[CONTRIBUTION FROM THE LABORATORIES OF PHYSIOLOGY, HARVARD MEDICAL SCHOOL]

LEAD STUDIES. VII. THE PHOSPHATES OF LEAD EQUILIBRIUM IN THE SYSTEM LEAD OXIDE-PHOSPHORIC ANHYDRIDE-WATER AT 25°

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The phosphates of lead are important from the view-point of the transportation and deposition of lead in the human organism. The realization that lead poisoning is associated with the gradual accumulation of lead in the body, especially in the bones,[1] has emphasized the need for a careful investigation of the exact compounds of lead formed under these conditions. This paper reports part of an extended study of the reactions and equilibria involved in the formation of the phosphates of lead.

The conditions under which lead phosphate is formed at room temperature are not very well defined. According to the early work of Mitscherlich[2] and of Heintz,[3] normal lead phosphate is formed when slightly acid lead acetate solution is added to boiling secondary sodium phosphate solution, while precipitation from cold solutions yields secondary lead phosphate $PbHPO_4$.[4] This is converted into the tertiary salt only after being boiled with water for several hours. Gerhardt[5] states that when lead nitrate is added in excess to the sodium salt, tribasic lead phosphate is formed; if the salts are mixed in the reverse order a double salt of lead nitrate and lead phosphate precipitates. Cold water does not affect this compound, but boiling water converts it into lead nitrate and tertiary lead phosphate. Surprisingly little attention has been paid to the reactions of lead compounds with sodium phosphate at ordinary temperatures, although the methods of preparation of the lead phosphates from boiling solutions have been clearly defined in the excellent paper by Alders and Stähler.[4] With the exception of their investigation, no extensive study of the phosphates of lead has been published for more than seventy years. The phosphates of lead have always been prepared under *synthetic* not under *equilibrium* conditions; it has, therefore, been the purpose of this investigation to define exactly the products obtained in the latter case.

A preliminary study showed that when disodium phosphate and lead nitrate react under equilibrium conditions the secondary lead phosphate, $PbHPO_4$, is formed. Further experiments, however, have indicated that this phosphate forms only under equilibrium conditions, and that when

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[1] Minot, *J. Ind. Hyg.*, **1924**.

[2] Mitscherlich, *Ann. chim. phys.*, 19, 359 (1821).

[3] Heintz, *Ann. Phys. Chem.*, **73**, 122 (1848).

[4] Alders and Stähler, *Ber.*, **42**, 2261 (1909).

[5] Gerhardt, *Ann. Chem. Pharm.*, **64**, 284 (1847).

the two reacting substances are first mixed, tertiary lead phosphate is formed. Evidence for this may be found in the curve (Fig. 1) showing the hydrogen-ion concentration of various mixtures of lead chloride and secondary sodium phosphate.

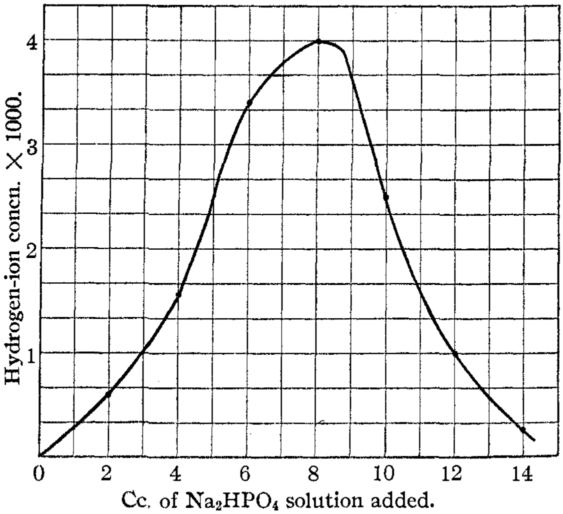

Fig. 1.

TABLE I

CHANGE IN HYDROGEN-ION CONCENTRATION DURING THE PRECIPITATION OF LEAD PHOSPHATE

10 cc. of 0.01797 *M* $PbCl_2$ solution was used in each experiment

0.01198 *M* Na_2HPO_4 cc...	0	2	4	6	8
Hydrogen-ion concentration	3.97×10^{-5}	6.06×10^{-4}	1.56×10^{-3}	3.15×10^{-3}	3.98×10^{-3}
0.01198 *M* Na_2HPO_4 cc...	10	12	14	16	
Hydrogen-ion concentration	2.49×10^{-3}	1.00×10^{-4}	2.50×10^{-5}	6.30×10^{-7}	

If these two substances react, as is generally stated, according to the equation, $PbCl_2 + Na_2HPO_4 \rightleftharpoons PbHPO_4 + 2NaCl$, the solution should remain neutral, whereas if tertiary lead phosphate is formed, $3PbCl_2 + 2Na_2HPO_4 \rightleftharpoons Pb_3(PO_4)_2 + 4NaCl + 2HCl$, the solution should become acid.

Table I and Fig. 1 show that the solution becomes progressively more acid with each successive addition of sodium phosphate until there is actually present almost the quantity of phosphate required to precipitate the lead in the form of tertiary lead phosphate (9.26 cc.). The filtrate was found to be lead-free, although the amount of sodium phosphate present was only 66% of that necessary to precipitate the lead as secondary lead phosphate. From this point the acidity of the solution decreases, owing to the presence of an excess of sodium phosphate. It was found impossible to make the hydrogen-ion concentration measurements electrometrically. Colorimetric determinations were therefore made. Denham and Allmand[6] experienced a similar difficulty in their attempts to measure the hydrolysis of lead salts by means of the hydrogen electrode. From the results obtained in Table I it is apparent that the tertiary salt forms under synthetic conditions or in slightly alkaline solution.

When suspended in boiling water, secondary lead phosphate is transformed into tertiary lead phosphate in the following manner: $3PbHPO_4 \rightleftharpoons Pb_3(PO_4)_2 + H_3PO_4$. Evidence for this reaction is found in the constant increase in acidity of the solution, as well as the changed microscopic appearance of the solid. The change is very slow, requiring several hours at least.

In order to test the range of stability of the various phosphates of lead of the system indicated, the isotherm at 25° was traced. The composition of the phosphates was found by extrapolation using Schreinemakers' residue method. In a ternary system such as this, of which the three components are lead oxide, phosphoric anhydride and water, variation of the solution indicates the existence of a single solid phase. The formation of a second solid phase produces a change in the degree of variability. That the system is invariant at this point is indicated by the formation of a solution of invariant composition. Analysis of the solid and liquid phases of a series of empirical mixtures which had been allowed to attain equilibrium would therefore define the conditions under which the compounds could exist. For this purpose analyses were made of the saturated solution and of the solid residue together with its adhering mother liquor or saturated solution. The two values thus obtained, when plotted on a coördinate system, lie on a line which, when projected, passes through a point representing the composition of the solid phase. Similar analyses of other saturated solutions in equilibrium with the solid phase served to locate other lines. Since these lines all pass through a common point which represents the composition of the solid phase, their intersection definitely establishes the composition of the solid phase present in given mixture.

Experimental Part

The materials were purified and the equilibrium measurements made in the following manner. Pure lead oxide was prepared from lead carbonate. The latter had been precipitated from a dilute solution of lead acetate by the addition of a slight excess of sodium carbonate. This precipitate was thoroughly washed, dried and carefully ignited in an electric muffle furnace. The oxide obtained was tested and found to be free from soluble salts and carbonate. The phosphoric acid used was selected from several lots of U. S. P. acid; analysis showed it to be free from chlorides, sulphates and nitrates.

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[6] Denham and Allmand, *J. Chem. Soc.*, **93**, 424 (1908).

Lead oxide was added to various mixtures of phosphoric acid and water, so that there was an excess of 2 or 3 g. of solid material. These mixtures, in securely sealed bottles, were then mechanically rotated end over end (at 38 r.p.m.) in a large electrically-heated thermostat. The temperature was maintained constant by this means at 25° (±0.05°) for very long periods. From time to time analyses were made until at the end of seven weeks equilibrium was found to have been established. The bottles were then allowed to stand for several hours to allow complete separation of the solid phase and liquid phase. Both solid and liquid phases were then analyzed for lead oxide and phosphoric anhydride. In the case of the solids, the phosphoric anhydride was precipitated as ammonium magnesium phosphate and weighed. In the solution phase, because of the large amount of phosphoric acid present, determinations were made volumetrically by titration against carbonate-free sodium hydroxide, using methyl orange as an indicator and a citrate-indicator solution[7] as standard. The sodium hydroxide solution had been standardized previously against an accurately analyzed phosphoric acid solution. In analyzing the solid phase for lead, weighed portions, together with some of the adhering mother liquor, were dissolved in sodium hydroxide and the lead was then precipitated as lead sulfide. This was converted to lead chromate and weighed as such. The small amounts of lead in the liquid phase were similarly separated and the chromate titrated.[8] Analyses of the solid phase were made in triplicate; of the solution phase in quadruplicate.

TABLE II

SUMMARY OF DATA

	Solution phase		Solid phase		Density	Composition of solution grams per liter	
No.	P_2O_5 %	PbO %	P_2O_5 %	PbO %	$d^{25°}_{4°}$	P_2O_5	PbO
1	5.09	0.134	18.76	54.61	1.036	52.73	1.38
2	9.91	.228	19.85	52.99	1.074	106.73	2.45
3	14.43	.329	21.41	56.30	1.113	160.60	3.66
4	18.84	.510	22.30	53.09	1.151	216.84	5.87
5	22.91	.690	23.52	49.89	1.190	272.63	8.21
6	26.74	.777	24.51	52.08	1.227	328.09	9.54
7	31.00	.792	25.79	50.53	1.264	391.84	10.01
8	34.82	.903	27.48	47.70	1.302	453.35	11.75
9	39.96	1.088	30.53	42.00	1.375	549.44	14.95
10	45.74	1.480	34.53	37.31	1.448	662.31	21.42
11	50.73	1.299	41.30	34.54	1.516	769.06	19.71
12	53.06	0.999	44.07	28.60	1.549	821.90	15.47
13	54.89	.756	42.41	35.78	1.576	864.06	11.90
14	58.53	.473	56.00	6.41	1.635	956.96	7.74

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[7] Prideaux, "The Theory and Use of Indicators," Constable and Co., London, **1917**, p. 287.

[8] Fairhall, *J. Ind. Hyg.*, 4, 9 (1922).

The averages of the data thus obtained, together with the density measurements which permit calculation of the volume figures, are assembled in Table II.

The phase diagram (Fig. 2) indicates the limits of existence of the lead phosphates over a wide range of acidity. ACE represents an area of complete solution with no solid phase present. Expts. 1–10 inclusive are represented along the straight line AC. The lines connecting these points with those representing the composition of the solid residues converge at B which represents the compound secondary lead phosphate. Since this series of experiments extends over a wide range of concentration it establishes the point B quite satisfactorily. The area ABC therefore represents the solid phase in contact with various solutions. At C the amount of lead in solution is maximal. This point, where the two branches AC and CE intersect, indicates the point at which a solution of invariant composition would be in contact with the two phases, secondary lead hydrogen phosphate and primary lead phosphate. The experiments plotted along the branch CE (11–14) are those in which the solid phase primary lead orthophosphate, $PbH_4(PO_4)_2$, is in contact with varying solutions. The lines connecting the composition of the solution phase

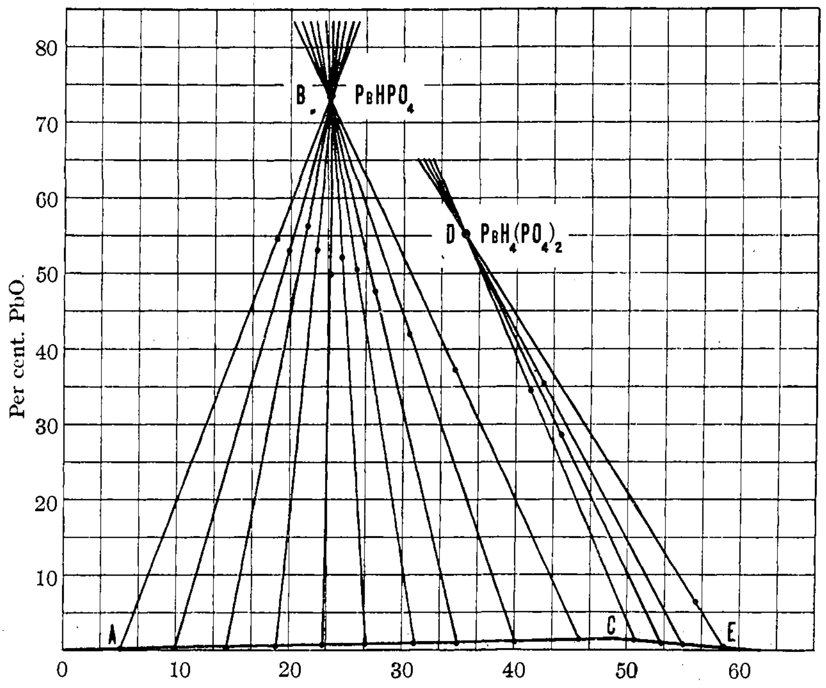

Fig. 2.

and solid phase when projected practically coincide with the point representing the theoretical composition of primary lead orthophosphate.

The stability of the secondary lead and primary lead phosphates at various acid concentrations is, therefore, quite clearly indicated by the diagram, which also furnishes us a means of predicting what happens when various mixtures are brought to equilibrium. Thus, any mixture whose representative points fall within the area ACE will yield a solution with no solid phase; and similarly one can predict the composition of the compound formed in the preparation of any empirical mixture which fall within the limits of the area ABC. The short branch CE delineates the solubility of primary lead phosphate in phosphoric acid at 25°. Its solubility rapidly decreases with increasing acid concentration.

Summary

The isotherm of the system, lead oxide-phosphoric anhydride-water has been traced at 25°.

The results indicate that secondary lead hydrogen phosphate is capable of existing over a considerable range of concentration of phosphoric acid under equilibrium conditions at 25°.

At equilibrium tertiary lead phosphate cannot exist in the presence of even a small amount of acid.

The product of the reaction between secondary sodium phosphate and a lead salt at room temperature is tertiary lead phosphate. This slowly shifts to the secondary lead salt which is the equilibrium product.

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A STUDY OF THE LUMINOUS DISCHARGE IN CHLORINE. THE ELECTRON AFFINITY OF HALOGEN MOLECULES

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In a recent article[1] it was shown that the potential necessary to maintain a luminous discharge in bromine was of the same order as that necessary in the case of iodine,[2] and that the potentials for these two electronegative gases were higher than in the case of electropositive gases such as hydrogen and mercury.[3] It was suggested that one could account for this fact without assuming that the halogen molecules as such possessed an electron affinity. The halogen atoms have definite electron affinities

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[1] Noyes, THIS JOURNAL, **45**, 1192 (1923).

[2] Noyes, *ibid.*, **45**, 337 (1923).

[3] (a) Gibson and Noyes, *ibid.*, **44**, 2091 (1922). (b) McCurdy, *Phil. Mag.*, **46**, 524 (1923).