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A CRITICAL STUDY OF THE POTASSIUM AND SODIUM DOUBLE SALTS OF LEAD TETRAFLUORIDE AS SOURCES OF FLUORINE.[1]

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The only strictly chemical method for the preparation of free fluorine which has shown satisfactory possibilities up to the present time is the decomposition of the double salt tripotassium lead hydrogen octafluoride $3KF.HF.PbF_4$, by heat. This compound was prepared in pure condition and studied for the first time by Brauner,[2] who showed that the molecule of hydrogen fluoride could be completely removed at temperatures below 250°, and that fluorine is evolved above 250°. In recent years doubts have been expressed by some chemists that such a discovery was really in accordance with the facts. By using this method, however, it has been found possible in the researches to be described

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[1] Published by permission of the Director of the Chemical Warfare Service.

The general problem of the preparation and use of tripotassium hydrogen lead octafluoride was suggested by Captain A. B. Ray, and the investigations begun under his supervision and with the assistance of Messrs. I. M. Colbeth and J. H. Card, at the American University Experiment Station, Washington, D. C.

The intensive solubility measurements, and all of the work on disodium lead hexafluoride were subsequently carried on by the author independently.

[2] *J. Chem. Soc.*, 65, 393 (1894).

in this paper to prepare quite successfully bromine trifluoride and iodine pentafluoride by permitting the fluorine evolved in the heating simply to pass over bromine and iodine, respectively.

The double salt $3KF.HF.PbF_4$ was prepared, following the directions of Brauner by dissolving potassium plumbate (made by fusing potassium hydroxide with lead dioxide) in fairly concentrated hydrofluoric acid and evaporating off the excess aqueous acid. The double salt crystallizes from the concentrates in well-formed monoclinic needles. In the present work, however, it has been found that there are several factors influencing yield and purity of the salt which make the apparently simple process one of relative complexity. Several samples prepared under slightly differing conditions were found to give different analyses. In some cases when the salt was being used for the purpose of generating fluorine, all of the hydrogen fluoride could not be driven off below 250°, indicating contamination with potassium hydrogen fluoride which does not readily evolve hydrogen fluoride below 500°. This study was undertaken, therefore, to discover if possible, the exact conditions necessary for the preparation of pure tripotassium lead hydrogen octafluoride and what yields might be expected. It has involved the preparation and properties of potassium plumbate, and the determination of various solubility and hydrolytic effects. In addition to this, inasmuch as the scarcity of potassium hydroxide at once makes commercial applications of the process doubtful, the problem of substituting sodium hydroxide was undertaken. This has resulted in the isolation and study for the first time of the sodium double salt of lead tetrafluoride, as a source of fluorine. The steps in the preparation of both potassium and sodium salts will be considered in order and comparisons made.

The Preparation and Properties of Potassium and Sodium Plumbates.

In the preparation of tripotassium hydrogen lead octafluoride Brauner[1] directs that potassium hydroxide and lead dioxide be fused directly together in a silver dish in the proportion of 3 molecular weights of potassium hydroxide to one of lead dioxide. Experiments of the author show that when the hydroxide is brought to a clear melt at 360° and the lead dioxide then added in small quantities, reaction takes place and the final product is in the form of a stiff paste almost the color of lead dioxide, having the approximate composition of $3KOH.PbO_2$, or more nearly $K_2PbO_3.KOH$ since water formed according to the reaction

$$3KOH + PbO_2 = K_2PbO_3.KOH + H_2O$$

is driven off at the high temperature of the melt. At this temperature also there is apparently some decomposition as shown by 3 facts: (1)

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[1] *Loc. cit.*

a yellowish color due to the presence of lead oxide; (2) the formation of some potassium tetraoxide either alone or loosely combined which results in the evolution of oxygen when the plumbate paste is added to water or aqueous hydrofluoric acid; and, (3) the precipitation of an insoluble crystalline complex fluoroxyperplumbate from the solution in hydrofluoric acid.

This decomposition is due in part to the action of heat upon lead dioxide in its loose combination in this salt, causing a complete breaking of the molecule into its constituents and the reduction of PbO_2 to Pb_3O_4 and then to PbO by oxidation of K_2O to K_2O_4, and in part to hydrolysis at this high temperature of the potassium plumbate to potassium hydroxide and colloidal plumbic acid by the water formed in the reaction.

The addition of a third molecule of potassium hydroxide, besides making available the requisite proportions for the preparation of the potassium double fluoride, also, as a mass action effect, stabilizes the fusion. Sufficient liquid potassium hydroxide is formed to make it possible for all the lead dioxide to be stirred into a homogeneous fused paste without necessitating elevation of the temperature as high as 350°. It was deemed advisable to try the effect of adding water in small quantities to the hydroxide, resulting in a solution more properly speaking of water in molten potassium hydroxide which can remain liquid at 100°. With this solution lead dioxide reacts easily to form a homogeneous paste from which excess water may be driven at 100° without decomposition.

In the presence of water a somewhat different condition is found than in fusion of dry potassium hydroxide and dry lead dioxide. True potassium plumbate is really a salt of hexoxyplumbic acid, $H_2Pb(OH)_6$ or $PbO_2.4H_2O$, and has been obtained as $K_2PbO_3.3H_2O$ in the form of pure crystals from strongly concentrated solutions evaporated in a vacuum. This verifies the work of Fremy,[1] Seidel,[2] and Bellucci and Barravano.[3] It is found, however, that this salt is not a true hydrate, inasmuch as the 3 molecules of water cannot be driven off without completely decomposing the salt. This leads to the belief that the water is a necessary integral part of the molecule and that the formula is more properly $K_2Pb(OH)_6$. At temperatures below 100° the salt is entirely stable even in the presence of the excess potassium hydroxide. At 150° decomposition is apparent only by a lighter color of the surface exposed to air. Decomposition seems to take place according to the equation

$$K_2Pb(OH)_6 = 2KOH + PbO + O + 2H_2O.$$

It is at once clear, therefore, inasmuch as the molecular identity of $K_2PbO_3.3H_2O$ is fairly certain while the existence of K_2PbO_3 is very

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[1] *Ann. chim. phys.*, [3] **12**, 488 (1844).

[2] *J. prakt. Chem.*, **20**, 200.

[3] *Z. anorg. Chem.*, **50**, 101 and 107 (1906).

doubtful, that by using water in making the fusion of potassium hydroxide and lead dioxide and thus avoiding high temperatures, a plumbate of much more definite composition is possible. While it is true that reduction of the tetravalent lead to lower oxides is brought about at much lower temperatures if $K_2Pb(OH)_6$ is present, than in a fused mixture of dry lead dioxide and potassium hydroxide, yet it is found to be unnecessary to raise the temperature above 150°. Another advantage of adding water is found in the fact that much of the powerful corrosive property of an oxidizing agent fused with an alkali upon the containing vessel is avoided, since such action is a function of concentration and temperature. Porcelain dishes are most suitable for this purpose, since the glazing is only slightly attacked, while nickel and copper vessels are strongly corroded.

Several experiments have been tried varying the amounts of water in the fusion. An amount not over $^1/_5$ the weight of the potassium hydroxide gives best results, while even $^1/_{10}$ permits homogeneous fusion below 200°.

Larger amounts of water exert a remarkably definite effect in hydrolyzing these compounds. For example, the action of water on $K_2Pb(OH)_6$ is

$$K_2Pb(OH)_6 + 2H_2O = 2KOH + H_2Pb(OH)_6$$

$$H_2Pb(OH)_6 = H_4PbO_4 + 2H_2O$$

or

$$K_2Pb(OH)_6 \rightleftarrows 2KOH + H_4PbO_4.$$

This proceeds from left to right preponderantly in the presence of 15 to 20% of water as indicated by the immediate precipitation of lead dioxide.

Sodium hydroxide acts quite differently from potassium hydroxide in its ability to form plumbates with lead dioxide. It has been shown already that by melting an excess of potassium hydroxide in water and adding lead dioxide, $K_2PbO_3.3H_2O$ may be obtained pure as crystals from the solution evaporated in a vacuum. There is only one statement to be found in the literature that any analogous sodium salt can be similarly prepared. Bellucci and Barravano[1] state that with great difficulty a very small quantity of powder was obtained which they thought to be the sodium salt. No analyses are given. Höhnel[2] claims that he obtained sodium plumbate by fusing together lead oxide and sodium peroxide, and that it is immediately hydrolyzed by water. It is quite clear that the sodium plumbates are very much less stable than the potassium. In this work it has been found mechanically impossible

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[1] *Loc. cit.*

[2] *Arch. Pharm.*, 232, 222 (1894).

to fuse together dry sodium hydroxide and lead dioxide. Impurities such as sodium carbonate in the caustic raise its melting point far above 318°. At such temperatures the lead dioxide is very rapidly reduced to plumboplumbic oxide and to lead oxide so that the resultant mass is simply a crumbling powder of a mixture of sodium hydroxide and lower oxides of lead. Practically no plumbate is formed; as shown by the fact that the hydrofluoric acid to which the substance is added dissolves selectively only the sodium hydroxide together with a small quantity of both bivalent and tetravalent lead oxides. While lead fluoride is soluble to the extent of 0.6491 g. per liter of water[1] no lead is detectable by any qualitative test in 50% hydrofluoric acid containing in solution more than 100 g. sodium hydrogen fluoride per 1000 g. of water.

In view of these difficulties all subsequent efforts to prepare plumbates of sodium have been made by means of very concentrated solutions of sodium hydroxide. Enough water is necessary in order that all of the lead dioxide may be stirred in homogeneously. Reaction occurs vigorously, forming first a greenish thin paste. As more dioxide is added the color more nearly approximates the dark brown. In any case the caustic solution is brought simply to boiling and the source of heat then entirely removed while the dioxide is being added. Sufficient heat is generated by the reaction to keep the mass warm. Temperatures above 100° cause rapid decomposition by combined action of the air and hydrolytic effect of the water present. Even while the reaction is carried on over a water bath, the sodium plumbate once formed rapidly undergoes change.

In the belief that the sodium double fluoride of lead tetrafluoride might be entirely analogous to the potassium salt, $3KF.HF.PbF_4$, a number of fusions were undertaken using the proportion of 3 molecules of sodium hydroxide to one of lead dioxide. With 150 g. of hydroxide and 300 g. of dioxide, it is found necessary for best conditions to add 75 g. of water, which is 50% of the weight of the caustic or 14% the weight of the total. Dissolving the sodium hydroxide in this and bringing to boiling, the source of heat is removed and the lead dioxide added with stirring. The resultant mass is a homogeneous, almost solid paste. When this stands in air, or when any attempt is made to dry it in the neighborhood of 100°, rapid decomposition takes place. Using only 50 g. of water with the same mixture as indicated above results in the solidification of the mixture before all the lead dioxide is added. The mass is therefore heterogeneous and considerable dioxide lost when solution in hydrofluoric acid is made. More than 75 g. of water enables the plumbate to be prepared easily, but the paste is thinner, depending upon the amount of water used. The excess water serves then simply to

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[1] Kohlrausch, *Z. phys. Chem.*, 50, 365 (1904).

dilute the hydrofluoric acid when solution is made, thus reducing materially the general efficiency of the acid in dissolving a maximum amount of the sodium double fluoride without hydrolysis.

It is quite apparent that sodium plumbates are much less well defined and much less stable than the potassium salts. The experiments just described seem to indicate that in the presence of water the compound $Na_2PbO_3.6H_2O$ is formed chiefly, whereas the potassium salt is a trihydrate. The latter is quite stable at 100° while the sodium salt is quite rapidly decomposed at that temperature. Hydrolysis takes place immediately when water is added. Thus when making a fusion of 150 g. of sodium hydroxide, 300 g. of lead dioxide and 75 g. of water, the caustic is dissolved in 50 g. of water, the dioxide added until the paste is thick, and then the other 25 g. of water is added with the remainder of the oxide, a complete hydrolysis of the plumbate already formed is indicated by the separation of lead dioxide. But if all the water is introduced into the solution of sodium hydroxide before any additions of dioxide, reaction takes place without difficulty. This indicates that the water is therefore *not* water of hydration but an integral part of the molecule which is unstable enough to decompose easily at low temperatures. The presence of the excess molecule of sodium hydroxide, just as in the case of the potassium salt, has a stabilizing influence upon the fusion.

When as a result of careful analysis it was found that the sodium double fluoride of lead tetrafluoride contains only two molecules of sodium fluoride and is not therefore the analog of the compound $3KF.HF.PbF_4$, the preparation of sodium plumbate was begun, using 2 instead of 3 molecular weights of sodium hydroxide to one of lead dioxide. The proportions most satisfactory are sodium hydroxide 160, lead dioxide 478, and water 100. The reaction runs quite the same as before, the only difference noted being a somewhat smaller stability towards the action of heat and air. The effect of the excess hydroxide in the first fusions upon the solubility relationships and percentage yields of the double salt from hydrofluoric acid solution will be fully discussed in another section of this paper.

The outstanding conclusion of this study and comparison of the plumbates is quite favorable to the use of potassium plumbate for preparing a double salt from which fluorine may be driven by heat. Great care is necessary in order to prepare and keep sodium plumbate of fair degree of purity. In this connection it may be noted with interest that one of the methods of preparing lead dioxide is by the hydrolysis of sodium plumbate, Na_2PbO_3, which is made by fusing together lead oxide, sodium nitrate and sodium hydroxide. With proper precautions, such as the proper amount of water and low temperature, $Na_2PbO_3.6H_2O$ may be prepared and used to advantage in forming the sodium double fluoride of lead tetrafluoride.

The Preparation and Properties of Tripotassium Lead Hydrogen Octafluoride.

In order to prepare this salt, the plumbate made as indicated in the preceding section is added a little at a time to strong aqueous hydrofluoric acid. Complete solution is observed at first but as the acid becomes weaker, some lead dioxide begins to separate out. At this point further addition of plumbate is stopped, since it would be decomposed, with separation of lead dioxide and solution of potassium hydroxide to form potassium hydrogen fluoride. This salt in turn decreases the solubility of the octafluoride in the aqueous hydrogen fluoride so that there is loss of material already dissolved. As the double salt dissolves, the solution warms. If the plumbate has been heated to too high a temperature and potassium tetraoxide formed, oxygen is evolved in the process of solution and a dark crystalline complex compound, probably a fluoroxyperplumbate, is precipitated even in the beginning.

After standing a short time in order to permit the lead dioxide and metallic fluoride impurities to settle, the solution is filtered through paper supported by several layers of cloth. The clear filtrate in lead dishes on sand baths is evaporated very gently in a stream of air. When crystals begin to form, the evaporation is carried on with extreme care. At this point there is great danger in obtaining crystals of the double salt contaminated with potassium hydrogen fluoride which remains in the mother liquor. If the addition of potassium plumbate has been carried only to the point where lead dioxide *just begins* to separate, the solution may very safely be evaporated to a very small residual volume with the possibility of only small contamination. It is essential, therefore, that an excess of hydrogen fluoride be kept always present. Very slight excess of plumbate after lead dioxide first begins to separate from the solution produces enormous solubility changes. In one instance 5 g. excess was added, the solution allowed to come to equilibrium, filtered and evaporated to dryness. The resulting pure white crystals upon analysis showed 24.22% lead while the pure octafluoride contains 43.4% lead. The mass is therefore almost half potassium hydrogen fluoride. Contamination with this salt is serious, inasmuch as the hydrogen fluoride cannot all be driven out below 250°, and therefore comes over with fluorine. It is true, however, that the hydrogen fluoride may be removed from the fluorine by passing the gases over fused potassium fluoride or through a condenser cooled with carbon dioxide-acetone mixture. In the preparation of the pure salt, $3KF.HF.PbF_4$, it is important, therefore, to separate as completely as possible the first crystals which form from the mother liquor.

Except for analysis of the double salt, Brauner's work on the octofluoride which is the only instance in the literature, was strictly of a qualitative nature. It was deemed advisable, therefore, to make as complete a study of this salt as possible with a view to controlling purity and yields.

Methods of Analysis.

The analysis of the complex salt once obtained presents no great difficulties. The most refined method for a quantitative determination of lead is to dissolve the double salt in strong nitric acid, the valence of lead thereby being reduced to two. The solution is diluted, sulfuric acid added and lead determined as the sulfate in the usual way. Potassium is determined as the sulfate in the filtrate by evaporating to fumes with excess sulfuric acid, and then igniting at a low red heat. In order to determine fluorine, another portion of the nitric acid solution and tripotassium lead hydrogen octafluoride is diluted and the lead precipitated as sulfide by hydrogen sulfide, some sulfur also being formed. The filtrate is made slightly alkaline with sodium carbonate and calcium chloride added in order to precipitate calcium fluoride.

In the course of these experiments, however, a very much simpler method of analysis has been found to be of great value as a time saver, at the same time being capable of a fair degree of accuracy. Water quantitatively hydrolyzes $3KF.HF.PbF_4$ according to the reaction

$$2(3KF.HF.PbF_4) + 4H_2O = 3K_2F_2 + 5H_2F_2 + 2PbO_2.$$

The lead dioxide precipitates out and may be filtered off and weighed as such. In some instances the product was collected on tared filter papers, but better results were obtained by the use of alundum crucibles. The dioxide is dried at 105°. Even at this temperature small amounts of water may be retained resulting in results slightly too high. This difficulty may be overcome by igniting to the monoxide and again weighing.

The filtrate is a solution of potassium fluoride in aqueous hydrogen fluoride. Part of it is titrated with standard alkali to determine fluorine as hydrofluoric acid formed by hydrolysis, together with the acid present as such in the original molecule. The rest of the solution is evaporated to complete dryness, ignited at 500° to decompose the potassium hydrogen fluoride and the residue weighed as potassium fluoride. These 3 very simple operations therefore enable the rapid determination of lead, fluorine and potassium.

In the preparation of samples of crystals of the pure double salt, of total solids, and of acid solutions for analysis, potassium plumbate carefully prepared as described was added in small quantities to aqueous hydrogen fluoride until the separation of lead dioxide became apparent.[1]

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[1] Commercial hydrofluoric acid analyzing 50% and containing hydrofluosilicic

The solution was then allowed to cool and to come to complete equilibrium by standing, and filtered. The clear filtrate was divided into several parts:

Part 1 was very carefully evaporated until well-shaped crystals began to form, and then placed in a vacuum desiccator until crystallization was complete. The crystals were removed from the mother liquor and dried repeatedly between filter papers. It is necessary that the operation proceed very rapidly as otherwise moisture in the air begins to cause darkening of the crystals by hydrolysis according to the equation

$$3KF.HF.PbF_4 + nH_2O = PbO_2.H_2O + 3KF.HF + 2H_2F_2 + (n - 3)H_2O.$$

The crystals so obtained were analyzed by the method outlined for lead, potassium and fluorine. The presence of one molecule of hydrogen fluoride was detected by titration after hydrolysis of the salt.

Part 2 of the solution was evaporated to complete dryness in order to determine the total double salt and the potassium hydrogen fluoride in solution. This was then subjected to complete hydrolysis, the lead dioxide filtered off, dried and weighed, and from the amount of lead so determined, the weight of the pure octafluoride was calculated. Subtraction of this value from the weight of the total solids gave the weight of potassium hydrogen fluoride. By titrating part of the filtrate from the lead dioxide for acidity and evaporating a part to dryness to determine potassium as potassium fluoride, a check could be established on the ratio of double salt to potassium hydrogen fluoride.

Part 3 of the solution was diluted with a large volume of water to complete hydrolysis, and the lead dioxide filtered off and weighed as a further check. The filtrate was then titrated with standard sodium hydroxide solution in order to determine what may be termed total acidity. This includes the concentration of hydrogen fluoride formed by the hydrolysis of the double salt and that of the acid in which the double salt is dissolved. Knowing the total solids in solution and having determined in Part 2 the so-called partial acidity, or the amount of hydrogen fluoride formed by their action with water, it was thus possible by subtraction to determine the strength of the acid solution and the amount of water present.

Part 4 of the solution was titrated carefully with water until a slight brownish tinge was apparent, indicative of incipient hydrolysis. This amount of water was then added to that known to be present in the solution as determined in Part 3 and the later concentration of free hydrogen fluoride in the solution thus determined. The solution was com-

and sulfuric acids as impurities was used in these experiments. The use of acid of lower concentration is entirely impracticable as will be evident from the solubility data. Anhydrous liquid hydrogen fluoride cannot be used because of its immediate evaporation by the heat generated in the reaction.

pletely hydrolyzed, the lead dioxide filtered off and weighed and the filtrate evaporated to dryness. The residue was ignited to red heat and weighed as potassium fluoride. All evaporations and titrations were conducted in nickel or "Bario" vessels.

The results of these determinations are summarized in Table I, the divisions of which correspond to the 4 parts of the solution just described. The solubility relationships of the octafluoride and potassium hydrogen fluoride alone and together in hydrofluoric acid at different concentrations are shown in Table II.

TABLE I.
Analyses.

	$3KOH.1PbO_2$ in H_2F_2.		$2NaOH.1PbO_2$ in H_2F_2.		$3NaOH.1PbO_2$ in H_2F_2.
1. Pure crystals:					
G. taken............	0.7433	0.3758 PbO_2 0.3233 PbO 0.4749 CaF_2	1.6770	1.1020 PbO_2 0.3840 (NaF)	
	0.6101	0.3088 PbO_2 0.2645 PbO 0.3330 K_2SO_4	2.7880	1.8885 PbO_2 0.6274 (HF)	
Calc. for $3KF.HF.PbF_4$.			($2NaF.PbF_4$):		
	3K	24.60	2NaF	22.89	
	Pb	43.35	Pb	56.40	
	8F	31.84	4HF	21.73	
			(Hydrolysis PbF_4)		
% composition:					
Found..........	K	24.53	NaF	22.86	
	Pb	43.36 43.35	Pb	56.90 56.45	
	F	31.23	HF	21.80	
2. Solute. *a.* Total solids:					
Wt. solution.............		6.3003	5.7067	23.4180	55.4120
Wt. dry residue..........		0.8153		2.2775	4.1030
% solids................		12.94		9.726	7.40
b. Pure double salt:					
Wt. solid................		0.8153		1.2490	4.1030
Wt. PbO_2 from hydrolysis.		0.3545	0.3353	0.1845	1.8300
Wt. pure, double salt.....		0.7075	0.6682	1.2020	2.810
% pure, double salt.......		11.23	11.27	9.358	5.07
c. Alkaline acid fluoride:					
Wt. in total solids (*a*).....		0.1078		0.0470	1.293
% in solution............		1.71		0.368	2.33
d. Normal fluoride (check):					
Calc. (double salt + acid fluoride)..............		0.3383			
Found..................		0.3367			
3. Solvent (original acid 49-50%):					
a. Partial acidity (hydrolysis of solids):					
Wt. solid................		0.8153		2.2775	4.1030
Wt. H_2F_2...............		0.1302		0.4900	0.7744
% H_2F_2.................		16.0	17.68 (calc.)	(17.87)	18.87

	3KOH.1PbO$_2$ in H$_2$F$_2$.	2NaOH.1PbO$_2$ in H$_2$F$_2$.	3NaOH.1PbO$_2$ in H$_2$F$_2$.
b. Total acidity (solvent + *a*):			
Wt. solution	5.7067	12.8439	103.3280
Wt. total solids	0.7379	1.2490	7.6460
Wt. $H_2F_2 + H_2O$	4.9688	11.5949	95.6820
Wt. total H_2F_2 (titration)	1.5638	4.700	37.0645
c. Solvent concentration (*b* — *a*):			
% H_2F_2	29.10	38.61	37.23
% H_2O	70.90	61.39	62.77
4. Solvent concentration at solute hydrolysis:			
Wt. solution	5.7067	12.8439	5.5650
Wt. H_2O added to incipient hydrolysis	3.50	5.85	20.0
Conc. of H_2F_2 (%)	17.0	24.5	8.0

Table II.

Solubility Relationships.

a. Solubility of K_2F_2 at 25° in 100 g. of H_2O.

G. H_2F_2.	% H_2F_2.	G. K_2F_2.	% K_2F_2.
0.0	0.0	96.3	48.0
1.61	1.5	61.0	37.5
6.05	5.7	30.4	22.3
12.5	11.1	30.5	21.3
16.0	13.8	33.4	22.3
20.7	17.2	38.4	24.1
28.6	22.3	46.9	26.7
42.0	30.0	61.8	30.0
100.0	50.0	136.0	40.5

b. Solubility of 3KF.HF.PbF$_4$ at 25° in 100 g. H_2O.

% H_2F_2.	% K_2F_2.	% salt.
0	0	Hydrolyzes
29.1	1.71	11.23
30.0	0	12.21
17.0	1.71	Hydrolyzes
20.0	0	Hydrolyzes
20.0	25.0[1]	1.7

The Preparation and Properties of Disodium Lead Hexafluoride.

No record is to be found in the literature of the isolation and study of any double salt of sodium fluoride with lead tetrafluoride. Confronted by the necessity of substituting sodium hydroxide for the more expensive potassium hydroxide in preparing a salt to serve as the basis for obtaining fluorine, this study has necessitated the isolation and analysis for the first time of the double salt containing sodium. It seemed upon first thought that the formula of the sodium compound should correspond exactly to the potassium compound. Sodium plumbate was therefore prepared in the proportion of 3 molecular weights of sodium hy-

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[1] At higher concentrations of potassium hydrogen fluoride, lead dioxide itself is soluble.

droxide to one of lead dioxide, observing the very particular conditions to prevent decomposition which have already been explained. Solution was made in hydrofluoric acid, the salt so formed analyzed and studied exactly as in the case of tripotassium hydrogen lead octafluoride. Repeated trials led to samples giving widely differing analyses so that it was impossible to calculate an exact formula. One sample analyzed according to the methods already described as used for the potassium double salt, contained 8.63% of lead, 32.37% sodium and 48.53% of fluorine, corresponding almost exactly to the formula $6NaF.4HF.PbF_4$. It soon was evident, however, that this sample was merely a large amount of sodium hydrogen fluoride containing a little of the true double salt. It was remarkably stable towards hydrolysis by water, was quite difficultly soluble and evolved hydrogen fluoride in amounts indicating the presence of sodium hydrogen fluoride. Another sample contained 14.46% of lead and 26.49% of sodium. It was reasoned from this that there must be excess sodium hydroxide in the plumbate which, when dissolved in hydrofluoric acid, resulted in the formation of sodium hydrogen fluoride along with the double fluoride of lead tetrafluoride, and that they could not be as easily separated from each other as are the corresponding potassium compounds because of the comparatively small solubility of sodium fluoride. The work of Marignac on the double fluorides of tin tetrafluoride furnished an analogy. This worker isolated tripotassium tin hydrogen octafluoride, which is isomorphous with the lead octafluoride, but found that the sodium compound was not analogous to the potassium, and possessed the formula $2NaF.SnF_4$.

Sodium plumbate therefore was prepared from sodium hydroxide and lead dioxide in the proportion of 2 to 1, and dissolved in 50% hydrofluoric acid until lead dioxide was just apparent. The crystals which formed were thick, short plates, instead of the needles of the potassium salt, and very much less stable. The salt was recrystallized 8 times, the crystals of sodium hydrogen fluoride which were first formed being rejected each time. By working very rapidly the plumbate crystals were separated from the mother liquor, dried between filters and weighed before they darkened. Analysis was made in the same way as outlined for the potassium salt. Solubilities and points of hydrolysis were also carried out in parallel with the determinations upon tripotassium lead hydrogen octafluoride. The results are summarized similarly in Tables I and III. Table I also shows the large influence upon solubility of the excess molecule of sodium hydroxide in fusions of $3NaOH + 1PbO_2$.

Attention is particularly called to the very remarkable effect of sodium hydrogen fluoride upon the solubility and hydrolysis of the double salt. The presence of 2.33% of the former, which lacks only 0.6% of being saturated, serves to diminish the solubility of $2NaF.PbF_4$ by over $^1/_2$

TABLE III.

Solubility Relationships.

a. Solubility of Na_2F_2 at 25° in 100 g. of H_2O.

G. H_2F_2.	% H_2F_2 (solvent).	G. Na_2F_2.	% Na_2F_2 (solution).
0.0	0.0	4.2	4.03
1.0	1.0	4.14	3.9
4.6	4.4	2.25	2.1
8.4	7.7	2.3	2.0
13.0	11.5	2.4	2.08
59.6	37.3	4.88	2.9
77.7	43.7	8.2	4.5

Note: The solubility of sodium fluoride decreases with increasing concentration of hydrogen fluoride until sodium hydrogen fluoride is formed, followed by increase in solubility.

b. Solubility of $2NaF.PbF_4$ at 25° in 100 g. of H_2O.

% H_2F_2.	% Na_2F_2.	% salt.
0	0	Hydrolyzes
38.61	0.368	9.358
40.0	Trace	10.49
24.5	0.4	Hydrolyzes
37.23	2.33	5.07
7.9	2.33	Hydrolyzes

(from 10.49 to 5.07) and to stabilize it towards the action of water by reducing the critical hydrolytic concentration of hydrogen fluoride from 24.5% to 8%. Another outstanding fact is that disodium lead hexafluoride is *more* soluble than is sodium hydrogen fluoride, although the solubilities are not greatly different, so that in fractional crystallization for separation, the pure, double salt *remains in the mother liquor.* The reverse relationships are observed in the separation of potassium hydrogen fluoride and tripotassium lead hydrogen octafluoride. The study of the very interesting 4 component system (H_2O–H_2F_2–$NaHF_2$–$2NaF.PbF_4$) will be continued further.

Comparison of the Potassium and Sodium Double Salts as Practical Sources of Fluorine.

Plumbates.—It has already been shown that potassium plumbate is more easily prepared, with more efficient use of the material. However, the greater availability and economy in the use of sodium hydroxide, especially inasmuch as the plumbate is prepared by fusing only 2 molecular weights instead of 3, may outweigh the mechanical and experimental difficulties.

Formulas.—If the salts could be prepared in pure condition exclusive of all other considerations, the advantage in the use of $2NaF.PbF_4$ over $3KF.HF.PbF_4$ as a source of fluorine is at once apparent, since no hydrogen fluoride must be driven from the molecule by preliminary heating.

Solubilities.—For a given weight of 50% hydrogen fluoride, the advantage is entirely on the side of the potassium salt, since under the most special conditions to avoid the formation of excess acid fluorides it is at least 4% more soluble than the sodium compound. There is manifestly much less difference between the solubilities of the double salts than between those of the fluorides (normal and acid salts, respectively).

In the second place, potassium hydrogen fluoride decreases the solubility of tripotassium lead hydrogen octafluoride far less than sodium hydrogen fluoride decreases that of disodium lead hexafluoride. This point deserves serious consideration, because even under the best conditions some of the acid fluoride will be present. The solubility of the potassium double fluoride is decreased only 1% by the presence of 2% of potassium hydrogen fluoride, while the solubility of the sodium compound is decreased $5^1/_2$% in a 2% solution of sodium hydrogen fluoride. Furthermore the potassium salt is in acid solution which is 10% weaker than the latter.

In the third place the potassium salt may be separated with ease from the contaminating potassium hydrogen fluoride by fractional crystallization, since the solubilities differ quite widely, whereas separation of the corresponding sodium compounds is almost impossible; indeed, the sodium hydrogen fluoride actually begins to crystallize out of solution first. There is a compensating advantage, however, in the fact that this compound gives up its hydrogen fluoride at temperatures considerably lower (160°) than does potassium hydrogen fluoride, so that even if hydrogen fluoride were evolved along with fluorine from the sodium double salt, it could be removed by condensation or absorbed in fused potassium fluoride.

Stabilities.—The pure potassium salt is considerably more stable than the pure sodium salt towards the action of moisture. In the invariable presence of the acid fluorides which exert a powerful stabilizing influence, however, there is little to choose between the salts in this respect.

Yields.—Weight for weight of materials used, the preparation of the potassium salt is almost twice as efficient a process as that of the sodium, as shown in the tables.

Recovery of By-products.—The evaporation of the saturated solutions to crystallization may be very successfully carried out as a distillation and the excess aqueous acid thus collected returned to the process. One sample so obtained from a solution of the sodium double salt analyzed 46.8% hydrogen fluoride. Similarly, the practically anhydrous hydrogen fluoride driven off at 250° may be condensed in a copper spiral cooled by carbon dioxide-acetone mixture and returned to the process. After fluorine has been evolved, salts of the formulas $3KF.PbF_2$ and $2NaF.PbF_2$ remain as residues. In either case the lead may be recovered as lead dioxide by dissolving in dil. nitric acid, filtering off any dioxide from the hydrolysis of unchanged lead tetrafluoride, adding alkaline hydroxide in excess and passing chlorine into the suspension of lead hydroxide below 50°. The precipitation of lead dioxide is practically quantitative according to the equation

$$PbO.H_2O + NaClO = PbO_2.H_2O + NaCl.$$

All fluorine remaining in solution may be recovered by precipitating as calcium fluoride which with sulfuric acid will regenerate the hydrofluoric acid used up. The entire recovery process as tested out on an experimental basis is 95% efficient.

Evolution of Fluorine.—The practically pure tripotassium lead hydrogen octafluoride has been used to advantage for the evolution of fluorine. Four hours at 250° usually suffice to drive off the hydrogen fluoride, and evolution of fluorine, as indicated by the formation of iodine crystals on potassium iodide paper, is evident at 300°. No experiments of this sort have been as yet possible with *pure* disodium lead hexafluoride because of the great difficulty in obtaining it pure. In every case the product has been contaminated with sodium hydrogen fluoride from which all the hydrogen fluoride could not be driven at 250°. There were strong indications of fluorine, however, from the salt even at 250°, so that undoubtedly the evolution from the pure salt would begin at quite low temperatures, which would of course be a distinct advantage.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF YALE UNIVERSITY.]

ON THE SULFITE METHOD FOR THE SEPARATION AND DETERMINATION OF GALLIUM WHEN ASSOCIATED WITH ZINC.

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The frequent occurrence of gallium with zinc makes the separation of these elements of especial importance. The usual method of separation consists in the precipitation of the gallium hydroxide by ammonium hydroxide in the presence of ammonium salts, the zinc remaining in solution.[1] This method has several disadvantages, for not only is it necessary to boil for a long time to expel the excess ammonia, in order that the precipitation may be complete, but in the process an appreciable amount of the gallium compound, the precipitate, usually adheres to the containing vessel; moreover, when extracting any considerable amount of gallium from material containing zinc, such as the leady residue from the purification of zinc or the gallium-indium alloy obtained from this

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[1] Lecoq de Boisbaudran, *Compt. rend.*, 94, 1625 (1882).