deposited by electrolysis either upon lead or upon platinum. A theory is offered for the non-reproducibility of certain solid electrodes.

The potential of solid lead in the presence of solid lead halides and solutions of the corresponding potassium halides was measured against the normal calomel electrode. From the measurements with lead iodide the normal electrode potential of lead is found to be 0.4125 against the normal calomel, and 0.1295 against the normal hydrogen electrode.

The solubility of lead iodide has been redetermined, and from the e. m. f. measurements the true solubility products of lead bromide and lead chloride are obtained and shown to differ greatly from those which would be calculated by ordinary methods.

From measurements of temperature coefficient of e. m. f. the heat of solution of lead in mercury and the heat of formation of lead chloride have been determined.

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[CONTRIBUTION FROM THE INSECTICIDE AND FUNGICIDE LABORATORY, MISCELLANEOUS DIVISION, BUREAU OF CHEMISTRY.]

THE DECOMPOSITION OF DILEAD ARSENATE BY WATER.

BY C. C. McDONNELL AND J. J. T. GRAHAM.

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Dilead arsenate, largely on account of the fact that it is very slightly soluble in water, is extensively employed as an insecticide for use on plants. Notwithstanding the fact that this lead arsenate is but very slightly soluble in water, its use often produces serious burning when applied to tender foliage. Although this is due in many cases, as shown by Headden,[1] and Haywood and McDonnell,[2] to the decomposition of the lead arsenate by dissolved salts in the water used in applying the material, still burning of the foliage has been noted even when the water employed was pure. Volck[3] states that lead hydrogen arsenate may be completely transposed to trilead arsenate by the prolonged action of fog, dew and rain. Tartar and Robinson,[4] however, were unsuccessful in their endeavor to verify Volck's statement. On account of the divergence of opinion on the subject, and in view of its economic importance, we were led to make this investigation.

Pure dilead arsenate, in the form of a fine amorphous powder, was prepared by adding to a solution of lead nitrate a solution of monopotassium arsenate in excess. The precipitate was separated by filtration and thoroughly washed.

Calc. for $PbHAsO_4$: As_2O_5, 33.11%; PbO, 64.29%. Found: As_2O_5, 33.11%; PbO, 63.93%.

The first set of experiments was carried out in the following way: Eight

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[1] Colo. Exp. Sta., *Bull.* **131**, 21 (1908).

[2] Bur. Chem., *Bull.* **131**, 46 (1910).

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

[4] THIS JOURNAL, **36**, 1850 (1914); Oregon Ag. Exp. Sta., *Bull.* **128**, 15 (1915).

2-g. portions of this dilead arsenate were treated in large flasks with 2 liters of freshly distilled water and maintained at 32° to 36° for varying periods, shaking daily at frequent intervals. The contents of two flasks were filtered at the end of 30 days, two at 60 days, two at 90 days, and two at 120 days. The residues were returned to the flasks from which they were taken (the 120-day flasks excepted), 2 liters of freshly distilled water were added in each case, and the flasks returned to the constant temperature bath. This was repeated every 30 days with the 30-day flasks for five periods, and the 60- and 90-day flasks ran for an additional 60 days. Arsenic and lead were determined in the filtrates, arsenic by the iodometric method,[1] using aliquots corresponding to 1 g. of the sample, and lead colorimetrically as the sulfide, using aliquots corresponding to 0.45 g. of the sample. The results are shown in Table I.

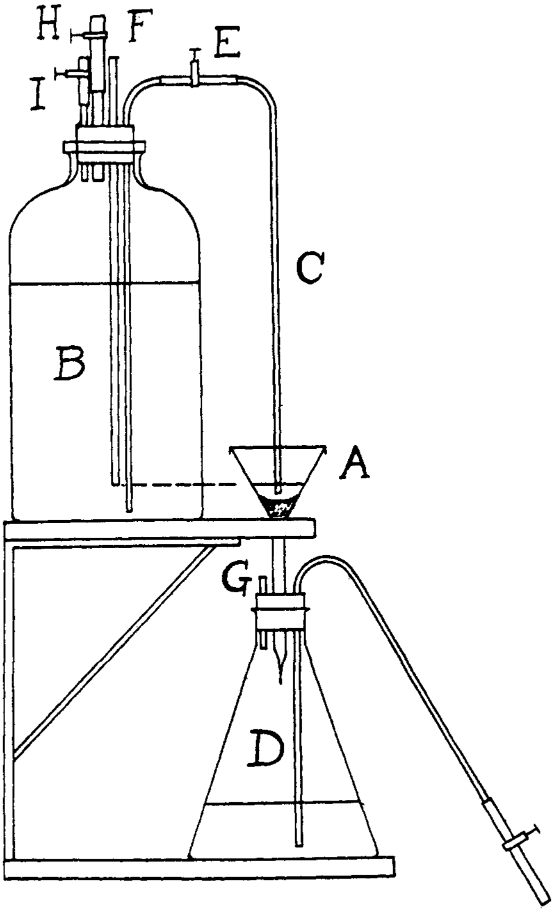

Fig. 1.—Apparatus for Continuous Extraction.

The funnel A, containing sample, is covered with a loosely fitting cap of copper foil to keep out the dust, etc. The height of the water in A remains at the level of the bottom of the air inlet tube F. In refilling the reservoir B, the stopcock E is closed, H and I are then opened and the water introduced through H by means of a funnel. When in operation E is opened and H and I remain closed. G = air vent.

It will be noted that the ratio of arsenic to lead in the filtrates is much greater than if it were simply a solution of the dilead arsenate; that the amount of arsenic and lead in solution is practically the same regardless of the length of the period of extraction and also the same in the case of each successive

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[1] *J. Assoc. Official Agr. Chemists*, 2 (No. 1, Pt. 2) 10 (1916).

treatment. These results show that dilead arsenate is decomposed by water, arsenic acid going into solution, the reaction reaching equilibrium, however, when the concentration of the arsenic acid is very low.

TABLE I.—ACTION OF WATER ON DILEAD ARSENATE (SUCCESSIVE EXTRACTIONS)

	As_2O_5.	PbO.	As_2O_5.	PbO.	As_2O_5.	PbO.	As_2O_5.	PbO.	As_2O_5.	PbO.
	Per cent.		Per cent.		Per cent.		Per cent.		Per cent.	
Successive 30-day periods	0.19	....	0.19	0.07	0.23	0.04	0.28	0.02	0.16	0.03
Successive 60-day periods	....	....	0.20	0.08	....	....	0.27	0.02	....	....
Successive 90-day periods	....	....	....	....	0.28	0.06	....	....	0.26	0.03
120-day period..........	....	....	....	....	....	....	0.28	0.02	....	....

In order to determine what the final product resulting from this action of water would be, apparatus was devised as shown in Fig. 1, whereby the dilead arsenate would be subjected to the action of constantly changing water for such a period as might be desired.

Four 2-g. portions of dilead arsenate were transferred to hardened filter papers which were fitted into funnels, A, the stems of which had been drawn out to such a size as to permit about a liter of water to pass through in 24 hours. Water was supplied from reservoirs, B, by means of siphons, C, so arranged as to give a constant level in the funnels. Large Erlenmeyer flasks, D, were used as receptors for the filtrates. This set of experiments was allowed to run for five months. Measured portions of the filtrates were withdrawn from time to time, concentrated by evaporation and the arsenic therein determined. It was observed, after the experiments had been running for several weeks, that crystals were forming in the receptors. These were recovered at the end of the period and analyzed. The results of analyses are given in Table II.

It is seen that the arsenic has dissolved at a fairly uniform rate, about 6.5% of the total amount in the dilead arsenate having gone into solution. Only a small amount of lead was dissolved. The molecular ratio (PbO/As_2O_5) of the lead arsenate originally taken has increased from 2 to about 2.23. A striking feature of the experiments is brought out by the results of the analyses of the crystals from the receptors, which show this compound to be a basic arsenate, with a molecular ratio of about 3.26.

A second set of four experiments, using one 1-g. and three 2-g. portions of dilead arsenate, was then started and allowed to run for twelve months. As in the previous experiments, crystals were deposited in the receptors. Some of the largest of these were examined with the petrographic microscope with results which are given later. The remaining crystals were dissolved from the flasks with nitric acid and analyzed for lead and arsenic. The residues on the filter papers were dried at 110° to constant weight and analyzed. The results are given in Table III.

These results are in general agreement with those in Table II, and show that the action of water has continued until, in the case of Expt. 1, in which

Table II.—Decomposition of Dilead Arsenate by Water (Continuous Extraction).

	1.			2.		
	As_2O_5.	PbO.	Vol. H_2O liters.	As_2O_5.	PbO.	Vol. H_2O liters.
Filtrate: First month	0.0193 g.		27.5	0.0232 g.		32.5
Second month	0.0174 g.		28.0	0.0168 g.		30.0
Third month	0.0152 g.		27.0	0.0145 g.		30.5
Fourth month	0.0095 g.		27.5	0.0121 g.		32.5
Fifth month	0.0117 g.		27.0	0.0102 g.		25.0
Total	0.0731 g.		137.0	0.0768 g.		150.5
Crystals deposited in receptors	0.0077 g.*	0.0244 g.*		0.0087 g.*	0.0275 g.*	
Total dissolved	0.0808 g.			0.0855 g.		
= % of total As_2O_5 originally present	6.28%			6.65%		
*Molecular ratio, PbO/As_2O_5 in crystals	3.26			3.26		
Analyses of residues on paper at the end of the fifth month	30.61%	65.57%		30.44%	65.79%	
Molecular ratio, PbO/As_2O_5 in residues	2.21			2.23		

	3.			4.		
Filtrate: First month	0.0221 g.		28.5	0.0193 g.		27.5
Second month	0.0162 g.		28.5	0.0160 g.		27.5
Third month	0.0166 g.		26.5	0.0168 g.		24.5
Fourth month	0.0098 g.		25.0	0.0123 g.		29.5
Fifth month	0.0131 g.		25.5	0.0102 g.		28.0
Total	0.0778 g.		134.0	0.0746 g.		137.0
Crystals deposited in receptors	0.0074 g.*	0.0215 g.*		0.0075 g.*	0.0238 g.*	
Total dissolved	0.0852 g.			0.0821 g.		
= % of total As_2O_5 originally present	6.63%			6.38%		
*Molecular ratio, PbO/As_2O_5, in crystals	3.00			3.27		
Analyses of residues on paper at the end of the fifth month	30.31%	66.34%		30.61%	65.97%	
Molecular ratio, PbO/As_2O_5 in residues	2.25			2.22		

1 g. was used, the dilead arsenate has been converted to a compound having the same molecular ratio as the crystals which deposited in the receptor. The filtrates contained a very small amount of lead in addition to that which deposited as a crystalline basic arsenate.

TABLE III.

	Crystals in receptors.		Molecular ratio of crystals.	Analysis of residues on paper.		Molecular ratio.	Total vol. H_2O in filtrate.
	As_2O_5, g.	PbO, g	PbO/As_2O_5.	As_2O_5, %.	PbO, %.	PbO/As_2O_5.	Liters.
No. 1	0.0097	0.0305	3.24	23.20	73.63	3.27	228.0
No. 2	0.0112	0.0337	3.10	25.90	71.27	2.83	264.5
No. 3	0.0182	0.0517	2.93	26.51	70.39	2.74	317.5
No. 4	0.0113	0.0352	3.21	24.80	72.39	3.01	305.5

The residues from the filters were examined with the petrographic microscope, and in all cases were seen to consist very largely of well formed crystals. That from the 1-g. charge was almost entirely crystallized. Many of the largest measured from 0.01 mm. × 0.05 mm. to 0.03 mm. × 0.08 mm. A photomicrograph of these crystals is shown in Fig. 2. They are in the form of hexagonal prisms, terminated by pyramids of the

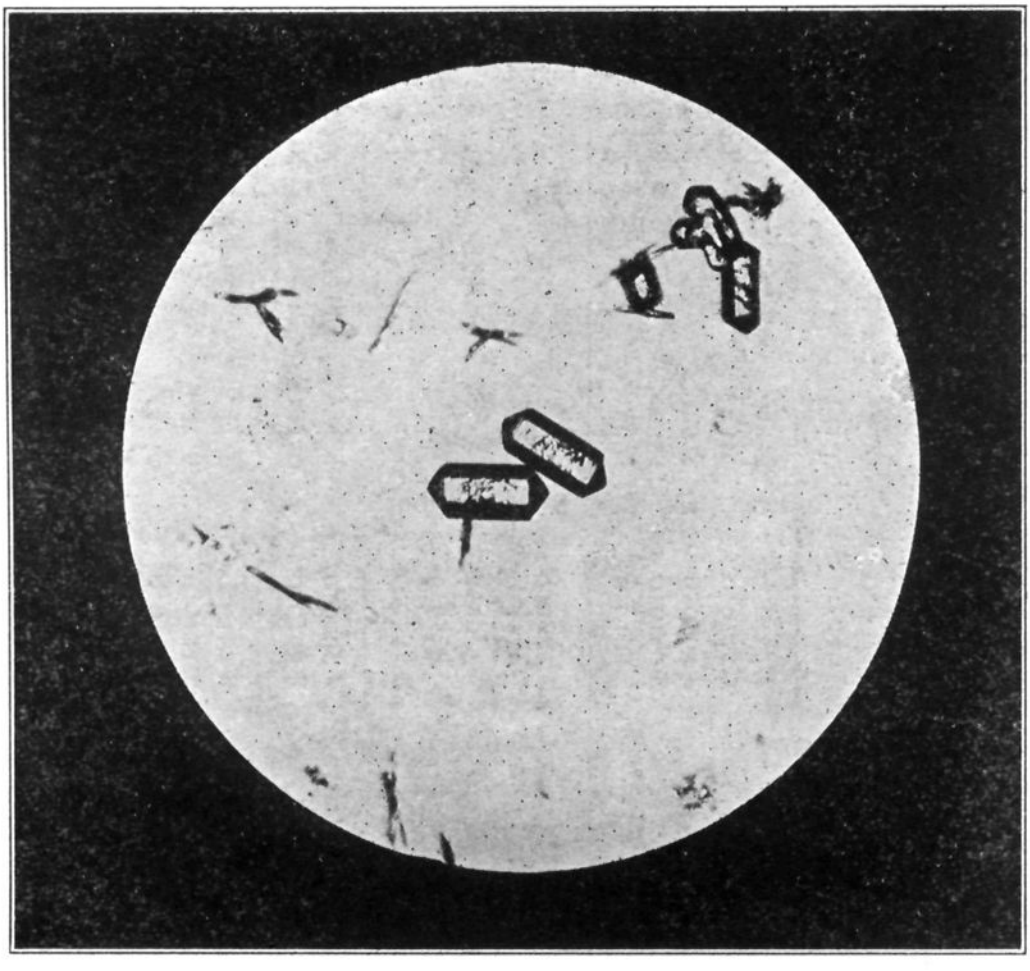

Fig. 2.—Lead-hydroxy arsenate (hydroxy mimetite) produced by the action of water on dilead arsenate (× 280).

first order. They show parallel extinction, are negative with low birefringence, apparently uniaxial, and have a mean refractive index of about 2.09. The crystals from the receptors were small and mainly in groups or bundles. The characteristics established definitely were parallel extinction, negative elongation, and index of refraction 2.09, which shows that both are undoubtedly the same compound.[1]

While the preceding set of experiments was running, two experiments were conducted in which the dilead arsenate was subjected to the action of hot water in Soxhlet extractors. S. & S. No. 603 extractor thimbles were reinforced on the outside with linen and each then charged with 2 g. of dilead arsenate. A thick pad of absorbent cotton was placed over the arsenate to prevent loss in case the water level should rise above the tops of the thimbles. These extractors were connected with flasks containing about 300 cc. of water and sufficient heat applied to distil approximately 100 cc. every 15 minutes. They were run 7 hours a day (6 days a week), for 9 months. Arsenic and lead were determined in the filtrates each month, and the residues in the thimbles were, at the end of the period, dried at 110° to constant weight and analyzed. The analytical results are given in Table IV.

TABLE IV.—DECOMPOSITION OF DILEAD ARSENATE BY WATER (SOXHLET EXTRACTION).

	1.		2.	
	As_2O_5.	PbO.	As_2O_5.	PbO.
Filtrate, first month	0.0438 g.	0.0029 g.	0.0182 g.	0.0006 g.
Filtrate, second month	0.0497 g.	0.0025 g.	0.0262 g.	0.0029 g.
Filtrate, third month	0.0469 g.	Trace	0.0274 g.	0.0000 g.
Filtrate, fourth month	0.0355 g.	None	0.0234 g.	None
Filtrate, fifth and sixth months	0.0587 g.	None	0.0511 g.	None
Filtrate, seventh and eighth months	0.0173 g.	None	0.0451 g.	None
Filtrate, ninth month	0.0029 g.	None	0.0188 g.	None
Total	0.2548 g.	0.0054 g.	0.2102 g.	0.0035 g.
= Per cent of As_2O_5 and PbO originally present	38.48%	0.42%	31.74%	0.27%
Analysis of residues on paper[2]	23.44%	74.34%	25.86%	71.80%
Molecular ratio, PbO/As_2O_5	3.27		2.86	

It is noted that the filtrate in No. 1, which ran a little faster than No. 2, contains 38.48% of the total As_2O_5 and 0.42% of the PbO originally present in the 2-g. charge of dilead arsenate taken, and that the arsenic and lead in the residue is in the same molecular ratio as in the crystals obtained from the extractors in the previous experiments. One striking

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[1] The writers are indebted to C. M. Smith of this laboratory for making the microscopic determinations, and to G. L. Keenan of the Microchemical Laboratory for making the photomicrograph.

[2] No. 1 lost on ignition at low temperature (water) 1.4%.

difference, however, is observed between these and the previous experiments in that a very much smaller amount of lead has gone into solution (no crystals deposited from the filtrates), showing that in so far as the lead is concerned, hot water (84° to 86° in the extractors) has a markedly less solvent action than does cold water.

An examination of the results given in this paper shows conclusively that continually changing water slowly decomposes dilead arsenate with the liberation of arsenic and traces of lead. Since the amount of arsenic in the filtrate is largely in excess of the amount necessary to combine with the lead, this cannot be a simple solution of the lead arsenate. In the experiments here recorded, the molecular ratio of the treated samples have increased from 2.00 (dilead arsenate) to a maximum of 3.27. The crystals deposited from the filtrates also have a molecular ratio of about 3.27. These results, taken in connection with the microscopical examination, show that the compound produced by the action of water on dilead arsenate and the crystals from the filtrates are the same basic arsenate.

The basic arsenate formed by the action of ammonium hydroxide on dilead arsenate, first mentioned by Tartar and Robinson,[1] and later shown by G. E. Smith[2] and C. C. McDonnell and C. M. Smith[3] to be a lead-hydroxy arsenate, $Pb_4(PbOH)(AsO_4)_3$, has a theoretical molecular ratio of 3.33. The last-named authors prepared this compound in crystalline form, showing it to be hydroxy mimetite, and to contain a small amount, apparently 1 molecule, of water of crystallization. For the transformation of dilead arsenate to this basic arsenate 40.00% of the total arsenic oxide present must be removed. In the case of the first experiment in the Soxhlet extractor, 38.48% of the total arsenic oxide was removed, which indicates a nearly complete transformation. The reaction may be represented by the equation

$$5PbHAsO_4 + HOH \rightleftarrows Pb_4(PbOH)(AsO_4)_3 + 2H_3AsO_4.$$

Summary.

It has been proven that dilead arsenate is decomposed by water. The reaction proceeds with the liberation of arsenic acid and the solution of a very small quantity of lead. The reaction reaches equilibrium while the concentration of arsenic acid is very low, but if the water is constantly changed, it proceeds until the residue is converted to a definite basic lead arsenate (hydroxy mimetite), $Pb_4(PbOH)(AsO_4)_3.H_2O$.

WASHINGTON, D. C.

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[1] *Loc. cit.*

[2] THIS JOURNAL, 38, 2016 (1916).

[3] *Ibid.*, 38, 2034 (1916); 39, 940 (1917).