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$CsCl-CaCl_2$ phase diagram [a]

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Abstract

The $CsCl-CaCl_2$ phase diagram was investigated following differences in published reports. The diagram contains two eutectics at 8 mol.% $CaCl_2$ (881 K) and 85 mol.% $CaCl_2$ (983 K), two peritectics appearing at approximately 15 and 17 mol.% $CaCl_2$ (931 K and 954 K) and a congruently melting compound, $CaCsCl_3$ (1182 K).

INTRODUCTION

Chemical reactions carried out in molten salts are now well established for the pyrochemical recovery and recycle of actinide metals [1]. One of these processes is americium extraction in which plutonium chloride (diluted with an inert salt) oxidises americium in plutonium metal [2]

$$Am^0 + PuCl_3 \rightarrow AmCl_3 + Pu^0$$

and/or

$$Am^0 + (2/3)PuCl_3 \rightarrow AmCl_2 + (2/3)Pu^0$$

As an alternative route, the formation of Cs_2PuCl_6 and subsequent reaction with americium in a $CaCl_2 - CsCl$ molten salt medium has been considered [3]. To aid our knowledge of this process the phase diagram for $CaCl_2$–CsCl needs to be known with some degree of reliability. Previous studies of this binary system by different research groups [4–7] have indicated differences in the physical characteristics of the melt and the resulting phase diagram.

The $CsCl-CaCl_2$ binary phase diagram data obtained by Seifert and Langenback [4] (see Fig. 1) contains most detail on the temperature arrests established to date. They found two eutectics at 8.5 mol.% $CaCl_2$ (608 ° C) and 84.0 mol.% $CaCl_2$ (706 °C), two peritectics at 14.0 mol.% $CaCl_2$

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[a]

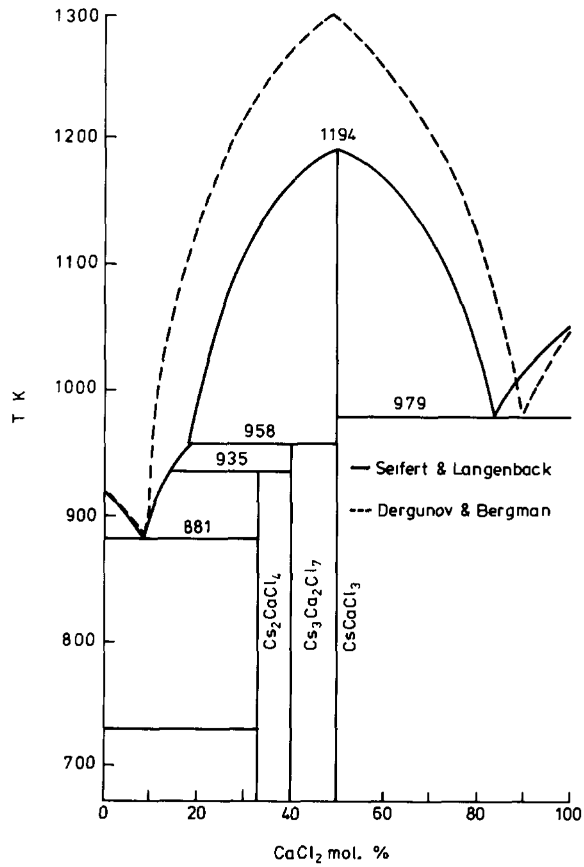

Fig. 1. The CsCl-$CaCl_2$ system.

(662 °C) and 18.5.% $CaCl_2$ (685 °C) and a congruently melting compound, $CsCaCl_3$ (921 °C).

However, not all these features were recorded by other researchers. Dergunov and Bergman [5] (see Fig. 1) reported two eutectics at 9 mol.% $CaCl_2$ (610 °C) and 91 mol.% $CaCl_2$ (708 °C), and a congruently melting compound, $CsCaCl_3$, at a higher liquidus temperature of 1030 °C but gave no indication of incongruently melting compound formation. Similarly, Plyushchev et al. [6] observed two eutectics at 11 mol.% $CaCl_2$ (612 °C) and 89 mol.% $CaCl_2$ (705 °C) and established that the chemical compound $CsCaCl_3$ melts without decomposition at 910 °C, but did not record any peritectics. In a thermochemical study of this system, Markov et al. [7] were able to determine the melting point of $CsCaCl_3$ as 934 °C and the two eutectic compositions of 12 mol.% $CaCl_2$ (608 °C) and 88.7 mol.% $CaCl_2$ (920 °C) but they did not investigate the peritectic compositions (Table 1). Because there is a lack of agreement between the published data, it was decided to re-examine the phase diagram.

EXPERIMENTAL

Materials

Ultra-dry calcium chloride and caesium chloride (both 99.999% pure) with melting points of 778 and 644 °C respectively were obtained from Johnson Matthey. These values were found to be in good agreement with the other workers (Table 1).

Cooling curve determination

A 10 g sample of the required composition of CsCl and $CaCl_2$ was weighed into a clean, dry silica test-tube in a nitrogen dry box. A chromel–alumel thermocouple, protected by a closed-end, recrystallised alumina tube, was inserted into the salt mixture.

The salt was melted in a resistance furnace controlled by a West MC 30 Mk. 2 furnace controller which allowed the salt to be held molten for a specified time and cooled at a predetermined rate. The furnace allowed the melt to cool at typically 3–4°C min^{-1} and the thermocouple output was recorded by a chart recorder. The thermocouples were calibrated against pure zinc metal (m.p. 420°C) and pure silver metal (m.p. 960°C), and corrections were found to be unnecessary for results quoted to the nearest degree. The samples were stirred while molten and during cooling to ensure complete mixing and to reduce supercooling effects.

RESULTS AND DISCUSSION

The cooling curve data from our study of this system are shown in Table 2 and the phase diagram is shown in Fig. 2. We found two eutectics, at 8 mol.% $CaCl_2$ (608°C) and 85 mol.% $CaCl_2$ (710°C), and two peritectics at approximately 15 and 17 mol.% $CaCl_2$ (658°C and 681°C). A maximum in

TABLE 1

Melting temperatures

Ref.	Temperature arrests observed (°C)						
	Eutectic	Peritectic (Cs_2CaCl_4)	Peritectic ($Cs_3Ca_2Cl_7$)	Compound ($CsCaCl_3$)	Eutectic	Melting point $CaCl_2$	Melting point CsCl
7	608	–	–	934	720	–	646
5	610	–	–	1030	708	772	647
6	612	–	–	910	705	772	646
4	608	662	685	921	706	778	646
This study	608	658	681	909	710	778	644

TABLE 2

Temperature arrests recorded on cooling $CaCl_2$–CsCl mixtures

Mol.% $CaCl_2$	Temperature arrests (°C)				
	1st	2nd	3rd	4th	5th
0	643	462			
5	620	601	442		
10	606				
15	651	604			
20	748	683	659	603	478
25	786	684	661	605	
30	814	681	658	601	473
33	827	685	661	604	450
40	891	681	656	600	478
45	909	678	656	601	
50	914				
55	915	690			
60	903	715			
65.6	870	708			
70	855	711			
75	812	713			
80	759	712			
84	712				
85	713				
90	725	713			
95	753	708			
100	778				

the liquidus temperature was observed at 50 mol.% $CaCl_2$ (909°C) indicating the formation of $CsCaCl_3$.

These values are compared with the previous determinations in Table 1 and show closer agreement to the data of Seifert and Langenback [4] than to the other studies [5–7]. Differential thermal analysis (DTA) and X-ray diffraction studies were undertaken to establish (a) the presence of suspected compounds formed in the course of melting known composition salts, and (b) the composition of compounds formed during melting of the constituent salts.

Of particular interest were the two peritectic compositions of 33 mol.% and 40 mol.% $CaCl_2$. The X-ray spectra for 33 mol.% $CaCl_2$ matched the reference data (JCPDS) for caesium calcium chloride ($CsCaCl_3$) and caesium chloride (CsCl), both of cubic structure. In addition, minor peaks were observed which matched the reference data for caesium calcium chlorides, Cs_2CaCl_4 and $Cs_3Ca_2Cl_7$, both tetragonal.

For the 40 mol.% $CaCl_2$ composition, the spectrum similarly matched the reference data for caesium chloride (CsCl), $Cs_3Ca_2Cl_7$, $CsCaCl_3$ and Cs_2CaCl_4. For the 50 mol.% $CaCl_2$ composition, only $CsCaCl_3$ was identi-

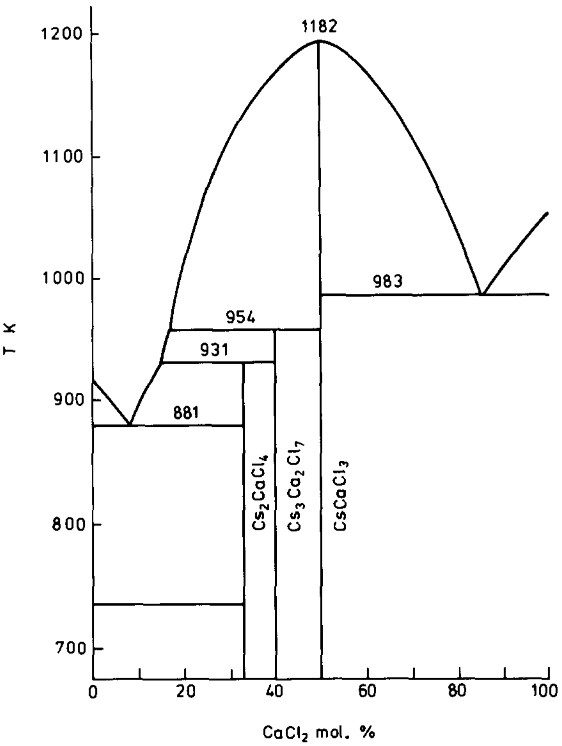

Fig. 2. The CsCl–$CaCl_2$ system (this study).

fied. All the X-ray investigations confirm the suspected compounds involved.

However, the presence of $CsCaCl_3$ and $Cs_3Ca_2Cl_7$ in the 33 mol.% $CaCl_2$ composition mixture, and $CsCaCl_3$ and Cs_2CaCl_4 in the 40 mol.% $CaCl_2$ composition mixture is a reflection of the non-equilibrium conditions which existed during operator-controlled cooling.

Further confirmation of these compounds was obtained by using DTA in the 12–18 mol.% $CaCl_2$ region of the composition range. Four endotherms were observed: 485.3°C, ±0.6%; 613.4°C, ±0.2%; 668.3°C, ±0.2%; and 692.4°C, ±0.3%. These investigations confirmed that the two peritectic compositions corresponded to Cs_2CaCl_4 and $Cs_3Ca_2Cl_7$ for 33 mol.% and 40 mol.% $CaCl_2$ respectively. $CsCaCl_3$ was also identified as the sole constituent in the 50 mol.% $CaCl_2$ salt mixture.

CONCLUSIONS

The CsCl–$CaCl_2$ phase diagram has been determined and confirms an earlier study of Seifert and Langenback in 1969. It contains two eutectics at 8 mol.% $CaCl_2$ (881 K) and 85 mol.% $CaCl_2$ (983 K), two peritectics at 15 and 17 mol.% $CaCl_2$ (931 K and 954 K), and the congruently melting compound $CsCaCl_3$ (1182 K).

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