

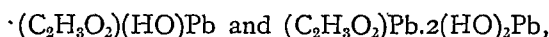
The System: Lead Oxide—Acetic Acid—Water.

By

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Many basic lead acetates have been described in literature; but in most cases it is doubtful whether they are single compounds. According to Löwe¹ there exist only two basic salts, namely:



the others being merely mixtures of these basic salts or of one of them and the neutral salt. So far as I know, there has been no systematic study of these compounds in modern times; and I have undertaken to investigate them from the point of view of heterogeneous equilibrium and to verify the conclusion of Löwe.

The materials used were as follows: Commercial pure lead oxide, fused in a platinum crucible to decompose such carbonate as might be contained in it, and used in a finely powdered state; acetic acid of the purest preparation of C. Merck, found to be pure enough for the purpose; and ordinary distilled water, freed from carbonic acid.

The experiments consisted of three series. In the first series of experiments, neutral lead acetate was dissolved in water and lead oxide was added to it, gradually increasing its quantity until the residue contained some lead oxide together with a basic salt. In the second series of experiments, some lead oxide was put in water and acetic acid was added to it in gradually increasing quantities until the residue contained only the basic salt and no oxide. In the third series of experiments, acetic acid was added to an aqueous solution of the neutral salt, the former being used in gradually increasing quantities.

Each experiment was carried out in the following way. The mixture was put in an Erlenmeyer flask of a capacity of about 50 cc., which was made to rotate in a thermostat at 25.0°. The thermometer

¹ J. prak. Chem., 98, 385 (1866).

used was compared with one with a certificate of Physikalisch-Technisches Reichsanstalt in Charlottenburg. In cases of acid solutions the equilibrium was attained in a short time, but in cases of basic salts two or three days were required. When the equilibrium was attained, the flask was allowed to stand still in the same thermostat until the suspended matter had completely subsided, then about 2 cc. of the mother liquor were taken out by a pipette, through a short glass tube filled with purified cotton and attached to its lower end, into a tared flask provided with a well-fitted stopper and subjected to analysis.

To prepare the residue for analysis, it was taken out by a small ladle bottomed with linen and put promptly on folded filter paper on a copper spoon with a long vertical handle held in a large test-tube in the same thermostat. Folded filter paper was placed on it and pressed down with a glass rod to remove as much as possible the adhered mother liquor from the residue. Then the residue, thus prepared, was subjected to analysis. When the residue was a basic salt, however, it was very finely divided, passed through linen even when doubled and was found impossible to remove for analysis in the manner above stated. As it was ascertained that a deviation of about 1° in temperature produces no appreciable change in the state of equilibrium, the residue was made to deposit in a glass tube by means of a centrifugal machine, the temperature of the surrounding air being kept approximately near 25° by means of lamps. The mother liquor was poured off; and the residue, still wet with mother liquor, was subjected to analysis.

For analysis, the mother liquor was diluted to about 30 cc., and the residue was dissolved in water and, if insoluble in it, with the addition of a known quantity of acetic acid. The lead in the solution was precipitated as lead sulphate by the addition of a given quantity of sulphuric acid; and the precipitate was made less soluble by means of some alcohol added. The precipitate was then treated in the usual way. The acetic acid radical was determined in the filtrate, usual precautions necessary in such a case being observed, by titration with a standard solution of caustic potash, using phenolphthalein as indicator.

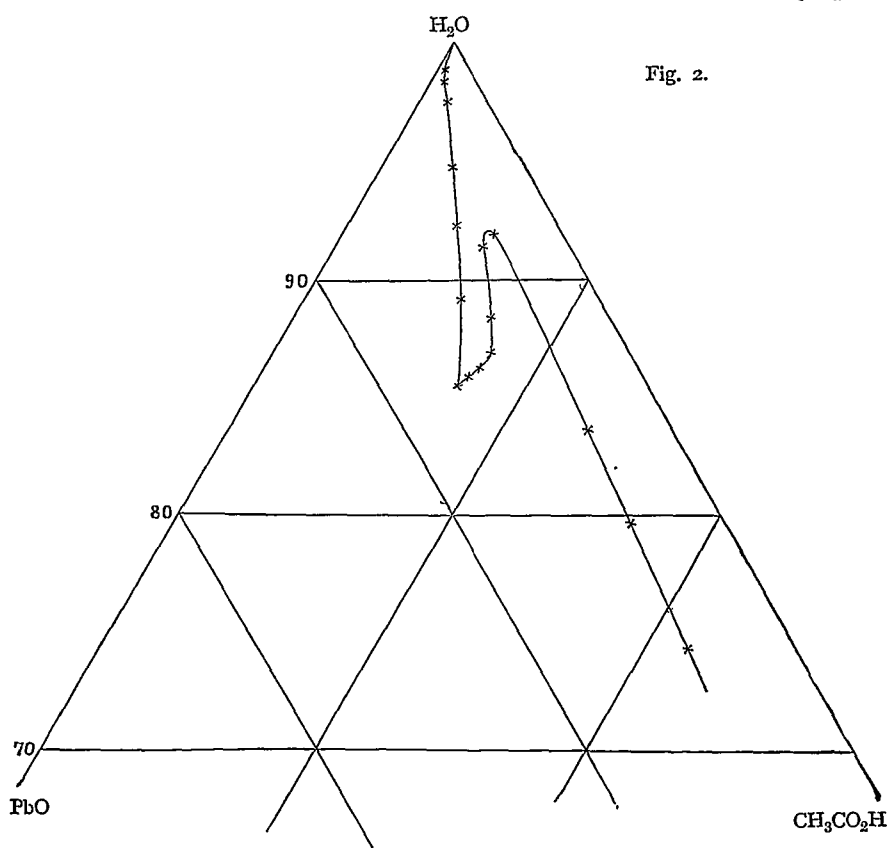
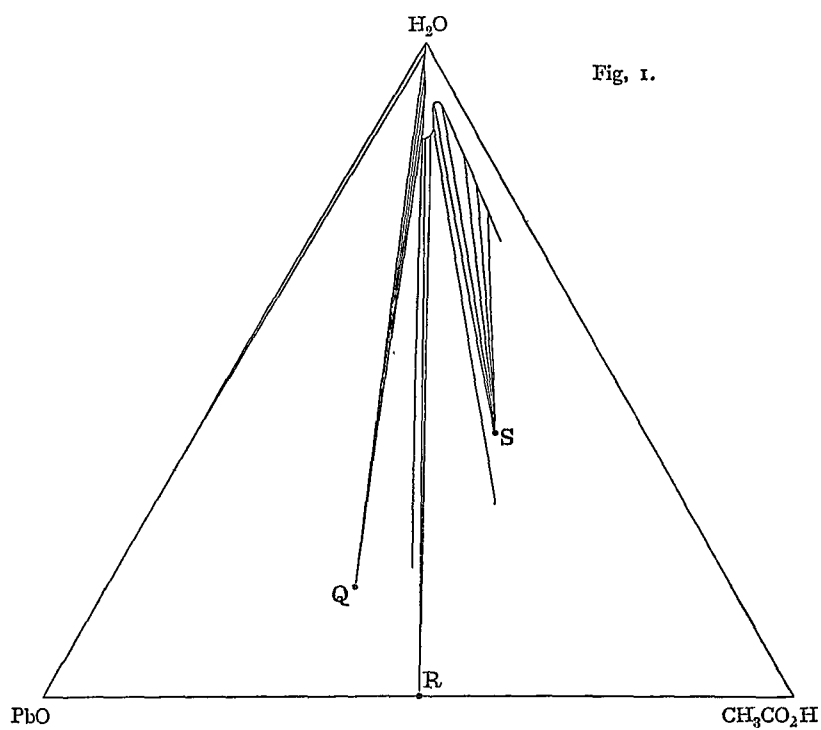
The results of analysis are given in the following table, the components being given in molar percentages:

TABLE I.

No.	Solution.			Residue, wet with some mother liquor.			Residue.
	Water.	Acetic acid.	Lead oxide.	Water.	Acetic acid.	Lead oxide.	
1	98.80	0.20	1.00	79.22	0.22	20.56	PbO
2	98.45	0.48	1.07	—	—	—	"
3	98.41	0.54	1.05	—	—	—	"
4	97.52	1.03	1.45	84.09	6.21	9.70	$(C_2H_3O_2)_2Pb.2(HO)_2Pb$
5	94.60	2.51	2.89	83.02	6.99	9.99	"
6	92.05	4.17	3.78	80.62	8.45	10.93	"
7	89.19	5.61	5.20	76.38	10.55	13.07	"
8	85.59	7.26	7.15	74.94	12.29	12.77	$\left\{ \begin{array}{l} (C_2H_3O_2)_2Pb.2(HO)_2Pb \\ (C_2H_3O_2)(HO)Pb \end{array} \right.$
9	85.70	7.79	6.51	76.42	12.26	11.32	$(C_2H_3O_2)(HO)Pb$
10	86.29	7.72	5.59	78.07	11.70	10.23	"
11	86.90	7.92	5.18	73.16	16.84	10.00	$\left\{ \begin{array}{l} (C_2H_3O_2)(HO)Pb \\ (C_2H_3O_2)_2Pb.3H_2O \end{array} \right.$
12	88.32	7.30	4.38	72.58	17.84	9.58	$(C_2H_3O_2)_2Pb.3HO$
13	91.30	5.36	3.34	75.72	15.71	8.57	"
14	91.87	5.49	2.64	82.92	11.39	5.69	"
15	83.77	13.07	3.16	55.77	30.13	14.10	"
16	79.42	16.78	3.80	50.71	33.62	15.67	"
17	74.29	21.53	4.18	60.55	29.25	10.20	"

The chemical compositions of the residues were graphically estimated by referring to triangular coordinates in the usual way, as shown in Fig. 1, and given in the last column of the table. Fig. 2 represents the upper part of the figure on a larger scale to show more clearly the course of the solution curves.

In order to test the existence of any acid salt, the neutral salt was mixed with anhydrous acetic acid; but no acid salt was obtained.



Summary.

1. The two basic lead acetates, $(C_2H_3O_2)(HO)Pb$ and $(C_2H_3O_2)_2Pb$, and no other basic salts, have been found to exist in contact with solutions at 25° ; and the conclusion of Löwe has been confirmed.
2. No acid salt has been found to exist in contact with solution at 25° .

The author's thanks are due to Prof. Y. Osaka for suggesting the subject of this research and for his interest and advice throughout the work.
