

## MASS SPECTROMETRIC IDENTIFICATION OF $\text{NaZnCl}_3$ AND $\text{Na}_2\text{Zn}_2\text{Cl}_6$

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Complex vapour species of the type  $\text{NaZnCl}_3$  have been proposed by Rice and Gregory<sup>1</sup> to explain differences in the vapour pressure above  $\text{ZnCl}_2 + \text{NaCl}$  melts when measured by relative and absolute methods. In a comparable system, Moss<sup>2</sup> has assumed the existence of  $\text{KZnCl}_3$  above  $\text{KCl} + \text{ZnCl}_2$  mixtures. The formation of such complexes is not unlikely as Bloom and Hastie<sup>3</sup> have identified by mass spectrometry complexes of the form  $\text{MPbX}_3$ ,  $\text{MCdX}_3$  ( $\text{M} = \text{Na, K, Rb, Cs}$ ;  $\text{X} = \text{Cl, Br}$ ) in the vapour above mixtures of either  $\text{PbX}_2$  or  $\text{CdX}_2$  with  $\text{MX}$ . Of the methods available the mass spectrometric technique gives unequivocal proof of the composition of the complexes. This is a preliminary report of the mass spectrometry of vapours above mixtures of  $\text{ZnCl}_2$  (42–51 mole %) with  $\text{NaCl}$  in the temperature range 250–450°.

### Experimental

Apparatus and techniques were based on those of Bloom and Hastie.<sup>3</sup> The salt mixture, well dispersed in an excess of alumina powder, was heated in a Kanthal wound boron nitride furnace and the relative vapour pressures of the gaseous species above the mixture measured with an E.A.I. Quad 300 mass spectrometer scanning from 0 to 500 a.m.u. The alumina powder served to ensure molecular flow from the cell to the ion source. The large alumina surface area compared to the area available for effusion gave pressure equilibrium as was indicated by the linear plots of  $\log(\text{ion intensity})$  against reciprocal temperature. Pressure within the sample was within the range  $10^{-6}$ – $10^{-7}$  mmHg, and the ionizing electron energy 50 V. Temperatures in the cell were measured with a calibrated chromel–alumel thermocouple. The possibility of ion–molecule reactions was examined by the method of Bloom and Hastie<sup>3</sup> and it was concluded that they had a negligible effect on the results.

### Results and Discussion

Table 1 lists the ions observed and the temperature at which they first appeared. To prove the assignment of an ion, isotopic abundances were measured and compared with theoretical abundances for possible ions of the assigned mass. Because of difficulty of measuring small peaks adjacent to larger ones the major peak in each isotopic cluster was chosen for measurement.

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<sup>1</sup> Rice, D. W., and Gregory, N. W., *J. phys. Chem.*, 1968, **72**, 4524.

<sup>2</sup> Moss, H. I., Ph.D. Thesis, Indiana University, Bloomington, Ind., 1960.

<sup>3</sup> Bloom, H., and Hastie, J. W., *Aust. J. Chem.*, 1966, **19**, 1003.

TABLE 1  
FRAGMENT IONS OBSERVED ABOVE NaCl-ZnCl<sub>2</sub> MIXTURES

Min. Temp.	Ion	<i>m/e</i>	Rel. Intensity <sup>a</sup>	Precursor
128°	ZnCl <sub>2</sub> <sup>+</sup>	136	250000	ZnCl <sub>2</sub>
	ZnCl <sup>+</sup>	99	22000	
	Zn <sup>+</sup>	64	16500	
	Cl <sup>+</sup>	35	72000	
180	ZnCl <sub>2</sub> <sup>++</sup>	68	14800	ZnCl <sub>2</sub>
	ZnCl <sup>++</sup>	49.5		
200	Na <sub>2</sub> Zn <sub>2</sub> Cl <sup>+</sup>	209	8	Na <sub>2</sub> Zn <sub>2</sub> Cl <sub>6</sub>
	Na <sub>2</sub> Zn <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	244	72	
	Na <sub>2</sub> Zn <sub>2</sub> Cl <sub>3</sub> <sup>+</sup>	279	17	
	Zn <sub>2</sub> Cl <sub>3</sub> <sup>+</sup>	237	140	
300	Na <sup>+</sup>	23	1200	(ZnCl <sub>2</sub> ) <sub>2</sub>
	NaCl <sup>+</sup>	58		NaCl
	Na <sub>2</sub> <sup>+</sup>	46		(NaCl) <sub>2</sub>
	Na <sub>2</sub> Cl <sup>+</sup>	81		
312	NaZnCl <sub>2</sub> <sup>+</sup>	159	39	NaZnCl <sub>3</sub>
330	NaZnCl <sub>3</sub> <sup>+</sup>	194	1	

<sup>a</sup> At 460°.

TABLE 2  
CALCULATED HEATS OF REACTION

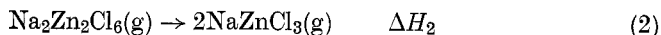
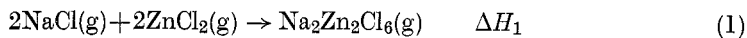
Ion	$\Delta H_1$ (kcal mole <sup>-1</sup> )	$\Delta H_2$ (kcal mole <sup>-1</sup> )
Na <sub>2</sub> Zn <sub>2</sub> Cl <sup>+</sup>	-52.9 ± 3.6	19.7 ± 3.1
Na <sub>2</sub> Zn <sub>2</sub> Cl <sub>2</sub> <sup>+</sup>	-54.3 ± 4.4	14.8 ± 2.5
Na <sub>2</sub> Zn <sub>2</sub> Cl <sub>3</sub> <sup>+</sup>	-54.3 ± 3.8	17.0 ± 3.2
Average	-53.8 ± 3.9	17.2 ± 2.9

Plots of the intensity ratios log  $K_1$  and log  $K_2$ , where

$$K_1 = \frac{[IT(\text{Na}_2\text{Zn}_2\text{Cl}_x^+)]}{[IT(\text{Na}^+)]^2[IT(\text{ZnCl}_2^+)]^2}$$

$$K_2 = \frac{[IT(\text{NaZnCl}_2^+)]^2}{[IT(\text{Na}_2\text{Zn}_2\text{Cl}_x^+)]}$$

$x = 1, 2$ , or  $3$ ,  $I$  = ion current at  $T^\circ\text{K}$ , against reciprocal temperature are given in Figure 1. From the least-squares slopes of the straight lines the heats of the following reactions were determined:



Calculations based on each of the fragments of Na<sub>2</sub>Zn<sub>2</sub>Cl<sub>6</sub> give the results shown in Table 2. The heat of formation,  $\Delta H_1$ , of Na<sub>2</sub>Zn<sub>2</sub>Cl<sub>6</sub> from NaCl and ZnCl<sub>2</sub> is

$-53.8 \text{ kcal mole}^{-1}$  and that of  $\text{NaZnCl}_3$  [i.e.  $(\Delta H_1 + \Delta H_2)/2$ ] is  $-18.3 \pm 3.4 \text{ kcal mole}^{-1}$ .

In both cases there is good agreement between heats of reaction calculated from each of the three separate fragments of  $\text{Na}_2\text{Zn}_2\text{Cl}_6$ .

In all cases intensities of complexes were at least a thousand times less than those of the zinc chloride fragments. This would account for the increased scatter in Figure 1(b) where the ratios of two weak peaks are being compared.

The figure given by Rice and Gregory<sup>1</sup> ( $-42 \text{ kcal mole}^{-1}$ ) for the heat of formation of  $\text{NaZnCl}_3$ , where monomer only was assumed, lies between those values

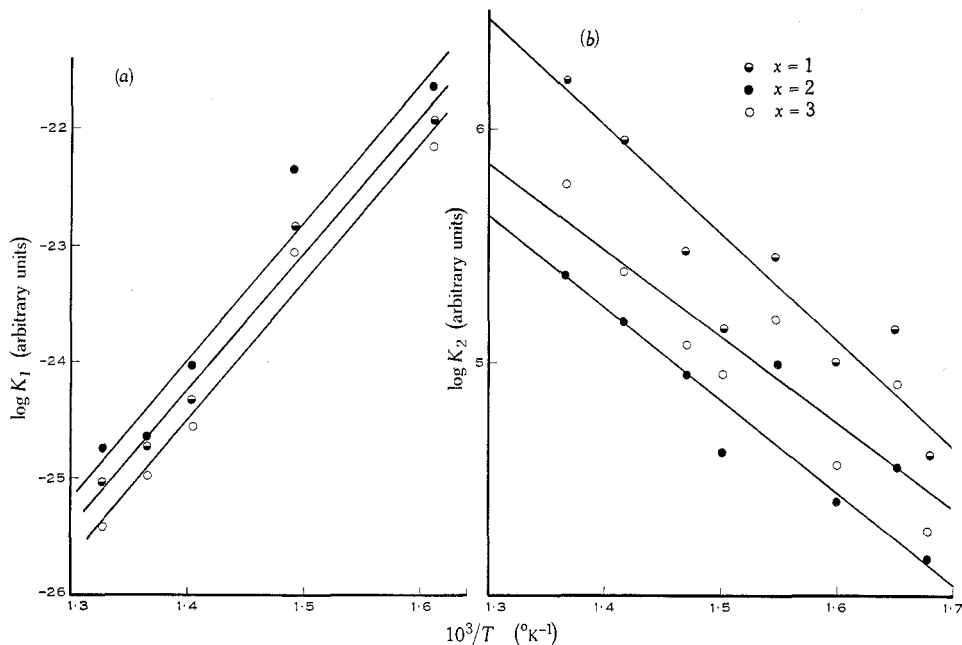


Fig. 1.—Plots against  $1/T$  of (a)  $\log\{[IT(\text{Na}_2\text{Zn}_2\text{Cl}_x^+)]/[IT(\text{Na}^+)]^2[IT(\text{ZnCl}_2^+)]^2\}$  and (b)  $\log\{[IT(\text{NaZnCl}_2^+)]^2/[IT(\text{Na}_2\text{Zn}_2\text{Cl}_x^+)]\}$ .

given here for monomer and dimer. It is interesting to note that the heat of formation of the monomer  $\text{NaZnCl}_3$  ( $-18.3 \text{ kcal mole}^{-1}$ ) is much less than that found by Hastie for the similar  $\text{NaPbCl}_3$  complex ( $-35 \text{ kcal mole}^{-1}$ ). Moreover, the heat of dimerization of  $\text{NaZnCl}_3$  is less than one half that of dimerization of pure zinc chloride ( $-40 \text{ kcal mole}^{-1}$ ) found by Keneshea and Cubicciotti.<sup>4</sup>

#### Acknowledgments

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<sup>4</sup> Keneshea, F. J., and Cubicciotti, D., *J. chem. Phys.*, 1964, **40**, 191.