Thermochimica Acta, 68 (1983) 341–348
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PHASE STUDIES OF THE KCl–$CaCl_2$–$ZnCl_2$ SYSTEM *

GEORGE S. PERRY, LINDSAY G. MACDONALD and STUART NEWSTEAD
Atomic Weapons Research Establishment, Aldermaston, Reading RG7 4PR (Gt. Britain)

(Received 12 April 1983)

ABSTRACT

The composition ranges in which the system KCl–$CaCl_2$–$ZnCl_2$ is molten are illustrated by liquidus lines drawn at 50° intervals in the range 500–1000 K on a ternary diagram. Solid and liquid phases were shown to coexist over a wide temperature range. Three eutectics were found with compositions (mole%): KCl(48)–$CaCl_2$(2)–$ZnCl_2$(50); KCl(27)–$CaCl_2$(6)–$ZnCl_2$(67); and KCl(72)–$CaCl_2$(2)–$ZnCl_2$(26) melting at 480, 495 and 690 K, respectively. The melting points agree with the calculated values of 490, 520 and 690 K. The two binary systems $CaCl_2$–$ZnCl_2$ and KCl–$ZnCl_2$ were also redetermined. In the $CaCl_2$–$ZnCl_2$ system, a eutectic was found at about 2 mole% $CaCl_2$ melting at 572 K and the KCl–$ZnCl_2$ phase diagram reported in 1941 was confirmed as correct.

INTRODUCTION

The use of metathetical reactions in molten halide salts for the recovery and separation of actinide metals is well-established [1]. One such process is the reaction of $ZnCl_2$ with plutonium metal in the presence of NaCl or KCl which moderates the reaction kinetics [2].

$$Pu + ZnCl_2/KCl \rightarrow PuCl_3/KCl + Zn$$

The plutonium can then be recovered by reduction of the resultant salt with calcium metal [3]

$$PuCl_3/KCl + Ca \rightarrow Pu + KCl/CaCl_2$$

To keep the amount of plutonium-contaminated waste to a minimum, the KCl–$CaCl_2$ salt produced in the reduction step could be recycled (in part) to the first-stage process. This would mean the use of the ternary salt, KCl–$CaCl_2$–$ZnCl_2$ being generated for that step.

There is no published data on this system and it was the purpose of this work to establish the liquidus diagram to determine whether any high melting compounds are formed in the temperature range of interest.

0040-6031/83/$03.00

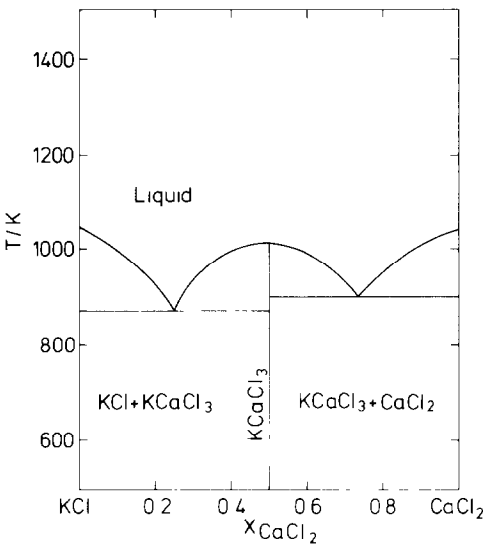

Fig. 1. $KCl–CaCl_2$ phase diagram.

A literature review of the binary salt systems comprising the ternary showed the $KCl–CaCl_2$ system to be reasonably well-established with the presence of two eutectics at about 26 and 73 mole% KCl. A high melting point double salt is formed at the equimolar composition, $KCaCl_3$ (Fig. 1).

The only available phase diagram of the $CaCl_2–ZnCl_2$ system is that reported by Menge [4] in 1911. An ill-defined eutectic was found at ap-

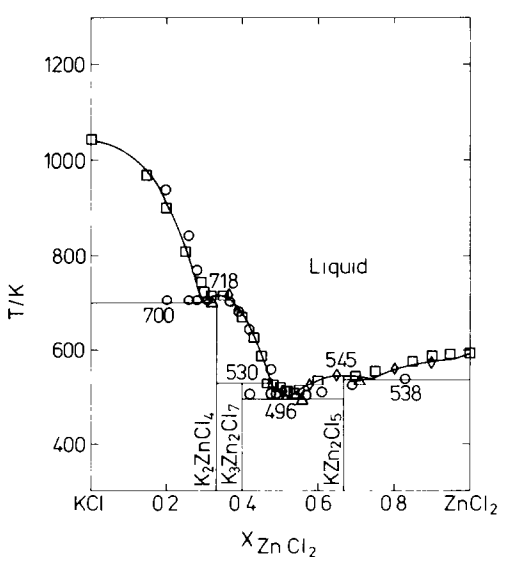

Fig. 2. $KCl–ZnCl_2$ phase diagram. □, Ref. 5; ◇, ref. 6; ○, ref. 7; △, this work.

proximately 1.5 mole% $CaCl_2$, melting at 572 K, although this is not shown in the published diagram There was no evidence of compound formation.

The KCl–$ZnCl_2$ phase diagram is not well-established and the most complete study has been made by Nikonova et al. [5] who observed eutectics at 30 mole %, 54 mole % and 72 mole % $ZnCl_2$, having melting points of 703, 503 and 535 K, respectively, with a peritectic at 46 mole % $ZnCl_2$, having a melting point of 523 K. Ugay and Shatillov [6] made a restricted study and found a eutectic at 49 mole % $ZnCl_2$. Later, Duke and Fleming [7] reported two eutectics at 31 mole % and 49 mole % $ZnCl_2$. Figure 2 shows the data available and clearly there was a need to confirm that part of the diagram, in the $ZnCl_2$-rich region.

EXPERIMENTAL

The study of $ZnCl_2$-containing systems is complicated by its hygroscopic nature, and variations in the melting point in the range 250–365°C are quoted in the literature. These variations are explained by the presence of impurities in the $ZnCl_2$ and the extent of dehydration, on the one hand, and the conditions used for drying the salt on the other. In determining the melting point of $ZnCl_2$, care must be taken because the absence of stirring can lead to a reduction in the freezing point by approximately 20°C, due to the tendency for $ZnCl_2$ to supercool.

Nikonova obtained a melting point of 318°C on a sample of $ZnCl_2$ dried in HCl by observing crystal formation and disappearance and Cubiccotti and Eding [8] report values in the range 314–318°C for vacuum-distilled $ZnCl_2$.

STARTING MATERIALS

Anhydrous $ZnCl_2$ (ultrapure) was obtained from Alfa Chemicals (Supplied by Lancaster Synthesis Ltd.) and had a melting point of 300°C. No significant increase in the melting point was observed on treatment with HCl gas. Vacuum-distilled $ZnCl_2$ (melting point, 308°C) was used for $ZnCl_2$-rich compositions in the $CaCl_2$–$ZnCl_2$ system.

Mallinckrodt anhydrous food-quality grade $CaCl_2$ had a melting point of 759°C compared with the published value of about 782°C [9]. The melting point remained the same after HCl gas treatment. Although impurities present in the calcium chloride reduce its melting point, and may influence the accuracy of temperature values for compositions close to pure calcium chloride in the ternary system, the effect will be minimal at higher concentrations of zinc and/or potassium chlorides. The Analar grade KCl used had a melting point of 771°C which agreed with the literature value [9].

The $KCl–CaCl_2$ and $KCl–ZnCl_2$ eutectics which were used as feed-stocks for most of the thermal analysis measurements were prepared by slow drying of the appropriate mixtures of the salts at temperatures below their melting points in a flow of dry HCl gas using Pyrex apparatus. The mixtures were fused under HCl, purged with argon to remove HCl from the melt and finally filtered through a sintered frit to remove particulate impurities. The resultant cast blocks of eutectic were reduced to powder using a mortar and pestle in a 'dry' box. The melting points of each eutectic were determined by the cooling curve method and the results are given in Table 1.

All reagents and glassware were dried in an oven at 120°C before use. A 25 g sample of the required composition was weighed into a Pyrex or silica tube in an inert atmosphere dry box (< 50 ppm water vapour) to minimise moisture uptake. A chromel–alumel thermocouple, protected by a closed-end glass or alumina tube was placed in the salts and the end of the tube was plugged with glass wool to limit the ingress of moist air. The tube was placed in a furnace and heated to above the expected melting point and the molten salt was vigorously stirred.

Power to the furnace was switched off and the sample allowed to cool slowly ($\sim 3°\ min^{-1}$) by covering with insulating material. The cooling curve was measured on a Lloyd Instruments CR600 chart recorder adjusted to suppress a fraction of the thermocouple output to display 20 mV full-scale deflection. Temperatures were calibrated by means of a precision potentiometer. The thermocouple was calibrated against pure zinc metal (melting point 419°C) and corrections were found to be unnecessary for results quoted to the nearest 1°. The sample was stirred in the region of the freezing point to eliminate super-cooling, especially in $ZnCl_2$-rich compositions.

Figure 3 shows the lines along which the experimental points were measured. Eutectic mixtures were used as the basis for most of the compositions because of their ease of preparation, drying and storage. For composition lines 1–3, $CaCl_2$ was added to $KCl–ZnCl_2$ eutectics of 31.6, 54.0 and 71.0 mole% $ZnCl_2$: $ZnCl_2$ was added to the two $KCl–CaCl_2$ eutectics for lines 4 and 5. Lines 6 and 7 stretch from 75 mole% $KCl–CaCl_2$ to 66 mole% $KCl–ZnCl_2$ and 26 mole% $KCl–CaCl_2$ to 37 mole% $KCl–ZnCl_2$, respec-

TABLE 1

Binary eutectics of KCl

Composition (mole%)	Melting point (K)	
	Found	Literature (Ref.)
$KCl–ZnCl_2$ (31.6)	705	703 [5]
$KCl–ZnCl_2$ (54.0)	490	505 [5]
$KCl–ZnCl_2$ (71.0)	533	535 [5]
$KCl–CaCl_2$ (25.0)	867	867 [9]
$KCl–CaCl_2$ (75.0)	900	913 [9]

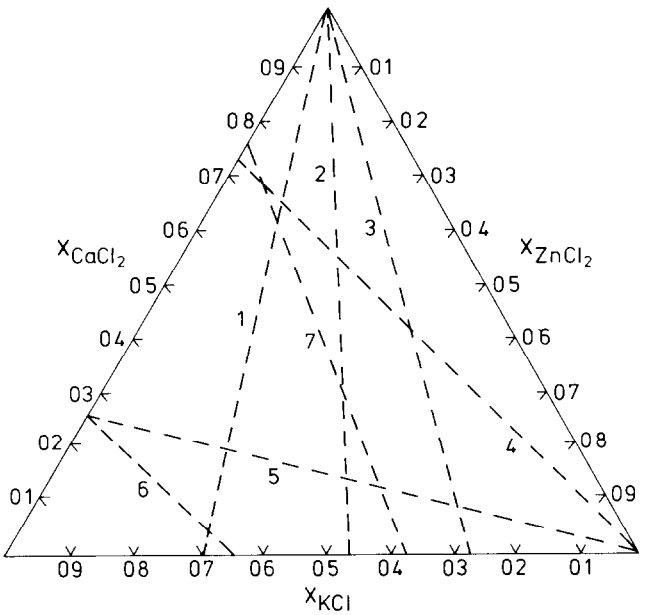

Fig. 3. Composition lines for the experimental data.

tively. The number of compositions measured along each line varied from 10 to 15, and about 90 points were measured in the whole system. After each thermal analysis, samples were analysed for zinc and calcium; potassium was obtained by difference and it was assumed that there were no significant amounts of cationic impurities present.

DISCUSSION

$ZnCl_2$ binary systems

In the determination of the $CaCl_2$–$ZnCl_2$ liquidus diagram, the chemical analysis of the $ZnCl_2$-rich compositions showed that losses of $ZnCl_2$ by volatilisation were negligible. The phase diagram obtained was similar to that found by Menge [4]; the only variation occurred in the 0–2 mole% $CaCl_2$ region. Figure 4 shows the presence of a single simple eutectic at about 2 mole% $CaCl_2$ with a melting point of 572 K.

The KCl–$ZnCl_2$ phase diagram (Fig. 2), determined between 40 and 80 mole% $ZnCl_2$ is in good agreement with that of Nikonova et al. [5], particularly in the region of the 72 mole% $ZnCl_2$ eutectic which was not observed by other workers [6,7]. Eutectic compositions were found at 54 mole% $ZnCl_2$ (497 K), compared with 503 K by Nikonova et al. and at 72 mole% $ZnCl_2$ (536 K). The peritectic composition of 48 mole% $ZnCl_2$ has a

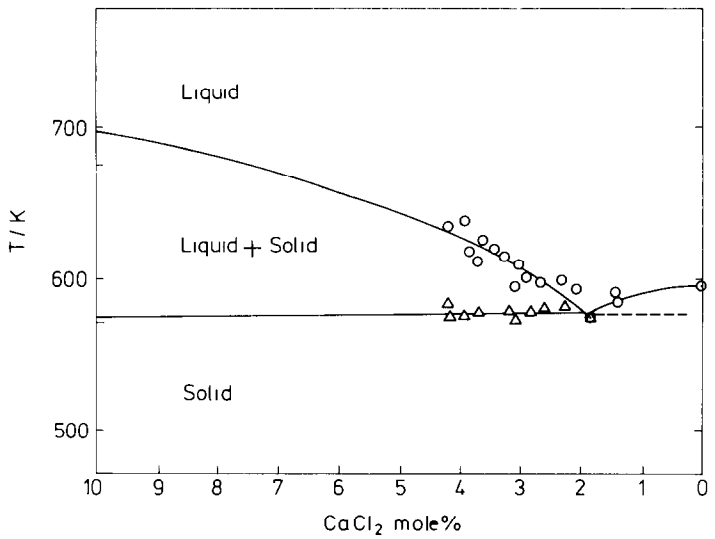

Fig. 4. $CaCl_2$–$ZnCl_2$ phase diagram. ⊙, 1st temperature of arrest; △, 2nd temperature of arrest.

melting point of 517 K (compared with 523 K). There was not such a large difference in temperature between the 72 mole% eutectic and the possible KZn_2Cl_5 compound at 539 K as found by Nikonova et al. Previous work in this laboratory has confirmed the eutectic at 31 mole% $ZnCl_2$ (750 K) and the composition equivalent to the K_2ZnCl_4 compound at 723 K.

KCl–$CaCl_2$–$ZnCl_2$ system

During the first part of the experimental programme only the compositions along the lines 1–5 were determined because these are based upon the use of the simple binary eutectics. It was only after the initial construction of the liquidus diagram that unusual features were found in the region of KCl(30)–$CaCl_2$(55)–$ZnCl_2$(15) and KCl(70)–$CaCl_2$(20)–$ZnCl_2$(10). Measurements were then carried out along the tie-lines between the KCl–$CaCl_2$ eutectics and the two $ZnCl_2$-rich KCl eutectics; these are the composition lines 6 and 7.

Using all the data points, Fig. 5 is the liquidus diagram for the ternary system KCl–$CaCl_2$–$ZnCl_2$ over the temperature range 500–1000 K. The most interesting experimental features were the three eutectics found at (mole%): KCl(72)–$CaCl_2$(2)–$ZnCl_2$(26), 690 K; KCl(48)–$CaCl_2$(2)–$ZnCl_2$(50), 480 K; and KCl(27)–$CaCl_2$(6)–$ZnCl_2$(67), 495 K whose compositions agree quite well with the calculated values: KCl(70)–$CaCl_2$(2)–$ZnCl_2$(28), 690 K; KCl(47)–$CaCl_2$(2)–$ZnCl_2$(51), 490 K; and KCl(22)–$CaCl_2$(5)–$ZnCl_2$(73), 530 K. At these compositions the melts

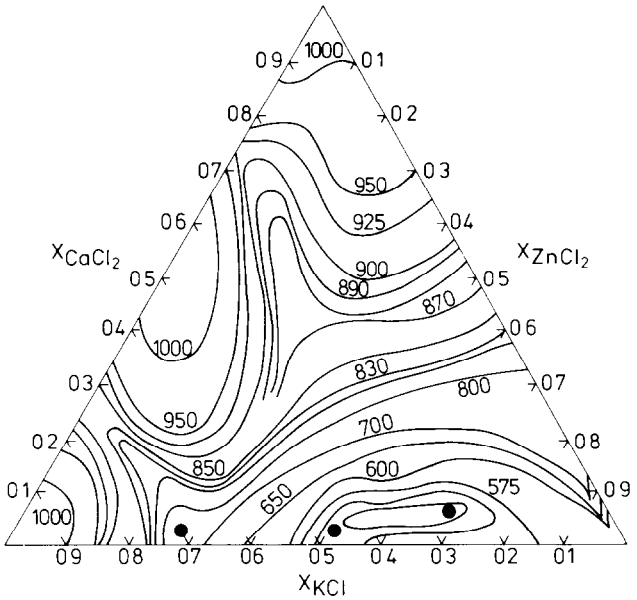

Fig. 5. $KCl-CaCl_2-ZnCl_2$ liquidus temperatures (K). ●, Ternary eutectics.

would solidify to $KCl + KCaCl_3 + K_2ZnCl_4$, $CaCl_2 + K_3Zn_2Cl_7 + KZn_2Cl_5$ and $CaCl_2 + ZnCl_2 + KZn_2Cl_5$, respectively [10]. No ternary compounds were found in the system.

The implications of these results on the pyrochemical recovery of actinide metals using $ZnCl_2$ in the presence of KCl and $CaCl_2$ are that there will be no interference from any high melting phases and therefore recycling of the $CaCl_2$ waste is a reasonable proposition.

ACKNOWLEDGEMENTS

We wish to thank S.D. Wilcox for his contribution to the experimental work.

REFERENCES

1 S. Lawroski and L. Burris, At. Energy Rev., 2 (1964) 3.
2 J.G. Reavis and J.A. Leary, U.S. Pat. 2, 886, 410 (1959).
3 D.C. Christensen and L.J. Mullins, Salt Stripping, A Pyrochemical Approach to the Recovery of Plutonium Electrorefining Salt Residues, Los Alamos Rep. LA-9464-MS, Oct. 1982.
4 O. Menge, Z. Anorg. Chem., 72 (1911) 162.
5 I.N. Nikonova, S.P. Pavlenko and A.G. Bergman, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, (1941) 391.

6 Ya A. Ugay and V.A. Shatillov, Zh. Fiz. Khim., 23 (1949) 744.
7 F.R. Duke and R.A. Fleming, J. Electrochem. Soc., 104 (1957) 251.
8 D. Cubiccotti and H. Eding, J. Chem. Phys., 40 (1964) 978.
9 G.J. Janz and R.P.T. Tomkins, Rep. NSRDS-NBS 61, Part IV, U.S. Dept. of Commerce and National Bureau of Standards, July 1981.
10 T.G. Chart, CALPHAD, submitted.