Summary

A report is given of a study of the variation with temperature, between 0 and 50°, of the dielectric constant of ethanol–diethyl ether and urea–water solutions as determined by a resonance method at wave lengths between 3.6 and 20 meters. The results are compared with data of previous investigators, and, in the case of the urea–water solutions, are applied to studies of Lange and Robinson on heats of dilution.

CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 13, 1933
PUBLISHED OCTOBER 6, 1933

[CONTRIBUTION FROM THE WALKER LABORATORY OF RENSSELAER POLYTECHNIC INSTITUTE]

The Binary System Lead Iodide–Potassium Iodide[1]

BY HENRY S. VAN KLOOSTER AND EDWIN I. STEARNS

The melting point of lead iodide has been reported at such variant temperatures as 358[2] and 412°.[3] The melting point of potassium iodide has been given as low as 634° (1878)[4] and as high as 723°.[5] Many workers have confirmed the fact that only the double salt $KPbI_3 \cdot 2H_2O$ exists in the ternary system PbI_2–KI–H_2O,[6,7] but the anhydrous binary system has not heretofore been examined.

C. H. Herty[8] has driven off the water from this hydrate, $KPbI_3 \cdot 2H_2O$, and states that at 310° the salt decomposes with the liberation of iodine. It was therefore the purpose of this work to find the melting points of these two iodides and to decide what anhydrous double salts they form by determining the phase diagram by means of cooling curves.

The difficulty in melting lead iodide is that it decomposes in the presence of air. Several oxyiodides have been reported[9] but they have not been examined in the light of the phase rule and are thus to be considered on probation.

Apparatus and Materials.—The tube used to melt the various mixtures consisted, as illustrated in Fig. 1, of an outer test-tube and an inner air-excluding and thermocouple-protecting tube. This inner tube excluded the air by three factors. Its volume expelled nearly all the air to begin with, and further access of air was hindered both by the snugness with which the two tubes fit together and by the bulge of the inner tube resting upon the rim of the outer. The amount of decomposition could be seen by the iodine

(1) A thesis presented 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) F. Matthes and K. Monkemeyer, *Neues Jahrb. B. B.*, **22**, i (1906).

(3) German and Metz, *J. Phys. Chem.*, **35**, 1944 (1931).

(4) "Phys.-Chem. Tabellen," Landolt und Börnstein, 1894.

(5) J. McCrae, *Wied. Ann.*, **55**, 95 (1895).

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

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

(8) Herty, *Amer. Chem. J.*, **18**, 292 (1896).

(9) Mellor, "Treatise," Vol. VII, p. 766.

that condensed on the upper part of the tube which protruded from the furnace. A cooling curve taken when nitrogen filled the space between the inner and outer tubes, in which case no decomposition occurred, could not be distinguished from a cooling curve taken with the inner tube as the sole protection, in which case a small ring of iodine was formed.

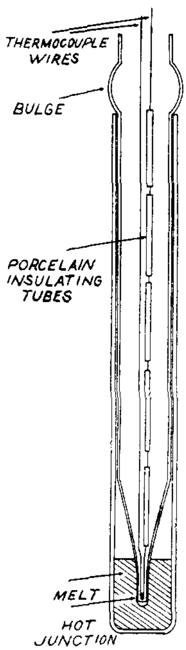

Fig. 1.

The thermocouple was of nichrome and alumel and the cold junction was kept at 20°. It was carefully calibrated with pure cadmium, lead, zinc and antimony. The calibration curve was very nearly a straight line and was extended as a straight line to beyond the melting point of potassium iodide.

An electric furnace was the source of heat and the e. m. f. was read with a millivolt meter made by Chas. Engelhard.

The lead iodide used in determining the equilibrium diagram was commercial lead iodide. Its purity is indicated by its cooling curve which has a long and strong horizontal and by the fact that its melting point, 412°, coincides with the melting point of C. P. lead iodide. The C. P. lead iodide was made by the admixture of solutions of C. P. lead nitrate (J. T. Baker Co.) and C. P. potassium iodide (J. T. Baker Co.) in the correct molar proportions. The precipitated lead iodide was washed by decantation ten times until a saturated ferrous sulfate solution placed above a 1 to 1 mixture of wash water and sulfuric acid no longer showed a brown color. It was then decanted five times more, placed on a filter, and washed ten times, allowing the previous water to drain off completely before adding more. It was then dried in an oven at 115° for two hours, pulverized, and further dried at 115° for three hours.

The potassium iodide was of U. S. P. quality (Eimer and Amend) and was crystallized twice from pure water. It was then dried for six hours at 115°.

EXPERIMENTAL RESULTS

Mole % PbI_2	Primary crystallization, °C.	Eutectic, °C.	Mole % PbI_2	Primary crystallization, °C.	Eutectic, °C.	Mole % PbI_2	Primary crystallization, °C.	Eutectic, °C.
100	412	...	65	330	321	30	504	346
95	404	321	60	337	321	25	548	346
90	395	321	55	345	321	20	585	346
85	383	321	50	349	...	15	609	347
80	367	321	47.5	...	346	10	641	...
75	349	321	45	378	346	5	660	...
70	324	321	40	422	346	0	686	...
69	...	321	35	475	346			

Discussion of Results.—The phase diagram (Fig. 2) is a common type in which the two components form a congruently melting compound. It shows definitely that the compound $KPbI_3$ is the only anhydrous double salt formed. The melting point found for lead iodide, 412 ± 1°, is in exact agreement with the work of German and Metz previously referred to. It is thus recommended that this value be accepted as the true melting point. The melting point of potassium iodide, 686 ± 1°, is reasonably close to the value 684° given by Rassow[10] but does not check exactly with any given in the literature. The 346° eutectic composition is exceptionally close to the compound composition, but this is to be expected from the great difference in the melting points of $KPbI_3$ and KI.

The method of locating eutectic composition by plotting the eutectic halts against the composition of the melts and choosing the maximum was only approximate here, because unequal weights of samples were used and unequal rates of cooling prevailed. However, the eutectic compositions could be quite satisfactorily found by the intersection of the lines drawn through the points of primary crystallization.

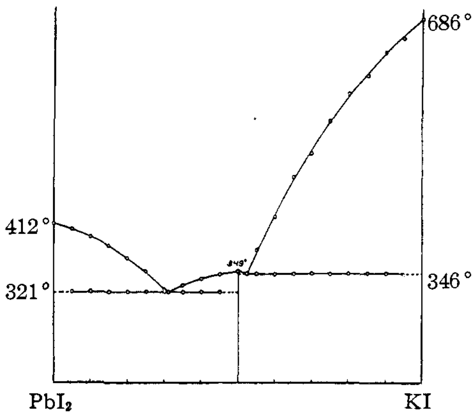

Fig. 2.—Phase diagram of PbI_2–KI.

Summary

The phase diagram of the binary system PbI_2–KI has been determined. Significant points are the three melting points, PbI_2 at 412°, $KPbI_3$ at 349°, KI at 686° and two eutectics, 69 mole % PbI_2 at 321°, and $47^1/_2$ mole % PbI_2 at 346°.

TROY, NEW YORK

RECEIVED JULY 15, 1933
PUBLISHED OCTOBER 6, 1933

(10) Rassow, *Z. anorg. allgem. Chem.*, **114**, 117 (1920).