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The $MgCl_2$–KCl–$CaCl_2$ phase diagram

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Abstract

The $MgCl_2$–KCl–$CaCl_2$ phase diagram has been determined using the method of thermal analysis. The liquidus system is a simple one with two eutectics at $MgCl_2$ (48 mol.%)–KCl (40 mol.%)–$CaCl_2$ (12 mol.%), m.p. 722 K; and $MgCl_2$ (35 mol.%)–KCl (63 mol.%)–$CaCl_2$ (2 mol.%), m.p. 700–725 K. There is a peritectic at $MgCl_2$ (47 mol.%)–KCl (35 mol.%)–$CaCl_2$ (18 mol.%), m.p. 725–750 K; the second peritectic near the compound K_2MgCl_4, was not found experimentally. There were no ternary compounds found and the diagram agrees very well with an earlier Russian determination.

INTRODUCTION

Phase diagram determinations are carried out to provide information on phase relationships at reaction compositions and temperatures. This study forms part of a programme of work investigating potential reaction media in pyro-chemical processes for the recovery and recycle of plutonium from metal residues.

Molten chloride systems are generally chosen for their thermal and radiation stability. The $MgCl_2$–KCl–$CaCl_2$ ternary phase diagram is of particular interest for potential application to the extraction of americium from plutonium metal

$$Am^0 + MgCl_2 \rightarrow AmCl_3 + Mg^0$$

and in plutonium electrorefining; it also has a general application in molten salt chemistry.

The only known previous determination of the $MgCl_2$–KCl–$CaCl_2$ ternary phase diagram was established by Ivanov in 1953 [1] (Fig. 1) from a very thorough study of the system.

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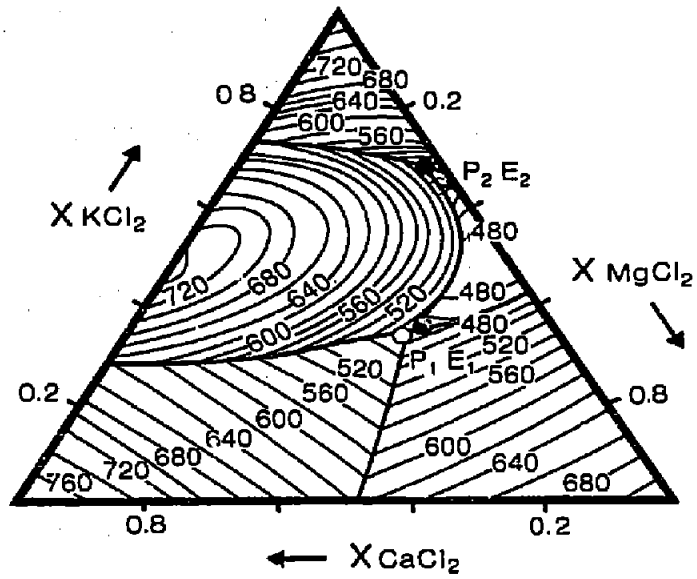

Fig. 1. Experimental $MgCl_2$–KCl–$CaCl_2$ phase diagram [1].

Phase diagrams of the binary systems

Liquidus points were not determined for the component binary systems; the values were taken from the literature phase diagrams.

The KCl–$CaCl_2$ phase diagram is well established and the liquidus points were taken from the Menge diagram [2] which has not been improved upon by later workers. The system has two eutectics at 26 mol.% (873 K) and

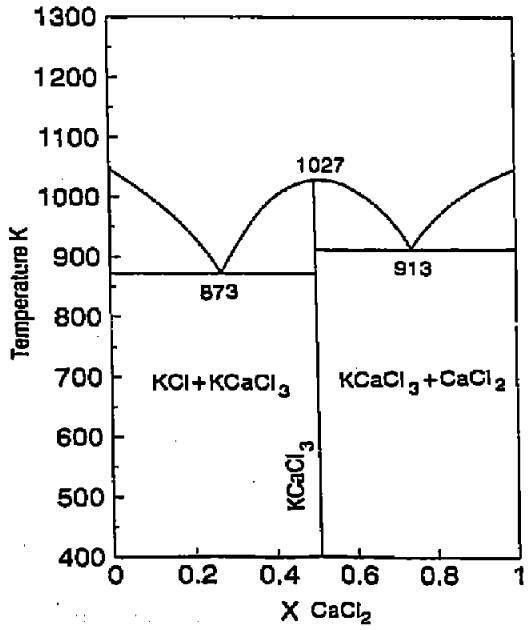

Fig. 2. KCl–$CaCl_2$ phase diagram [2].

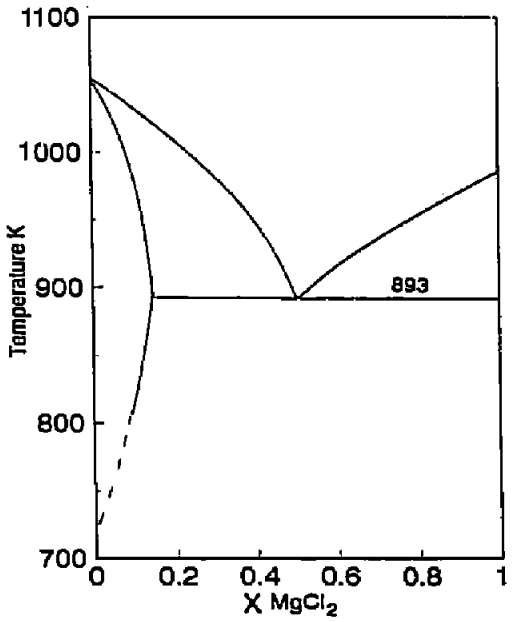

Fig. 3. $MgCl_2$–$CaCl_2$ phase diagram [3].

73 mol.% $CaCl_2$ (913 K) with a congruently melting compound $KCaCl_3$ (1027 K) (Fig. 2).

The $MgCl_2$–$CaCl_2$ phase diagram is also well established and liquidus points were taken from the diagram of Grjotheim et al. [3]. They found a simple eutectic at 53 mol.% $MgCl_2$ (893 K) and solid solubility in the $CaCl_2$-rich region (Fig. 3).

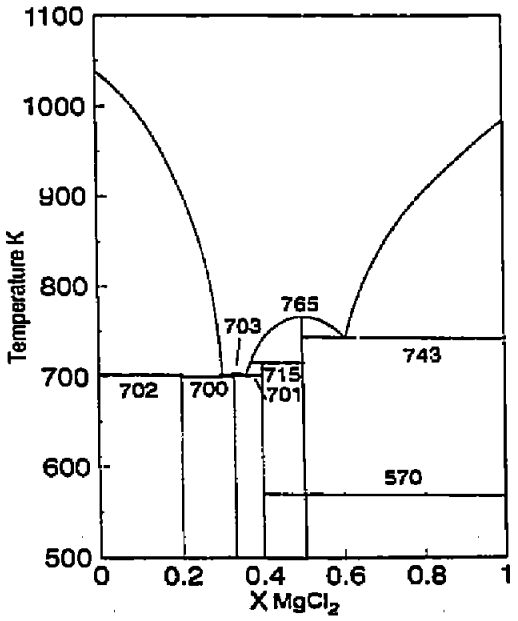

Fig. 4. $MgCl_2$–KCl phase diagram [4].

The $MgCl_2$–KCl system has been examined by several authors, with discrepancies over the existence of the compound K_2MgCl_4. The diagram of Seifert and Uebach [4] was used to provide liquidus points. They found three eutectics, two congruently melting compounds and two incongruently melting compounds, K_2MgCl_4 (703 K) and $KMgCl_3$ (765 K), K_4MgCl_6 (702 K) and $K_3Mg_2Cl_7$ (715 K) (Fig. 4). This phase diagram has also been redetermined by us [5] and although we found a system similar to that of Seifert and Uebach, the incongruent compound K_4MgCl_6 was not identified and, in addition, metastability was found in the composition range 40–50 mol.% $MgCl_2$ at 424°C.

EXPERIMENTAL

Materials

The potassium chloride was AnalaR grade from Merck (BDH). This was dried prior to use by heating until molten, holding for 1 h, and cooling under argon. This typically gave a water content of 0.07 (±0.02) wt.%, determined by Karl Fischer analysis.

The magnesium chloride used was Merck Technical Grade Anhydrous. This was dried prior to use by heating to 750°C in a silica tube in an argon atmosphere. Once the salt was molten, HCl was bubbled through the melt for 30 min before allowing it to cool under argon. This treatment is necessary to prevent the $MgCl_2$ from hydrolysing and forming the oxychloride. Karl Fischer analysis showed the product to contain 0.32 (±0.05) wt.% water.

The calcium chloride used was Ventron Ultrapure which was dried prior to use by heating to 400°C in an argon atmosphere; this contained 0.19 (±0.02) wt.% water.

The melting points by cooling curve were as follows: KCl, 768°C (cf. 722 ± 1°C [6]), $MgCl_2$, 704°C (cf. 714 ± 2°C [6]), $CaCl_2$, 767°C (cf. 782 ± 5°C [6]). These are low, possibly owing to the oxygen content of the compounds, but this is thought unlikely to affect the liquidus temperatures by more than a few degrees, particularly in the ternary system.

Methods

A free-standing furnace, designed [illegible] graphite holder, housed in a nitrogen dry [illegible] used for the cooling curve determinations.

The $MgCl_2$–KCl–$CaCl_2$ liquidus [illegible] ing thermal arrests on cooling of 90 different [illegible] the required compositions were weighed into dry silica [illegible] a dry box. Chromel–Alumel thermocouples, protected [illegible] recrystallised alumina tube, were inserted into [illegible] connected to an

analogue input interface board. The temperatures of the salts were monitored by a PC, using a data acquisition program. The furnace was controlled by a West 2050 furnace controller, which was programmed to heat to 830°C in 3 h, dwell for 30 min and cool at a rate of 1–2°C min^{-1}. The samples were stirred whilst molten to ensure mixing and to eliminate the possibility of supercooling. The phase changes occurring during the cooling of the molten salt produced temperature arrests which were detected visually on plotted traces of the cooling curves. The temperature arrest was read at the highest point on the plateau and quoted to the nearest 0.5°.

RESULTS AND DISCUSSION

Based upon the previously determined binary phase diagrams $CaCl_2$–KCl [2], $MgCl_2$–$CaCl_2$ [3], $MgCl_2$–KCl [4] and their eutectics and compound compositions, nine sets of ten different compositions were chosen to analyse. Figure 5 shows the nine lines along which the experimental points were measured, and where the eutectics and compounds lie.

The liquidus temperatures were then used to construct nine pseudo-binaries, one for each of the nine composition sets. From the pseudo-binaries, the ternary was constructed (Fig. 6) with liquidus lines drawn at 25 K intervals in the range 675–1075 K.

The $MgCl_2$–KCl–$CaCl_2$ is a simple ternary phase system with no ternary compounds present. The main features are the two eutectics (E_1 and E_2) and the peritectic (P_1) located in the 18 mol.% $CaCl_2$ region of the diagram. The boundary curves originate from the binary eutectic points and meet to form the ternary eutectics at 48:40:12 mol.% $MgCl_2$–KCl–$CaCl_2$ at 722 K,

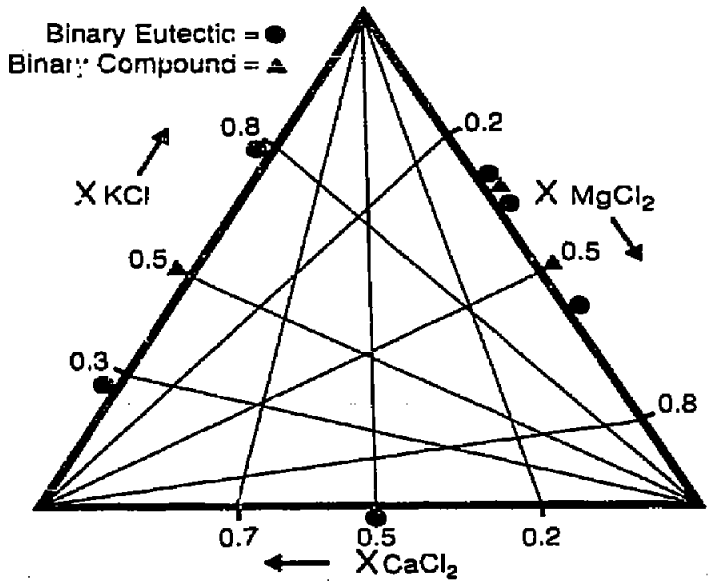

Fig. 5. Composition lines.

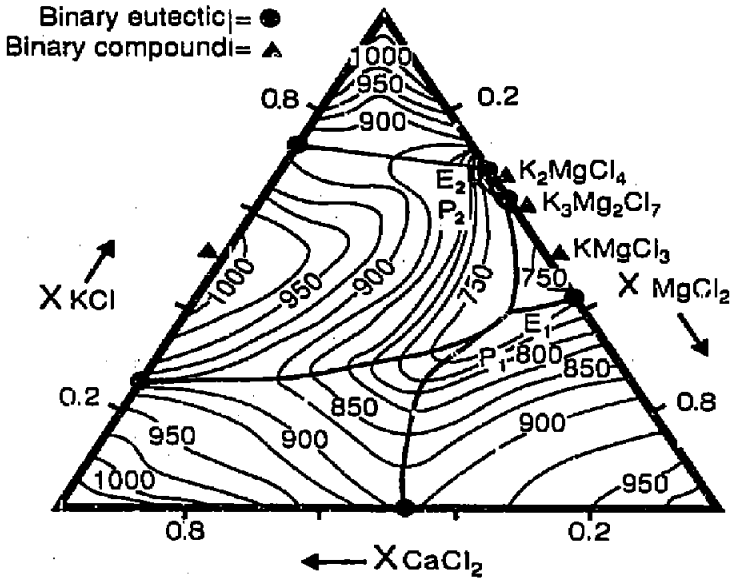

Fig. 6. Experimental $MgCl_2$–KCl–$CaCl_2$ phase diagram (this work).

and at 35:63:2 mol.% $MgCl_2$–KCl–$CaCl_2$ between 725 and 700 K. The peritectic was at 47:35:18 mol.% $MgCl_2$–KCl–$CaCl_2$ between 725 and 750 K. The second peritectic (P_2) is very close to K_2MgCl_4 at 37:62:1 mol.% $MgCl_2$–KCl–$CaCl_2$ and 700–725 K.

The component binary systems influence the direction of the isotherms. The strongest influences are from the KCl–$CaCl_2$ and the KCl–$MgCl_2$ compounds. The $KCaCl_3$ compound projects the isotherms in the $CaCl_2$-rich region towards the low $CaCl_2$ region. The $KMgCl_3$ and K_2MgCl_4 compounds shift the isotherms towards an area of minimum energy, the 50 mol.% eutectic of the $CaCl_2$–$MgCl_2$ binary system. However the additional phase transition found at 35–50 mol.% $MgCl_2$ appears to have no effect on the ternary system.

An unusual feature are the isotherms in the $CaCl_2$-rich corner: they curve away from each other at 950 and 925 K, opening a larger than expected gap. This region was examined in detail by the cooling curve analysis of several additional compositions. It was initially thought that this area may contain a ternary compound, but the primary temperature arrests obtained did not provide any evidence for this. It is now thought that the gap may arise from the latent solid solubility which exists in the $MgCl_2$–$CaCl_2$ binary phase diagram (Fig. 3).

For the ternary, Ivanov [1] used thermal analysis and microstructural methods in the 653–1073 K range to analyse 17 polythermal sections in order to construct the liquidus ternary diagram with 20° interval isotherms. Figure 1 shows his ternary phase diagram converted from weight per cent data to molar units. He found two eutectics E_1 and E_2, two peritectic points P_1 and P_2 and discusses the basic system in terms of two secondary

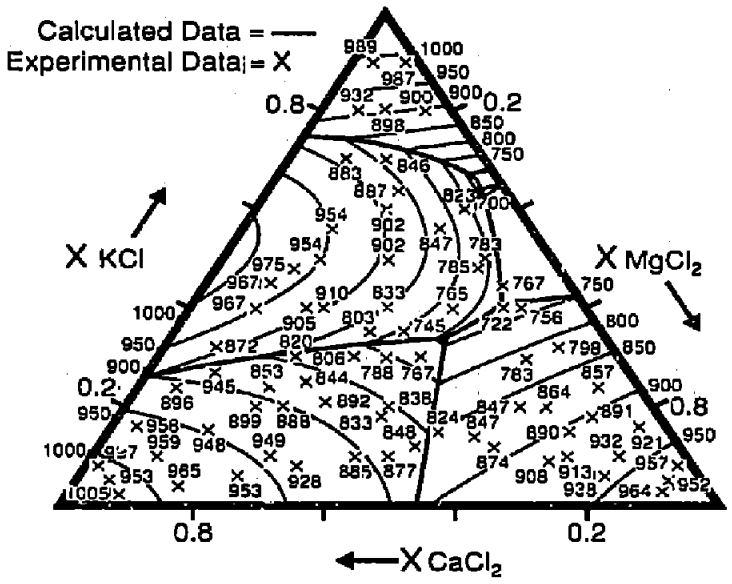

Fig. 7. Calculated $MgCl_2$–KCl–$CaCl_2$ phase diagram [7].

diagrams, a ternary KCl · $CaCl_2$–KCl · $MgCl_2$–KCl and a ternary reciprocal $CaCl_2$ + KCl · $MgCl_2$ = $MgCl_2$ + KCl · $CaCl_2$.

In both experimentally determined phase diagrams, two ternary eutectics and two peritectics were found. The ternary system does not appear to be influenced by the $MgCl_2$–KCl binary compounds ($KMgCl_3$ and K_2MgCl_4), but by the $KCaCl_3$, the isotherms of the $CaCl_2$-rich region being pushed right across to the $CaCl_2$-low region.

A calculation of the $MgCl_2$–KCl–$CaCl_2$ ternary phase diagram has recently been carried out at NPL [7]; Fig. 7 shows the calculated liquidus and our temperature data.

Table 1 compares the eutectics and peritectics for the experimentally

TABLE 1

Comparison of $MgCl_2$–KCl–$CaCl_2$ ternary phase diagrams

Author	Method	Eutectics/ peritectics	Mol.% $MgCl_2$:KCl:$CaCl_2$	Temperature (K)
Ivanov [1] 1953	Thermal analysis	E1	47:34:19	713
		E2	30:68:2	707
		P1	49:26:25	719
		P2	33:65:2	710
This work	Thermal analysis	E1	48:40:12	722
		E2	35:63:2	700–725
		P1	47:35:18	725–750
		P2	37:62:1	700–725
Chart [7] 1991	Computer calculation	E1	46:40:14	717
		E2	33:65:2	693

determined $MgCl_2$–KCl–$CaCl_2$ ternary phase diagrams which, taking into account the different experimental techniques, shows good agreement. The calculated diagram also shows very good agreement, which must be attributed to the relatively simple binary systems and the model used to derive the liquidus temperatures.

CONCLUSION

The experimental determination of the $MgCl_2$–KCl–$CaCl_2$ liquidus ternary phase diagram by thermal analysis has shown the system to be a simple one. There are two ternary eutectics and two peritectics. No ternary compounds are present. The $CaCl_2$ corner merits attention; the possibility of solid solubility in this region needs to be investigated further.

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