CCXXIII.—*Studies of Equilibria in Systems of the Type Lead Halide–Potassium Halide–Water.*

By Leslie James Burrage.

The purpose of this work was the investigation of those complex salts formed by lead halides and potassium halides which are capable of existence in contact with aqueous solutions.

The method employed was to vary the concentration, from zero to saturation, of each of the component salts in turn in presence of excess of the other. The solution of potassium salt was put into a bottle of about 600 c.c. capacity in contact with excess of solid lead salt. After its neck had been sealed off, the bottle was attached in a horizontal position to a revolving framework in the thermostat, and rotated at such a speed as to hold the solid salt in suspension.

In order to ensure that the solid phases in equilibrium with any particular solution were homogeneous, the following method was adopted. After one day's shaking at 25°, the whole contents of the vessel were raised to 30° in another thermostat and kept at this temperature for several hours. The liquid phase was then transferred to another bottle in the thermostat at 25° and rotated in the shaker. The solid phase deposited by this means would be quite homogeneous unless the liquid phase corresponded in composition to the eutectic point.

At the end of 24 hours the bottle was removed from the shaker, and, after the solid had been allowed to settle, a certain amount of the liquid was pipetted into a weighing-bottle and analysed. The bottle was then resealed and put back in the shaker, the whole process of cutting off and resealing being conducted with only the neck of the bottle above the liquid. These operations were repeated at the end of 48 hours to ensure that the solution was saturated. Special precautions were taken to prevent solid from being sucked up into the pipette.

The thermostat was regulated at $25° \pm 0{\cdot}01°$. All the materials used were previously recrystallised from water. The lead was usually estimated gravimetrically as chromate, and the halide as the silver salt.

Colorimetric Determination of Lead.—At low concentrations of potassium iodide the lead was estimated by a colorimetric method, as the amount of lead iodide in solution was very small. The method was essentially that used in water analysis (Clowes and Coleman, " Quantitative Chemical Analysis," 1909, p. 315), but it was found advisable to use 10 c.c. of saturated ammonium acetate solution in each 100 c.c. Nessler tube in order to regulate the hydrogen-ion concentration.

This method gave excellent agreement with the gravimetric estimations, although in the latter case a very large amount of liquid had to be used for analysis.

Analysis of the Solid Phase.—The solid phases were determined by the " rest " method. Some of the solid in contact with the solution was weighed rapidly without being dried. The whole was then analysed and the percentage of potassium and lead halides found; by the analysis of the solid phase from two solutions the composition was obtained. If, on the other hand, the solid phase were dried by pressure between filter-papers, its analyses gave widely varying results, owing to the occlusion of small amounts of alkali halide.

Since in all previous work on this subject the latter method was employed for determining the constitution of the complex salts, it is probable that many of these salts which have been described have no actual existence.

The results in the tables are the average of those obtained after 24 and 48 hours' rotation, the difference between them being 0·1—0·5%. The compositions of the solutions were plotted in the

FIG. 1.

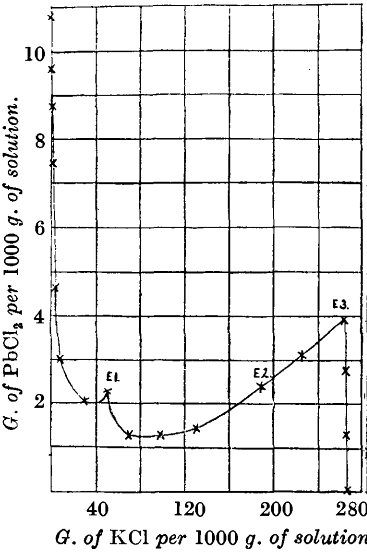
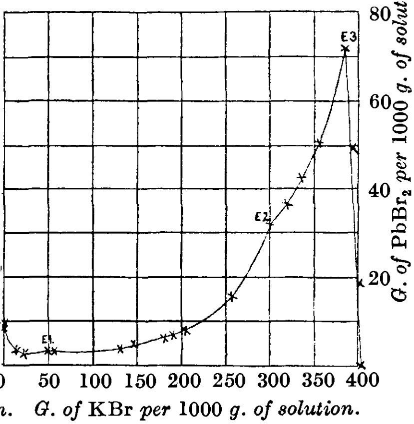


FIG. 2.



manner shown, as triangular diagrams were unsuitable, being too cramped to show the results clearly. In each case, the eutectic points in the tables are indicated by E in the diagrams.

Lead Chloride–Potassium Chloride–Water.

Previous work on the system $KCl–PbCl_2–H_2O$ indicates that several double salts can be obtained, but the results are not in agreement. Herty (*Amer. Chem. J.*, 1892, **14**, 125) obtained a salt to which he gave the formula $PbCl_2,KCl$; although his results were approximately 1% lower than were required for this formula, he considered the salt to be anhydrous. Kendall and Sloan (*J. Amer. Chem. Soc.*, 1925, **47**, 2306) have recently claimed that the definitely anhydrous salt $PbCl_2,KCl$ is formed at 25°. Wells (*Z. anorg. Chem.*, 1893, **3**, 195) found two double salts—$KCl,PbCl_2,\frac{1}{3}HO$ and

$KCl,2PbCl_2$—the former being obtained from concentrated and the latter from dilute potassium chloride solutions. Von Ende (*Z. anorg. Chem.*, 1901, **26**, 129) stated that only one existed at 25°—$KCl,2PbCl_2$. Since the commencement of the present work, Demassieux (*Ann. Chim.*, 1923, **20**, 233) has studied the solubility of lead chloride in solutions of potassium chloride at 100°, 50°, and 14°, with results in complete agreement with those recorded in this paper : two compounds exist, *viz.*, $KCl,2PbCl_2$ and $KCl,PbCl_2,\frac{1}{3}H_2O$; the former was obtained as white, transparent needles and the latter as brilliant, prismatic crystals which lost their water of crystallisation when heated to 200°.

TABLE I (see Fig. 1).

Composition of equilibrium solutions at 25° for the system KCl–$PbCl_2$–H_2O. (Concentrations are expressed as g. per 1000 g. of solution.)

	KCl.	$PbCl_2$.	Solid phase.		KCl.	$PbCl_2$.	Solid phase.
	—	10·83	$PbCl_2$.		70·48	1·28	$KCl,2PbCl_2$.
	0·37	10·08	,,		97·87	1·27	,,
	0·75	9·61	,,		129·3	1·42	,,
	1·52	8·77	,,	(E 2)	187·4	2·36	$KCl,2PbCl_2$ and $KCl,PbCl_2,\frac{1}{3}H_2O$.
	2·96	7·47	,,		225·4	3·03	$KCl,PbCl_2,\frac{1}{3}H_2O$.
	7·35	4·62	,,	(E 3)	264·3	3·86	$KCl,PbCl_2,\frac{1}{3}H_2O$ and KCl.
	14·69	3·01	,,		265·2	2·67	KCl.
	30·22	2·05	,,		264·9	1·22	,,
(E 1)	49·69	2·27	$PbCl_2$ and $KCl,2PbCl_2$.		265·3	—	,,

Solid Phases.—$KCl,2PbCl_2$. Found : KCl, 11·9; $PbCl_2$, 88·1; ($KCl : PbCl_2 = 1 : 1·99$). Calc., KCl, 11·8; $PbCl_2$, 88·2%.

$KCl,PbCl_2,\frac{1}{3}H_2O$. Found : KCl, 20·6; $PbCl_2$, 77·6; H_2O, 1·8; ($KCl : PbCl_2 : H_2O = 1 : 1·01 : 0·36$). Calc., KCl, 20·8; $PbCl_2$, 77·5; H_2O, 1·7%.

Lead Bromide–Potassium Bromide–Water.

The first work on this system was carried out by Berthelot (*Ann. Chim. Phys.*, 1883, **29**, 293), who reported a compound, $3PbBr_2,2KBr$. Herty (*Amer. Chem. J.*, 1892, **14**, 107) obtained $KBr,PbBr_2,H_2O$ as colourless crystals. According to Wells (*loc. cit.*), four compounds can be obtained : $PbBr_2,2KBr,H_2O$; $PbBr_2,KBr,\frac{1}{3}H_2O$; $PbBr_2,KBr,H_2O$ and $KBr,2PbBr_2$. In the present work two compounds have been found : $KBr,2PbBr_2$ and $KBr,PbBr_2,\frac{1}{3}H_2O$.

It seems possible that Wells's first compound is really $KBr,PbBr_2,\frac{1}{3}H_2O$ together with a small quantity of ice, since it is only formed at low temperatures and is described as losing two-thirds of a molecule of water by standing over sulphuric acid.

His $PbBr_2,KBr,H_2O$ may be the same complex salt together with occluded potassium bromide, since it is said to exist only in contact with very concentrated solutions of the latter salt.

Both the complex bromides and lead bromide itself discolour on exposure to light. The white crystals assume a brownish-grey tint which deepens almost to black.

FIG. 3.

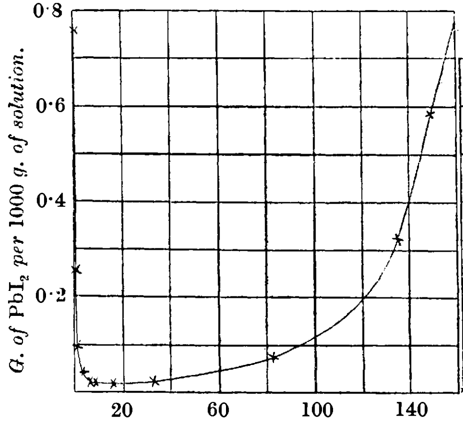
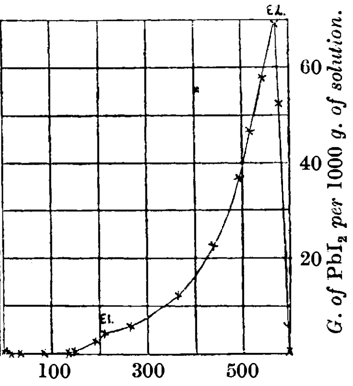


FIG. 4.



G. of KI *per* 1000 *g. of solution.*

TABLE II (see Fig. 2).

Composition of equilibrium solutions at 25° for the system $KBr–PbBr_2–H_2O$. (Concentrations are expressed as g. per 1000 g. of solution.)

KBr.	$PbBr_2$.	Solid phase.	KBr.	$PbBr_2$.	Solid phase.
—	9·69	$PbBr_2$.	190·5	6·66	$KBr,2PbBr_2$.
0·56	9·46	,,	206·4	7·53	,,
1·31	8·75	,,	216·1	8·68	,,
4·23	7·82	,,	256·9	14·94	,,
13·25	3·47	,,	(E 2) 301·1	31·60	$KBr,2PbBr_2$ and $KBr,PbBr_2,\frac{1}{3}H_2O$.
22·92	2·56	,,	319·7	36·22	$KBr,PbBr_2,\frac{1}{3}H_2O$.
(E 1) 49·67	3·10	$PbBr_2$ and $KBr,2PbBr_2$.	338·0	42·48	,,
56·09	2·95	$KBr,2PbBr_2$.	356·8	50·38	,,
129·4	3·30	,,	(E 3) 388·7	72·05	$KBr,PbBr_2,\frac{1}{3}H_2O$ and KBr.
131·8	3·45	,,	393·2	49·29	KBr.
145·4	4·27	,,	402·8	18·35	,,
182·7	5·60	,,	405·2	—	,,

Solid Phases.—$KBr,2PbBr_2$. Found: KBr, 13·9; $PbBr_2$,86·1; ($KBr : PbBr_2 = 1 : 2·01$). Calc.: KBr, 13·95; $PbBr_2$, 86·0%.

$KBr,PbBr_2,\frac{1}{3}H_2O$. Found: KBr, 24·3; $PbBr_2$, 74·4; H_2O, 1·3;

(KBr : $PbBr_2$: H_2O = 1·01 : 1 : 0·36). Calc.: KBr, 24·2; $PbBr_2$, 74·6; H_2O, 1·2%.

Lead Iodide–Potassium Iodide–Water.

Boullay (*Ann. Chim. Phys.*, 1827, **34**, 366) obtained two compounds: PbI_2,KI and PbI_2,4KI; and Ditte (*ibid.*, 1881, **24**, 226) added PbI_2,2KI,4H_2O. Berthelot (*ibid.*, 1883, **29**, 293) claimed the existence of two more: PbI_2,2KI,2H_2O and 3PbI_2,4KI,6H_2O. Herty (*loc. cit.*; *Amer. Chem. J.*, 1896, **18**, 290) examined these and eliminated all except one, PbI_2,KI,2H_2O, which was confirmed by Wells (*loc. cit.*). Field (*Chem. News*, 1893, **67**, 157) reported the existence of 3PbI_2,4KI. Since the commencement of this work, Demassieux (*Compt. rend.*, 1923, **177**, 51) has studied this system at 50° and 13°, and the results are in entire agreement with those of the author—only one compound can exist, PbI_2,KI,2H_2O, crystallising in long, pale yellow needles.

TABLE III (see Figs. 3 and 4).

Composition of equilibrium solutions at 25° for the system KI–PbI_2–H_2O. (Concentrations are expressed as g. per 1000 g. of solution.)

KI.	PbI_2.	Solid phase.	KI.	PbI_2.	Solid phase
—	0·758				
0·83	0·234	PbI_2.	(E 1) 213·2	4·28	KI,PbI_2,2H_2O and PbI_2.
1·66	0·092	,,	268·2	5·53	KI,PbI_2,2H_2O.
3·32	0·040	,,	367·3	12·21	,,
6·64	0·020	,,	438·0	22·49	,,
8·30	0·019	,,	494·3	37·12	,,
16·61	0·016	,,	516·1	46·54	,,
33·20	0·020	,,	546·0	58·76	,,
83·07	0·073	,,	(E 2) 565·9	74·21	KI,PbI_2,2H_2O and KI.
136·1	0·316	,,	578·2	52·35	KI.
149·1	0·578	,,	591·3	5·49	,,
194·5	2·53	,,	597·2	—	,,

Solid Phase.—KI,PbI_2,2H_2O. Found: KI, 25·0; PbI_2, 69·5; H_2O, 5·5; (KI : PbI_2 : H_2O = 1 : 1 : 2·03). Calc.: KI, 25·0; PbI_2, 69·5; H_2O, 5·4%.

Summary.

(1) Equilibria existing at 25° in the systems KX–PbX_2–H_2O (where X = Cl, Br, or I) have been investigated over the whole range of concentrations.

(2) At this temperature following double salts are capable of existence: KCl,2$PbCl_2$; KCl,$PbCl_2$,$\frac{1}{3}H_2O$; KBr,2$PbBr_2$; KBr,$PbBr_2$,$\frac{1}{3}H_2O$; and KI,PbI_2,2H_2O.

(3) Some of the compounds whose existence is thus discredited are discussed.

A further investigation of the systems is now being carried out by an electrometric method.

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