[CONTRIBUTION FROM THE WALKER LABORATORY OF RENSSELAER POLYTECHNIC INSTITUTE]

The Ternary System KI–PbI_2–H_2O at 0 and 25°[1]

BY HENRY S. VAN KLOOSTER AND PAUL A. BALON

The purpose of this investigation was to study the phase equilibria of the ternary system KI–PbI_2–H_2O. This system has been investigated at 13 and 50° by Demassieux[2] and at 25° by Burrage.[3]

Apparatus and Material.—The solubility apparatus was similar to that used by Goldschmidt.[4] The solution of one salt was put into the solubility vessel in contact with an excess of the other salt and the container was then placed in a thermostat. The contents were stirred for three hours by a Witt stirrer. At the end of this time part of the liquid was run into the weighing flask and analyzed. The method employed consisted of varying, in turn, the concentration of each of the component salts from zero to saturation in the presence of the other.

EXPERIMENTAL RESULTS

	0°		25°	
Solid phase	G. PbI_2 in 100 g. soln.	G. KI in 100 g. soln.	G. PbI_2 in 100 g. soln.	G. KI in 100 g. soln.
PbI_2	0.043	...	0.075	...
PbI_2	.003	0.166	.010	0.159
PbI_2	.001	2.21	.001	.645
PbI_2	.002	4.55	.020	9.97
PbI_2	.012	7.26	.033	12.52
PbI_2	.030	10.35	.256	19.58
PbI_2			.408	21.03
PbI_2			.410	21.09
PbI_2			.413	21.26
$PbI_2 + KPbI_3 \cdot 2H_2O$	.037E_1	11.42	.422E_2	21.29
$KPbI_3 \cdot 2H_2O$	.044	15.26	.461	22.56
$KPbI_3 \cdot 2H_2O$	.074	19.60	.808	30.77
$KPbI_3 \cdot 2H_2O$	.146	25.56	1.166	32.98
$KPbI_3 \cdot 2H_2O$	.263	29.72	1.537	38.38
$KPbI_3 \cdot 2H_2O$	.445	35.20	2.348	43.48
$KPbI_3 \cdot 2H_2O$	.724	40.56	4.491	51.42
$KPbI_3 \cdot 2H_2O$	1.300	46.20	5.011	53.07
$KPbI_3 \cdot 2H_2O$	2.410	53.10	5.901	55.75
$KPbI_3 \cdot 2H_2O + KI$	3.110E_3	55.10	7.30E_4	56.60
KI	2.00	55.28	5.22	57.75
KI	1.23	55.65	3.663	58.40
KI	...	56.07	2.267	58.53
KI			...	59.77

COMPOSITION OF SOLID PHASE

Solution	0.445	35.2	0.81	30.77
Wet residue	38.48	29.81	39.25	27.61
Solution	2.41	53.1	2.35	43.48
Wet residue	49.50	33.51	36.50	34.10

The composition of the solid phase was determined by the method of wet residues.[5] Part of the solid phase, together with the adhering mother liquor, was removed from the vessel, weighed and analyzed. As in the case of the solutions, the iodine was determined as silver iodide, the lead as lead sulfate, while the potassium was determined by difference.

The 25° temperature was maintained in the thermostat by means of a knife type immersion heater, mercury thermoregulator, relay and mechanical stirrer. The 0° temperature was maintained by a constant temperature bath using melting ice. The ice was finely shaved, and too much liquid was not allowed to collect. The ice and water were stirred by the mechanical stirrer. At both temperatures there was no variation greater than ±0.1°.

Both the lead iodide and the potassium iodide (Eimer and Amend) were recrystallized twice from pure water.

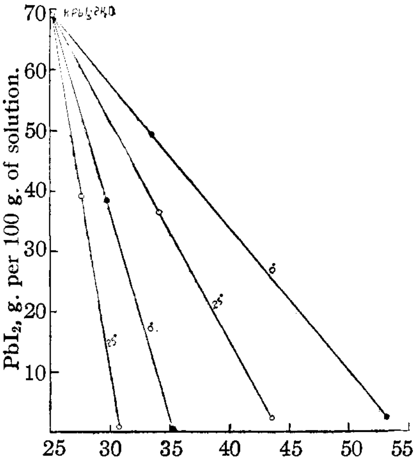

Fig. 1.

Discussion of Results

The data are plotted, for the sake of clearness, on rectangular coördinates as grams of salt in 100 g. of solution. From the results obtained as plotted in Fig. 1, it is seen that the solid phase

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(1) A thesis presented by Paul A. Balon in partial fulfilment of the requirements for the degree of Master of Science in the Graduate School of Arts and Science of Rensselaer Polytechnic Institute.

(2) N. Demassieux, *Compt. rend.*, **177**, 51 (1923).

(3) L. J. Burrage, *J. Chem. Soc.*, **129**, 1703 (1926).

(4) H. Goldschmidt, *Z. physik. Chem.*, **17**, 153 (1895).

(5) Schreinemakers, *ibid.*, **11**, 76 (1893).

separating out at 25 and at 0° is the hydrate $KPbI_3 \cdot 2H_2O$ (the lines meet at PbI_2 = 69 g., KI = 25.5 g. and H_2O = 5.5 g. The ratio of PbI_2 : KI : H_2O = 1:1:2). Only one double salt, formed from an incongruently saturated solution, exists. This is in agreement with the work of Herty,[6] Burrage and Demassieux.

The time allowed for equilibrium to be reached was considered to be sufficient, for the results obtained at 25° are in fair agreement with those of Burrage,[3] who allowed more than forty-eight hours for the equilibrium to be reached.

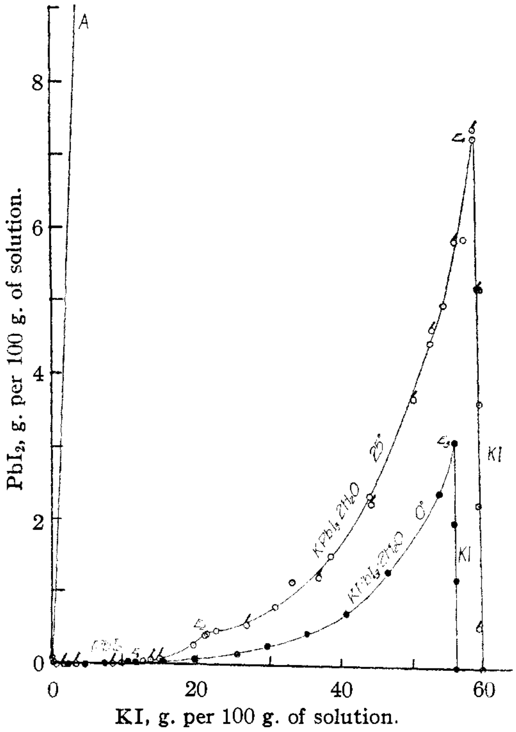

Fig. 2.—♂, 25° (Burrage's) isotherm; ○, 25° isotherm; ●, 0° isotherm.

In Fig. 2 we have the 0 and 25° isotherms while in Fig. 3 on an enlarged scale are found the solubility data for very small concentrations of potassium iodide and lead iodide. The points E_1 and E_2 indicate saturation with respect to lead iodide and double salt; while E_3 and E_4 indicate saturation with respect to double salt and potassium iodide. The line OA in Fig. 2 represents the ratio of 1 PbI_2 to 1 KI.

The precipitation of lead iodide by the addition of potassium iodide or lead nitrate to a saturated solution of lead iodide has often been used as a lecture example of the law of mass action. The addition of large amounts of potassium iodide to a saturated solution of lead iodide produces different effects as follows from the shape of the isotherms at 25 and 0° shown in Fig. 2.

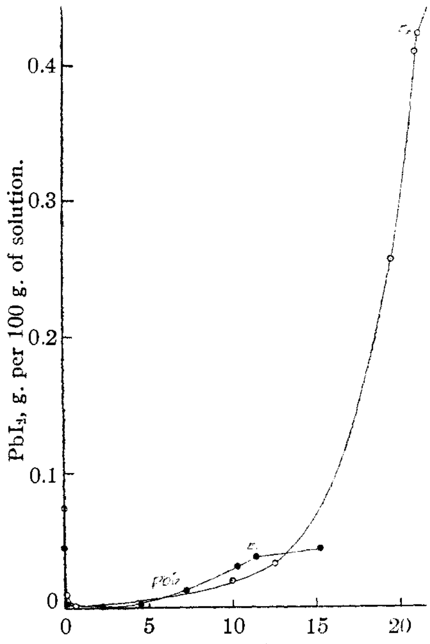

Fig. 3.—○, 25° isotherm; ●, 0° isotherm.

To 85 g. of lead iodide solution saturated at 25°, solid potassium iodide was added. Lead iodide was precipitated but when 15 g. of potassium iodide had been added, all the precipitated lead iodide redissolved, and when still more potassium iodide was added an unsaturated solution resulted. Finally on further addition of potassium iodide, a solution saturated with respect to potassium iodide was formed.

Summary

The equilibria at 0 and 25° in the system KI–PbI_2–H_2O have been investigated over the whole range of concentration. At both temperatures only one double salt exists, $KPbI_3 \cdot 2H_2O$.

TROY, N. Y.

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[6] C. H. Herty, *Am. Chem. J.*, **14**, 107 (1892).