XXIII.—*Lead Tetracetate and the Plumbic Salts.*

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Introduction.

IN a note published in this Journal in September, 1893 (Trans., 1893, **63**, 1136), we pointed out that the crystals obtained when minium is dissolved in glacial acetic acid were to be regarded as lead tetracetate, a salt of lead dioxide, and that it would in all probability be possible to prepare other salts of quadrivalent lead from this substance. During the past two years we have, as opportunity offered, attempted a fuller study of the properties of this compound, and, although some points are still under investigation, we venture now to lay before the Society the results we have so far obtained.

Lead Tetracetate.

Historical.—Since the time of Berzelius, chemists have been aware that minium is soluble in acetic acid, and a method of detecting and estimating certain impurities found in the commercial article has been based on this fact. Little, however, was known of the properties of this solution till Jacquelain noticed (*Comptes rendus mensuels des Travaux Chimiques*, 1851, 1; Abstr., *J. pr. Chem.*, 1851, **53**, 151), as Dumas had done before him, that a solution of minium in aqueous acetic acid soon decomposed and deposited lead dioxide; he found, also, that this decomposition was greatly accelerated by heat or by the addition of water, and further observed that when he employed glacial acetic acid at 40° as the solvent, the solution, on cooling, deposited a crop of slender, colourless, oblique prisms. The formation of these crystals had, Jacquelain tells us, been previously noted by Balard, who did not, however, study them.

A few years later, Schönbein (*J. pr. Chem.*, 1858, **74**, 315) made similar observations on the behaviour of the solution of minium in acetic acid, and found that sulphuric acid precipitated only a part of the lead from this liquid, leaving in solution the "acetate of lead peroxide;" Schönbein does not appear to have been acquainted with Jacquelain's work, nor to have obtained any crystals from his solutions. On filtering off the crystals of "acétate de bioxide de plomb," and attempting to dry them between filter paper, Jacquelain found that they quickly turned brown, decomposing into lead peroxide and acetic acid. On the addition of water, this decomposition became complete, and he was therefore able to determine the percentage of acetic anhydride in the substance by titrating the aqueous solution with standard alkali. The lead was estimated as chloride in another portion.

The results led him to adopt the improbable formula

$$PbO_2,3(C_4H_3O_3)\ [O = 100,\ Pb = 129{\cdot}4,\ H = 12{\cdot}5,\ C = 75],$$

which requires lead dioxide = 43·86 and acetic anhydride = 56·14 per cent. Finding that Jacquelain's improbable formula was based on insufficient data, we determined to submit the substance anew to investigation.

Preparation.—Commercial red lead was added little by little to hot glacial acetic acid till no more dissolved and lead peroxide began to separate; the solution was then either filtered hot, or the crystals deposited on cooling were subsequently freed from peroxide by collecting them in a funnel on a porcelain filtering plate, and washing away the finely divided peroxide by cold acetic acid. The crystals were purified by recrystallisation from hot glacial acetic acid, and dried over sulphuric acid in a vacuum.

As regards the interaction which takes place, Jacquelain seems to have held the view that a compound of minium with acetic acid is first formed, for he speaks of an "acetate of minium" which, as the solution crystallises, splits up, yielding crystals of acetate of dioxide of lead, and ordinary lead acetate which remains dissolved. Schönbein, on the other hand, believed that when minium dissolved in acetic acid, the two oxides contained in the former separated, and that both lead acetate and acetate of the peroxide were present in solution. As, however, lead peroxide is insoluble in acetic acid, Schönbein adopted the hypothesis that lead peroxide can exist in two conditions, in one of which it is capable of union with acetic acid and in the other incapable of such combination.

We are inclined to think that Schönbein's view is in the main the correct one, for it is conceivable that the peroxide set free from minium by abstraction of lead monoxide should, at the moment of its formation, be capable of combining with acetic acid, although it is insoluble when once formed. We have not, however, so far been able to obtain fresh direct experimental evidence bearing on this point.

The substance can be readily analysed by taking advantage of the extraordinary ease with which water decomposes it; a weighed portion was treated with hot water, the PbO_2 collected on a tared filter, dried at 110°, and weighed, the acetic acid being estimated in the filtrate by titration with a standard alkali. The lead determinations were checked by direct conversion of other portions into chloride and sulphate by evaporation with the respective acids.

Analyses I, II, and IV were made on different samples, II and III on the same.

I. 0·8757 gave 0·4735 PbO_2, and required 98·4 c.c. of potash solution (1 c.c. = 0·00448 KOH).

II. 0·8770 gave 0·4755 PbO_2, and required 79·9 c.c. of soda solution (1 c.c. = 0·00395 NaOH).

III. 0·6403 gave 0·4040 $PbCl_2$.

IV. 0·5474 gave 0·3760 $PbSO_4$.

	I.	II.	III.	IV.	Calculated for $Pb(C_2H_3O_2)_4$.
PbO_2........	54·07	54·22	54·26	54·16	53·93
$(CH_3{\cdot}CO)_2O$..	45·85	45·88	—	—	46·07
	99·92	100·10			100·00

The pure crystals begin to melt at 175°, and decompose at a temperature a few degrees higher. The only substance known to us which dissolves the tetracetate without change is glacial acetic acid, in which it is readily soluble when hot, crystallising out again on cooling. Before using this solvent for the molecular weight determinations, we estimated the amount of tetracetate contained in a solution saturated at 17°. For this purpose, two portions of the solution were weighed, and the lead determined in the one case as chloride, and in the other as sulphate.

I. 10·57 grams of solution gave 0·178 of $PbCl_2$. Hence 100 grams of acetic acid dissolve 2·76 grams of lead tetracetate at 17°.

II. 10·57 grams of solution gave 0·1947 gram of $PbSO_4$. Hence 100 grams of acetic acid dissolve 2·77 grams of lead tetracetate at 17°.

Lead tetracetate is easily soluble in cold chloroform, but, owing to partial decomposition, gives a muddy-brown solution. If, however, the acetate is previously moistened with a small quantity of acetic acid a clear solution is obtained. Boiling carbon tetrachloride (dried over fused calcium chloride or over phosphoric anhydride) dissolves it slightly, the greater part of the salt crystallising out on cooling. Hot benzene (dried over sodium) dissolves it somewhat more readily; in both these cases a small quantity of acetic acid is necessary to prevent the solution turning brown. The tetracetate is very slightly soluble in ether and light petroleum, and only slowly attacked by these solvents if they are thoroughly dry.

The specific gravity was determined in a pyknometer in the ordinary way, but, owing to the difficulty of finding any other liquid which would neither dissolve nor act on the salt we were obliged to use a saturated solution of the tetracetate in glacial acetic acid.

The specific gravity of the solution saturated at 16·4 was 1·0692 at 16·4°/4°.

A second determination made as a control, in a small pyknometer, on a portion of the solution which had just been used for finding the specific gravity of the solid gave the value 1·0678 at 17·2°/4°.

Two determinations of the specific gravity of the solid as compared with the solution gave the values 2·084 at 16·9° and 2·075 at 18·2°. Hence the specific gravity of the solid, as compared with water at 4°, is (A) 2·228 at 16·9° and (B) 2·218 at 18·2°; of these results, A is probably the more accurate, and was got by using 8·484 grams of the solid in a 25 c.c. pyknometer, especial care being taken to get rid of all air bubbles.

Crystallography of Lead Tetracetate.

The crystals are typically monoclinic, colourless, transparent prisms, greatly elongated in the direction of the *c* axis. They are usually 10 to 25 mm. in length, and 1 to 2 × 1 to 2 mm. in section.

The faces *m* and *b* are often about equally developed, their combination giving a nearly hexagonal prism. The form *n*{210} is not of very frequent occurrence, and is always narrow and subordinate. Cleavage *b* perfect.

The crystals decomposed so easily that no complete optical examination could be made.

The extinction observed through *b* makes an angle of $-16\frac{1}{2}°$ with the c axis, and this is the direction of vibration of the ray traversing the plate with the greatest velocity.

System: Monoclinic.

Ratio of axes:

$$a : b : c = 0{\cdot}5874 : 1 : 0{\cdot}48485. \quad \beta = 74^\circ\ 24'.$$

Forms observed:

$$b = \{010\},\ m = \{110\},\ n = \{210\},\ q = \{01\bar{1}\}.$$

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
$mm''' = 110 : 1\bar{1}0$	8	59° 36′— 58° 34′	59° 0′	59° 0′
$mb = 110 : 010$	12	60 17 — 60 47	60 30	*
$nn''' = 210 : 2\bar{1}0$	2	31 43 — 31 37	31 40	31 36
$nb = 210 : 010$	6	74 20 — 74 2	74 12	74 12
$nm = 210 : 110$	5	13 52 — 13 19	13 38	13 42
$qq' = 011 : 0\bar{1}1$	4	50 14 — 49 54	50 4	50 4
$qb = 011 : 010$	11	65 12 — 64 45	64 58	*
$qm = 011 : \bar{1}10$	5	90 20 — 90 3	90 13	*
$qm' = 011 : 110$	1	—	65 4	65 8

Molecular Weight of Lead Tetracetate by Raoult's Methods.—The only solvent available for this purpose was glacial acetic acid; the specimen employed was carefully purified by recrystallisation, and melted at 16·58°.

The freezing-points of solutions of various concentrations were determined in Beckmann's apparatus (*Zeit. physikal. Chem.*, 1891, **7**, 323), and the precautions taken by him to prevent the acid absorbing moisture from the air, were found highly necessary, and were duly observed. The earlier boiling point determinations were made with Beckmann's original apparatus (*Zeit. physikal. Chem.*, 1889, **4**, 543); better results were, however, subsequently obtained with the improved form described by him in 1891 (*Zeit. physikal. Chem.*, 1891, **8**, 223). Preliminary experiments made by adding successive portions of acetate to the boiling solvent proved unsatisfactory, probably because a slight decomposition of the acetate was brought about either by the long-continued boiling of its solution, by the action of moisture, or by organic matter derived from the cork, and we found it advisable to eliminate as far as possible these sources of error by making a separate determination at each concentration. The constants of the acid were taken as 39 and 25·3 respectively. Our results are contained in the following tables.

The molecular weight of $Pb(C_2H_3O_2)_4$ is 443. The numbers tabulated on p. 217 leave but little doubt, therefore, that in solution lead tetracetate consists essentially of molecules of the formula $Pb(C_2H_3O_2)_4$.

Freezing Point Method.

Experiment.	Grams of solvent.	Grams of substance.	Rise observed.	Grams of substance in 100 of solvent.	Molecular weight.
I	26·2	0·1915	0·070	0·73	407·0
	,,	0·4538	0·164	1·73	412·0
	,,	0·5544	0·202	2·11	408·5
	,,	0·6690	0·243	2·55	410·0
II	25·9	0·3616	0·138	1·40	394·5
	,,	0·6513	0·238	2·52	412·0
III	25·0	0·1250	0·049	0·50	398·0

Boiling Point Method.

Experiment.	Grams of solvent.	Grams of substance.	Rise observed.	Grams of substance in 100 of solvent.	Molecular weight.
I	21·1	0·2578	0·087	1·02	355
II	50·4	0·5620	0·075	1·11	376
III	25·3	0·4830	0·132	1·91	366
IV	51·5	0·9950	0·134	1·93	365
V	52·4	1·2363	0·167	2·36	357
VI	26·5	1·4733	0·377	5·56	373
VII	23·9	2·0860	0·609	8·72	362

It is interesting in this connection to compare these numbers with the value 69 obtained by Beckmann for the mean molecular weight of sodium acetate dissolved in boiling glacial acetic acid (*Zeit. physikal. Chem.*, 1890, **6**, 450).

It will be noticed that the ratio of the mean molecular weight observed (by boiling point method) to the true molecular weight i 365/443 = 0·824 for lead tetracetate, and 69/82 = 0·841 for sodium acetate.

Molecular Volume of Lead Tetracetate.—The formula $Pb(C_2H_3O_2)_4$ obtained some slight additional support from the fact that, taking the specific gravity as 2·228, we find that the molecular volume is 199, a number which agrees well with that calculated by the aid of the empirical law enunciated by Schröder (*Ber.*, 1881, **14**, 1607), namely, that for a large number of anhydrous acetates the molecular volume of the salt is the same as that of the molecules of acetic acid from which it has been derived. This statement is illustrated in the following table.

Salt.	MV.	Salt.	MV.	Salt.	MV.
$C_2H_4O_2$.......	48·7	$2C_2H_4O_2$.......	97·5	$4C_2H_4O_2$.......	195
$C_2H_3O_2 \cdot Na$....	53·8	$(C_2H_3O_2)_2Mg$ ..	99·9	$(C_2H_3O_2)_4Pb$ ...	199
$C_2H_3O_2Ag$	51·5	" Zn ..	99·5		
		" Ni ..	98·5		
		" Mn ..	99·1		
		" Sr ..	97·9		
		" Hg ..	97·2		
		" Pb ..	99·9		

Action of Water.—Lead tetracetate is extraordinarily sensitive to the presence of water, so much so, indeed, that exposure to the air for a few moments suffices to turn it brown. The interaction represented by the equation $Pb(C_2H_3O_2)_4 + 2H_2O = PbO_2 + 4C_2H_4O_2$, takes place quantitatively, and forms the basis of the method of analysing the salt used by Jacquelain and ourselves. This salt might sometimes be useful for detecting the presence of moisture in gases.

Action of Hydrochloric acid.—Lead tetracetate is readily dissolved by concentrated aqueous hydrochloric acid, giving a deep yellow solution, which contains lead tetrachloride, produced in accordance with the equation $Pb(C_2H_3O_2)_4 + 4HCl = PbCl_4 + 4C_2H_4O_2$. The lead tetrachloride cannot, however, be directly isolated, and, on standing, or more quickly on warming, the yellow colour disappears, chlorine is given off and lead dichloride is left, whilst, in all probability, partial chlorination of the acetic acid occurs at the same time.

The existence of lead tetrachloride in this liquid may, nevertheless, be readily demonstrated by pouring it into dilute aqueous hydrochloric acid, saturated with ammonium chloride, when the double salt, $PbCl_4,2NH_4Cl$, at once separates as a yellow precipitate. A salt of this nature was isolated in 1885 by Nikolukine (Abstr., 1886, 123; from *J. Russ. Chem. Soc.*, 1885, 207) from the solution of lead dioxide in hydrochloric acid, but he does not appear to have assigned any formula to it. Some years later, Classen and Zahorski (*Zeit. anorg. Chem.*, 1893, **4**, 100) prepared the salt $2PbCl_4,5NH_4Cl$, by adding concentrated ammonium chloride solution to the homogeneous liquid obtained when lead dichloride, concentrated hydrochloric acid, and liquid chlorine were digested together for some hours.

Substituting quinoline hydrochloride for ammonium chloride, they obtained from the same solution the salt $PbCl_4,2C_9NH_7HCl$.

Wells (*Zeit. anorg. Chem.*, 1893, **4**, 335), on the other hand, and Friedrich (*Ber.*, 1893, **26**, 1434) are both of opinion that the formula of the ammonium salt is really $PbCl_4,2NH_4Cl$. The former obtained it by adding ammonium chloride dissolved in hydrochloric acid to a solution of lead dioxide in the same acid, and made the corresponding potassium, rubidium, and cæsium compounds by a similar process. The latter worked with a solution of lead tetrachloride prepared by passing chlorine gas into lead dichloride dissolved in aqueous hydrochloric acid.

Goebbels (*Ber.*, 1895, **28**, 792) has recently sought to explain this discrepancy by assuming that two sets of double salts exist, of the types $PbCl_4,2M'Cl$ and $2PbCl_4,5M'Cl$ respectively, and claims to have prepared the two corresponding lutidine compounds, and also a picoline salt, $3PbCl_4,7C_6NH_7,HCl$, belonging to a different type.

Finding that ammonium chloride was precipitated from its saturated aqueous solution on the addition of hydrochloric acid, we endeavoured, when preparing our salt, to avoid this source of impurity by using, as Wells had done, a solution of ammonium chloride in hydrochloric acid.

The following analyses show that the salt obtained by us under these conditions is identical with those prepared by Wells and Friedrich.

I. 0·6888 gave 0·4590 $PbSO_4$. Pb = 45·51.
II. 0·5437 „ 1·0234 AgCl. Cl = 46·54.
III. 0·7905 required 35·1 c.c. of $Na_2S_2O_3$. Cl (active) = 15·21.
(1 c.c. = 0·2396 $Na_2S_2O_3$).

$PbCl_4,2NH_4Cl$ requires Pb = 45·39, Cl = 46·71, Cl (active) = 15·57 per cent.

Action of Gaseous Hydrogen Chloride.—This gas, dried by means of sulphuric acid, acts energetically on lead tetracetate in accordance with the equation given above, and in the early part of 1893, we made numerous attempts to separate the acetic acid from the tetrachloride by means of carbon tetrachloride and other liquids. Our efforts in this direction met with no success until we learnt from Friedrich's paper (*Ber.*, 1893, **26**, 1434) that lead tetrachloride is not acted on by sulphuric acid, when by employing this acid we were able to prepare small quantities of lead tetrachloride direct from the tetracetate. For this purpose, a few grams of the finely powdered salt were placed in a test tube and covered with concentrated sulphuric acid.

The tube was then quickly cooled in ice, and dry hydrogen chloride was passed in; after a short time, a globule of lead tetrachloride collected at the bottom of the tube. The yield was unfortunately small, the greater portion of the lead being converted into sulphate. A similar result, but a still poorer yield, was obtained by passing hydrogen chloride over lead tetracetate kept cool in ice; on adding cold, concentrated sulphuric acid, the acetic acid was dissolved, and a small globule of lead tetrachloride remained.

Action of Hydrobromic and Hydriodic acids.—Lead tetracetate dissolves in the concentrated acids, but almost immediate separation of the halogen and corresponding haloïd occurs. We have not succeeded in isolating double salts from the solutions, but Classen and Zahorski have prepared the two quinoline derivatives, $PbBr_4,2C_9NH_7,HBr$ and $PbI_4,2C_9NH_7,HI$, by decomposing the chloride with potassium bromide and iodide respectively.

Action of Hydrofluoric acid.—The aqueous acid (37 per cent.) dissolves lead tetracetate readily, and gives a colourless solution, which, in all probability, contains either PbF_4 or H_2PbF_6. If excess of acid is present, the solution is stable at the ordinary temperature, but, like the liquid obtained when hydrochloric acid is used, it is entirely broken up on evaporation even in a vacuum; the decomposition in this case, however, takes a somewhat different course, and results in the quantitative deposition of lead dioxide in accordance with the equation $PbF_4 + 2H_2O = PbO_2 + 4HF$.

The explanation of this difference in the behaviour of the two haloïds is most likely to be sought in the small relative affinity of hydrofluoric acid as compared with hydrochloric acid.

The hydrofluoric acid solution of the tetracetate may, however, be evaporated to dryness without separation of lead dioxide if a small quantity of ammonium fluoride is first added to it, and leaves then a residue rich in quadrivalent lead. This is, doubtless, due to the formation of an ammonium double salt analogous to those derived from lead tetrachloride.*

Action of Hydrogen Sulphide.—In view of the ease with which water and lead tetracetate interact to form lead dioxide, we thought it desirable to see if a corresponding sulphide, PbS_2, could be prepared by passing hydrogen sulphide over the salt or into its solutions in glacial acetic acid or chloroform. The product, in all cases, appeared to consist of lead sulphide and free sulphur, and we have been quite unable to obtain any evidence of the existence of the bisulphide PbS_2.

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* We obtained the above results in the summer of 1893, but were unable to continue the research till the following spring. In the meantime, several points we had proposed to investigate, were cleared up in an interesting paper by Brauner (Trans., 1894, **65**, 393), who, unknown to us, had been working on the same lines as ourselves, and who by a similar method to the above, succeeded in preparing considerable quantities of the salt PbF_4, 3KF, HF, isomorphous with the corresponding tin compound, pink salt, SnF_4, 3KF, HF, and pointed out that after hydrofluoric acid had been expelled by heating at 250°, the residue yielded fluorine on ignition.

Action of Sulphuric acid.—Lead tetracetate is insoluble in aqueous sulphuric acid, which rapidly converts it into lead dioxide. When treated with the concentrated acid at ordinary temperatures, no change occurs at first, but after a time the salt turns yellow, slowly gelatinises, and finally decomposes, lead sulphate being deposited, and a small quantity of gas chiefly consisting of carbon dioxide evolved. This change takes place at once if the acid and salt are warmed together on the water bath; under these conditions, lead tetrasulphate, $Pb(SO_4)_2$, if formed, is exceedingly unstable, and we have not been able to obtain any satisfactory proof of its existence Brauner (*Zeit. anorg. Chem.*, 1894, **7**, 11), however, found that a clear solution of lead tetrafluoride in excess of concentrated sulphuric acid deposited yellow crusts, believed by him to be $Pb(SO_4)_2$ when it was warmed to 100° from time to time, during a period of more than two months.

Lead Tetraphosphate.

When a 50 per cent. aqueous solution of orthophosphoric acid is allowed to act on lead tetracetate, the latter is converted into a pale yellow gelatinous mass, which readily turns brown on adding excess of water, and evolves chlorine when treated with hydrochloric acid. These observations led us to make numerous attempts to prepare phosphates of quadrivalent lead, and though we have not so far been successful in preparing a pure specimen of such a compound, we believe, nevertheless, that our results warrant the assertion that $Pb(HPO_4)_2$ is capable of existence, and we attribute our inability to obtain it pure chiefly to the lack of a suitable solvent for lead tetracetate, and also to the difficulty of washing away excess of phosphoric acid, without at the same time decomposing the tetraphosphate formed. In the course of this part of our work, a large number of preparations has been made and analysed; we only propose, however, to describe a few experiments which either illustrate our methods or give information as to the nature of the compounds obtained.

1. Lead tetracetate was dissolved in glacial acetic acid, excess of aqueous phosphoric acid added, and the white gelatinous precipitate, after being collected on a filter plate, and washed first with acetic acid and finally with absolute alcohol, was then placed over sulphuric acid in a vacuum till all smell of acetic acid had disappeared. The solid obtained turned brown when treated with water, and contained 7·9 per cent. of quadrivalent lead, Pb^{IV} (determined by distillation with hydrochloric acid) 52 per cent. of bivalent lead, Pb'' (total lead $- Pb^{IV}$) and 12·54 per cent. of phosphorus. $Pb : P = 1 : 1·417$. Two orthophosphates of lead $Pb_3(PO_4)_2$ and $PbHPO_4$ have been described. They contain Pb and P in the ratio 1 : 0·666 and 1 : 1 respectively.

Corresponding phosphates of quadrivalent lead would be $Pb_3(PO_4)_4$ and $Pb(HPO_4)_2$, with the ratio Pb : P = 1 : 1·333 and 1 : 2. The analysis shows that the sample contains more phosphorus than would be found if all the bivalent lead were present as $PbHPO_4$, and the quadrivalent lead as $Pb(HPO_4)_2$; this is doubtless due to imperfect washing, while the explanation of the small amount of quadrivalent lead is to be sought in the reducing action of the absolute alcohol.

2. It was subsequently found that much better results could be obtained by adding a solution of tetracetate in acetic acid to a concentrated solution of aqueous phosphoric acid, mixed with two or three times its volume of acetic acid. The precipitate which formed was sucked up, washed quickly with acetic acid only, and dried as completely as possible in a vacuum over sulphuric acid and solid caustic soda. This specimen proved, on analysis, to be entirely free from bivalent lead, whilst quadrivalent lead and phosphorus were present in the ratio 1 : 2·36. Owing to the presence of excess of phosphoric acid as an impurity we have not been able to assign a definite formula to this compound, the fact that all the lead is quadrivalent proves, however, quite conclusively that tetraphosphates of lead can be prepared by precipitation.

3. Lead tetracetate is only slightly soluble in cold glacial acetic acid, and any method involving the use of large quantities of such a solvent is open to so many objections that we resolved to try and precipitate chloroform solutions of the tetracetate by alcoholic phosphoric acid. Preliminary experiments showed us that the salts obtained in this way contained considerable quantities of quadrivalent lead, and were fairly stable in the presence of alcoholic phosphoric acid.

a. Five grams of lead tetracetate were moistened with acetic acid, dissolved in 75 grams of chloroform, and the solution poured slowly into 14·75 grams of a 30 per cent. alcoholic solution of H_3PO_4 (4 mols. H_3PO_4 : 1 mol. $PbAc_4$), the precipitate at first redissolved, but became permanent after the greater part of the solution of lead tetracetate had been added. On adding ether, a bulky solid came down, which filtered readily, and was soluble in water, giving a brown liquid from which lead dioxide was precipitated on boiling. Alcohol acted on the precipitate, dissolving some of it, and converting the rest into a yellow, semi-transparent jelly, which it was almost impossible to filter. After sucking it up as completely as possible with the aid of a pump, it was placed in a vacuum till it dried to a white mass.

The lead in this substance was probably all quadrivalent, for although, owing to the presence of alcohol in the apparently dry mass, no satisfactory determination could be made, still, in spite of the reducing action of the alcohol, upwards of 80 per cent. of the total lead was found to be present as Pb^{IV}. After heating for some time at 150°, a portion of the substance was gently ignited; the residue contained Pb, 50·45; P, 19·68 per cent. Pb : P = 1 : 2·605.

b. Another specimen, prepared in a similar way, gave a salt which, after drying at 150°, was found to contain Pb, 52·9; P, 15·63 per cent. It lost, on ignition, 5·07 per cent., and the composition of the residue, calculated from these data, is Pb, 56·2 and P, 16·61 per cent. Pb : P = 1 : 1·99 (mean of three analyses). From these numbers it will be seen that in this sample the ratio Pb : P is that required by the formula $Pb(HPO_4)_2$. This may be a mere coincidence, but it seems to us highly probable that this substance was actually formed, for its composition, Pb, 51·88 and P, 15·54 per cent., agrees fairly well with that of our preparation. Again, if we grant that such a substance as $Pb(HPO_4)_2$ may exist, we may fairly be allowed to assume that it will give off water and oxygen on ignition, and be converted into the metaphosphate $(Pb(PO_3)_2$. This change will result in a loss of 7·39 per cent., and the residue will contain Pb, 56·71 and P, 16·98 per cent. The numbers quoted above as representing the actual composition of the ignited substance agree fairly well with these. It is probable that our preparation while drying at 150° underwent a certain amount of decomposition, and this would account for its containing rather more lead and phosphorus than the formula $Pb(HPO_4)_2$ demands, and also to some extent for the small loss when it was subsequently ignited.

It is, perhaps, worth noticing in this connection that the composition of the residue obtained in Experiment 3*a* may be also fairly satisfactorily explained if we assume that the substance before ignition consisted of a mixture of $Pb(HPO_4)_2$ and H_3PO_4, and that these on heating were converted into $Pb(PO_3)_2$ and HPO_3 respectively, for if we calculate and subtract the weight of HPO_3, which corresponds to the excess of phosphorus present, the residue has the composition Pb = 57·21 and P = 17·17 per cent., while $Pb(PO_3)_2$ requires Pb, 56·71 and P, 16·98 per cent.

If all the lead in these two compounds had been present in the quadrivalent state, a strong case would have been made out for assigning the formula $Pb(HPO_4)_2$ to our precipitate.

Determinations made by distillations with hydrochloric acid showed, however, that of the total lead in 3*a*, only 80 per cent., and in 3*b*, only 65 per cent. was present as quadrivalent lead. We are, however, inclined to think that this result was due, partly to reduction of the tetraphosphate during its preparation, and possibly also to the presence of small quantities of alcohol in the apparently dry substance, which, being acted on by the chlorine evolved, vitiated the determination. We believe, however, that th facts we have quoted, though insufficient to establish the formula $Pb(HPO_4)_2$, make it extremely probable that this compound was actually precipitated.

This point cannot, however, be satisfactorily settled without further experimental work, and we hope to find an early opportunity of submitting this substance to a more thorough examination.*

Lead Tetrapropionate.

This salt resembles the corresponding acetate very closely, and was prepared and analysed in a precisely similar way. It crystallises from its solution in propionic acid in thin needles, which melt at 132°, and decompose at a somewhat higher temperature. The substance can be recrystallised from hot propionic acid, but the process is attended with loss, a portion of the tetrapropionate being apparently reduced to propionate.

The sample analysed was recrystallised twice.

0·6389 gave 0·3077 PbO_2, and required 51·7 c.c. of soda solution [1 c.c. = 0·00395 gram NaOH], whence PbO_2 = 48·16 and $(C_3H_5O)_2O$ = 51·94 per cent.

0·3870 gave 0·2172 $PbCl_2$, whence PbO_2 = 48·26 per cent.

The formula $Pb(C_3H_5O_2)_4$ requires PbO_2 = 47·87 and $(C_3H_5O)_2O$ = 52·13 per cent.

Analogous Salts of other Metals.

The existence of a stable crystalline acetate derived from lead dioxide led us to enquire if the higher oxides of other metals afford similar compounds. We find that several such substances have been described, the most interesting of which are the thallic and manganic acetates. According to Willm (*Ann. Chim. Phys.*, 1865, [4], **5**, 5), the acetate, $Tl(C_2H_3O_2)_3$, obtained by dissolving freshly precipitated thallic oxide in strong acetic acid, is the most stable of the thallic salts. Like lead tetracetate, which it resembles extraordinarily closely, it is quantitatively decomposed, on treatment with water, into Tl_2O_3 and acetic acid. It is soluble in hydrochloric acid, giving thallic chloride; added to potassium iodide it sets free iodine, thallous iodide being precipitated, whilst phosphoric and arsenic acids give gelatinous precipitates, probably consisting of $TlPO_4,2H_2O$ and $TlAsO_4,2H_2O$ respectively. Thallic chloride and the thallic salts generally are,

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* By methods somewhat similar to those employed for preparing the lead tetraphosphate described above, we have recently succeeded in obtaining a lead tetrarsenate, containing 42·01 per cent. of lead, and 30·59 per cent. of arsenic; the formula $Pb(HAsO_4)_2$ requires Pb, 42·48 per cent., and As, 30·83 per cent. This substance, together with some others made by acting with a hydrofluoric acid solution of lead tetracetate on solutions of phosphoric acid, are still under investigation, and we hope soon to make a further communication to the Society on this subject.

however, somewhat more stable than the plumbic salts, and the nitrate, sulphate, and oxalate have been prepared.

Like lead dioxide, manganic oxide, Mn_2O_3, is not attacked by acetic acid, the oxide Mn_3O_4, however, dissolves readily enough, and on adding a little water, crystals of $Mn(C_2H_3O_2)_3,2H_2O$ are deposited (Christensen, *J. pr. Chem.*, 1883, [2], **28**, 1). This salt is apparently the most stable of the manganic compounds, and its behaviour towards reagents is similar to that of lead tetracetate; a sulphate, $Mn_2(SO_4)_3H_2SO_4,8H_2O$; phosphates, $MnPO_4,H_2O$, and $MnNaP_2O_7,5H_2O$, and an arsenate, $MnAsO_4,H_2O$, have been prepared from it. Christensen has also described a fluoride, $MnF_3,3H_2O$, and numerous double salts of the type $2M'F,MnF_3$ (*J. pr. Chem.*, 1887, [2], **35**, 57).

Cobaltic acetate exists in the solution prepared by dissolving hydrated cobaltic oxide in strong acetic acid (Beetz, *Ann. Phys. Chem.*, 1844, **61**, 472). With the exception of the sulphate described by Marshall (Trans., 1891, **59**, 767), it seems to be the most stable of the simple cobaltic salts. When the oxide, CrO_3, dissolves in glacial acetic acid, an acetate may possibly be found; we have not, however, been able as yet to obtain any evidence of this.*

List of Salts of Quadrivalent Lead.

Leaving out of consideration the numerous organo-metallic derivatives of lead, and omitting a few compounds whose nature is not yet fully elucidated (Wells, *Zeit. anorg. Chem.*, 1895, **9**, 305), the following list comprises the salts of quadrivalent lead which have, up to the present, been described by Brauner, Classen and Zahorski, Friedrich, Goebbels, Wells, and ourselves.

PbF_4? $PbCl_4$.
$PbF_4,3KF,HF$.
K_2PbCl_6.
Rb_2PbCl_6.
Cs_2PbCl_6.
$(NH_4)_2PbCl_6$.
$(C_9NH_7)_2,H_2PbCl_6$, $(C_9NH_7)_2,H_2PbBr_6$, and $(C_9NH_7)_2,H_2PbI_6$.
$(C_7NH_9)_2,H_2PbCl_6$.
$2PbCl_4,5NH_4Cl$.
$2PbCl_4,5(C_5NH_5,HCl)$ (pyridine salt).
$2PbCl_4,5(C_7NH_9,HCl)$ (lutidine salt).
$3PbCl_4,7(C_6NH_7,HCl)$ (picoline salt).
$Pb(SO_4)_2$? $Pb(HPO_4)_2$? $Pb(C_2H_3O_2)_4$ $Pb(C_3H_5O_2)_4$.
$Pb(HAsO_4)_2$.

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* The remarkable compound obtained by Tafel (*Ber.*, 1894, **27**, 816) by acting with Na_2O_2 on acetic acid, does not appear to belong to this class of substances.

Brauner, Friedrich, and Wells have pointed out that several of these compounds present analogies not only in composition, but also in behaviour and crystalline form, with certain of the stannic salts, and the relationship between lead and tin is further exhibited by the existence of plumbates allied to the stannates. Of them the potassium, sodium, barium, strontium, and calcium salts have been prepared, whilst the two oxides Pb_2O_3 and Pb_3O_4, may be regarded as derivatives of meta- and ortho-plumbic acids respectively, and may therefore be written PbO,PbO_2 and $\left.\begin{matrix}PbO\\PbO\end{matrix}\right\} PbO_2$.

In conclusion, the principal results of our work, and our deductions from them, may be summed up as follows.

1. The substance obtained by dissolved Pb_3O_4 in glacial acetic acid has the molecular formula $Pb(C_2H_3O_2)_4$. It is decomposed quantitatively by water into lead dioxide and acetic acid; hydrochloric acid converts it into lead tetrachloride, and orthophosphoric acid into a phosphate. Its general behaviour is analogous to that of the thallic and manganic acetates, and its molecular volume agrees with that calculated for the acetates by Schröder's empirical law.

These facts lead us to regard it as a salt of lead dioxide.

2. A similar propionate exists.

3. When acted on by orthophosphoric acid, the tetracetate is converted into a phosphate, to which in all probability the formula $Pb(HPO_4)_2$ must be assigned.

4. Numerous lead salts exist which bear the same relation to the stannic salts that the ordinary lead compounds do to the stannous salts. The former should therefore be termed plumbic salts, and the latter plumbous salts.

5. Like stannic oxide, lead dioxide is capable of playing the part of either an acid or a basic oxide. The appropriate name for it is plumbic oxide, which should be used in preference to the term peroxide, which in this connection is both unsuitable and misleading.

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