Thermochimica Acta, 211 (1992) 323–330
Elsevier Science Publishers B.V., Amsterdam

Phase studies of the $CeCl_3$–KCl–$ZnCl_2$ ternary system and of the component binary systems

George S. Perry and Colin H. Hawthorn
Atomic Weapons Establishment, Aldermaston, Reading, Berks. RG7 4PR (UK)
(Received 18 March 1992)

Abstract

The $CeCl_3$–KCl–$ZnCl_2$ ternary has been established; solid and liquid phases were shown to co-exist in the range 500–1100 K. It was found to be similar to the $CaCl_2$–KCl–$ZnCl_2$ system. The previously unreported $CeCl_3$–$ZnCl_2$ phase diagram has been determined; it is a simple system with a eutectic at about 1 mol.% $CeCl_3$, melting point 570 K. The peritectic composition (46 mol.% $ZnCl_2$) and temperature (548 K) in the KCl–$ZnCl_2$ system were determined experimentally.

INTRODUCTION

Pyrochemical processes for the recovery and purification of actinide elements are under development in the US [1, 2] and the UK [3]. These processes are based upon the use of molten inorganic salts, usually chlorides, because of their thermal and radiation stability. Phase diagrams play an important role in molten salt chemistry, providing fundamental data about compositions and reaction pathways.

In the study of the reactions of $ZnCl_2$ with actinide metals, e.g. plutonium, it is often convenient to carry out preliminary experiments with a simulant metal. Cerium fulfils this role because its chemistry closely resembles that of plutonium. Its trichloride is well known but there is a paucity of data on its phase relationships with $ZnCl_2$ and KCl–$ZnCl_2$.

In this paper we describe the determination of the $CeCl_3$–KCl–$ZnCl_2$ ternary system and the previously unreported component binary, $CeCl_3$–$ZnCl_2$. The binary system $CeCl_3$–KCl is known [4] (Fig. 1) although the eutectic composition (at about 71 mol.% KCl) and its temperature are not well established. The third binary phase diagram, KCl–$ZnCl_2$, is also well established [5–8] (Fig. 2) although the peritectic temperature has not been experimentally determined; we report this here.

Correspondence to: G.S. Perry, Atomic Weapons Establishment, Aldermaston, Reading, Berks, RG7 4PR, UK.

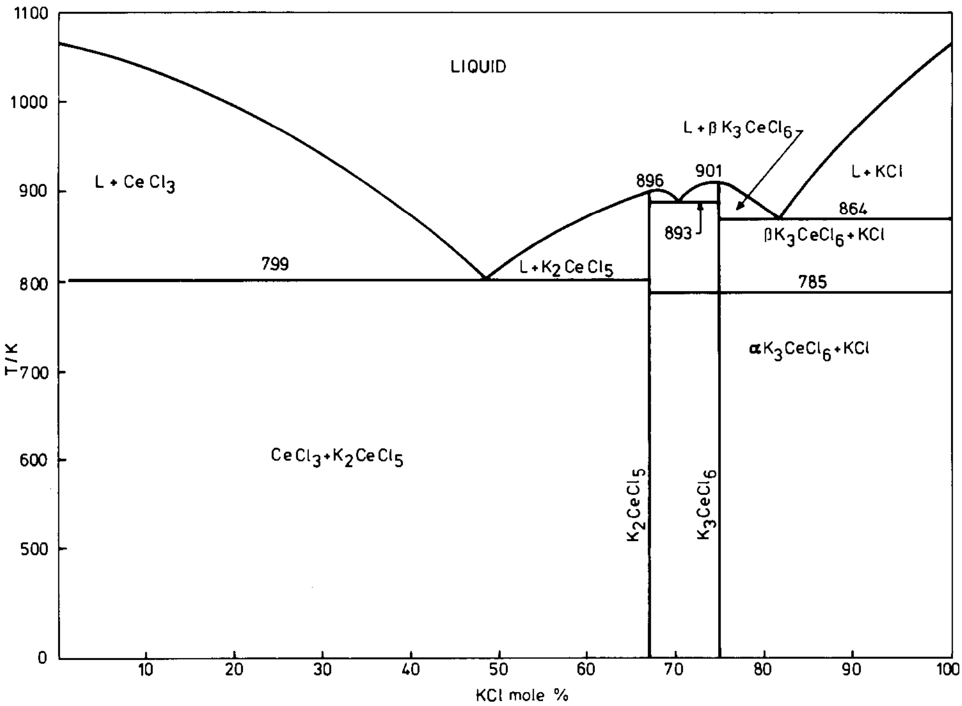

Fig. 1. $CeCl_3$–KCl phase diagram.

EXPERIMENTAL

Materials

Anhydrous zinc chloride (Ventron ultrapure) was obtained from Alfa Chemicals and had a melting point of 309°C, which is 9°C lower than the literature value [9] although there is evidence that it varies with the method of determination. Anhydrous KCl was Merck AnalR grade with melting point 771°C (cf. 772°C [10]). The cerium trichloride was purchased from Ventron and had a melting point at 790°C (cf. 822°C [9]). Qualitative spectrographic analysis was carried out and the salts dried in vacuo before use.

Method

The liquidus diagrams of the systems $CeCl_3$–KCl–$ZnCl_2$, $CeCl_3$–$ZnCl_2$ and KCl–$ZnCl_2$ were obtained by determining the thermal arrest temperatures on cooling a range of compositions. A 20 g sample of the salt mixture was weighed into a dried silica or Pyrex tube in a dry nitrogen atmosphere glovebox (less than 25 ppm water vapour). A Chromel–Alumel thermocouple protected by a recrystallised alumina sheath was

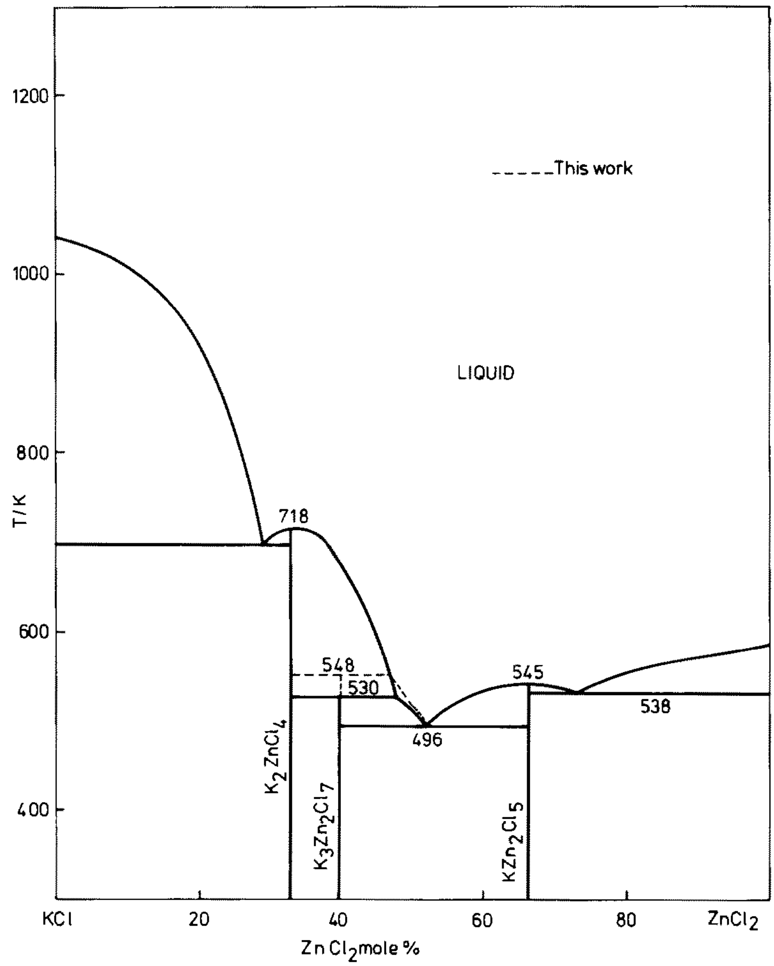

Fig. 2. KCl–$ZnCl_2$ phase diagram (refs. 5–8).

inserted into the salt mixture and the tube closed by a glass cover. The tube was then placed inside a temperature-controlled furnace and the temperature raised above the melting point of the salt mixture. The molten salt was stirred and inspected visually to ensure complete melting and the absence of immiscibility. The furnace was then cooled by about 1–2°C min^{-1} and the temperature of the melt was recorded using a microcomputer system, giving an accuracy of ±1°C.

RESULTS

Chemical analysis of the $ZnCl_2$ showed that the major impurities were silicon (180 ppm) and oxygen (0.35 wt.%) and analyses for 50 other elements showed levels below 100 ppm of each. The KCl was very pure with no impurity elements at greater than 100 ppm each. Selected chemical analysis of the salts for Al on completion of each experiment showed that there was no appreciable attack on the thermocouple sheath by the salt mixtures under study.

Analysis of the $CeCl_3$, however, showed that it contains about 55.4 wt.% Ce (plus other lanthanides), i.e. 97% pure. The other impurities amounted to about 3 wt.%, of which 2.6 wt.% was oxygen (probably oxy-chloride); but an X-ray diffraction examination was not carried out.

DISCUSSION

In the determination of the ternary system, it is expected that impurities will only have a strong influence in those regions close to the pure compounds. However, our main interest was in those compositions where either compound formation or a miscibility gap occurs.

The $CeCl_3$–$ZnCl_2$ system

This phase diagram (Fig. 3) has not previously been reported. In its general form, however, the liquidus curve resembles those of the $ZnCl_2$–alkaline earth chloride systems [8, 11], e.g. $CaCl_2$, Fig. 4. The phase diagram is the simple melting type; the eutectic occurs at about 1 mol.% $CeCl_3$ and melting at 570 K.

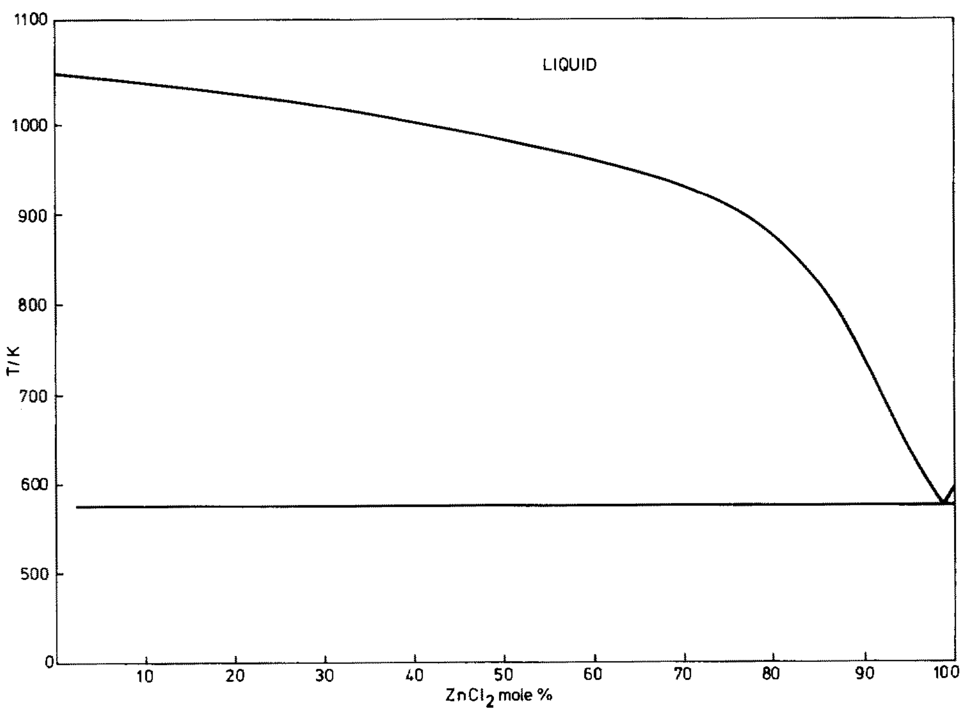

Fig. 3. $CeCl_3$–$ZnCl_2$ phase diagram.

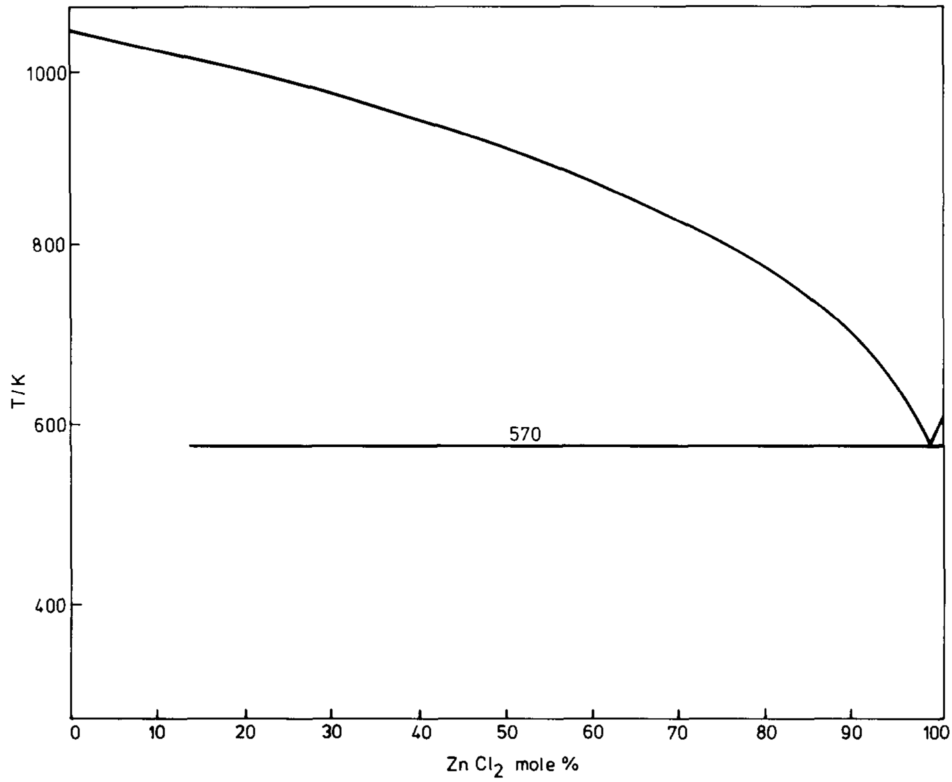

Fig. 4. $CaCl_2$–$ZnCl_2$ phase diagram.

The $CeCl_3$–KCl system

The published diagram for this system is shown in Fig. 1 [4]. The system contains two binary compounds, K_2CeCl_5 (melting point, 896 K) and K_3CeCl_6 (melting point, 901 K), and three eutectics at 799, 893 and 864 K.

The KCl–$ZnCl_2$ system

This system has been well studied [5–8], yet there are no experimental data reported for the peritectic composition $K_3Zn_2Cl_7$ at about 530 K. We here report the measured peritectic temperature and the data are given in Table 1 and Fig. 2.

The results confirmed most of the previous liquidus data [5, 6, 8] but the peritectic temperature was found to be 548 K, 18° higher than the value reported by Nikonova et al. [5]. The temperatures were confirmed by measuring the thermal arrest in the heating mode.

TABLE 1

KCl–$ZnCl_2$ peritectic

Composition (mol.%)		Temperature (K)		
KCl	$ZnCl_2$	First arrest (liquidus)	Second arrest (solidus)	Third arrest (solidus)
62	38	701	532	
60	40	682	548 [a]	507
58	42	646	538	500
57	43	624	544	500
		–		
Heating curve				
58	42	–	549 [a]	–

[a] Agreement of heating/cooling data suggests 548 K to be the reliable temperature.

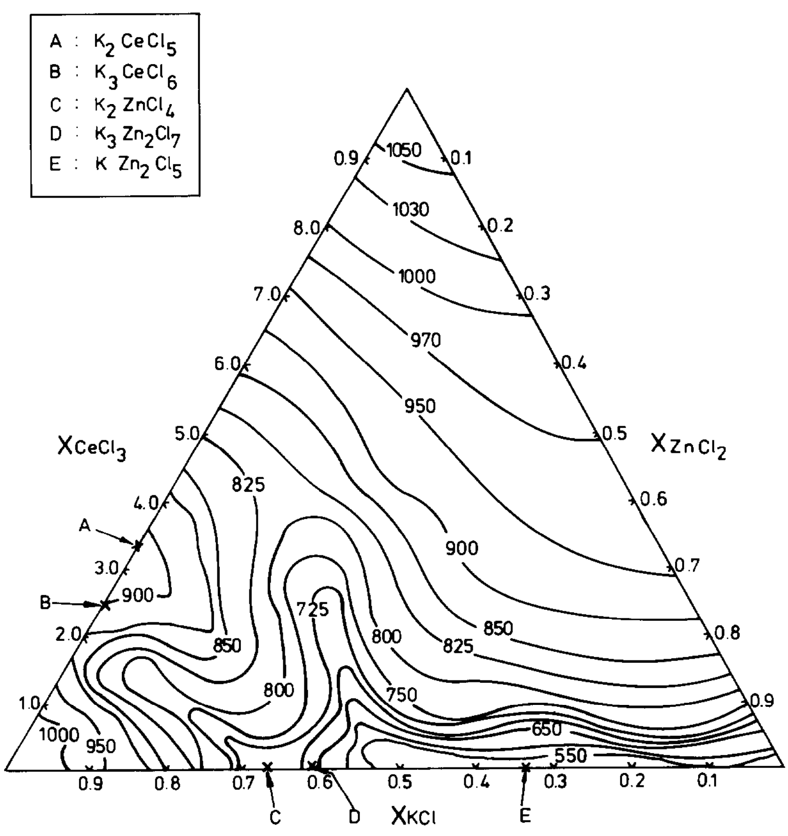

Fig. 5. $CeCl_3$–KCl–$ZnCl_2$ phase diagram.

The $CeCl_3$–KCl–$ZnCl_2$ system

The ternary liquidus diagram is shown in Fig. 5, and there is a close similarity to the $CaCl_2$–KCl–$ZnCl_2$ system [8].

In this system, the influence of the $CeCl_3$–KCl binary, with its two compounds, K_3CeCl_6 and K_2CeCl_5, is shown by the intrusions of the liquidus isotherms into the KCl-rich region. The region of the ternary bounded by the area 60 mol.% $CeCl_3$–10 mol.% KCl and pure $ZnCl_2$, contains liquid and solid below about 850 K, with fairly evenly spaced isotherms over much of the composition. This is a result of the influence of the $CeCl_3$–$ZnCl_2$ binary, which is of the simple eutectic type.

The KCl–$ZnCl_2$ binary has three eutectics and three compounds, K_2ZnCl_4, $K_3Zn_2Cl_7$ and KZn_2Cl_5, which, in the $CaCl_2$–KCl–$ZnCl_2$ system lead to the formation of three ternary eutectics. However no corresponding eutectics were found in the $CeCl_3$–KCl–$ZnCl_2$ system, although it is possible that they exist in the very low $CeCl_3$-containing region which we have not examined in detail. There were no ternary compounds found or any evidence of immiscibility in the liquidus.

CONCLUSIONS

(a) The $CeCl_3$–$ZnCl_2$ binary is the simple eutectic type.

(b) In the $CeCl_3$–KCl–$ZnCl_2$ system, there are no ternary compounds or ternary eutectics.

(c) The $CeCl_3$–KCl–$ZnCl_2$ ternary is similar to the $CaCl_2$–KCl–$ZnCl_2$ system, as predicted by the similarity of the binary systems.

(d) The peritectic temperature in the KCl–$ZnCl_2$ system was found to be 548 K, 18° higher than previously reported.

ACKNOWLEDGEMENT

The authors thank Mr. S.J. Shaw for his contribution to the experimental work on the KCl–$ZnCl_2$ system.

REFERENCES

1 M.S. Coops, J.B. Knighton and L.J. Mullins, Pyrochemical Processing of Plutonium, in W.T. Carnall and G.R. Choppin (Eds.), ACS Symposium Series No. 216, Plutonium Chemistry, 1983, p. 381.
2 J.A. McNeese, D.F. Bowersox and D.C. Christensen, in M.L. Saboungi, K. Johnston, D.S. Newman and D. Inman (Eds.), Proc. 5th Int. Symp. Molten Salts, Oct. 1985, The Electrochem. Soc., NJ, 1986, p. 474.
3 G.S. Perry and L.G. Macdonald, J. Nucl. Mater., 130 (1985) 234.
4 E.M. Levin, C.R. Robbins and H.F. McMurdie, Phase Diagrams for Ceramists. The American Ceramic Society, Columbus, OH, 1964.
5 I.N. Nikonova, S.P. Pavlenko and A.G. Bergman, Izv. Akad. Nauk SSR Otd. Khim. Nauk, (3) (1941) 391.

6 F.R. Duke and R.A.J. Fleming, J. Electrochem. Soc., 104 (1957) 774.
7 Y.A. Ugay and V.A. Shatillov, Zh. Fiz. Khim., 23 (1949).
8 G.S. Perry, L.G. Macdonald and S. Newstead, Thermochim. Acta, 68 (1983) 341.
9 G.J. Janz, Molten Salts Handbook, Academic Press, London, 1967.
10 G.J. Janz, C.B. Allen, N.P. Bansal, R.M. Murphy and R.P.T. Tomkins, Physical Properties Data Compilation Relevant to Energy Storage; Data on single and multi-component salt systems, NSRDS-NBS, Part 2, US Dept. Commerce./NBS Rep., US Govt. Printing Office, Washington, April 1979.
11 O. Menge, Anorg. Chem., 72 (1911) 162.