

and MnB_4 is easily seen if the C -centered MnB_4 cell is transformed to an I -centered one with $a=4.6303 \text{ \AA}$, $b=5.3669 \text{ \AA}$, $c=2.9487 \text{ \AA}$, and $\beta=90.309^\circ$. The I -centered orthorhombic CrB_4 unit cell has the dimensions $a=4.744 \text{ \AA}$, $b=5.477 \text{ \AA}$, and $c=2.866 \text{ \AA}$.

It was observed that there were marked preferred orientation effects in the MnB_4 powder specimen used for recording the intensities, and accordingly the preliminary structure data quoted above are less accurate. Efforts are now being made to obtain improved diffraction data, and the results from this work together with the results from a careful phase analysis of the region MnB_2 -B will be published later.

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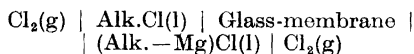
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Partial Free Energies of the Alkali Chlorides in Fused Mixtures with Magnesium Chloride

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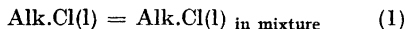
For systems of the type magnesium chloride-alkali chloride the partial molar Gibbs free energy has been measured. The data were obtained from electromotive force measurements of galvanic cells of the type:



where

Alk. = Na, K, Rb, and Cs.

The cell reaction for this galvanic cell is



In two previous papers by Førland and Østvold^{1,2} the liquid junction potential was discussed for galvanic cells of the type mentioned above. They concluded that this potential was negligible as long as $t_{\text{Alk}^+} \approx 1$. In the present investiga-

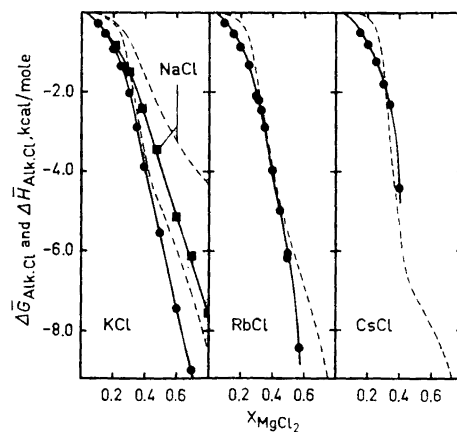


Fig. 1. Partial molar Gibbs free energies and partial molar enthalpies of mixing (dotted lines) of the alkali chlorides in mixtures with magnesium chloride. The temperatures are 1123°K, 1073°K, 998°K, and 928°K, respectively, for the sodium, potassium, rubidium, and cesium chloride systems.

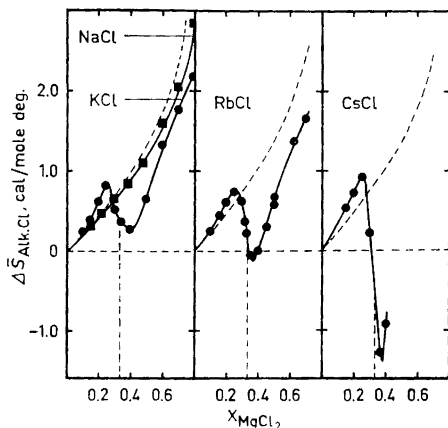


Fig. 2. Partial molar entropies of mixing of the alkali chlorides in mixtures with magnesium chloride. The dotted lines represent the ideal partial entropy of mixing: $-R \ln X_{\text{Aik.Cl}}$

tions glass membranes were used where $t_{\text{Na}^+} = 0.996$, $t_{\text{K}^+} = 0.998$, $t_{\text{Rb}^+} = 0.99$ and $t_{\text{Cs}^+} = 0.99$ in the sodium,² potassium,² rubidium,³ and cesium³ glasses, respectively. The emf values will therefore according to eqn. (1) give the partial molar Gibbs free energy of mixing of the alkali chlorides in the mixtures with magnesium chloride:

$$\Delta \bar{G}_{\text{Aik.Cl}} = \bar{G}_{\text{Aik.Cl}} - G^{\circ}_{\text{Aik.Cl}} = -nF\Delta E \quad (2)$$

A summary of the results is given in Figs. 1 and 2 where the partial molar Gibbs free energies, the partial molar enthalpies and the partial molar entropies are plotted versus the composition of the melt. The partial enthalpies are calculated from integral enthalpies of mixing from a work by Kleppa and McCarthy.⁴

The entropy curves show inflection points at $X_{\text{MgCl}_2} = 0.33$ and a sharp dependence on composition at this concentration. This may be accounted for in terms of a high degree of local order associated with this composition for the magnesium chloride-alkali chloride melts except for the magnesium chloride-sodium chloride melt where the entropy function is closely related to the ideal configurational entropy of mixing ($-R \ln X_{\text{NaCl}}$).

A similar entropy effect to that observed in the magnesium chloride-alkali chloride systems was found by Østvold and Kleppa⁵ in the lead oxide-silicon oxide melt at the composition $X_{\text{SiO}_2} \approx 0.35$. This entropy effect was attributed to the formation of the ortho-silicate anion, SiO_4^{4-} .

The magnesium chloride-alkali chloride systems have attracted considerable interest due to the possible formation of the complex anion, MgCl_4^{2-} , in the melt. Flood and Urnes,⁶ Førland,⁷ Kleppa and McCarthy,⁴ Neil, *et al.*⁸ and Krohn and Ikeuchi⁹ have discussed these systems in terms of complex formation. As pointed out by Kleppa and McCarthy,⁴ this problem could perhaps also be discussed by a suitable modification of the statistical model developed by Wagner and Schottky¹⁰ and Ölander¹¹ for nearly ordered solid compounds. The entropy behaviour reported in the present paper for the magnesium chloride-alkali chloride melts resembles the S-shaped entropy function observed by Ölander¹¹ for some solid binary mixture of metals, and indicate strongly the presence of an ordered structure in these melts at the composition $X_{\text{MgCl}_2} = 0.33$. An extensive discussion of this work will be given later in this journal.

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