

SHORT COMMUNICATIONS

THE PHASE DIAGRAM OF THE SYSTEM AgCl-PbCl_2 *

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In the course of investigations of thermodynamic properties of molten salt mixtures, the solid-liquid equilibrium diagram of the system AgCl-PbCl_2 has been redetermined. The published phase diagrams for this system¹⁻³ indicated that AgCl-PbCl_2 mixtures form a simple eutectic system.

However, the need for a reinvestigation of this system is clearly shown by the disparity in the reported eutectic points. The eutectic compositions reported have ranged from 39 mole % PbCl_2 ¹ to 40.5 mole % PbCl_2 ² while their melting temperatures have varied between 291°¹ and 314°.³

In this investigation, a differential thermal analysis technique was used to determine the temperatures which define phase changes in the mixtures.

Experimental

A sheathed Pt/Pt-10% Rh thermocouple was sealed into each of the Pyrex sample cells so that the thermocouple junction was always maintained in intimate contact with the melt. These sample cells were sealed under vacuum after charging with the calculated aliquot of salt mixture. The mixtures used in these phase equilibrium studies were prepared from the dried pure components, each of which had an analysed purity of not less than 99.9%. For both AgCl and PbCl_2 the major impurities were traces of alkali metal chlorides but there was insufficient to detect any depression of melting point of the pure components. Mixtures were synthesized by accurately weighing the pure component and their compositions checked by chemical analysis. During all handling operations, exposure to light was minimized to prevent surface decomposition of the AgCl . The samples were heated in the uniform temperature zone of a Nichrome resistance furnace. The furnace power controls were programmed for uniform heating and cooling rates of 2°/min. Phase changes were detected from inflections in the T° against ΔT° plot recorded on an X-Y recording potentiometer. The ΔT° signal was amplified to read 0.05 mV/in. on the chart paper while the output of the T° signal was equivalent to 0.1 mV/in.

Each thermocouple used was accurately calibrated both before and after use, as were the measuring instruments. The combined errors due to thermocouple calibration and instrumentation were $\pm 0.5^\circ$. Likewise, for a given sample, the reproducibility of inflexion points determined from differential thermal analysis cooling curves was found to be better than $\pm 0.5^\circ$. Each sample of the mixture was subjected to at least five heating and cooling cycles to minimize errors. During the cooling cycle, the samples holder was subjected to continuous (but slight) mechanical vibrational shock. This was found to eliminate supercooling which occasionally occurred in static samples rich in lead chloride.

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¹ Pélabon, H., and Laude, M., *Bull. Soc. Chim. Fr.*, 1929, **45**, 489.

² Treis, K., *Jb. Min. (Beil.-Bd)*, 1914, **37**, 766.

³ Tubant, C., and Eggert, S., *Z. anorg. allg. Chem.*, 1920, **110**, 196.

Results and Discussion

The liquid-solid equilibrium diagram constructed from the experimental results is presented in Figure 1. The generally accepted liquidus curve as reported by Treis² is illustrated also as a comparison of the two sets of data. From this figure it can be seen that there is considerable difference in the liquidus curves for the two sets of data on the lead chloride side of the diagram. The discrepancies are outside the limits of experimental error of the curve determined in this investigation.

The solidus curve for this diagram is incomplete outside the mixture limits investigated. Since Wagner and Ziemens⁴ have shown that 0.63 mole % PbCl_2 is soluble in solid silver chloride at 270° , this must also be represented to completely define the phase equilibrium.

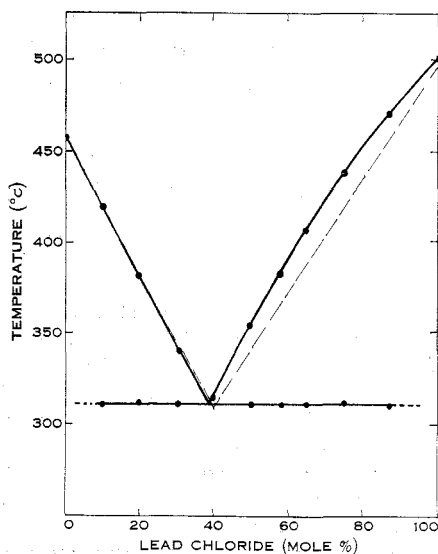


Fig. 1.—Solid-liquid equilibrium diagram for the system AgCl-PbCl_2 . The broken line indicates Treis's results.

From these results the eutectic composition (38.5 mole % PbCl_2) melts at 311.5° . This may be compared with a eutectic of 40 mole % PbCl_2 melting at 314° as reported by Tubandt and Eggert, 40.5 mole % PbCl_2 melting at 310° as reported by Treis, and 39 mole % PbCl_2 melting at 291° as quoted by Pélabon and Laude. Silver chloride was found to melt at 455° while the measured melting point of lead chloride was 500° . During the last 10 years published values for these components have varied between 452° ⁵ and 456° ⁶ for silver chloride and 496° ⁷ and 501° ⁸ for lead chloride. Therefore within experimental accuracy the results obtained for the pure components in this work are in agreement with the most acceptable published data.

⁴ Wagner, C., and Ziemens, K., *Acta Chem. Scand.*, 1947, **1**, 539.

⁵ Lifshits, G. M., *Zh. Obshch. Khim.*, 1955, **25**, 2414.

⁶ Palkin, A. P., and Shehirova, N. A., *Zh. Neorg. Khim.*, 1956, **1**, 2155.

⁷ Il'yasov, I. I., Bostandzhian, A. K., and Bergman, A. G., *Zh. Neorg. Khim.*, 1956, **1**, 2543.

⁸ Palkin, A. P., and Redchenko, V. T., *Zh. Neorg. Khim.*, 1956, **1**, 133.

The liquidus curve determined in this investigation was, for the corresponding composition, up to 15° higher than that previously published. This large discrepancy might be due to impurities of components and supercooling in the earlier work. The former^{1,2} is indicated from the published melting points of pure components (PbCl_2 , 496°), while it was found in this work that precautions had to be taken to prevent supercooling.

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