of lead hydroxyarsenate if the precipitates are filtered immediately after the precipitation.

The precipitate that is first formed is lead hydroxyarsenate; diplumbic arsenate is produced by a secondary reaction.

As the excess of the alkaline disodium arsenate increases greater amounts of lead hydroxyarsenate are produced.

As the concentration increases, when the reactions have come to an equilibrium, the relative amount of diplumbic arsenate increases.

As the temperature rises more lead hydroxyarsenate is formed.

From the determination of the point of equilibrium in the systems

$$5PbHAsO_4 + 4NaNO_3 + H_2O \rightleftarrows Pb_5OH(AsO_4)_3 + 2Na_2HAsO_4 + 4HNO_3$$

$$5PbHAsO_4 + 4CH_3COONa + H_2O \rightleftarrows Pb_5OH(AsO_4)_3 + 2Na_2HAsO_4 + 4CH_3COOH,$$

the composition of the resulting lead arsenate of the respective reactions can be calculated.

BOZEMAN, MONT.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, OF THE U. S. DEPARTMENT OF AGRICULTURE.]

THE ARSENATES OF LEAD.

[FIRST PAPER.]

BY C. C. McDONNELL AND C. M. SMITH.

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Arsenate of lead, until comparatively recent years, was of no commercial importance; however, since it was first recommended as an insecticide,[1] it has come into very extensive use, and several thousand tons are used annually for the destruction of certain leaf-eating insects. Fourteen U. S. patents[2] relating to commercial processes for its production have been issued. Despite its large and increasing use and importance, the chemical and physical properties of the several arsenates of lead have not been very thoroughly investigated. Most of the recent work has been directed toward determining what products result from the reaction between lead nitrate or lead acetate, and disodium hydrogen arsenate, Na_2HAsO_4, which compounds have been widely recommended for its preparation for spraying purposes.

The references in the literature concerning the prepa ation and properties of the arsenates of lead are based mostly upon the work of the earlier chemists, Berzelius, Mitscherlich, Wittstein, Graham, H. Rose, and Salkowski, whose conclusions are somewhat contradictory, and

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[1] Report Mass. Board of Agr., 1893, p. 282.

[2] Nos. 870,915, 892,603, 903,389, 929,952, 1,014,742, 1,056,340, 1,064,023, 1,064,639, 1,100,673, 1,100,686, 1,141,920, 1,169,114, 1,172,741, 1,175,565.

frequently misquoted by more recent writers. The latter condition has been due in part no doubt to changes in nomenclature.

The older investigators recognized "neutral" lead arsenate (which term was applied indiscriminately to both dilead orthoarsenate and lead pyroarsenate) and "basic" or "sub" arsenate (later designated trilead arsenate). The naturally occurring mineral now known as mimetite was for many years regarded as "sub" arsenate of lead until the researches of V. Rose[1] and Wöhler[2] showed it to be lead chloroarsenate of the formula $Pb_4(PbCl)(AsO_4)_3$.

The work of the more recent investigators will be considered under the several subheadings.

Arsenic acid, as is well known, forms several distinct classes of salts—orthoarsenates, derived from orthoarsenic acid, H_3AsO_4, which are subdivided into mono-, di- and tri-metallic salts; pyroarsenates, derived from pyroarsenic acid, $H_4As_2O_7$; and metarsenates, derived from metarsenic acid, $HAsO_3$.

Representatives of all of these classes are found among the various metallic arsenates, and, theoretically, lead should also form corresponding compounds.

Monolead Orthoarsenate, $PbH_4(AsO_4)_2$.—One might naturally suppose that monolead arsenate would result from the interaction of solutions of lead nitrate or acetate and a monoalkali arsenate, such as potassium dihydrogen arsenate, KH_2AsO_4.[3] However, this does not occur, at least at moderate dilutions. Under such conditions we invariably obtained dilead arsenate, $PbHAsO_4$, with simultaneous liberation of free acid in the solution, according to the following equation:

$$Pb(NO_3)_2 + KH_2AsO_4 = PbHAsO_4 + KNO_3 + HNO_3$$

Likewise, dilead arsenate is formed when arsenic acid is permitted to react with lead nitrate at ordinary dilutions. These facts suggested that monolead arsenate is unstable in moderately acid media, but might exist at higher acid concentrations. When 20 g. of dilead arsenate were boiled for two hours with 50% arsenic acid and the liquid filtered off, the latter was found to contain but a trace of lead, and the residue, after washing with 95% alcohol (in which arsenic acid is readily soluble), was found to have been practically unchanged. When the arsenic acid concentration was raised to 86% H_3AsO_4, transposition took place. 400 g. of 86% arsenic acid were brought to boiling (about 130 °), and pure dilead arsenate was added in successive small portions. The first few additions dissolved completely, and 7 g. went into solution before a permanent

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[1] *Neues Allgemeines Journal der Chemie*, 3, 65 (1804).

[2] *Ann. Phys. Chem.*, 4, 161 (1825).

[3] Commercial potassium arsenate is the dihydrogen salt, KH_2AsO_4, although frequently labeled K_2HAsO_4.

residue remained. A total of 10 g. was added and the heating continued for several minutes. The solution was then filtered through asbestos and allowed to stand until cold, when a bulky mass of moderate sized crystals had deposited. They were separated from the mother liquor as well as possible by centrifuging, then washed with absolute alcohol and dried at 110°. Analysis showed this compound to be monolead orthoarsenate (*a*).

By the addition of a small amount of nitric acid to the boiling arsenic acid solution a larger yield of this material may be obtained. One such experiment, using a solution containing 86% arsenic acid and 2% nitric acid, gave a product of almost theoretical composition (*b*).

	Found. (*a*).	Found. (*b*).	Calc. for $PbH_4(AsO_4)_2$.
Lead oxide, PbO	45.03%	45.59%	45.62%
Arsenic oxide, As_2O_5	47.42	47.14	47.01
Water of constitution (by ignition)	7.55	7.34	7.37
	100.00	100.07	100.00

The concentration at which the change from di- to monolead arsenate takes place was determined approximately by using arsenic acid of various concentrations. It was found that 93, 91, 88 and 86% H_3AsO_4 deposited monolead arsenate, while concentrations of 80% H_3AsO_4, or less, gave dilead arsenate, showing that the transition concentration lies somewhere between 80 and 86% arsenic acid.

Properties.—Under the microscope the monolead arsenate prepared as described was seen to consist entirely of long, narrow, rhomboidal plates. The acute angle at the end is 68° (measured by rotating stage). They are biaxial, probably negative, and extinguish at an angle of 8° with reference to the longer edge. The minimum index of refraction, normal to the face upon which the crystals naturally lie, is about 1.75, and the birefringence is very strong. (These results indicate that they are mono- or triclinic, probably the latter, as the normal to the crystal did not coincide with any one of the three ether axes.)

The specific gravity, determined on 2.5 g. of material, using a 25 cc. specific gravity bottle and benzene as the liquid, was found to be 4.46 at 15° compared with water at the same temperature.

Chemically, monolead arsenate is very unstable. In contact with water it gives up arsenic acid immediately; 0.5 g. treated with 100 cc. of water for 3 hours at room temperature gave 21.89% soluble As_2O_5. The same proportions boiled for 5 minutes gave 22.91% soluble As_2O_5. The lead dissolved was practically *nil* in both cases, showing that water causes complete decomposition of monolead arsenate into dilead arsenate and arsenic acid. The crystals which had been treated with water retained their shape, as shown by microscopical examination, but were almost without exception of a brown color, and nearly opaque, with the appearance of having been fractured throughout.

Monolead arsenate, when heated very slowly, begins to lose water at 140°. Heated at 150° for 7 hours it lost approximately one half its total content, corresponding to one molecule of water. Upon further heating at this temperature it continued to lose weight slowly, but the entire theoretical amount was not lost after heating 5 hours a day for three successive days, nor after three additional 5-hour periods at 210°. Total loss during this heating, 6.83%. When heated over a low flame below redness it lost 7.34% (theory for water of constitution, 7.37%). Heated to fusion it was partially reduced and lost As_2O_3, which could be seen escaping from the crucible.

Dilead Orthoarsenate, $PbHAsO_4$.—The material derived from orthoarsenic acid by the replacement of two of the hydrogen atoms by lead has been known by various names, such as neutral lead arsenate, acid lead arsenate, bibasic lead arsenate, lead hydrogen arsenate, diplumbic hydrogen arsenate, diplumbic arsenate, and simply lead arsenate. It would seem that dilead arsenate is sufficiently specific; in fact, in commercial usage when the term "lead arsenate" is used it is generally this compound that is meant. It is by far the most important arsenate of lead. The formula may be expressed as $Pb_2H_2(AsO_4)_2$, or, since its molecular weight is not known, simply $PbHAsO_4$.

There are numerous references in the literature to the preparation and properties of this material. They are, however, in some cases, contradictory.

Berzelius (*Neues Journal für Chemie und Physik*, **23**, 174 (1819); *Ann. chim. phys.*, [2] 11, 229 (1819)) states that it is produced when a solution of nitrate of lead is added to a solution of arsenate of soda with the precaution that the whole amount of the arsenic acid be not precipitated, and describes the product (*Lehrbuch der Chemie*, **3**, 72 (1845)) as a white powder, insoluble in water, soluble in HCl and HNO_3, melting at white heat to an opaque yellowish mass.

Mitscherlich (*Ann. chim. phys.*, **19**, 368 (1821)).—Lead acetate completely decomposes the bin-arsenates ($M'H_2AsO_4$), for the arsenate of lead is insoluble in acetic acid. The precipitate is ordinarily the neutral salt (dilead arsenate), but one can never be sure that the neutral salt is not mixed with the sub-salt (trilead arsenate). Distinguished from the sub-salt by melting easily and crystallizing on cooling.

Wittstein, "Entymologisch Chemisches Handwörterbuch," **2**, 929 (1847).—Neutral lead arsenate precipitates as a white insoluble powder when lead acetate is mixed with neutral arsenates of the alkalies. It melts at white heat to a yellow nontransparent glass.

H. Rose, "Ausführliches Handbuch der Analytischen Chemie," 1, 381 (1851).—A solution of nitrate or acetate of lead produces in solutions of arsenic acid, or alkali arsenates, an immediate white precipitate of lead arsenate, soluble in nitric, insoluble in acetic acid; does not crystallize when melted before the blowpipe. In certain cases the lead arsenate may contain more lead and be, therefore, more basic (*Ibid.*, **2**, 406).

Gmelin, "Handbook of Chemistry," trans. by Watts, **5,** 173 (1851).—It is formed by the slow action of arsenic acid and air upon metallic lead; also by the precipitation of lead chloride with arsenic acid. Soluble in hydrochloric acid.

Salkowski, *J. prakt. Chem.*, 104, 160 (1868).—Produced by the addition of neutral sodium arsenate to lead acetate as long as a precipitate forms. Crystalline. Converted to lead pyroarsenate upon ignition.

Duvillier, *Compt. rend.*, **81,** 1251 (1875).—If a boiling solution of arsenate of lead in nitric acid be diluted with water it quickly deposits little plates of dilead arsenate.

Goguel, "Memoires de la Societe des Sciences Physiques et Naturelles de Bordeaux," Ser. [5] 1, 135 (1896).—By the addition of concentrated arsenic acid to a boiling solution of lead nitrate containing about 1% nitric acid obtained crystals in micaceous leaflets, unctuous to the touch, insoluble in water, soluble in dilute nitric acid; water of constitution lost above 200°; not further decomposed at red heat. Optical measurements of the crystals showed them to belong to the monoclinic system.

De Schulten, *Bulletin de la Societé Française de Mineralogie,* **27,** No. 6, 113 (1904).—Well formed monoclinic crystals of dilead arsenate were obtained by the slow addition of a 0.3% solution of ammonia to a hot nitric acid solution of lead arsenate. Sp. gr. 6.076 at 15°. Optical and goniometric measurements are given.

Holland and Reed (Mass. Agr. Expt. Station, *24th Ann. Report,* Part I, 204 (1912)) state that acid lead arsenate of theoretical composition is readily prepared from nitrate of lead and sodium arsenate, provided dilute solutions are employed and the sodium salt added carefully in excess (10%).

Tartar and Robinson (THIS JOURNAL, **36,** 1846 (1914)).—Pure dilead arsenate was obtained as a white amorphous powder by the addition of dilute ammonia, with constant stirring, to a saturated solution of lead arsenate in nitric acid until three-fourths of the nitric acid used was neutralized. Sp. gr. 5.786.

The most frequently quoted method for the production of dilead orthoarsenate is the reaction between solutions of lead acetate, or nitrate, and the "neutral" arsenate of soda, Na_2HAsO_4. R. E. Curry and T. O. Smith,[1] after a phase rule study, conclude that "in the system disodium hydrogen arsenate, lead nitrate and water there exists at 25° only one compound, lead hydrogen arsenate;" however, F. J. Smith,[2] Pickering[3] Haywood[4] and Tartar and Robinson[5] have noted that the action between lead nitrate and disodium arsenate is not constant, resulting in a product usually slightly more basic than dilead arsenate. Experiments made by us are in agreement with the latter view. (It should be noted that Curry and Smith worked with very dilute solutions.) Using lead acetate and disodium arsenate in suitable proportions we have obtained a material even more basic than trilead arsenate.

Mitscherlich used as his source of arsenic the "binarsenates" of ammonia, soda, and potash, by which he meant salts of the type $M'H_2AsO_4$, and not those of the type M'_2HAsO_4, as is stated in several later quotations of his work. We have found that if lead nitrate or acetate in moderately

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[1] THIS JOURNAL, **37,** 1685 (1915).

[2] Mass. State Board of Agr., *45th Ann. Report,* 357 (1897).

[3] *J. Chem. Soc.*, **91,** 310 (1907).

[4] Bur. Chem., *Bull.* **105,** 165 (1907).

[5] *Loc. cit.*

strong solutions is precipitated by means of an excess of monopotassium arsenate, dilead arsenate is produced, which, when dried, is a very bulky, amorphous powder, of practically theoretical composition. The use of very dilute solutions results in the formation of a crystalline product having a silky appearance.

Arsenic acid in conjunction with lead acetate or nitrate, as stated by H. Rose, is as efficient as the method just described for making a pure product and the tendency to crystallization is greater owing to the greater acidity of the solution.

The few experiments made by us on the reaction between lead chloride and arsenic acid, gave, instead of dilead arsenate (which Gmelin states is so formed), a chloroarsenate approximating to natural mimetite, $Pb_4(PbCl)(AsO_4)_3$, as we have shown in a previous paper.[1] It may be that under certain conditions dilead arsenate would also deposit from such solutions. In a number of experiments with saturated lead chloride and soluble arsenates (0.04 mol As_2O_5 per l.), a lead chloroarsenate was always obtained, except that when a solution of lead chloride was added to potassium or sodium dihydrogen arsenate, the latter in excess, pure dilead arsenate was precipitated.

We first obtained crystals by placing a solution of cold dilute nitric acid, saturated with dilead arsenate, under a bell jar by the side of an open dish of concentrated ammonia. The slow absorption of the ammonia vapors neutralized the acid and precipitated dilead arsenate in the form of long, slender, glistening crystals. A pure crystalline product was also obtained by adding a dilute solution of ammonium acetate to a solution of dilead arsenate in boiling nitric acid. We found the method of Duvillier to be the most satisfactory for producing a pure crystallized compound, as it permits of successive recrystallizations. On pouring a solution of nitric acid (1 : 4) saturated at the boiling point with dilead arsenate into about six times its volume of boiling water, a mass of beautiful crystals separated, consisting of very thin plates of sufficient size to be visible to the eye. The analysis of this product gave results in practical accord with theory.

	Found.	Theory for $PbHAsO_4$.
Lead oxide, PbO	64.20%	64.29%
Arsenic oxide, As_2O_5	33.13%	33.13%
Water of constitution (by diff.)	2.67%	2.58%
	100.00%	100.00%

When the nitric acid solution was allowed to cool without dilution a smaller crop of much larger crystals was obtained, some being as large as 1 × 1 × 0.03 mm.

Properties.—Goguel and de Schulten both described the product as oc-

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[1] *Am. J. Sci.*, [4] **42**, 139 (1916).

curring in monoclinic leaflets, tabular parallel to the plane of symmetry, the latter containing the optic axes. The crystals in both cases had an acute angle of about 84°. Goguel states that extinction occurred at 21–22°, while de Schulten gives for this measurement 38°, both in reference to the obtuse angle of the crystal. Those prepared by us had an acute angle of 85° and extinguished at 29° within the obtuse angle. They are optically positive and the birefringence is quite high.

The determination of the density of two lots of dilead arsenate crystals, using a 10 cc. specific gravity bottle, 6 g. of material, and water[1] as the liquid, gave sp. gr. 15/15 6.042 and 6.053, agreeing with the value 6.076 as given by de Schulten. A determination made on 4.5 g. of amorphous material, using benzene as the liquid, gave sp. gr. 15/15 5.93. Tartar and Robinson[2] report a value of 5.786. (The results obtained on the crystalline compound are no doubt more nearly correct.)

Dilead arsenate is very little soluble in water; 5 g. boiled for 6 hours under a reflux condenser with 200 cc. of water gave but 4 mg. of As_2O_5 in solution. Cold water has even less effect. Experiments being conducted by C. C. McDonnell and J. J. T. Graham (the results of which have not yet been published), show that long-continued exposure to constantly changing water brings about decomposition, both lead and arsenic dissolving, but the latter at a relatively greater rate, leaving the residue more basic than dilead arsenate.

Upon heating, dilead arsenate loses its water of constitution and is converted into the pyroarsenate. Experiments made by heating small portions at various constant temperatures in an air oven, showed that the temperature of conversion to pyroarsenate is within a few degrees of 280°. The material used in these tests did not lose its crystalline appearance. It melts at a bright red heat and on cooling crystallizes to lead pyroarsenate.

Trilead Orthoarsenate, $Pb_3(AsO_4)_2$.—It is stated by Berzelius[3] that trilead arsenate is formed by the action of ammonia on "neutral" lead arsenate ($PbHAsO_4$), and[4] when a neutral arsenic acid salt (M'_2HAsO_4) is mixed with neutral lead acetate. Mitscherlich[5] says it is produced by the addition of neutral lead salts to a solution of an arsenate, the latter in excess; and[6] by the addition of lead acetate in excess to bi-arsenates ($M'H_2AsO_4$), with subsequent boiling. Graham[7] claims to have produced it by the addition of lead acetate to subarsenate of soda (Na_3AsO_4).

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[1] The action of water on dilead arsenate is so slight that no error is here introduced.

[2] *Loc. cit.*, p. 1849.

[3] *Ann. chim. phys.*, [2] 11, 229 (1819).

[4] *Lehrbuch der Chemie*, **3**, 72 (1845).

[5] *Ann. chim. phys.*, **19**, 363 (1821).

[6] *Ibid.*, p. 368.

[7] *Philosoph. Trans. Royal Society*, **123**, 266 (1833).

The double decomposition between soluble arsenates and lead salts has been used by a number of more recent investigators. Holland and Reed,[1] using disodium arsenate and lead acetate, obtained, under restricted conditions, a product containing lead and arsenic in the proper ratio for trilead arsenate. Tartar and Robinson,[2] however, state that pure trilead arsenate cannot be prepared by the reaction of these two compounds. Our work, as well as the observations of others, shows that the compound resulting from such reactions varies with changing conditions. In a series of experiments the reactions between the two lead salts, nitrate and acetate, and the two arsenates Na_2HAsO_4 and Na_3AsO_4 were studied, first with lead salt in excess and then with arsenate in excess, the concentrations employed being 0.4 mol PbO and As_2O_5, respectively, per liter. The results are here tabulated.

Salt in excess.	Precipitant.	Molecular ratio $\frac{PbO}{As_2O_5}$ in precipitate
$Pb(Ac)_2$	Na_2HAsO_4	3.29
$Pb(Ac)_2$	Na_3AsO_4	3.36
$Pb(NO_3)_2$	Na_2HAsO_4	2.19
$Pb(NO_3)_2$	Na_3AsO_4	3.14
Na_2HAsO_4	$Pb(Ac)_2$	2.96
Na_2HAsO_4	$Pb(NO_3)_2$	2.12
Na_3AsO_4	$Pb(Ac)_2$	3.25
Na_3AsO_4	$Pb(NO_3)_2$	3.27

An inspection of this table shows that the only case in which the molecular ratio is very close to 3.00 is in the reaction between lead acetate and excess disodium arsenate. In two cases a product approximating to dilead arsenate was obtained and in all the others basic compounds or mixtures having molecular ratios from 3.14 to 3.36 resulted.

According to Tartar and Robinson the action of aqueous ammonia on dilead arsenate produces, instead of trilead arsenate, a basic arsenate, to which they ascribe the formula $21Pb_3(AsO_4)_2.2Pb(OH)_2.10H_2O$. As a result of phase rule experiments (results to be published shortly), we have found that ammonia does change dilead to trilead arsenate, but the latter has a very limited range of existence, and with slight excess of ammonia is converted to a basic arsenate. We have prepared this basic arsenate in crystalline form. All of its properties indicate that it is hydroxy mimetite containing, however, one molecule of water of crystallization, $Pb_4(PbOH)(AsO_4)_3H_2O$. It will be more fully described in a subsequent paper on the basic arsenates of lead.

When small portions of litharge are added to molten lead pyroarsenate combination takes place with incandescence, showing that a chemical reaction, and not merely solution, is taking place. A mixture of dilead arsenate (or pyroarsenate) and litharge in theoretical proportions to form

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[1] *Loc. cit.*, p. 203.

[2] *Ibid.*, p. 1847.

trilead arsenate fuses with difficulty before the blast lamp, but can be rendered fluid in a furnace. The melt solidifies to a light yellowish brown, crystalline mass, which is easily broken up. No single crystals were revealed, even after breaking up and examining with the microscope. Most of the pieces were irregularly twinned throughout their mass, giving a speckled appearance when viewed in parallel polarized light. Practically all of the clear transparent pieces appeared to be perpendicular to the acute bisectrix, giving a poor figure very little different from a uniaxial cross. Birefringence low and positive. Specific gravity 7.32 at 15°.

Small portions fused before the mouth blowpipe and allowed to form into hanging drops, on cooling assumed polyhedral forms somewhat resembling crystals of garnet. They were dark brown, iridescent and opaque. The faces were of a resinous luster, somewhat conchoidal in appearance and probably are not true crystallographic faces.

Lead Metarsenate, $Pb(AsO_3)_2$.—Metarsenates in general may be prepared from monoarsenates by ignition. Monolead arsenate loses its water of constitution completely below a red heat and forms lead metarsenate. We also produced it directly from its constituents. When solid arsenic acid and litharge (PbO) or red lead (Pb_3O_4), in the correct proportion to form lead metarsenate, are heated, the mixture fuses very readily to a rather thin liquid. When permitted to cool slowly, and undisturbed, the melt solidifies at a dull red heat to a transparent glassy mass, very brittle and devoid of crystalline structure. When, however, this material is broken up and the lumps again heated until semiliquid, the whole mass becomes crystalline almost immediately. A product prepared in this way analyzed as follows:

	Found.		Theory for $Pb(AsO_3)_2$.
Lead oxide, PbO	49.75%		49.25%
Arsenic oxide, As_2O_5	47.12%		50.75%
Arsenious oxide, As_2O_3	2.65%	=○= 3.07% As_2O_5	.....
	99.52%		100.00%

It is seen that the arsenate has been partially reduced to arsenite, and this occurred even when red lead was used in an attempt to prevent the reduction. A similar experiment, using lead nitrate, produced the same compound. It also contained some arsenite (3.54% As_2O_3).

Properties.—Crystallized lead metarsenate appears to consist of hexagonal tablets. Pieces viewed perpendicular to these tablets were dark under crossed nicols, but gave no recognizable interference figure, even when 1 mm. or more in thickness. All pieces which showed any interference color at all were of an intense blue, regardless of their thickness. This may be the ultra-blue mentioned by Dana[1] as being sometimes seen in minerals such as Danburite, which have very low birefringence.

[1] "Textbook of Mineralogy," p. 428 (1906).

The specific gravity, determined with about 10 g. of material in benzene, was 6.42, referred to water.

Lead metarsenate is decomposed by water. The amorphous glassy material takes up moisture quickly from the air, becoming opaque, but the crystallized product is less readily attacked. Some material powdered to pass a No. 100 sieve was allowed to stand in contact with water at room temperature for 42 hours when it gave only 1.96% soluble As_2O_5 and 2.60% As_2O_3 (the latter represents the total As_2O_3 in the preparation). Boiling for 10 minutes gave practically the same result. However, when ground to an impalpable powder, decomposition into dilead arsenate and arsenic acid occurs almost completely. One gram treated with 100 cc. of water at about 70° for 40 hours gave 21.34% As_2O_5 and 2.59% As_2O_3 in the solution.

Lead Pyroarsenates.—It is theoretically possible to have two lead pyroarsenates, with the formulas $PbH_2As_2O_7$ and $Pb_2As_2O_7$. Pyroarsenic acid and pyroarsenates cannot exist in aqueous solution, and lead pyroarsenates are not obtained by double decomposition. All of our work was therefore confined to ignition methods.

Monolead Pyroarsenate, $PbH_2As_2O_7$.—This may be regarded as the semidehydration product of monolead orthoarsenate, $PbH_4(AsO_4)_2 = PbH_2As_2O_7 + H_2O$. As a matter of fact, monolead arsenate loses approximately one-half of its water of constitution rapidly at 150° and the remainder is expelled with much more difficulty, as previously noted under monolead arsenate. This is proof that dehydration takes place in steps, and indicates that monolead pyroarsenate is formed as an intermediate product.

Brünnich and F. Smith[1] claim to have found this compound in commercial lead arsenates. Their results, however, are not conclusive and it does not appear, from the properties of this compound, that it could exist in a commercial lead arsenate paste or be isolated from a dry mixture which might contain it by the method employed by these authors.

Dilead Pyroarsenate, $Pb_2As_2O_7$.—There is a conflict in the literature concerning methods of making this compound. According to Dammer[2] it may be prepared by the action of arsenic acid and air on metallic lead, also by the precipitation of lead nitrate with ammonium, potassium or sodium diarsenates, giving as the reference for the latter statement the work of Berzelius and Mitscherlich. Upon consulting the original articles it was found that Berzelius[3] obtained a product of the percentage composition corresponding to pyroarsenate, but he had ignited the material resulting from the precipitation of lead nitrate by sodium arsenate. Mit-

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[1] *Queensland Agric. J.*, **26**, 333 (1911).

[2] *Handbuch der Anorganischen Chemie*, **2**, Pt. 2, 566 (1894).

[3] *Neues Journal für Chemie und Physik*, **23**, 174 (1818).

scherlich[1] quotes Berzelius' results just given and[2] states that "neutral" lead arsenate results by the interaction of lead acetate and "bi-arsenates." The statement by Luther and Volck[3] that lead pyroarsenate results from the action of arsenic acid on basic lead carbonate, and Volck[4] that lead pyroarsenate may occur in lead arsenate pastes, are not supported by experimental proof.

Lefevre,[5] by saturating fused potassium metarsenate with litharge, produced lead pyroarsenate in the form of transparent orthorhombic leaflets.

The simplest means of producing lead pyroarsenate is to heat pure dilead orthoarsenate to about 300°. It may also be made by fusing a mixture of PbO and As_2O_5, or $Pb(NO_3)_2$ and $NH_4H_2AsO_4$ in equivalent amounts. Fusion always results in a slight reduction to arsenite.

Properties.—Lead pyroarsenate melts before a blast lamp, becoming quite fluid, and solidifies on cooling to a light yellow crystalline mass, which is easily broken and powdered between the fingers, probably owing to pronounced cleavage in the crystals. The crushed material when examined under the polarizing microscope showed no well formed crystals but a predominance of irregular pieces almost perpendicular to one optic axis. Such pieces, whenever they had any straight edges, showed slightly inclined extinction. They were biaxial and positive, with medium birefringence.

The specific gravity, determined on about 55 g. of material in benzene, was found to be 6.85 referred to water.

Lefevre states[6] that lead pyroarsenate crystals slowly became opaque under the action of water. We found that when finely powdered it rapidly absorbs water when moistened. Amorphous dilead arsenate, heated to redness but not fused, lost 2.73%. When moistened and allowed to stand for three days and then dried at 110°, it regained 2.29%. A second moistening and drying resulted in a further gain of 0.29% or a total of 2.58%, which is the theoretical amount of water of constitution in dilead arsenate.

Summary.

1. Monolead arsenate has been prepared and its physical and chemical properties described for the first time.

2. The methods of preparing crystalline dilead arsenate have been reviewed, and its physical and chemical properties more fully investigated.

3. Crystallized trilead arsenate has been prepared.

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[1] *Ann. chim. phys.*, [2] **19**, 360 (1821).

[2] *Ibid.*, p. 368.

[3] U. S. Patent No. 903,389.

[4] *Science*, **33**, 868 (1911).

[5] *Ann. chim. phys.*, [6] **27**, 25 (1892).

[6] *Loc. cit.*

4. Lead metarsenate has been made and its physical and chemical properties described.

5. Dilead pyroarsenate has been prepared in crystalline form, and certain of its physical and chemical properties determined.

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THE EFFICIENCY OF CALCIUM CHLORIDE, SODIUM HYDROXIDE AND POTASSIUM HYDROXIDE AS DRYING AGENTS.

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In a recent paper upon the efficiency of certain drying agents, Baxter and Warren[1] make the statement that Dibbits[2] found the aqueous vapor pressures of the lowest hydrate of calcium chloride to be 0.29 mm., 2.17 mm., and 3.50 mm. at 0°, 24° and 30°, respectively. Our attention has been called by Dr. W. F. Hillebrand to the fact that these figures refer to a hydrate containing 26% of water. As we have been unable to discover reliable data upon the drying efficiency of anhydrous calcium chloride,[3] the matter has been investigated experimentally. We have found the efficiency of this salt to be far greater than the above values indicate. In addition we seized the opportunity to test two other common drying agents, fused sodium and potassium hydroxides.

The air current method was employed, the details of the apparatus and procedure being essentially identical with those described by Baxter and Warren. Calcium chloride was prepared in an anhydrous condition by fusion in an open platinum dish.[4] While still warm it was crushed to pieces the size of a small pea and packed in a glass stoppered U-tube about 15 mm. in diameter, the column of salt being about 30 cm. long.[5] In most of the experiments the air was passed over a 20% solution of sodium hydroxide to ensure an excess of moisture before being conducted through the calcium chloride tube. After a considerable amount of moisture had been absorbed by the calcium chloride, in a few experiments the air was first dried by means of concentrated sulfuric acid in order that the equilibrium might be approached from the reverse side. The

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[1] THIS JOURNAL, 33, 340 (1911).

[2] *Z. anal. Chem.*, 15, 159 (1876).

[3] See however, Marden and Elliott, *J. Ind. Eng. Chem.*, 7, 320 (1915).

[4] The calcium chloride was undoubtedly basic after fusion. It is, however, unlikely that the basic impurity was present in quantity sufficient to affect the results even if of a greater efficiency than the neutral salt.

[5] In the paper by Baxter and Warren it is erroneously stated that the column of salt was 30 mm. long, as in reality it was ten times this length.