

## Note

### THERMODYNAMICS OF THE DISSOCIATION OF $\text{ZnCl}_2(\text{NH}_3)_2$ BY MODIFIED ENTRAINMENT

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(Received 23 March 1988)

Molten zinc chloride has been proposed as a hydrocracking solvent for coal slurries and heavy oil fractions [1]. Nitrogen is one of several heteroatoms inevitably introduced with the feedstock and is reduced to  $\text{NH}_3$  under the usual operating conditions ( $420^\circ\text{C}$  and 180 atm hydrogen overpressure). The  $\text{NH}_3$  forms strong complexes, principally  $\text{ZnCl}_2(\text{NH}_3)_2$  and  $\text{ZnCl}_2\text{NH}_3$ , with zinc chloride and these steadily accumulate in the melt. As part of a programme [2,3] to study the thermodynamics of reactions involving molten zinc chloride and its regeneration from contaminated melts, the thermal decomposition of  $\text{ZnCl}_2(\text{NH}_3)_2$  has been examined by modified entrainment.

#### EXPERIMENTAL

The modified entrainment method has been described in detail previously [4,5]. Briefly, a spherical quartz capsule containing  $\text{ZnCl}_2(\text{NH}_3)_2$  was suspended from one arm of a recording microbalance. The capsule contents are in contact with a downward flowing argon stream (ca.  $90\text{ cm}^3$  (s.t.p.)  $\text{min}^{-1}$ ) via a capillary (ca. 20 mm long  $\times$  1 mm internal diameter) fused to the top of the capsule; this capillary acts as a diffusive resistance and isolates the diammine from the irreproducible effects of the flowing carrier gas. The experimental parameter is the rate of mass loss  $\dot{w}$  from the capsule at a preset temperature in the range  $165\text{--}230^\circ\text{C}$ . Temperature was measured with a calibrated chromel–alumel thermocouple positioned immediately below the capsule.

#### Materials

Diamminedichlorozinc(II) was prepared by the method of Perchard and Novak [6] from ethanolic zinc chloride into which ammonia was passed. Zinc was determined by EDTA titration and chloride was determined

argentometrically. Found: Cl = 41.55%, Zn = 38.9%; calculated: Cl = 41.6%, Zn = 38.4%. The purification of zinc chloride has been described previously [2]. The argon was purified by passage through a rare gas purifier (model RGP-4, BOC Ltd.).

## RESULTS

### *Stoichiometry of the thermal decomposition*

Zinc chloride forms several ammines,  $\text{ZnCl}_2(\text{NH}_3)_n$ , where  $n = 6, 4, 2, 1.5, 1, 0.5$  and  $0.167$ . Their thermal stability and phase interrelationships have been well documented [7–12]. The monoamine and the diammine have been most thoroughly characterized, namely by X-ray diffraction [13], vibrational spectroscopy [6], temperature dependence of viscosity and conductivity [10], thermogravimetric analysis [7,8], thermomechanical analysis [7] and molecular mass in solution [10]. The starting material in this work,  $\text{ZnCl}_2(\text{NH}_3)_2$ , remains solid on heating to over  $190^\circ\text{C}$  when the presence of a liquid phase ( $\text{ZnCl}_2\text{NH}_3$ , see below) becomes apparent. Quantitative analysis [11] of all of the phases present in a closed system between  $220$  and  $540^\circ\text{C}$  initially charged with diammine has established the equilibrium stoichiometry as  $\text{ZnCl}_2(\text{NH}_3)_2 \rightleftharpoons \text{ZnCl}_2\text{NH}_3 + \text{NH}_3$ . The product of the reaction under investigation,  $\text{ZnCl}_2\text{NH}_3$ , may be prepared by the controlled thermal decomposition [7,10] of the diammine in an open system at  $200^\circ\text{C}$  until the proportional mass loss is 10%. The thermal stability of  $\text{ZnCl}_2\text{NH}_3$  has been examined in open systems by Zubakhina [8] and Volova et al. [7] who report insignificant decomposition (to  $\text{ZnCl}_2(\text{NH}_3)_n$  (where  $n < 1$ ) and  $\text{NH}_3$ ) below  $320^\circ\text{C}$  and  $380^\circ\text{C}$ , respectively.

The physical properties of  $\text{ZnCl}_2\text{NH}_3$  have been extensively studied [7,10]. The room temperature phase is a glassy polymer,  $(\text{ZnCl}_2\text{NH}_3)_m$ , where  $m \approx 30$ . On heating it passes through an elastic phase ( $34$ – $60^\circ\text{C}$ ) and becomes increasingly viscous to  $90^\circ\text{C}$ . From  $90$  to  $140^\circ\text{C}$  it displays increasing crystallinity, and finally undergoes a reversible depolymerization and melting from  $140$  to  $148^\circ\text{C}$ .

The work reported here was confined to 11 temperatures in the range  $166$ – $228^\circ\text{C}$  where the diammine is solid and the monoamine is liquid (and is insignificantly decomposed to lower ammines). Furthermore, the cumulative proportional mass loss throughout the experiments was 4.1%, less than the 10% required for quantitative conversion to  $\text{ZnCl}_2\text{NH}_3$ . Taken together the above evidence supports a reaction stoichiometry given by



### Modified entrainment

For equilibrium (1), involving a single gaseous species, the partial pressure of  $\text{NH}_3$  is given [4] by

$$p_{\text{NH}_3}^0 = P(1 - e^{-\xi_{\text{NH}_3}}) \quad (2)$$

where

$$\xi_{\text{NH}_3} = \dot{\omega}RTl/\mathcal{D}MPA \quad (3)$$

In eqn. (3),  $\dot{\omega}$  is the rate of mass loss at temperature  $T$ ,  $l/A$  is the length over the cross-sectional area of the capsule capillary ( $2.006 \times 10^4 \text{ m}^{-1}$ ),  $M$  is the molecular mass of  $\text{NH}_3$ ,  $P$  is the total system pressure (usually a few mmHg above atmospheric pressure) and  $\mathcal{D}$  is the binary diffusivity of  $\text{NH}_3$  in Ar. The diffusivity was estimated over the experimental temperature range (438–503 K) from the Lennard–Jones potential parameters for Ar and  $\text{NH}_3$  [14]

$$\mathcal{D}(\text{NH}_3, \text{Ar})(\text{m}^2 \text{ s}^{-1}) = 1.825 \times 10^{-5} (T/273.15)^{1.842} \quad (4)$$

Only limited experimental evidence [15] exists for this system and not within our temperature range. The equilibrium constant for reaction (1),  $p_{\text{NH}_3}^0/p^\ominus$  ( $p^\ominus = 101\,325 \text{ N m}^{-2}$ ), was obtained from eqns. (2)–(4) and the corresponding  $\Delta G_1^0$  value was linearly regressed against  $T$  (K) to give eqn. (5)

$$\Delta G_1^0(\text{J mol}^{-1}) = (118\,500 \pm 3800) - (218 \pm 8)T \quad (5)$$

The uncertainty intervals in eqn. (5) are standard deviations of the regression coefficients. The dissociation pressure above  $\text{ZnCl}_2(\text{NH}_3)_2(\text{cryst})$  has been reported before [16,17] at five temperatures in the range 401–490 K. The decomposition reaction was quoted as eqn. (1) except that the monoamine phase was written as solid. Converting these early results to free energies we obtain

$$\Delta G^0(\text{J mol}^{-1}) = (118\,800 \pm 9600) - (219 \pm 21)T \quad (6)$$

The coefficients in eqn. (6) have large uncertainty intervals but are close to those of eqn. (5) and it seems likely that Biltz and Messerknecht [16] failed to identify the monoamine phase correctly.

### ACKNOWLEDGEMENTS

We are indebted to Dr. K. Holder (BP plc) for helpful discussions and to BP plc for financial support.

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