

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE MONTANA EXPERIMENT STATION, UNIVERSITY OF MONTANA.]

LEAD ARSENATES.

A STUDY OF THE FACTORS CONTROLLING THE REACTIONS OF LEAD NITRATE AND LEAD ACETATE WITH DISODIUM ARSENATE.

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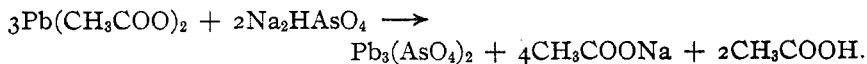
Since Moulton¹ in 1893 first demonstrated the economic value of lead arsenate, numerous publications have appeared discussing the different compounds of lead and arsenic acid. These have dealt chiefly with the methods of preparation, the composition, some of the physical properties, and their efficiency as insecticides. While it has been generally stated that the composition varies with the source, mode of preparation, concentration, temperature, and every other conceivable condition that may vary in the production, yet there has been no attempt to define how these factors cause the variation; in fact, there has been a general evasion of even stating the direction and the extent to which the composition is influenced by the different factors.

The object of this paper will be to attempt to define the conditions in the production of lead arsenate that regulate the composition, and when the conditions are varied to demonstrate the influence that the variation will exert on the reaction, and on the composition of the resulting products.

It is not considered necessary to give a historical review of literature on lead arsenates as that has been given in a recent volume² of *THIS JOURNAL*. In general the various investigators have contended that the reaction of lead nitrate and disodium arsenate can be represented in the main by the equation



though the composition of the resulting lead arsenate would indicate that there was slight deviation and that the reaction of lead acetate with disodium arsenate can be represented closely by the equation



While working on another problem with commercial lead arsenates, some experiences suggested that the reactions given by the various investigators were not correct and that there might be a movable equilibrium in the products of the reactions, and thus a study of this problem was undertaken. Before reliable results could be obtained, however, it was necessary to prepare pure samples, at least of the lead and sodium compounds which may be components of the systems to be examined.

¹ Mass. Board, *Agr. Report*, 41, 282 (1893).

² Tartar and Robinson, *THIS JOURNAL*, 36, 1843 (1914).

Experimental.

Preparation of the Lead Compounds.—Tartar and Robinson¹ claimed that they had prepared pure diplumbic arsenate, and a basic lead arsenate of a constant composition by the reaction of diplumbic arsenate with ammonium hydroxide. They stated that triplumbic arsenate is not formed under the ordinary aqueous conditions employed in the manufacture of commercial lead arsenate and that the precipitates obtained from the reactions of lead acetate and lead nitrate with disodium arsenate are mixtures of diplumbic arsenate and the basic lead arsenate.

When the results of Tartar and Robinson were examined it was observed that there was a great discrepancy. They claim that the composition of the basic lead arsenate, produced by the reaction of diplumbic arsenate with ammonium hydroxide, may be represented closely by the formula $21\text{Pb}_3(\text{AsO}_4)_2 \cdot 2\text{Pb}(\text{OH})_2 \cdot 10\text{H}_2\text{O}$. There are 65 Pb atoms and 42 As atoms in this formula and as the number of Pb and As atoms is identical in diplumbic arsenate, then it must be concluded that an amount corresponding to 23 atoms As or 35.38% of the arsenic of diplumbic arsenate has gone into solution. In outlining a method for a quantitative determination of diplumbic arsenate by the same reaction of diplumbic arsenate with ammonium hydroxide, they state that "the amount of soluble arsenic calculated as As_2O_5 and then multiplied by the factor 7.6034, gives the amount of lead hydrogen arsenate," which would indicate that 39.71% of the arsenic of the diplumbic arsenate has gone into solution. On account of this discrepancy the reaction of diplumbic arsenate with ammonium hydroxide was studied.

The diplumbic arsenate was prepared from solutions of lead nitrate and disodium arsenate of equimolar proportions (concentration 0.01 *M*); when the precipitate had formed one-half the molecular proportion of nitric acid was added. After standing eighteen hours the supernatant liquid was decanted and the precipitate was then washed by decantation, first with water acidulated with nitric acid, then with distilled water, and dried at 110°. This is a modification of the method suggested by Tartar and Robinson. (The reason for the modification will be discussed later on.) By this method two samples were prepared which, on analysis, showed an arsenic content of 33.08% and 33.1% of As_2O_5 , respectively, which would indicate that there had been a fairly complete isolation of diplumbic arsenate. When prepared in this manner diplumbic arsenate takes the form of comparatively large, transparent, crystalline plates, showing a general rhombohedral direction when seen through the microscope.

Weighed samples of the diplumbic arsenate were digested with a 5% solution of ammonium hydroxide on a steam bath for three hours. They

¹ *Loc. cit.*

were then filtered, washed, and dried at 110° . The amount of soluble arsenic in the filtrate, the loss in weight of the samples, and the lead and arsenic content of the dried insoluble residue were determined. It was noted that the soluble arsenic approached 40% of the arsenic of the di-plumbic arsenate, therefore, in the products of the reaction the ratio of the soluble arsenic to the insoluble arsenic approaches two to three. Thus it may be that the reaction can be represented by the following equation:

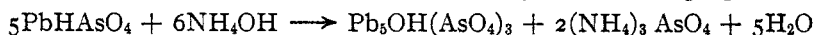


TABLE I.

Analyses of the Products of the Reaction of Diplumbic Arsenate with Ammonium Hydroxide.

	Soluble arsenic in filtrate. Per cent.	Loss of wt. of the lead compound. Per cent.	Insoluble residue.	
			Lead as PbO. Per cent.	Arsenic as As_2O_5 . Per cent.
Sample No. 1.....	39.9	15.22	74.98	23.43
Sample No. 2.....	39.94	15.28	75.05	23.46
Theoretical for $\text{Pb}_5\text{OH}(\text{AsO}_4)_3$	40.00	15.32	75.924	23.463
As found by Tartar and Robinson.....	39.71 ¹	74.72 ²	23.43 ²
Theoretical for $21\text{Pb}_3(\text{AsO}_4)_2 \cdot 2\text{Pb}(\text{OH})_2 \cdot 10\text{H}_2\text{O}$	35.38	74.2	24.694
Theoretical composition of PbHAsO_4	64.292	33.113

These results would indicate that the reaction can be represented by the above equation and that the formula $\text{Pb}_5\text{OH}(\text{AsO}_4)_3$ more closely represents the insoluble product of the reaction of diplumbic arsenate with ammonium hydroxide, than the formula suggested by Tartar and Robinson.

The results of the lead determination do not correspond very closely with the theoretical, but it is generally accepted that the method of the Association of Official Agricultural Chemists for the determination of lead gives low results. For this reason, in this paper, more emphasis will be laid on the arsenic determination, and the results of the lead determination will be given only where it is considered to be essential. It might be inferred from the lead determination that it was a hydrated compound. Instead of carrying out a lengthy investigation of the lead determination, it was decided to determine the loss of weight of the lead compound during the reaction, to find out if it corresponds to the theoretical decrease in weight when diplumbic arsenates is converted into the compound, $\text{Pb}_5\text{OH}(\text{AsO}_4)_3$. The results of that determination show that it is not a hydrated compound, which is substantiated by the results of the arsenic determination. The formula may be written $3\text{Pb}_3(\text{AsO}_4)_2 \cdot \text{Pb}(\text{OH})_2$, which would indicate that it is a tritri-plumbic lead hydroxy-arsenate but the formula $\text{Pb}_5\text{OH}(\text{AsO}_4)_3$ is preferred and the compound will be referred to in this paper as the lead hydroxyarsenate. The com-

¹ Calculated from the factor 7.6034.

² The average of four samples.

pound occurs as a fine amorphous powder and does not show any definite structure when seen under the microscope.

Preparation of the Sodium Compounds.—Disodium arsenate occurs as two well-defined salts, which are generally represented, respectively, by the formulas $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$. The compound $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$ crystallizes out of solution of disodium arsenate at low temperatures and is efflorescent. The compound $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ crystallizes out of solution of disodium arsenate at temperatures above 18° and is not efflorescent.¹

Samples of both these salts were prepared. Disodium arsenate is prepared commercially in the presence of an excess of sodium carbonate, and the salt, as it is put onto the market, is generally alkaline.

The crystals of $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$ were prepared by saturating a solution at 0° with the fairly pure disodium arsenate and then adding a small amount of arsenic acid until the solution was neutral to phenolphthalein. During the crystallization the solution was kept at a low temperature. The crystals obtained in this manner were further purified by recrystallization three or four times, the precaution being taken not to use heat to dissolve the crystals. The crystals obtained in this manner were efflorescent and were only slightly alkaline with phenolphthalein.

The crystals of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ were prepared by taking part of the solution that had been neutralized for the production of the crystals $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$, heating the solution to boiling and allowing the salt to crystallize from the warm solution and then recrystallize from warm solutions. The crystals obtained in this manner were not efflorescent and were decidedly alkaline with phenolphthalein.

Sodium nitrate, sodium acetate and sodium baborate were prepared by recrystallization of the so-called pure commercial salts.

The Reaction of Diplumbic Arsenate with Sodium Baborate.—The reaction of diplumbic arsenate with sodium baborate was examined, using the sample of diplumbic arsenate that had been isolated from all other compounds. The lead arsenate and the solution of sodium baborate were shaken intermittently for two days and then filtered. The soluble arsenic in the filtrate and the loss of weight of the lead compound were determined.

TABLE II.

	Vol. of soln. (Cc.).	% arsenic soluble.	Loss of wt. of lead compd. (%).	Sol. As calc. as $\text{H}_4\text{As}_2\text{O}_7$. (%).	Sol. As calc. as H_3AsO_4 . (%).
1 g. PbHAsO_4	500	37.15	14.28	14.23	15.19
5 g. Sodium baborate.....					
1 g. PbHAsO_4	500	37.8	14.56	14.49	15.46
5 g. Sodium baborate.....					

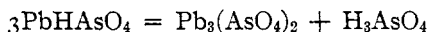
¹ Fresenius, *J. prakt. Chem.*, 56, 30.

When sodium silicate and the sodium compounds of the higher fatty acids were used very similar results were obtained. With the latter compounds, when the diplumbic arsenate was added in excess the fatty acids were precipitated:

When diplumbic arsenate is converted into lead hydroxyarsenate, pyroarsenic acid ($\text{H}_4\text{As}_2\text{O}_7$) is eliminated from the lead compounds, which corresponds to 40% of the arsenic of the diplumbic arsenate and can be represented by the following:



If diplumbic arsenate should be converted into triplumbic arsenate, orthoarsenic acid (H_3AsO_4) is eliminated from the lead compounds, which corresponds to 33.33% of the arsenic of the diplumbic arsenate and can be represented thus:



The above results then show:

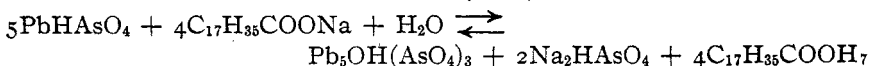
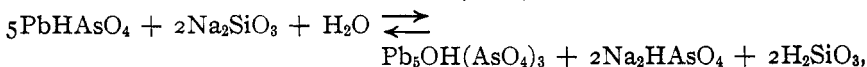
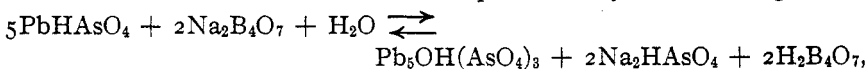
(1) That the diplumbic arsenate has been converted into lead hydroxyarsenate.

(2) That when diplumbic arsenate is converted into lead hydroxyarsenate, 40% of the arsenic of diplumbic arsenate has changed to a soluble arsenic compound as has been previously demonstrated.

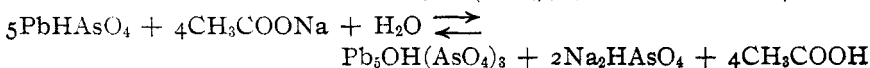
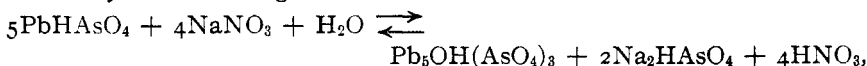
(3) That a free acid has been formed.

It will be demonstrated later that the ratio of the soluble arsenic to the free acid approaches one HAsO_4 to two H.

Thus it can be inferred that the reactions of diplumbic arsenate with the sodium salts of weak acids can be represented by the following:



In each of the three reactions given above, the free acid is to a great extent thrown out of solution or has a very low degree of dissociation, therefore the reactions tend towards completion in that direction. Naturally the next step would be to study the reactions of diplumbic arsenate with sodium nitrate and sodium acetate, which are by products in the manufacture of lead arsenate. Then the reactions to be studied can be represented by the following:



The results of Tartar and Robinson indicate that lead arsenate prepared from aqueous solutions is a mixture of diplumbic arsenate and lead hydroxyarsenate, which is corroborated by the results obtained in the examination of the reaction of diplumbic arsenate with sodium bismorate, and by other results which will be brought forward later; therefore, if a definite point of equilibrium could be established in the above systems, the products of the reactions of lead nitrate and lead acetate with disodium arsenate could accurately be defined as when disodium arsenate is added in excess, the products of the reactions are identical with the components of the systems which are to be studied.

Reaction of Lead Nitrate with Disodium Arsenate. Point of Equilibrium.—The mixtures were placed in bottles which were then attached to a shaker and intermittently shaken for the period stated in the tables. After the shaking the mixtures were filtered and the soluble arsenic and acidity in aliquot parts of the filtrate were determined.

To ascertain if the composition of the lead arsenate, produced by the reaction of lead nitrate with disodium arsenate agreed with that calculated from the concentrations of the system when they had come to an equilibrium, unless otherwise stated, the solutions of lead nitrate and disodium arsenate were placed in a container and attached to a shaker and were shaken until the composition became constant.

TABLE III.

Temperature.	Initial concentrations.			Period. Days.	Concentrations at equilibrium.	
	PbHASO ₄ . Mol.	NaNO ₃ . Mol.			HNO ₃ . Mol.	Na ₂ HASO ₄ . Mol.
10-16°.....	0.01	0.008	5		0.00004	0.0000175
	0.1	0.08	5		0.00004	0.0000175
	Pb ₂ OH(AsO ₄) ₃ . Mol.	Na ₂ HASO ₄ . Mol.	HNO ₃ . Mol.			
10-16°.....	0.002	0.004	0.008	60	0.00005	
	0.02	0.04	0.08	60	0.00005	

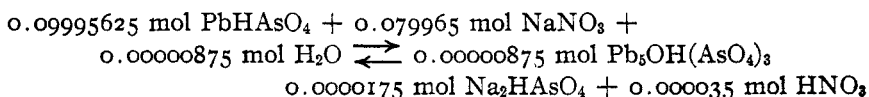
It was noted that the amounts of the concentration of HAsO₄ to the concentration of H⁺ were approximately in the proportion of 1 to 2. With varying conditions there was a wide variation from this ratio, the variation being constant under similar conditions. As a study of the equation shows that the amount of soluble arsenic accurately defines the progress of the reaction, and as it can be more accurately determined than the acidity, the results of the soluble arsenic determination were adopted to designate the point of equilibrium when it was approached from PbHASO₄ and NaNO₃. The possibility of error being introduced into the system with these samples was also practically *nil*.

When the equilibrium was approached from Pb₂OH(AsO₄)₃, Na₂HASO₄ and HNO₃, as the large amount of soluble arsenic introduced into the system was reduced to a low concentration, the experimental error in its

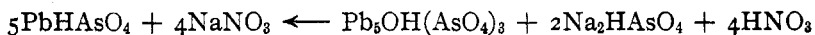
determination was greatly multiplied. And as the acidity gave constant results, then, when the concentration of the acid approached within experimental error of the concentration of the acid, when the equilibrium was approached from PbHAsO_4 and NaNO_3 , it was assumed that the systems had come to an equilibrium.

When the equilibrium was approached from PbHAsO_4 and NaNO_3 , constant results could readily be obtained and the system came to an equilibrium in a relatively short period; but when it was approached from $\text{Pb}_5\text{OH}(\text{AsO}_4)_3$, Na_2HAsO_4 and HNO_3 , the rate of reaction was extremely slow. This was probably due to the physical condition of the lead hydroxyarsenate. That this is a factor will be apparent when the "Progress of the Reaction" is discussed. It was very difficult to obtain corroborative results and it was only after each component was thoroughly examined, that constant results could be obtained.

The above results show that the following equation represents the concentrations of the components of the system when it has arrived at an equilibrium at stated concentration and temperature:

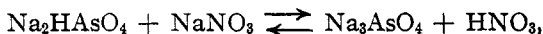


The Effect of the Concentration of the Disodium Arsenate on the Equilibrium.—The influence of increasing the concentration of disodium arsenate would be to move the equilibrium in the direction



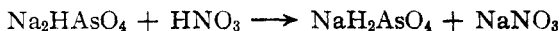
and, therefore, there would be a tendency to produce more diplumbic arsenate. If the disodium arsenate does function in this manner then the effect is masked by other influences.

If, in the presence of an excess of disodium arsenate in the system, lead nitrate is added, if the excess is only slight, the lead compounds of the arsenic acids are distributed in practically the same ratio as the other lead compounds of the system; from this it might be inferred that the sodium compounds were in an equilibrium which can be represented thus:



in which case, under certain conditions, the effect of the concentration of the disodium arsenate would be an effect of a much lower order than its mass action.

The compounds, Na_3AsO_4 , Na_2HAsO_4 and NaH_2AsO_4 , are all alkaline to congo red and methyl orange and these indicators can be used to indicate the completion of the following reaction at low temperatures:

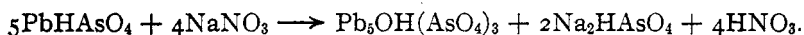


If solutions of disodium arsenate are made strongly acid, using either

of these two indicators, and are then heated, they become decidedly alkaline, and when cooled, become acid again.

It is not intended in this paper to make a detailed examination of the movable equilibrium of the sodium compounds, but this phenomenon has been mentioned because it can be readily seen that it will give an insight into the influence of disodium arsenate upon the equilibrium and upon the products of the reaction of lead nitrate and disodium arsenate.

While it was found that a slight excess of neutral disodium arsenate did not affect the equilibrium, yet a slight excess of solutions of the compound $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ always moved the equilibrium in the direction



The system must produce more acid to neutralize the alkalinity of the disodium arsenate before it can proceed to an equilibrium; therefore, more lead hydroxyarsenate would be produced.

TABLE IV.

Composition of Lead Arsenates.

	As_2O_5 .
Prepared from 0.1 mol $\text{Pb}(\text{NO}_3)_2$ and 0.1 mol $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$...	33.08
Prepared from 0.1 mol $\text{Pb}(\text{NO}_3)_2$ and 0.2 mol $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$...	32.00

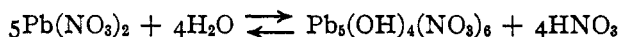
These results disproved the contention of Holland and Reed¹ that the influence of an excess of the alkaline disodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$) would be to produce a compound approaching nearer to the theoretical composition of diplumbic arsenate.

It is worthy of note that while the alkalinity of the excess of disodium arsenate exerts such an influence on the equilibrium and on the composition of lead arsenate, yet the effect of the alkalinity is not apparent when the arsenate is completely precipitated. This may be due to the alkalinity being neutralized by the acidity of the lead nitrate solution or to the distribution of the arsenic acids before and after precipitation.

The Effect of the Concentration of the Lead Nitrate on the Reaction.—The methods by which the point of equilibrium was established cannot be used when there is an excess of lead nitrate, as the soluble arsenic is eliminated and general acidimetric methods are not applicable in the presence of the lead compound. From the arsenic content of the resulting lead arsenates the point of equilibrium could be established, but that would not be very satisfactory, as it is possible that the limit of error in the determination of the arsenic content might be greater than the influence of the lead nitrate.

A probable indication of the influence of the lead nitrate upon the reaction might be obtained from a study of the solution of the compound. When lead nitrate is dissolved in dilute solutions there is a turbidity and the solution becomes acid; this is due to hydrolysis, which may be represented in part by the following:

¹ Mass. Agr. Exp. Sta., *24th Ann. Report*, p. 201.



As none of the general titration methods can be used to determine the acidity of the lead nitrate solution, a rather crude colorimetric method was employed to obtain a rough approximation of the acidity of the solution. Strips of litmus paper were dipped, for a short interval, simultaneously into lead nitrate solutions and acid solutions of known strength. The acidity of the solution being fairly great, an excess would tend to produce more diplumbic arsenate but a measure of the acidity is also a measure of the amount of the hydroxy compound. The tendency of this hydroxy compound would be to produce more lead hydroxyarsenate, thus an excess of lead nitrate solution exerts two influences which are directly opposed to each other. Each may offset the effect of the other, in which case an excess of lead nitrate would not affect the composition of the precipitate.

The Effect of Concentration and Temperature on the Equilibrium.

TABLE V.

The Initial and Final Concentrations of the System at Different Temperatures and Concentrations.

Temperature.	Initial concentrations.		Period.	Concentrations at equilibrium.	
	PbHAsO ₄ . Mol.	NaNO ₃ . Mol.		HNO ₃ . Mol.	Na ₂ HAsO ₄ . Mol.
10-16°	0.01	0.2	5 days	0.00004	0.0000175
	0.01	0.02	5 days	0.00004	0.0000175
19-23°	0.01	0.2	5 days	0.00011	0.00007
	0.01	0.02	5 days	0.00011	0.00007
Boiling; Barometric pressure, 637 mm. ¹	0.01	0.2	8 hrs.	0.000575	0.000525
	0.01	0.02	8 hrs.	0.00045	0.000425

TABLE VI.

Composition of Lead Arsenate Produced at Different Concentrations and Temperatures.

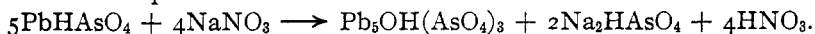
Temperature.	Concentration of reacting compounds.	Composition.		
		Calculated.		Found. Arsenic as As ₂ O ₃ .
		Lead as PbO.	Arsenic as As ₂ O ₃ .	
10-16°	0.1	64.296	33.11	33.08
	0.01	64.331	33.076	33.05
19-23°	0.1	64.309	33.091	33.05
	0.01	64.46	32.886	32.9
Boiling; Barometric pressure, 638 mm.	0.1	64.421	33.006	32.95
	0.01	65.355	32.26	32.32

As the solubilities of diplumbic arsenate and lead hydroxyarsenate are only very slight, as long as these compounds are in contact with the solution, their active masses can be considered constant. Therefore, an in-

¹ The altitude of the Chemistry laboratory of the Montana Experiment Station is 4910 feet above sea level.

crease in the amounts of the lead arsenates in the system would not affect the equilibrium.

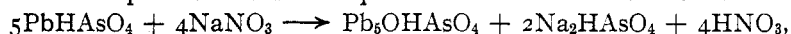
An increase in the concentration of the sodium nitrate would be expected to move the equilibrium in the direction



At low temperatures, although the concentration of the sodium nitrate was increased ten and one hundred fold, there was the same amount of soluble arsenic produced. It is probable that the influence of a variation in the concentration of the sodium nitrate at low temperatures is so slight that it cannot be detected by the methods used. The results show that as the temperature rises the influence of a variation in the concentration of the sodium nitrate becomes apparent.

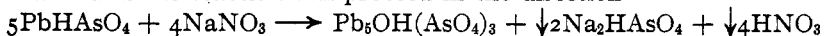
In the production of lead arsenate, when the reaction has come to an equilibrium, as the concentration increases, the relative amount of lead hydroxyarsenate will decrease. Therefore, as the concentration increases the composition of the resulting lead arsenate will approach nearer to the theoretical composition of diplumbic arsenate. This is not in accord with the deductions of other investigators. The error in their conception was due to the fact that the products of the reaction were not allowed to come to an equilibrium, and that the progress of the reaction in dilute solutions, within certain limits, is faster than in the more concentrated.

As the temperature rises the equilibrium moves in the direction



and more lead hydroxyarsenate is formed; therefore, as the temperature rises the composition of the resulting lead arsenate will recede from the theoretical composition of diplumbic arsenate. There are probably two factors that cause the movement of the equilibrium Pt: the depression of the dissociation of the acid and the tendency of the sodium compounds of the system to become more alkaline as the temperature rises.

The Effect of Washing Away the Soluble Products.—In Table VI the calculated compositions of the precipitates at different concentrations are given, which represent the compositions of the precipitates as they exist before they have been isolated from the soluble products of the reactions. The results have shown that when the concentration of the sodium nitrate is decreased the systems attain to the same concentrations of soluble arsenic and acid. After each removal and addition of the washing fluid the concentrations of soluble arsenic and acid have been greatly reduced. Therefore, as the concentration of sodium nitrate still remains relatively great, the system will tend to produce more soluble arsenic and acid and the reaction will proceed in the direction



and more lead hydroxyarsenate will be formed which will be proportional to the rate at which the concentration of the sodium nitrate is reduced

by the removal of the washing fluid. While the increased amount of lead hydroxyarsenate produced is comparatively small, yet it is sufficient to materially alter the composition of the precipitate. It would probably be an economic advantage to use a slightly acidulated water as the washing fluid in the commercial production of lead arsenate. There is a loss of disodium arsenate by each addition of the washing fluid when distilled water is used. This loss is greatly multiplied on account of the general alkalinity of the average water supply. If sufficient nitric acid were added to neutralize the alkalinity of the water and leave a slightly acid solution, the loss of soluble arsenic would be reduced to a minimum.

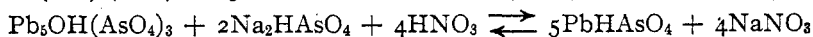
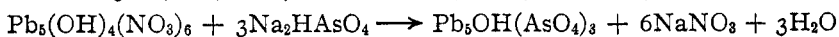
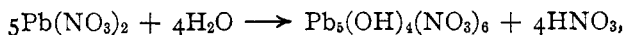
Progress of the Reaction.—Various investigators claim that the reaction between lead nitrate and disodium arsenate takes place as represented by the equation



and some have added that a same amount of the tribasic arsenate is formed due to a secondary reaction. While this equation, to a certain extent, represents the initial and final stages, it does not represent the reaction as it actually takes place.

It has been pointed out that diplumbic arsenate occurs in comparatively large crystalline plates and that lead hydroxyarsenate is a very fine amorphous precipitate. When solutions of lead nitrate and disodium arsenate are mixed, the precipitate as it first appears is extremely fine and then quickly changes to a relatively large flocculent crystalline precipitate. The transformation is too rapid to be a physical change due to the growth of the crystal by solution, as the diplumbic arsenate is only very slightly soluble. While the precipitate clings together, a microscopic examination shows that the change is not due to the coagulating power of sodium nitrate. It is contended that there has been a reaction between the precipitate and the solution and that the compound which is precipitated is lead hydroxyarsenate which reacts with disodium arsenate and the nitric acid of the solution, the reaction proceeding to an equilibrium, as in the system that has been studied.

The course of the reaction between lead nitrate and disodium arsenate can probably be represented by the following:



Attempts were made to regulate the progress of the reaction. If the influence of the action of the solution upon the precipitate could be retarded then it might be possible to isolate the precipitate in an initial stage of the reaction. When the precipitates were produced at infinite dilutions (under 0.001) and the solution decanted as soon as the pre-

cipitate had settled, then washed and dried, it was found that the precipitates were composed practically of pure lead hydroxyarsenate.

TABLE VII.

Composition of Precipitate from Lead Nitrate and Disodium Arsenate at Infinite Dilution.

	Lead as PbO.	Arsenic as As ₂ O ₃ .
Sample 1.....	74.6	23.52
Sample 2.....	74.2	23.94

Although the progress of the reaction is rapid in the concentrated solutions, it was found that in infinitely dilute solutions the progress was extremely slow. This is probably due to the condition of the lead hydroxyarsenate, which might account for the slow rate of reaction when the equilibrium was approached from $\text{PbOH}(\text{AsO}_4)_3 \cdot 2\text{Na}_2\text{HAsO}_4$ and 4HNO_3 .

When the attempt was made to isolate diplumbic arsenate it was thought advisable to avoid the production of lead hydroxyarsenate in such a condition that it would not be readily acted upon by the solution. As it seemed probable that this might occur if it was endeavored to prepare diplumbic arsenate by re-precipitating with ammonium hydroxide, lead arsenate that had been dissolved with nitric acid, as suggested by Tartar and Robinson, the previously mentioned modification was adopted.

The Reaction of Lead Acetate with Disodium Arsenate.—The same methods as were used in the examination of the reaction of lead nitrate with disodium arsenate were employed to examine the reaction of lead acetate with disodium arsenate.

TABLE VIII.

Temperature.	Initial concentrations. (Mol.)		Period.	Concentrations at equilibrium. (Mol.)	
	PbHAsO ₄ .	CH ₃ COONa.		CH ₃ COOH.	Na ₂ HAsO ₄ .
15-22°.....	0.01	0.008	10 days	0.00016	0.000065
	0.01	0.02	10 days	0.00022	0.0000738
	0.01	0.2	10 days	0.00108	0.00053
Boiling; Bar. press.					
633 mm.....	0.01	0.2	8 hrs.	0.0056	0.00275
	Pb ₂ OH(AsO ₄) ₃ . Na ₂ HAsO ₄ . CH ₃ COOH.				
15-22°.....	0.002	0.004	6 mos.	0.00012	

TABLE IX.

Composition of Lead Arsenates Produced by the Reaction of Lead Acetate with Disodium Arsenate at Different Concentrations and Temperatures.

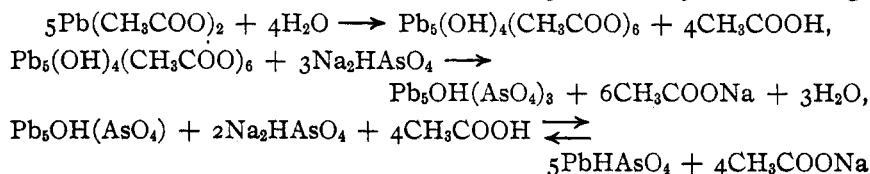
Temperature.	Concentration of reacting compounds.	Composition.				
		Calculated.		Found.		
		Lead as PbO.	Arsenic as As ₂ O ₃ .	Immediately.	After two weeks.	After two months.
				Arsenic as As ₂ O ₃ .	Arsenic as As ₂ O ₃ .	Arsenic as As ₂ O ₃ .
15-22°.....	0.01	64.47	32.95	24.5	31.52	31.74
	0.1	64.42	33.00	24.5	30.75	31.92
Boiling; Bar. press. 633 mm.	0.1	64.97	32.54	30.5 ¹

¹ After being boiled for eight hours under reflux condenser.

TABLE X.
The Composition of Lead Arsenate from Lead Acetate and Disodium Arsenate at Infinite Dilution.

	Lead as PbO.	Arsenic as As ₂ O ₃ .
Sample No. 1.....	74.9	23.26
Sample No. 2.....	74.3	23.9

These results show that the progress of the reaction of lead acetate with disodium arsenate is similar to the progress of the reaction of lead nitrate with disodium arsenate and can be represented by the following:



The results also show that, when the reaction of lead acetate with disodium arsenate has come to an equilibrium, the resulting lead arsenate is composed principally of diplumbic arsenate. As the reaction of lead acetate with disodium arsenate has been employed so extensively for the commercial production of lead arsenate and has also been studied by numerous investigators, it appears to be remarkable that the fact has been so completely overlooked that there was a reaction between the precipitate as it was formed and the solution. Haywood and McConnell¹ appear to be the only investigators that have found it was possible to produce a lead arsenate by the reaction of lead acetate with disodium arsenate that was composed principally of diplumbic arsenate, though they make no mention of how their results were obtained.

There has been no attempt in this paper to derive the equilibrium constants. Before these can be obtained with any degree of accuracy it will probably be necessary to make a more thorough examination of the influence of the sodium compounds on the equilibrium and also to attain the point of equilibrium of the systems within a narrower range of temperature than has been attempted in this investigation.

Conclusions.

In the reactions of lead nitrate and lead acetate with disodium arsenate:

The lead arsenates produced are mixtures of diplumbic arsenate, PbHAsO_4 , and lead hydroxyarsenate, $\text{Pb}_5\text{OH}(\text{AsO}_4)_3$.

The products of the reactions at low temperatures, when the reactions have come to an equilibrium, whether lead acetate or lead nitrate is used, consist principally of diplumbic arsenate.

The products of the reactions at infinite dilutions (less than 0.001 mol) whether lead acetate or lead nitrate is used, consist principally

¹ U. S. Dept. Agr., Bur. Chem., *Bull.* 131.

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

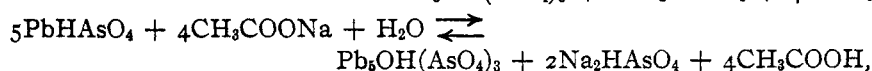
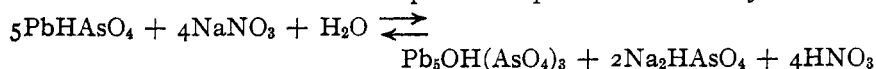
The precipitate that is first formed is lead hydroxyarsenate; diplumbic arsenate is produced by a secondary reaction.

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



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. patents² 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 preparation 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

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.