Thermochimica Acta, 157 (1990) 329–333
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

$NaCl–ZnCl_2$ PHASE DIAGRAM *

STEPHEN J. SHAW and GEORGE S. PERRY
Atomic Weapons Establishment, Reading, Berkshire, RG7 4PR (U.K.)
(Received 12 June 1989)

ABSTRACT

The $NaCl–ZnCl_2$ phase diagram has been investigated following differences in published reports. It contains a eutectic at 35 mol% NaCl (526 K), a peritectic at 60 mol% NaCl (650 K) and an incongruently melting compound Na_2ZnCl_4.

INTRODUCTION

The $NaCl–ZnCl_2$ binary phase diagram was first determined in 1941 by Nikonova et al. [1] (Fig. 1). They found a eutectic at 41.5 mol% (555 K) and a peritectic at 63.5 mol% NaCl (683 K) but they did not determine the composition of the corresponding compound, which they thought might be Na_2ZnCl_4. Although they gave data for the NaCl-rich region of the phase

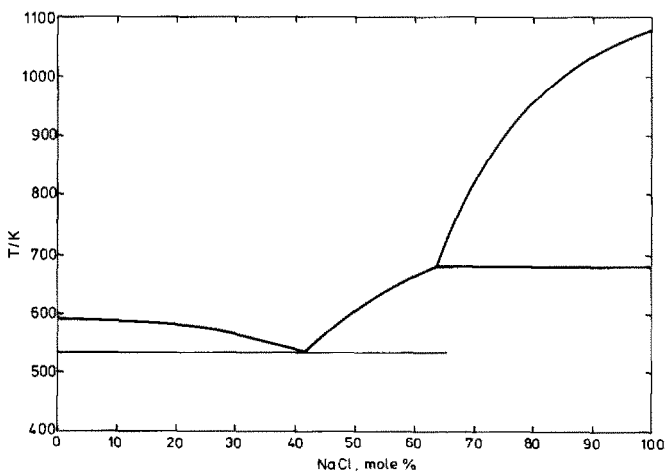

Fig. 1. $NaCl–ZnCl_2$ phase diagram from ref. 1.

* Copyright © Controller HMSO, London, 1989.

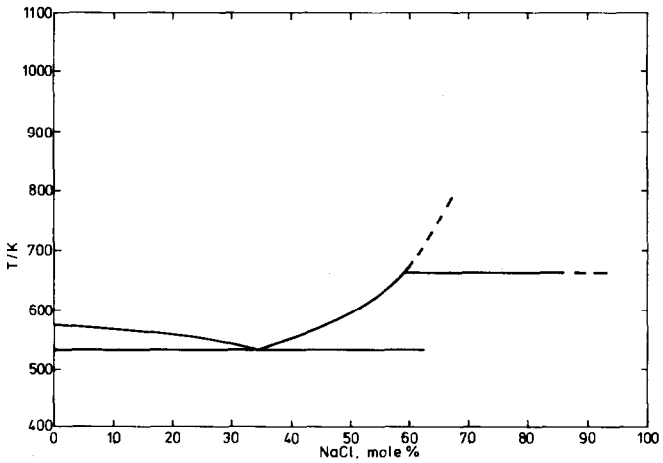

Fig. 2. NaCl–$ZnCl_2$ phase diagram from ref. 2.

diagram, they admitted it should be regarded as only approximate. Johnstone and Winsche [2] (Fig. 2) found a eutectic at 34 mol% NaCl (530 K) and a peritectic at 60 mol% NaCl (662 K) but again they did not investigate the NaCl-rich region. Since there is a lack of agreement between the published data it was decided to determine the phase diagram.

EXPERIMENTAL

Materials

Polarographic grade zinc chloride was obtained from Andersons Physics Laboratories (APL), and had a melting point by the cooling curve method of 574 K; cf. 591 K [1]. Reviews on the melting point of $ZnCl_2$ [1,3] have quoted a wide range of values from 512 K to 638 K. Craw and Rogers [3] obtained 591 ± 4 K by the capillary tube method, which showed good agreement with previous work. A DTA study of $ZnCl_2$ gave a value of 586.3–589.3 K for the melting of crystalline $ZnCl_2$ [4]. Analytical grade NaCl was dried under vacuum at 180 °C for 5 days and then melted under argon before use, and gave a melting point of 1070 K, cf. 1073 K [5]. Both NaCl and $ZnCl_2$ contained less than 0.05% of H_2O (Karl-Fischer method).

Method

A 20 g sample of the required composition of NaCl and $ZnCl_2$ 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. Comparison of weights

before and after experiments indicated that less than 0.02 g of $ZnCl_2$ was lost by volatilisation.

The salt was melted in a resistance furnace controlled by a West 2050 furnace controller, which allowed the salt to be held molten for a specified time and cooled at a constant rate. The furnace was programmed, allowing the melt to cool at 0.5 °C min^{-1}, and the thermocouple output was stored by a microcomputer. The thermocouples were calibrated against pure zinc metal (melting point 692 K), 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.

X-ray diffraction studies

A fine powder of the sample was prepared by crushing using an agate mortar and pestle in a dry-box. A thin walled silica capillary tube was loaded with the sample and sealed using picene wax (unsealed samples hydrated rapidly). The sample tube was loaded into a Debye–Scherrer powder camera, rotated slowly, and the sample was exposed to Cu $K\alpha$ radiation (wavelength 1.54 Å). The diffraction pattern on the photographic film was read into a computer using a digitiser, and compared with values in the Joint Committee on Powder Diffraction Standards (JCPDS) compilation.

RESULTS AND DISCUSSION

The phase diagram obtained from our study of this system is shown in Fig. 3. We found a eutectic at 35% NaCl (526 K) and a peritectic at 60% NaCl (650 K). These values are compared with the previous determinations in Table 1, and show closer agreement to the data of Johnstone and Winsche [2] than to those of Nikonova et al. [1]. Both Nikonova et al. [1] and Johnstone and Winsche [2] believed the compound formed to be Na_2ZnCl_4, although neither had determined this experimentally. In addition, Rice and Gregory [6] had studied a compound using X-ray diffraction which chemical analysis showed to be Na_2ZnCl_4.

Samples containing 66 mol% NaCl and 80 mol% NaCl were analysed using X-ray diffraction and the results are shown in Fig. 4, together with those for JCPDS reference standards for Na_2ZnCl_4, NaCl and $ZnCl_2$. Both samples show the main lines corresponding to Na_2ZnCl_4 and NaCl, although in the 66 mol% NaCl sample the intensities of the lines at 0.28 and 0.20 nm are unexpected. In both samples there is some splitting of lines due to the inability to grind the sample to a sufficiently fine powder. Neither of the strongest lines due to $ZnCl_2$ (0.308 and 0.479 nm) is observed in either

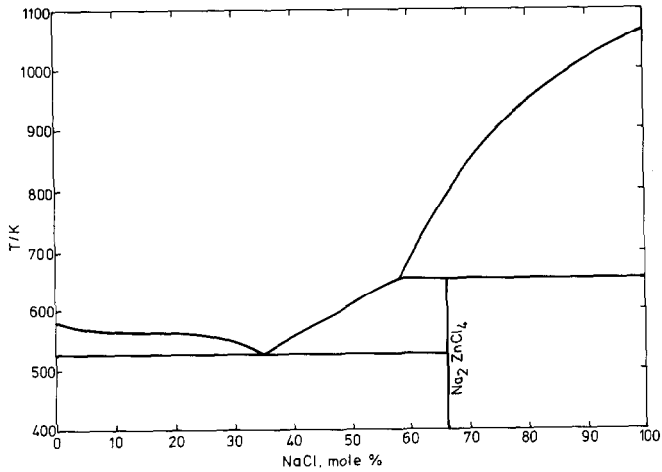

Fig. 3. $NaCl–ZnCl_2$ phase diagram (this work).

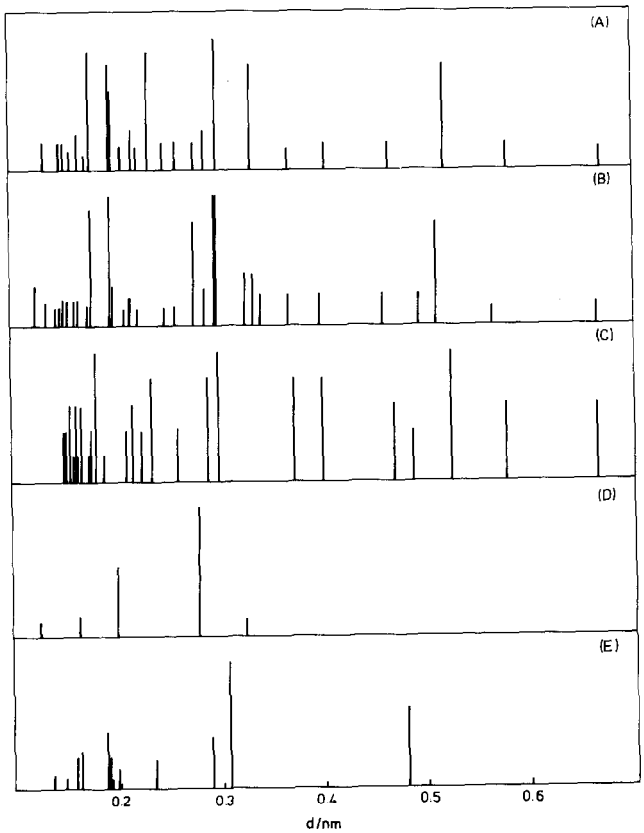

Fig. 4. X-ray diffraction studies. (A) 66% $NaCl–ZnCl_2$; (B) 80% $NaCl–ZnCl_2$; (C) Na_2ZnCl_4; (D) NaCl; (E) $ZnCl_2$.

TABLE 1

Comparison of $NaCl–ZnCl_2$ phase diagrams

	Eutectic		Peritectic	
	Composition (mol% NaCl)	Temperature (K)	Composition (mol% NaCl)	Temperature (K)
Nikonova et al. [1].	41.5	555	63.5	683
Johnstone and Winsche [2]	34	530	60	662
This study	35	526	60	650

case.

Since almost all the lines in the samples can be assigned to either NaCl or Na_2ZnCl_4, it is unlikely that any other compound is present. However, the X-ray diffraction analysis of a 66 mol% NaCl sample showed that some NaCl was present, indicating that the formation of the compound may be slow and equilibrium had not been attained. If cooling rates greater than $0.5\,°C\ min^{-1}$ were used, a temperature arrest corresponding to the eutectic was seen beyond 66 mol% of NaCl.

ACKNOWLEDGEMENT

The authors wish to thank M.R. Clay, who carried out the X-ray analysis.

REFERENCES

1 I.N. Nikonova, S.P. Pavlenko and A.G. Bergman, Izv. Akad. Nauk. SSR, Otd. Khim. Nauk, (1941) 391.
2 H.F. Johnstone and W.E. Winsche, Ind. Eng. Chem., 36 (1944) 435.
3 D.A. Craw and J.L. Rogers, J. Chem. Soc., (1956) 217.
4 Y. Takagi and T. Nakamura, Summary of the Nineteenth Symposium on Molten Salt Chemistry, Osaka, Japan, 5–6 November 1986, p. 69.
5 L.B. Pankratz, Thermodynamic Properties of Halides, Bull. U.S., Bur. Mines, No. 674, 1984, p. 456.
6 D.W. Rice and N.W. Gregory, J. Phys. Chem., 72 (1968) 4524.