DEACON : STUDIES OF EQUILIBRIA IN THE SYSTEMS, ETC. 2063

CCLXXII.—Studies of Equilibria in the Systems Sodium Chloride-Lead Chloride-Water, Lithium Chloride-Lead Chloride-Water.

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THE purpose of this work was the investigation of those complex salts, if any, formed by lead chloride with sodium or lithium chloride, which are capable of existence in contact with aqueous solutions at 25°, and to obtain the isothermal diagrams for these systems.

The method used was the same as that described by Burrage



(J., 1926, 1703). The lead was estimated gravimetrically as chromate and the total chloride as silver chloride, water being found by difference. The analytical results for the liquid and wet solid phases were plotted on triangular diagrams according to Schreinemakers's method of residues; they exhibit the nature of the results more clearly, however, when plotted as in Figs. 1 and 2.

Lead Chloride-Sodium Chloride-Water.

Previous work on this system has led to conflicting results. (Mme.) Demassieux (Ann. Chim., 1923, 20, 233) studied the system at 100°, 50°, and 13°, and found that no double compounds existed. Kendall and Sloan (J. Amer. Chem. Soc., 1925, 47, 2306), working at 25°, describe the compound $2PbCl_2$, NaCl. The present investigation shows the absence of any such compound, the solid phases being lead chloride and sodium chloride only.

TABLE I (see Fig. 1).

Composition of the equilibrium solutions at 25° for the system NaCl-PbCl₂-H₂O. (Concentrations are expressed as g. per 1000 g. of water.)

		Solia			
NaCl.	PbCl ₂ .	phase.	NaCl.	PbCl ₂ .	Solid phase.
	10.87	PbCl ₂ .	143.0	3.52	PbCl.
5.0	7.24	,, -	160.0	4.14	*
8.8	4.22	,,	200.0	6.01	,,
15.57	2.52	,,	240.0	8.87	,,
20.0	2.09	,,	280.0	13.77	,,
30.0	1.80	"	300-0	17.30	,,
40·0	1.72	,,	320.0	21.50	,,
50.0	1.67	,,	340.0	26.40	,,
60.0	1.75	,,	369.9	34.80	$PbCl_{2} + NaCl_{2}$
80.0	1.88	,,	367.0	20.10	NaCl.
100.0	2.14		363.0	8.20	
121.0	2.79	,,	359.6		,,

Lead Chloride-Lithium Chloride-Water.

This system has been investigated at 50° by Demassieux (*loc. cit.*), and some measurements have also been made at 25° by Kendall and Sloan (*loc. cit.*), who claimed the existence of the salt LiCl,2PbCl₂. The present work shows the absence of this salt at 25° , and that of Demassieux shows that no compound is formed at 50° .

The system is singular in that the decrease in solubility of the lead chloride to 1.39 g. and the subsequent increase to 103.5 g. are followed by a slight decrease in solubility to 101.6 g. before the eutectic point is reached. The curve undergoes a break at the eutectic point, and a second solid phase LiCl,H₂O separates. The separation of the monohydrate is in agreement with the work of Bogorodsky (J. Russ. Phys. Chem. Soc., 1893, 25, 316), who describes this hydrate as the stable form between 12.5° and 98° .

TABLE II (see Fig. 2).

Composition of equilibrium solutions at 25° for the system LiCl-PbCl₂-H₂O. (Concentrations are expressed as g. per 1000 g. of water.)

		Sona			
LiCl.	PbCl ₂ .	phase.	LiCl.	PbCl ₂ .	Solid phase.
	$10.8\bar{7}$	PbCl _a .	257.7	8.02	$PbCl_2$.
3.88	4.74	,, -	$329 \cdot 2$	16.36	
6.67	2.68	,,	453.9	48.71	,,
7.16	2.58	••	458.8	52.34	**
20.24	1.67		621.8	94.43	33
21.64	1.58		$735 \cdot 2$	103.5	••
29.74	1.53		794 ·1	103.4	••
43.77	1.39	,,	834.9	101.6	$PbCl_{*} + LiCl_{*}H_{*}O.$
59.94	1.52	,,,	835.0	72.0	LiĊl,H.O.
75.88	1.53	,,,	835.0	31.0	
156.2	2.58	"	830.0	17.2	~
221.6	5.61	"	830.5		,,

Treis (Jahrb. Min. Beil.-Bd., 1914, 37, 766), investigating the binary systems $PbCl_2$ -XCl (where X = Li, Na, K, or Rb), found that whilst potassium gave two double compounds, and rubidium three, no combination was obtained between lithium or sodium chloride and lead chloride. Double salts are also formed between potassium and lead chlorides in aqueous solution (Burrage, loc. cit.).

Summary.

1. Equilibria existing at 25° in the systems NaCl-PbCl₂-H₂O, and LiCl-PbCl₂-H₂O have been investigated over the whole range of concentrations.

2. At this temperature, no double salts are capable of existence in either system.

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