second reaction takes place depends upon the dilution and the temperature. If the amount of water present is not too great, a state of equilibrium is reached when a sufficient amount of alkaline chloride, hydrochloric acid and chlorine have gone into solution, and the decomposition stops. The caesium salt is more slowly decomposed by water than others. All the salts are decomposed by boiling with an excess of hydrochloric acid, but the decomposition of the caesium compound is remarkably slow, especially in solutions containing much caesium chloride.

When free chlorine is present the caesium salt is almost completely insoluble in strong solutions of caesium chloride and in hydrochloric acid. Although the rubidium salt is considerably more soluble, the difference is not great enough so that a quantitative separation can be made. It will be shown in the following article that caesium can be approximately separated from potassium, sodium and lithium by this means, and that when rubidium is also present the caesium can be approximately determined indirectly.

The salts to be described can be washed with hydrochloric acid containing chlorine. They are perfectly stable on exposure to the air. When heated in capillary tubes the ammonium salt begins to whiten at about 225°, the potassium salt at about 190° and the caesium and rubidium salts at about 280°. This temperature for the decomposition of the ammonium salt is about 100° higher than that given by Nikolukine. It is probable that difference is due to a typographical error.

Attempts were made to prepare corresponding sodium and calcium salts, without success.

In analyzing the salts, lead was separated and weighed as sulphate, and, in the filtrate from this, the alkali-metal was determined as sulphate. To determine chlorine, a separate portion was decomposed by a solution of sodium arsenite and chlorine was determined in this as usual.

Ammonium-Plumbic Chloride, $(\text{NH}_4)_2\text{PbCl}_6$.—In preparing this salt, Nikolukine's method of using sealed tubes was found to be unnecessary. A solution of lead tetrachloride was made by adding slightly diluted hydrochloric acid to an excess of lead dioxide at 0°. This solution was quickly filtered through asbestos, and a saturated, cold solution of ammonium chloride in dilute hydrochloric acid was added until an abundant, yellow, crystalline precipitate was produced. The salt was pressed on paper, and then air-dried.

	Found.	Calculated for (NH ₄) ₂ PbCl ₆ .
Ammonium	----	7.90
Lead	44.61	45.39
Chlorine	46.53	45.71

Potassium-Plumbic Chloride, K₂PbCl₆.—Chlorine was passed into a solution saturated with potassium chloride, lead chloride and hydrochloric acid at 0°, without producing the double salt. Nikolukine has stated that the salt is soluble in an excess of potassium chloride, and, acting upon this suggestion, another solution was made, like the former except that no potassium chloride was used. On mixing about equal volumes of the two solutions and letting the mixture stand at 0° for several hours, a well crystallized crop of the yellow double-salt was obtained. The air-dry salt was analyzed.

	Found.	Calculated for K ₂ PbCl ₆ .
Potassium	15.30	15.70
Lead	41.91	41.55
Chlorine	42.49	42.75
	99.70	100.00
Loss on heating	15.07	Cl ₂ 14.25

The above method of preparation gives a small yield, and it would probably be better to use a method analogous to that by which the ammonium salt was prepared.

Rubidium-Plumbic Chloride, Rb₂PbCl₆.—When 65^g of rubidium chloride were dissolved in 250^{cc} of water with 4^g of lead chloride, no precipitate was produced by saturating the solution with chlorine, but, on adding an equal volume of concentrated hydrochloric acid to this solution, an abundant, yellow, crystalline precipitate was produced. This was collected on a filter, washed with hydrochloric acid containing chlorine and air-dried.

	Found.	Calculated for Rb ₂ PbCl ₆ .
Rubidium	28.62	28.93
Lead	34.98	35.03
Chlorine	35.85	36.03
	99.45	100.00
Loss on heating	12.41	Cl ₂ 12.01

A solution 35^{cc} in volume, made of equal volumes of concentrated hydrochloric acid and water, and containing .0619^g of rubidium and double the theoretical quantity of lead chloride was saturated with chlorine. A precipitate of the double salt was produced, which, after standing several

hours was collected upon a Gooch filter. The rubidium in this precipitate was determined and found to amount to $\cdot 0318^g$. One cubic centimeter of the solution dissolved, therefore, $\cdot 003^g$ of the lead salt, equivalent to $\cdot 00086^g$ of rubidium. The experiment was made at about 20° .

Cæsium-Plumbic Chloride, Cs_2PbCl_6 .—This salt is very readily prepared by passing chlorine into solutions containing lead chloride and a large excess of cæsium chloride. When hydrochloric acid is present, the excess of cæsium chloride is unnecessary, but in that case the precipitate is very finely divided. The precipitate begins to form in solutions that are nearly at a boiling temperature. A crop obtained without the use of hydrochloric acid was analyzed. It was washed with hydrochloric acid containing chlorine and air-dried.

	Found.	Calculated for Cs_2PbCl_6 .
Cæsium	38.51	38.78
Lead	30.05	30.17
Chlorine ...	30.99	31.05
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	99.55	100.00
Loss on heating	10.96	Cl_2 10.35

The salt usually has a lemon-yellow color, but, when very strong hydrochloric acid is used and a large excess of lead chloride is present the precipitate has a dark brown color. Such a crop gave the following analysis:

	Found.	Calculated for Cs_2PbCl_6 .
Cæsium	38.19	38.78
Lead	29.64	30.17
Chlorine	31.35	31.05
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	99.18	100.00
Loss on heating	11.09	Cl_2 10.35

This is evidently the same compound as the lemon-yellow salt. The cause of the brown color is not known. The presence of lead dioxide in it does not seem probable on account of the strong acid that was used, and, moreover, experiment showed that this oxide was instantly dissolved by the mother-liquor. It was suspected that this was a dimorphous form of the compound, but Mr. Louis V. Pirsson, who has kindly made a microscopic examination of both products, has found that both are isometric and octahedral in habit. He noticed that while the yellow salt forms perfect octahedrons, the brown compound occurs in octahedral

groups composed of combinations of the cube and octahedron. The accompanying figure, by Mr. Pirsson, shows the prevailing habit of these crystals. The groups are very small, usually not over 0.015^{mm} in diameter.

Sheffield Scientific School, March, 1893.