CLXXXVIII.—*The System Lead Chloride–Lead Iodide–Water.*

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The literature yields only the most conflicting and unsatisfactory accounts of double salts of the type $x\mathrm{PbCl_2},y\mathrm{PbI_2}$, and a systematic investigation of their stability and properties was therefore undertaken.

Various workers (*e.g.*, Dietzell, *Dingler's Poly. J.*, 1868, **190**, 41; Field, J., 1893, **63**, 540) have prepared salts to which they ascribed formulæ of this type, without sufficient evidence that they were true double salts. Herty (*Amer. Chem. J.*, 1896, **18**, 290) claims to have shown that these substances were not true chemical compounds, but isomorphous mixtures of lead chloride and lead iodide; and later (Herty and Boggs, *ibid.*, 1897, **19**, 820), he concluded that " all the evidence thus far obtained tends to show that lead iodide and lead chloride will crystallise together, the lead chloride being in excess."

Thomas (*Compt. rend.*, 1898, **126**, 1349), reviewing previous work in conjunction with his own, concluded that PbICl could exist as a true compound.

Two-component Systems.

To the system lead iodide–lead chloride–water there correspond three two-component systems, *viz.*, each salt and water, and the two salts only. The first two systems show no points of particular interest within the temperature range over which they have been investigated (0—100°); in neither case is there any report of a hydrate, and the solubility is sufficiently small to make the temperature of the eutectic point approximate closely to that of pure water. At high temperatures, there is considerable hydrolysis, however, and the two-component systems lead chloride–water and lead iodide–water become special cases of the three-component systems lead oxide–water–hydrochloric or hydriodic acid, the solubility curves really representing the locus of the isothermal invariant points where lead hydroxide or a basic salt exists as a solid phase beside the normal salt.

The binary system lead iodide–lead chloride was investigated by Mönkemayer (*Neues Jahrbuch für Mineralogie*, Beilageband, 1906, **22**, 1) who concluded that it belonged to Roozeboom's Type V of mixed crystals (Roozeboom, *Z. physikal. Chem.*, 1899, **30**, 403). The evidence upon which he based this conclusion appears to be insufficient; he observed the rate of cooling of fused mixtures of the two salts, and by plotting the time of the eutectic halt against composition, and extrapolating to zero eutectic halt, he obtained values for the limiting compositions of the mixed crystals. On re-plotting the figures given by Mönkemayer and extrapolating as described, the limiting compositions appear to be 100% $PbCl_2$ and 100% PbI_2, respectively. There is no other evidence in the paper of the formation of mixed crystals, nor is any compound formed at these temperatures. It is therefore very doubtful whether the relations are not those of the simplest possible two-component system—two melting-point curves meeting in a eutectic point at 306°.

EXPERIMENTAL.

All results were obtained by the analysis of solutions and solids which had been allowed to attain equilibrium in a thermostat, the analysis normally comprising a volumetric estimation of total halides by Volhard's method and an independent estimation of iodide by another method. Since in all cases the concentration of chloride was high compared with that of iodide, the errors in determining the former by difference are not appreciably greater than if the chloride had been directly determined.

Determination of Iodide.—The determination of the iodide in presence of a large excess of chloride offered considerable difficulty, especially as the concentration of lead iodide never exceeded 0·09 g. per 100 c.c. of solution (corresponding to less than 0·05 g. of iodine per 100 c.c.).

Of the many methods tried and abandoned, two only are of interest. The first depends upon the statement of Pisani (Fresenius, "Quantitative Analysis," Sixth Ed., 444) that if silver nitrate solution be run into a solution containing mixed iodides and chlorides to which have been added a few c.c. of starch iodide solution of known silver value, the metallic iodide is first precipitated, and next the iodine from the starch iodide, thus giving an end-point before the chlorides begin to be precipitated. On trial with very dilute solutions, using the equivalent of 0·05 c.c. of $N/10$-solution of iodide for each titration and $N/1000$-silver nitrate, it was found that this statement is correct, provided that the chloride concentration is not much greater than that of the iodide. In the presence of a large excess of chloride, however, the end-point was delayed, the quantity of silver nitrate required increasing by about 40% as the chloride concentration was increased up to about 100 times that of the iodide. For analysis of the solutions in the present work, this method was therefore valueless, but it was found convenient for the analysis of the solids, of which only small amounts were available. Trustworthy results were obtained, provided that (*a*) the normality of the chloride was not more than double that of the iodide, (*b*) the total volume of the solution being titrated was kept constant in all cases, and (*c*) the silver nitrate solution was standardised against an iodide solution of known concentration under operating conditions.

The second method that proved unsuccessful in its original form is due to Benedict and Snell (*J. Amer. Chem. Soc.*, 1903, **25**, 1139); in this method, the iodine is liberated by iodate and acetic or nitric acid, and extracted with carbon disulphide. The resulting pink solution is washed and titrated with thiosulphate. Three difficulties, all due to the extreme smallness of the amount of iodide to be measured, were encountered:

(*a*) The acetic acid available (ordinary laboratory reagent) appeared to re-absorb, by some secondary reaction, the iodine at first liberated, so that the results obtained depended on the length of time that elapsed between the liberation and the final extraction, and were invariably low, although not by a constant amount. Nitric acid of ordinary purity was free from this objection, and was consequently used for further experiments.

(*b*) The carbon disulphide used reacted with iodine slowly, the titration value of the solution falling to about one-half in 15 hours, but carbon tetrachloride proved to be satisfactory and was used throughout.

(*c*) The very dilute solution (approx. 0·005*N*) of thiosulphate used gave erratic variations of the order of 20% in the titrations. Every attempt to eliminate this source of error failed completely, and solutions of arsenious oxide gave rise to similar variations.

Finally, a colorimetric method, based on the method of Benedict and Snell, was adopted : Ten c.c. of the solution to be examined were diluted with a little water to prevent crystallisation, and the lead was precipitated as sulphate and filtered off. Filtrate and washings were made up to 300 c.c. in a separating funnel. A known volume of a standard lead iodide solution was made up to the same volume in a second funnel. The iodine was then liberated in both funnels by the addition of potassium iodate and nitric acid, extracted with carbon tetrachloride, and the two resulting solutions were made up to the same volume in small standard flasks. These solutions were then matched in a Dubosc colorimeter, illuminated preferably by daylight. From the colorimeter readings and the known concentration of one solution, that of the other could readily be calculated. This method was found to be accurate to within 2%, even in estimating no more than 0·5 mg. of iodine.

Results.

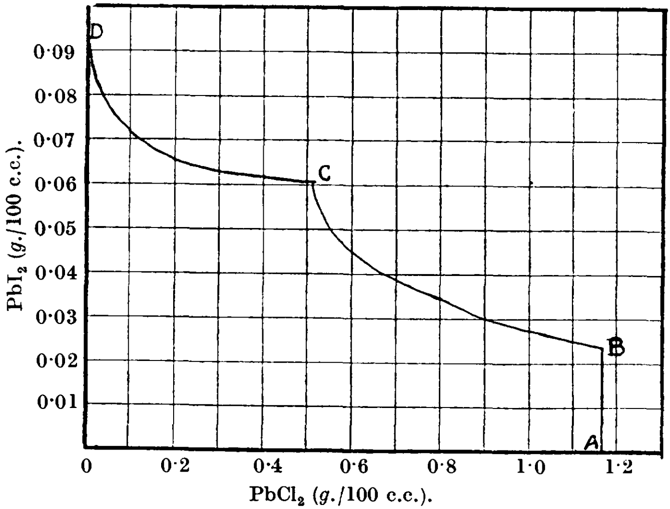
Table I and Fig. 1 summarise the results obtained at 30°. The letters in the first column of the table refer to the corresponding points in the diagram. The points B and C are isothermal invariant points. The continuity of the curve BC is evidence of the existence of only one solid over this range of concentrations. Analysis of the solid obtained from solutions represented by the curve BC was attempted, but the quantity obtained was so small as to preclude accuracy.

In order to obtain larger quantities of this solid, the necessary quantities of lead iodide and lead chloride were boiled with water until they dissolved, and the solution was allowed to come to equilibrium in the thermostat. A sample of the solution was then withdrawn and analysed for total halides in order to determine with sufficient accuracy the point on the curve to which the solution

TABLE I.

	Solution.		
	PbI_2 (g./100 c.c.).	$PbCl_2$ (g./100 c.c.).	Solid phase.
A.	—	1·171	$PbCl_2$
	0·0081	1·171	,,
	0·0120	1·171	,,
	0·0168	1·171	,,
B.	0·0235	1·171	$PbCl_2$ & PbICl
	0·0241	1·140	PbICl
	0·0277	0·969	,,
	0·0278	0·958	,,
	0·0334	0·820	,,
	0·0390	0·717	,,
	0·0421	0·631	,,
	0·0432	0·631	,,
	0·0520	0·550	PbICl
	0·0531	0·545	,,
C.	0·0602	0·518	PbICl & PbI_2
	0·0606	0·417	PbI_2
	0·0620	0·352	,,
	0·0630	0·270	,,
	0·0647	0·209	,,
	0·0687	0·144	,,
	0·0712	0·100	,,
	0·0788	0·046	,,
D.	0·091	—	,,

FIG. 1.



System $PbCl_2$–PbI_2–H_2O.

corresponded. Larger amounts of solid, often as much as 0·5 g., were thus obtained. These solids were analysed, after drying, by Volhard's method for total halides, and by Pisani's method (see above) for iodide. As a check, chlorides were estimated again after liberating and boiling off the iodine. No attempt was made to estimate lead in the solid, since the boiling involved in its preparation caused a small amount of basic salt to be formed. The results are summarised in Table II, and it is seen that the solid in equilibrium with solutions having the concentrations expressed by the curve BC is PbICl. No other compounds are formed at this temperature.

TABLE II.

Solution.		Solid.		
$PbCl_2$ (g./100 c.c.).	PbI_2 (g./100 c.c.).	$PbCl_2$ (equivs./100 g.).	PbI_2 (equivs./100 g.).	Ratio $PbI_2 : PbCl_2$.
0·86	0·032	0·271	0·265	0·978
0·765	0·036	0·268	0·269	1·004
0·67	0·041	0·270	0·271	1·004
0·56	0·051	0·269	0·268	0·996

A line drawn from the origin of Fig. 1 through the points corresponding to solutions containing lead iodide and chloride in equimolecular quantities does not cut the solubility curve, BC, of lead chloroiodide, but the curve CD. In accordance with this, it is found that the double salt is decomposed by water at the temperature of the isotherm.

An attempt was made to determine the isotherm for 70°, but hydrolysis was so considerable that the work was abandoned.

Summary.

The isotherm for 30° in the system lead chloride–lead iodide–water has been completely investigated. Three solubility curves have been found, corresponding to the two salts and to the binary compound PbICl. This salt has been shown to be decomposed by water, and the composition of solutions with which it can remain in equilibrium has been determined.

Methods have been developed by which small amounts of iodide can be estimated in presence of chloride.

The author's thanks are due to Professor F. G. Donnan for his kindly interest in the work, and to the late Miss K. A. Burke for many valuable suggestions in connexion with methods of analysis.

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[*Received, April 7th,* 1927.]