# XXXVI.—Fluorplumbates and Free Fluorine.

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TWELVE years ago (Trans., 1882, **41**, 68), the compounds  $CeF_4H_2O$  and  $3KF_2CeF_4, 2H_2O$  were described by me, and it was shown that, when carefully heated, they lose their water, and then, if heated more strongly, they evolve fluorine, that is, a gas which smells of hypochlorous acid and decomposes potassium iodide with liberation of iodine.\*

About the same time (1882, Abstr., 8), it was stated by me that similar compounds of quadrivalent lead had been prepared, but that I was unable to obtain them in a pure state.

In the year 1885, Nikoljukin (Journ. Russ. Chem. Soc., 1885) announced the existence of a double salt of ammonium chloride with lead in which the lead is present as tetrachloride.

This salt was subsequently investigated (1887) in this laboratory by Friedrich, and lead tetrachloride was obtained from it (1890, Abstr., 699). The salt has the formula  $2NH_4Cl,PbCl_4$  (Friedrich: Abstr., 1893, ii, 415; compare Classen and Zahorski, Abstr., 1893, ii, 464, and Wells, *ibid.*, ii, 523). Another interesting compound of quadrivalent lead, the tetracetate, has been studied recently by Hutchinson and Pollard (Trans., 1893, **63**, 1136).<sup>+</sup>

The work on the fluorides of quadrivalent lead referred to above was taken up from time to time, but my laboratory not being arranged for this kind of work, the deleterious effects of hydrofluoric acid often compelled me to postpone it. I beg now to lay before the

\* Moissan regards it as possible that some higher fluorides may decompose by heat to lower fluorides with liberation of fluorine, but he makes no reference to my experiment, by which this was proved. Mendeléeff, however, in his well-known *Principles of Chemistry*, says: "It is evidently fluorine."

+ Last year Mr. Husník, one of my advanced students, was engaged in investigating Jacquelain's salt,  $PbO_2(C_4H_3O_3)_4$ ; it was found that the true formula is  $Pb(C_2H_3O_2)_4$ , and that it can be easily obtained by following Jacquelain's direction. When Mr. Husník began to prepare other salts of tetratomic lead from it, the paper of Hutchinson and Pollard was published, and I regarded it as an act of courtesy due to these English chemists to discontinue the research.

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Society some of the results of intermittent work carried on during some years.

The salt I have obtained is the first member of a new series of salts: the *fluorplumbates*, derivatives of fluorplumbic acid. It can be prepared by the following methods.

1. By treating the freshly-precipitated oxide  $Pb_5O_{7,3}H_2O$  with a mixture of hydrogen potassium fluoride and hydrofluoric acid. As lead diffuoride is formed at the same time, the fluorplumbate must be separated from it by dissolving it in hydrofluoric acid and crystallising it from this solvent.

The oxide  $Pb_5O_7, 3H_2O$  was first obtained by me in 1881 and described in 1885 (Royal Society of Bohemia, 295-299); it is intermediate between the oxides  $Pb_2O_3$  and  $Pb_3O_4$  for  $Pb_2O_3 + Pb_3O_4 = Pb_5O_7$ . This is also seen from the following comparison.

 $\begin{array}{cccc} Pb_{2}O_{3}. & Pb_{3}O_{7}. & Pb_{3}O_{4}. \\ 2PbO, 2PbO_{2} & 3PbO, 2PbO_{2} & 4PbO, 2PbO_{2} \end{array}$ 

It dissolves more readily in acids than the anhydrous double oxides.

2. By substituting fluorine for oxygen in Fremy's plumbates. For this purpose, lead dioxide is fused with potassium hydroxide in a silver crucible in the proportion 3KOH, PbO<sub>2</sub>, and the mass obtained\* is moistened with water, after which it is added, in small portions at a time, to a large excess of pure strong hydrofluoric acid. At first the brown paste dissolves completely with a violent action, but as soon as the acid becomes weaker, some lead dioxide (partly in the hydrated state) separates, together with other impurities. The solution, which has meanwhile become warm, is separated by filtration from the insoluble impurities, among which some silver fluoride is found, and is concentrated either by spontaneous evaporation in a good current of air or at a very gentle heat. As soon as crystals of the salt begin to form, the solution is placed in a specially-constructed vacuum desiccator, when, after some time, the potassium fluorplumbate separates in long, needle-shaped crystals. In this way, any quantity of the pure salt may be obtained without great difficulty, except the disagreeable work entailed in operating with large quantities of warm hydrofluoric acid, especially its injurious effect on the eyes.

3. Theoretically interesting is the following method of preparation, that of displacing the acetic acid in lead tetracetate by fluorine; three molecular proportions of potassium hydrogen fluoride, KF,HF (2343)

<sup>\*</sup> This is brown when the fusion takes place at a low temperature, and yellow at higher temperatures. In the latter case, the hard yellow melt obtained will contain not only potassium plumbate, but also large quantities of potassium peroxide, which dissolves in hydrofluoric acid with liberation of oxygen. At the same time an insoluble crystalline substance is obtained which, judging from analogy, is most probably potassium fluoroxyperplumbate; the latter is being investigated.

parts), are dissolved in an excess of hydrofluoric acid, and one of lead tetracetate (442.9 parts), prepared by Jacquelain's method, is added; if some bivalent lead should be present, the diffuoride can be easily separated by filtration. Crystals of potassium fluorplumbate are obtained on evaporating the solution, either in the air, or over sulphuric acid and quicklime in a vacuum desiccator so constructed that the vapours do not come into contact with glass.

The salt, obtained by any of these three methods has the composition 3KF,HF,PbF<sub>4</sub>, as is shown by the analyses made in the following manner.

The salt was taken out of the mother liquor, which contains potassium hydrogen fluoride, if there is any excess of it present; dried between perfectly dry and pure filter paper, and weighed quantities decomposed by large quantities of water in a platinum dish. Some of the dioxide formed adheres firmly to the walls of the dish, and must be dried and weighed with it. The major part of the dioxide is collected on a tared paper filter, previously washed with hydrofluoric acid, and placed in a platinum funnel. As the dioxide seemed to contain some water, even after continued drying at 105°, thus giving higher results for the lead, an aliquot part of it was converted into lead oxide by heating it to incipient fusion. In the filtrate from the dioxide, the fluorine was determined as calcium fluoride, and in another portion the potassium was determined as sulphate, the latter being finally heated in an atmosphere of ammonium carbonate; for this purpose the carbonate was suspended in a little

this purpose the carbonate was suspended in a little platinum tray, a, in the upper part of the crucible. This method has the advantage that the salt does not begin to evaporate until the bottom of the crucible has become red hot, so that the red-hot sulphate is brought into contact with ammonia, and any nonvolatile impurities in the carbonate are left in the little tray.



The fluorine was also determined by Penfield's method, but, as the lead present might form the insoluble sulphate, which would probably inclose some of the original salt and prevent its being attacked, 15 grams of powdered quartz and 50 c.c. of sulphuric acid were used, and the digestion continued, not merely for two hours, as recommended by Penfield, but, better, from the morning till the evening, and then left over night, after removing the lamp, so as to insure the complete expulsion of the gas from the developing vessel. The arrangement of the apparatus is seen from the adjoining figure (next page).

A and A' contain sulphuric acid, and B potassium hydroxide; C is the developing flask, standing on asbestos cardboard and closed with

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a stopper perforated with three holes. Through the first passes a funnel by which sulphuric acid is poured in, and by which, afterwards, air is passed in; through the second, the tube to convey the escaping gas; through the third, a tube of thin glass containing mercury in the sealed lower end, into which a thermometer is plunged; the latter is thus insured against corrosion, and must not be placed in a *separate* vessel with sulphuric acid, as recommended by Fresenius, Penfield, and others. D is a perfectly dry, empty



U-tube. E is a wide test-tube, closed with a rubber stopper pierced with three holes; through the one hole a carefully-dried tube passes to the bottom of the test-tube; through the second, the tube which leads the air away; through the third hole, after the apparatus has been put together, mercury is first poured in, and then a solution of potassium chloride (50 c.c. of water, 50 c.c. of alcohol, 2 grams of KCl), after which it is closed by a glass rod. In this test-tube the final titration is done. The U-tube F contains water, coloured by neutral litmus, which, however, never became red, and the tube at its other extremity leads to the pump G, the current of air being regulated by two pinchcocks. This form of apparatus has often proved convenient for the determination of fluorine.

The hydrogen was determined by heating the dry salt, after it had been crushed between platinum to a fine powder, with a large excess of sodium carbonate, and collecting the water in a weighed chloride of calcium tube. The sodium carbonate should be prepared just before the experiment by heating sodium hydrogen carbonate below its melting point.

I. 0.3227 gram of the salt gave 0.1766 gram of  $K_2SO_4 = 24.57$  per cent. K, and 0.1637 gram PbO<sub>2</sub> (= 43.93 per cent. Pb); this dioxide, on careful heating, yielded 0.14 gram PbO = 43.41 per cent. Pb.

- II. 0.7433 gram gave 0.3758 gram  $PbO_2$  (= 43.79 per cent. Pb) and 0.3233 gram PbO = 43.36 per cent. Pb. From the filtrate 0.4749 gram CaF<sub>2</sub> was obtained = 31.23 per cent. F. (This method always gives low results.)
- III. 0.6101 gram gave 0.3088 gram  $PbO_2$  (= 43.84 per cent. Pb) and 0.26446 gram PbO = 43.35 per cent. Pb. From the filtrate 0.3333 gram  $K_2SO_4$  was obtained = 24.53 per cent. K.
- IV. 0.5042 gram treated by Penfield's method, with quartz and sulphuric acid, yielded SiF<sub>4</sub>, which, from a solution of potassium chloride in alcohol of 50 per cent., liberated hydrochloric acid, requiring 28.0 c.c. of decinormal ammonia for neutralisation = 0.1596 gram F = 31.65 per cent. F.
- V. 0.5869 gram heated with sodium carbonate, gave 0.0116 gram  $H_2O = 0.22$  per cent. H.

Calculated for			Found.				
	3KF·HF·POF <sub>4</sub> .		í.	11.	III.	IV.	$\overline{\mathbf{v}}$ .
3К	117.42	24.60	24.57		24.53		
Pb	206.9	43.35	43.41	43.36	43.35	—	
8F	152.0	31.84		31.23		31.65	
н	1.0	0.21		—			0.22
	477.32						

The analysis shows that the substance contains no oxygen. The crystallographic examination was, in so far, of theoretical interest, as Marignac has described a perfectly analogous compound of quadrivalent tin, namely, 3KF,HF,SnF<sub>4</sub> (see Gmelin-Kraut's Handbuch), for it shows that both substances are isomorphous.

Professor Ch. Vrba, of our University, gives the following account:—"The needle-shaped crystals have a thickness of about 1/3 mm. and a length of up to 10 mm.; they are generally grouped radially. The faces of the prisms, as well as those of the pyramids, are uneven, convex, striated, and corroded; the connection of the zones is loose. Most of the faces give hardly any reflection of the slit, but usually an indistinct glimmer; if signal images are reflected, they are indistinct, scattered, and feeble. The results of the measurements are so uncertain that no definite conclusion can be drawn from them as regards the symmetry of the crystals, and no better results were obtained on examining the crystals optically. From the values of the angles obtained, however, it seems highly probable that the form of the salt is similar to that of the analogous fluorstannate obtained and measured by Marignac."

Assuming the monoclinic symmetry for the fluorplumbate, as has been assumed by Marignac for the fluorstannate, and founding the calculation upon the most trustworthy values of the angles (which in the following table are marked with an asterisk) the elements are approximatively the following.

$$a:b:c = 0.6223:1:0.4818$$
 and  
 $\beta = 86^{\circ} 41'.$ 

The forms observed are:  $m(110) \propto P$ ;  $b(010) \propto P \propto$ ; p(111) - P;  $\pi(11\overline{1}) P$ ; the same forms have been observed by Marignac upon the fluorstannate, and in addition to them c(001) 0P was found by him. The angles calculated from the above axial relations for the normals of the planes are given below, together with the inclinations observed; Marignac's values of the analogous fluorstannate, are appended for comparison.

	Calculated.	Found.	Marignac for 3KF·HF·SnF <sub>4</sub> .
$m(110): m'(1\bar{1}0) \ldots$	$63^\circ$ $42'$	63° 39′	64° 8'
: b (010)	—	*58 9	57 54
: p (111)		<b>*4</b> 6 <b>7</b>	
$p(111): p'(1\overline{1}1) \dots$		<b>*4</b> 0 <b>37</b>	40 49
: b (010)	69 <b>41</b> '	$69 \ 45$	·
$\pi(11\bar{1}):\pi'(\bar{1}11)$	$42 \ 45$	$41 \ 15$	43 12
: b (010)	$68 \ 37$	$69 \ 31$	

The salt is stable in dry air but turns brown in moist air, being decomposed by water in the following manner.

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

The water must be present in excess, however, as the hydrated dioxide would otherwise remain dissolved, being soluble in a concentrated solution of potassium hydrogen fluoride, although the anhydrous dioxide is insoluble in it and in hydrofluoric acid; consequently decomposition does not take place, or only partially, in presence of a small quantity of water.

The following experiment shows that 1 mol. of the salt, after decomposition by water, yields 5 mols. of free HF, corresponding to 5 atoms F of PbF<sub>4</sub> and HF.

0.512 gram was decomposed by water, and the filtrate required for neutralisation 53.2 c.c. of decinormal sodium hydroxide, corresponding to 20.77 per cent. HF, instead of the calculated quantity of 20.95 per cent. HF.

The weight of the salt remained absolutely constant, even when heated at  $100-110^{\circ}$  for many hours; at  $200^{\circ}$ , hydrogen fluoride began to escape, the loss amounting to 1.72 per cent.; and after heating at 250° for four hours more, the loss was 5.43 per cent., showing that some fluorine was given off (1.24 per cent. of the total available quantity) of 7.96 per cent. of fluorine).

In order to study the behaviour of the salt at a higher temperature, some of the salt was placed in a small platinum tube, closed at one end, and dried for several hours at  $230-250^\circ$ ; the middle of the tube was then surrounded with asbestos cardboard, and heated carefully with a Bunsen. Long before the tube became red hot, a gas began to be evolved, having the characteristic odour of fluorine, and crystals of iodine were liberated in large quantity from a strip of iodinestarch paper held in the gas at the exit. Fumes of hydrofluoric acid issued from the nose after inhaling and exhaling the gas.

Some small crystals of silicon were placed in the open end of the tube, and when the closed end of the tube was heated, the silicon burned with vivid incandescence, and even with explosive violence (Moissan's test for fluorine). The residue is white, or sometimes slightly yellow, and consists of a mixture of lead difluoride with potassium fluoride, when the heating takes place in a closed tube without access of moisture. When, however, the salt is heated in the open air—on a platinum basin, for example—a brown, deliquescent residue is left.

This experiment, which was repeated several times, confirms the accuracy of the results obtained by me 13 years ago, when it was generally believed that fluorine could not exist in the free state. Although Moissan has since then obtained fluorine by a *physical* method, we have here the first trustworthy *chemical* process of obtaining this gas. If potassium fluorplumbate loses its hydrogen fluoride, say at 230°, without losing more than traces of fluorine, 1 gram of the salt should yield, on heating, 47 c.c. of fluorine; the fluorine could be freed from any hydrogen fluoride by passing it over potassium fluoride (Moissan).

If the sodium salt which is now being investigated by me is, like the potassium salt, analogous in composition to Marignac's sodium fluorstannate, 2NaF, SnF<sub>4</sub>, it would give fluorine at once, without its being necessary previously to drive off hydrogen fluoride.

Qualitative experiments have shown that a whole series of *fluor*plumbates exists, the metals forming them being the same as those in Marignac's series of fluorstannates.

# Fluorplumbic acid and Lead Tetrafluoride.

A solution of *fluorplumbic acid* is obtained on dissolving lead tetraacetate in strong hydrofluoric acid, acetic acid being liberated, for on adding soluble fluorides to this solution, it gives the corresponding fluorplumbates. This solution, however, cannot be evaporated to

dryness, even at the ordinary temperature, a crust of the brown lead dioxide being deposited on the upper part of the platinum vessel.

In order to prepare anhydrous *lead tetrafluoride*, potassium fluorplumbate was reduced to fine powder in a platinum dish, using a pestle coated with platinum foil; a dry agate mortar cannot be used, as it is attacked by the dry salt, which becomes brown:

$$4(3KF,HF,PbF_4) + SiO_2 = SiF_4 + 2H_2O_1$$

and the water formed at once decomposes the salt. The powdered salt (0.874 gram) was then thrown on to the surface of cold, concentrated, sulphuric acid (5 c.c.). Hydrogen fluoride escapes in abundance, and a pale-yellow solution is obtained, having the same characteristic colour as that of lead tetrachloride. Dense fumes soon begin to come off, having an extremely pungent smell, resembling that of hypochlorous acid; they seem to contain some gaseous lead tetrafluoride, as they have a taste like that of the dust of potassium fluorplumbate, which escapes into the air on powdering it. After the salt has completely dissolved in the acid, 3KF, HF,  $PbF_4 + 3H_2SO_4 = 4HF + 3KHSO_4 +$ PbF4, the clear, yellow liquid begins to get turbid, and after half an hoar or so it is converted into a thick, lemon-yellow jelly. From this emulsion, which probably contains the colloïdal modification of lead tetrafluoride, the latter cannot be separated at the ordinary temperature. On heating the mass to 100-110°, some hydrofluoric acid escapes, and a heavy, lemon-yellow powder is deposited on the bottom of the crucible, this in all probability being the third modification of lead tetrafluoride. In the experiment described, the sulphuric acid could be easily poured off from the yellow precipitate, and it is remarkable that it did not contain any lead in solution, for it gave neither a turbidity of lead sulphate with water, nor any precipitate with excess of aqueous hydrogen sulphide.

After pouring off the first sulphuric solution of potassium hydrogen sulphate, it was replaced by fresh sulphuric acid, stirred with a platinum rod, and heated again at 100° for a day or two; no change took place. After pouring off this acid, which was also free from lead, fresh acid was added to wash away any potassium hydrogen fluoride. On heating now for some time at 115° complete decomposition took place, and a white mass of pure lead sulphate was left at the bottom of the sulphuric acid in the crucible.

On repeating the experiment with about 1.5 gram of the fluorplumbate and 20 c.c. of sulphuric acid, complete solution took place, and an extremely strong "hypochlorous" smell was evolved, together with dense fumes, but nothing separated from the clear yellow liquid after 24 hours at the ordinary temperature. On heating this solution on a water bath for two days, a yellow substance began to fall to the

bottom of the crucible, and hard, crystalline, yellow crusts were deposited on the walls of the crucible above the level of the liquid. The greater part of the tetrafluoride remained in solution, for, on adding water, it was decomposed with separation of brown hydrated lead dioxide, the hydrofluoric acid remaining in the solution; the yellow substance is decomposed in the same way, in accordance with the equation  $PbF_4 + 3H_2O = PbO_2, H_2O + 4HF$ .

I have not yet been able to isolate lead tetrafluoride, in spite of numerons attempts, as no liquid could be found which would displace the sulphuric acid without at the same time decomposing the tetrafluoride. Plates of plaster of Paris, previously dried or very old, absorb the greater part of the acid, but not all, and, after some time, decomposition takes place, and the brown dioxide is formed. Hydrofluoric acid dissolves it only partly, and the liquid contains fluorplumbic acid which liberates iodine from potassium iodide, &c. At the same time the greater part of the original substance remains undissolved, and assumes a paler sulphur-yellow colour.

On comparing the properties of the incompletely studied tetrafluoride with those of lead tetrachloride, which I often had an opportunity of observing, as it was discovered by Friedrich in this laboratory, it will be seen that both substances are set free from their double salts by strong sulphuric acid without being decomposed by it, but the tetrafluoride seems to me to be the less stable of the two; moreover the tetrachloride is a liquid, whilst the tetrafluoride seems to exist in several allotropic modifications. All these, as well as other questions, *e.g.*, the action of anhydrous hydrogen fluoride on lead tetracetate, will require careful examination.

It is, perhaps, unnecessary to point out that the existence of the substances described in the present paper gives additional confirmation to the position which lead occupies in Mendeléeff's periodic system. Thirty years ago hardly anyone could have predicted that lead would form compounds analogous to those of carbon, silicon, cerium, &c.

I hope my English colleagues will pardon me for thus laying before them an account of results which I myself regard, in some points, as very imperfect and incomplete; but I must urge, in excuse, the consideration that this difficult and delicate work had to be done without any assistance and during the time which could be snatched from the little leisure afforded by numerous official duties.

Note on the Density of Fluorine.—Ever since I first became acquainted with some of the properties of free fluorine, I have been struck by its unusually great affinity for many other elements, and I came to the conviction that the gas may probably contain not only molecules  $F_2$ , but possibly also free atoms  $F_1$ , just as has been found in the case of another halogen, iodine, at high temperatures, by Victor Meyer, and by Craffts.

This conviction was still more firmly established when Moissan's classical research became known, for Moissan has found by the most careful determinations the following numbers as the density of free fluorine at normal temperature and pressure. D. = 1.264, 1.262, 1.265, and 1.270 (Ann. Chim. Phys., [6], 25, 131). He could not explain the discrepancy of these values from the theoretical value d = 1.3165 (F = 19.05).

On calculating, on the above assumption, the degree of dissociation by Naumann's formula,  $p = \frac{100(d-D)}{D}$ , in which d = 1.3165 and D = 1.265, we obtain p = 4.07, that is, free fluorine contains for 96 mols. of F<sub>2</sub>, 8 atoms of F<sub>1</sub>.

It is probable that at a higher temperature, at which even platinum is attacked, the degree of dissociation will be found to be greater.