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The Solution of Alkaline Earth Metals in Their Molten Halides

I. On the Phase Diagram of the System Barium-Barium Chloride

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Phase relationships in the system barium-barium chloride have been remeasured in the region from 0 to 15 mole percent of metal additions to the salt.

Special attention has been given to the solidus curve of the system. A maximum solubility of 2 mole percent barium metal in the solid salt has been found. The results are compared with previous work on this system. It is pointed out that the data seem to confirm the presence of only one foreign particle in the melt for each barium atom added.

There is still considerable doubt about the nature of solutions of alkaline earth metals in molten alkaline earth halides.[1-3] An analysis of the melting point depression of the salt by additions of metal is one way of learning more about these systems. This method was in 1954 applied to the comparable system of cadmium in cadmium chloride by the authors,[4] and the study has now been extended to the barium-barium chloride system.

Essentially the melting point depression may be used to estimate the number of foreign particles associated with each metal atom added to the melt. This approach obviously requires reliable phase diagram data. Phase diagrams for the system barium-barium chloride have appeared in the literature twice previously.[5,6] A new phase diagram study has also been announced by Bredig and collaborators.[3] Moreover the monotectic temperature and composition (at about 15 mole% Ba) have been reported separately in two other papers.[7,8] The two published diagrams are somewhat conflicting and no accurate data for the solubility of barium in the crystalline barium chloride is presented in these papers. A reinvestigation of the system was therefore undertaken.[9]

EXPERIMENTAL

Pro analysi barium chloride dihydrate from E. Merck, AG Darmstadt, was dehydrated by the following procedure: The salt was dried in a furnace for 2 to 3 days at 200°C. Then the furnace was evacuated to a total end pressure between 1 and 5 mm Hg and the temperature subsequently raised to 400°C for 24 h. At the end of this period, purified argon gas was let in to the furnace and the sample melted. The operation was performed in molybdenum crucibles. Molybdenum appears to resist very well chemical attack by the salt and by mixtures of the salt with barium metal. The salt would thus not have to be transferred to another crucible for the subsequent preparation of the mixtures with barium.

The barium metal was delivered by Dr. T. Schuckart, GmbH, München, and guaranteed to contain no more than 0.05 mole % of contaminations. The melting point of this metal was determined to be 726°C (as compared with 729°C for barium metal purified by vacuum distillation[6]). The metal pieces were handled (cut and weighed) in a glovebox containing an inert atmosphere of purified argon. Prior to use they were kept immersed in dry toluene. The pieces thus had a thin protective coating of toluene during the brief (15 sec) exposures to the atmosphere, when transferred from the storage to the furnace.

All measurements were performed in an argon atmosphere. The argon gas obtained from Norsk Hydro, was labelled as spectroscopically pure. It was further purified by passing through a tube with metallic copper at 500°C and a dehydrite tower.

The furnace used in the present investigations was of a standard type designed by Motzfeldt.[10] The furnace has a working region of 10 cm length, within which the temperature was found to vary with position no more than 1°C. It could be evacuated down to 1 mm Hg in less than 10 sec.

The temperature was measured with a calibrated Pt/Pt10Rh thermoelement (protected from the melt by a molybdenum tube), and a precision potentiometer, (W.C. Pye and Co. Ltd., Cat. No. 790115). The liquidus curves were determined from holds in the cooling curves. Samples of 100 g were cooled at a rate of 0.8°C/min. Supercooling was prevented by stirring the melt. A tendency for supercooling could not be entirely eliminated, and is probably the most important source of errors in the result. The accuracy in the determination of the liquidus temperature is judged to be ± 0.5°C.

The solidus curve could not be determined from the cooling curves. Instead the following method was used: A 100 g sample of the pure salt was molten and then frozen to a compact mass in the bottom of a molybdenum crucible. Known amounts of barium metal was placed on the top of the salt phase and the system equilibrated about 20°C below the liquidus temperature given by the overall composition. A molten phase (of lower specific gravity than the solid phase) would form above the salt phase. By rapidly removing the crucible from the furnace, the molten phase could be poured off. The excess

Table 1. Monotectic temperature and composition in the system $BaCl_2-Ba$ as observed by various investigators.

	temp. °C	mole% Ba
Cubicciotti and Thurmond[4]	840	39
Schäfer and Niklas[5]	878	15
Peterson and Hinkebein[6]	890	15
Emons[7]	880	16
This investigation	884	14.8

Table 2. Observed liquidus temperatures, t_{liq}; transition temperatures, t_{tr}; monotectic temperatures, t_{mon}; solidus temperatures, t_{sol}; for different mole percentages of barium in barium chloride. Temperatures are given in degrees centigrade.

mole% Ba	t_{liq}	t_{tr}	t_{mon}	t_{sol}
0.00	961.5	925.9		
0.52				932.3
0.97				918.2
1.64				900.5
1.66				893.9
1.98				887.4
1.84				873.2
1.91	948.3			
2.89	941.2	926.3		
3.62	935.0	926.2		
4.07	931.5			
5.81	922.1			
6.88	918.5			
7.51	915.1			
8.57	910.4		884.6	
11.3	899.2		883.9	
13.1	891.1		884.0	
14.3	885.5			

of barium in the remaining solid was then determined by chemical analysis. Sections of the solidified salt close to the interface were discarded, and sections from other parts of the sample were then found to have a uniform metal concentration. No sign of any penetration of the metal-rich phase into possible cracks and crevices in the solid salt could be discerned. Equilibrium was established in less than 2 h, as shown by preliminary trials.

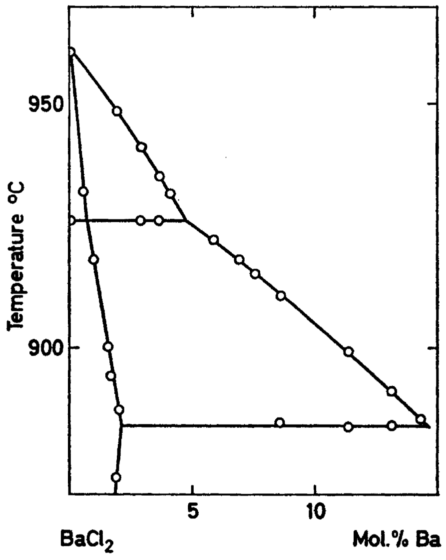

Fig. 1. The barium chloride side of the phase diagram $BaCl_2-Ba$.

RESULTS AND DISCUSSION

In Table 1 the experimental values for the monotectic point as observed by different investigators are given. In Table 2 the experimental values obtained in the present investigation are listed. Fig. 1 gives the remeasured part of the phase diagram. The liquidus curve presented here agrees roughly with the earlier work.[5,6] The solidus curve given by Schäfer and Niklas,[6] however, differs from the present results. Thus we found a maximum solid solubility of 2 mole percent barium in the chloride as compared with some 8 mole percent read off from the figure in the earlier paper. We observed no significant change in the transition temperature of barium chloride when the maximum 2 mole percent of barium in solid solution was introduced.

In a subsequent paper, a discussion of various physico-chemical measurements on the alkaline earth metal-alkaline earth metal chloride system will be given. The experimental results on the melting point depression will then be evaluated in a broader context. In anticipation of this discussion, it may be pointed out that the experimental melting point depression and the solid solubility observed by us are compatible with the formation of approximately one foreign particle for each barium atom added to the melt. This seemingly contradicts vapour pressure measurements by van Westenburg[11] who concluded that each dissolved alkaline earth atom produces two foreign particles. The result of van Westenburg, however, is based on the assumption that Henry's law is valid for the dissolved particles, which is not necessarily true.[9]

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