# Emf Measurements for the Determination of Partial Gibbs Energies and Entropies of Mixing of the Alkali Chlorides in Liquid Mixtures with MnCl₂

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The partial Gibbs energies of mixing of the alkali chlorides in liquid mixtures with $MnCl_2$ have been measured using concentration cells of the following type:

C, $Cl_2(g)$ | $MeCl-SrCl_2(l)$ | Me-glass | $MeCl-MnCl_2(l)$ | $Cl_2(g)$, C
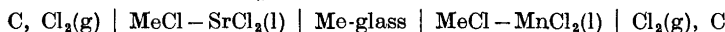
The binary $MeCl-SrCl_2$ ($X_{SrCl_2}=0.500$) was used as a reference melt for the $NaCl-MnCl_2$ and $KCl-MnCl_2$ systems. The cell temperature was then reduced compared to the higher melting point temperatures of the pure alkali salts. We thus avoided difficulties with the higher vapor pressures of $MnCl_2$ above the binary, $MeCl-MnCl_2$, melts at the melting points of NaCl and KCl. For Me = Li and Rb pure LiCl and RbCl, respectively, were used as reference melts. The concentration range for the binary systems, $MeCl-MnCl_2$, was $0 < X_{MnCl_2} < 0.7$.

The results of the present investigation are in agreement with the assumption that the $MnCl_4^{2-}$ ion is formed in the binary $MnCl_2-NaCl$, $-KCl$, and $-RbCl$ melts. The tendency for complex formation is enhanced by an increase in the radius of the alkali ion. The experimental data did not predict any formation of the complex ion in the $LiCl-MnCl_2$ melts.

During the past decade many equilibrium and emf investigations of simple binary charge-unsymmetrical molten salt mixtures ($MeX-MX_2$) have been reported. A review of much of this work can be found in paper by Blander,[1] Ricci,[2] and Førland[3] and in two bibliographies by Janz[4] and Janz and Dijkhuis.[5] Some recent emf investigations were carried out by Ikeuchi and Krohn[6] on the alkali chloride−magnesium chloride systems and by Østvold,[7] who investigated the alkali chloride−alkaline earth chloride binary melts using concentration cells with ion selective glass membranes separating the two half cells. Other thermodynamic data on charge-unsymmetrical systems have been obtained through vapor pressure measurements on binaries which contain volatile species, such as $PbCl_2$,[8] $CdCl_2$,[9] and $FeCl_2$,[10] and also through the study of decomposition pressures.[11]

Recently the integral enthalpies of mixing, ΔH, of several charge-unsymmetrical fused salt binaries have been measured by Kleppa and coworkers. Studies of mixtures of the alkali chlorides with lead chloride,[12] magnesium chloride,[13] nickel(II) chloride,[14] manganese, iron(II), and cobalt chlorides,[15] cadmium chloride,[16] and the alkaline earth chlorides [17] have been reported. The enthalpies of mixing of these binary melts were found to decrease sharply when the monovalent cation is replaced in the sequence $Li - Na - K - Rb - Cs$. For the binaries of $MgCl_2$, $PbCl_2$, $CdCl_2$, $NiCl_2$, $MnCl_2$, $FeCl_2$, and $CoCl_2$ with KCl, RbCl, and CsCl the enthalpy interaction parameter, $\lambda = \Delta H / X_1 X_2$, (where X_i is the mol fraction of the ith component) depends strongly on composition and shows a minimum value at $X_{MCl_2} = 0.33$. This supports the view originally advanced by Flood and Urnes [18] for the alkali chloride-magnesium chloride mixtures, that the mixture is stabilized by a preferred coordination of four anions around the divalent cation, MCl_4^{2-}. The stability of this configuration increases markedly as the radius of the monovalent cation increases.

The partial entropies of mixing of the alkali chlorides KCl, RbCl, and CsCl in the binary mixtures with magnesium chloride obtained by Østvold [7,19] show inflection points at $X_{MgCl_2} = 0.33$ and a sharp dependence on composition at this concentration. This was accounted for in terms of the high degree of local order associated with this composition. A similar entropy effect to that observed in the magnesium chloride − alkali chloride melts was found by Østvold and Kleppa [20] in the lead oxide − silicon oxide melts. This entropy effect was attributed to the formation of the ortho-silicate anion, SiO_4^{4-}.

In the present investigation the chemical potentials of the alkali chlorides of solution in the liquid mixtures with manganese chloride were measured by an emf technique using concentration cells with an alkali ion conducting glass separating the two half cells. In these cells, therefore, the chemical work carried out in the junction between the two half cells was negligible and the chemical potential of the alkali chloride was obtained directly from the emf data. Due to swelling of the graphite electrodes at high manganese chloride concentrations we were unable to study melts richer in manganese chloride than $X_{MnCl_2} = 0.65$.

EXPERIMENTAL

Chemicals. The analytical reagent grade salts were obtained from E. Merck AG, Germany, and were melted before use in order to remove moisture. The manganese chloride contained water and was heated slowly from room temperature to 200°C under vacuum over a period of 2 days. The salt was then moved to a drying device consisting of a 6 cm o.d. and 30 cm long Pyrex tube with a Pyrex frit at the bottom. $250 - 500$ g of the predried $MnCl_2$ were added to a fused silica cylinder mounted in the Pyrex tube. This drying device was then heated to 450°C over a period of 20 h. Pure dry HCl was passed through the salt bed. The gases leaving the drying apparatus passed through a mercury trap and a second water trap. The manganese chloride was then fused under a continuous flow of HCl. The purity of the dehydrated salts was tested by passing a water solution of the salts through a hydrogen-cation exchanger. The resultant solutions were titrated with a standard 0.1 N sodium hydroxide solution. The following results were obtained:

$$MnCl_2: \quad 99.9 \pm 0.1 \text{ mol } \% \quad MnCl_2$$
$$LiCl: \quad 100.1 \pm 0.1 \quad \text{»} \quad LiCl$$

$$
\begin{array}{llll}
\text{NaCl:} & 100.0 \pm 0.1 & \text{»} & \text{NaCl} \\
\text{KCl:} & 100.1 \pm 0.1 & \text{»} & \text{KCl} \\
\text{RbCl:} & 99.9 \pm 0.1 & \text{»} & \text{RbCl}
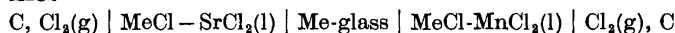\end{array}
$$

Hand picked crystals of each of the salts were used in loading the cells, the manganese chloride and lithium chloride being handled in a dry-box. The exposure to air never amounted to more than 10 sec. The silica cells were always filled with dry N_2 before the salts were introduced to prevent the oxidation of the divalent manganese ion.

Apparatus. The silica cells employed in these experiments are described elsewhere.[7,21] The composition of the four glasses used in the present investigation is given in Table 1.
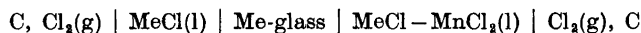
Table 1. Composition of the alkali-membrane-glasses (mol %).

Oxide	Lithium glass	Sodium glass	Potassium glass	Rubidium glass
SiO_2	70	70	64.8	75
Li_2O	20			
Na_2O		12.3		
K_2O			15	
Rb_2O				20
Al_2O_3	10	12.7	15.2	5
TiO_2		2	2	
ZrO_2		2	2	
Ce_2O_3		1	1	

The relatively high vapor pressure of $MnCl_2$ over these binary mixtures made it difficult to work with pure alkali chloride as reference melts in these cells at high concentrations of $MnCl_2$. The following cells were therefore used in the present investigation: when $X_{MnCl_2} > 0.3$
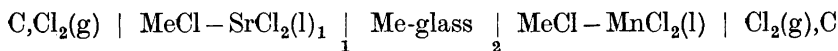
$$\text{C, } Cl_2(g) \mid MeCl - SrCl_2(l) \mid \text{Me-glass} \mid MeCl\text{-}MnCl_2(l) \mid Cl_2(g), \text{C}$$

when $X_{MnCl_2} < 0.3$

$$\text{C, } Cl_2(g) \mid MeCl(l) \mid \text{Me-glass} \mid MeCl - MnCl_2(l) \mid Cl_2(g), \text{C}$$

For the $LiCl - MnCl_2$ and $RbCl - MnCl_2$ mixtures pure alkali chloride, however, could be used in the left hand side compartment since the temperatures of fusion for these salts are low enough to keep a moderate pressure of $MnCl_2$ over the fused manganese chloride containing mixtures.

RESULTS

The emf, E, of the galvanic cell

$$\text{C,} Cl_2(g) \mid \underset{1}{MeCl - SrCl_2(l)_1} \mid \text{Me-glass} \mid \underset{2}{MeCl - MnCl_2(l)} \mid Cl_2(g), \text{C}$$

is connected to the change in Gibbs energy for the cell reaction by the following equation [7,22,23]

$$
\begin{aligned}
\varDelta G = -FE = {} & \mu_{MeCl(2)} t_{Me^+(2)} + \tfrac{1}{2}\mu_{MnCl_2(2)} t_{Mn^{2+}(2)} \\
& - \mu_{MeCl(1)} t_{Me^+(1)} - \tfrac{1}{2}\mu_{SrCl_2(1)} t_{Sr^{2+}(2)} \\
& - \int_1^2 \{ [\mu_{Me\text{-sil}} \mathrm{d}t_{Me^+} + \tfrac{1}{2}\mu_{Mn\text{-sil}} \mathrm{d}t_{Mn^{2+}} + \tfrac{1}{2}\mu_{Sr\text{-sil}} \mathrm{d}t_{Su^{2+}} \}
\end{aligned}
\tag{1}
$$

over
membrane

where t_{Me^+}, $t_{Mn^{2+}}$ and $t_{Sr^{2+}}$ refer to the transport numbers in the glass membrane of Me^+, Mn^{2+}, and Sr^{2+} ions, respectively, and $t_{Me^+(1)}$ or $t_{Me^+(2)}$ etc. refer to the values of these transport numbers in the glass membrane at the interfaces between glass and salt mixtures denoted 1 or 2. Introducing the equations for the equilibria between ions in solution and ions in glass at the contact between the two phases and integrating eqn. (1) by parts, we obtain

$$\Delta G = -FE = \mu_{MeCl(2)} - \mu_{MeCl(1)} + \mu_{Me\text{-sil}(1)} - \mu_{Me\text{-sil}(2)}$$
$$+ \int_1^2 \{t_{Me^+}\mathrm{d}\mu_{Me\text{-sil}} + \tfrac{1}{2}t_{Mn^2+}\mathrm{d}\mu_{Mn\text{-sil}} + \tfrac{1}{2}t_{Sr^2+}\mathrm{d}\mu_{Sr\text{-sil}}\} \qquad (2)$$
$$\text{over}$$
$$\text{membrane}$$

We cannot simplify eqn. (2) further without introducing assumptions regarding the transport properties of the ions in the glass membrane. The transport numbers of the alkaline earth ions in glasses of the same type as used as membranes in the above galvanic cells were measured previously.[23,24] The transport numbers of these ions were all found to be negligible compared to the transport numbers for the alkali ions. The charge and size of the Mn^{2+} ion is the same as for the Ca^{2+} ion and it is therefore reasonable to believe that the transport number of Mn^{2+} in these glasses is very small. If we assume that $t_{Me^+} = 1$, eqn. (2) gives

$$\Delta G = -FE = \Delta\mu_{MeCl(2)} - \Delta\mu_{MeCl(1)} \qquad (3)$$

where $\Delta\mu_{MeCl} = \mu_{MeCl} - \mu_{MeCl}^\circ$ (μ_{MeCl}° is the chemical potential of pure liquid MeCl) has been introduced. Since the chemical potentials of mixing of the alkali chlorides in mixtures with strontium chloride, $\Delta\mu_{MeCl(1)}$, are known,[7] we can calculate the chemical potentials of mixing of the alkali chlorides in mixtures with manganese chloride, $\Delta\mu_{MeCl(2)}$, from eqn. (3). When pure alkali chloride is used as a reference melt, eqn. (3) takes the form

$$\Delta G = -FE = \Delta\mu_{MeCl(2)} \qquad (4)$$

Table 2. Thermodynamic data for the $MnCl_2 - MeCl$ mixtures. $Me = Li$, Na, K and Rb. Emf's for the galvanic cell

$$C, Cl_2(g) \mid MeCl(l) \mid Me\text{-glass} \mid MeCl - MnCl_2(l) \mid Cl_2(g), C$$
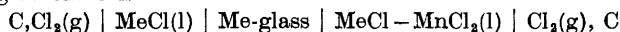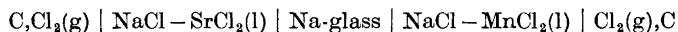
are measured. The thermodynamic data for MeCl in the fused $MeCl - MnCl_2$ mixtures are calculated from the present emf values and the enthalpy of mixing data given by Papatheodorou and Kleppa.[15]

System and temperature	X_{MnCl_2}	Emf mV	$-\Delta\mu_{MeCl}$ cal/mol	$-\Delta\bar{H}_{MeCl}$ cal/mol	$\Delta\bar{S}_{MeCl}$ cal/mol deg.
$MnCl_2 - LiCl$	0.101	8.2	190	50	0.15
$T = 918$ K	0.200	21.0	485	130	0.39
	0.250	29.8	685	170	0.56
	0.300	37.0	850	210	0.70
	0.350	47.7	1100	270	0.90
	0.400	54.6	1260	370	0.97
	0.450	70.0	1610	490	1.21
	0.500	81.1	1870	590	1.40
	0.600	105.3	2430	700	1.89

Table 2. Continued.

$MnCl_2 - NaCl$	0.129	17.1	394	70	0.30
$T = 1085$ K	0.241	44.9	1040	360	0.63
	0.353	87.4	2010	950	0.98
	0.409	113.0	2600	1700	0.83
$MnCl_2 = KCl$	0.124	16.9	390	0	0.37
$T = 1063$ K	0.185	32.6	750	200	0.51
	0.243	54.0	1245	700	0.51
	0.266	65.4	1510	800	0.67
	0.277	71.3	1640	950	0.65
	0.300	85.5	1970	1050	0.87
$MnCl_2 - RbCl$	0.125	15.6	360	0	0.36
$T = 998$ K	0.198	35.2	810	100	0.71
	0.231	48.7	1120	500	0.62
	0.254	60.2	1390	800	0.59
	0.300	89.8	2070	1800	0.27
	0.354	136.9	3150	3600	− 0.45
	0.376	154.5	3560	4000	− 0.44
$MnCl_2 - RbCl$	0.430	201.0	4630	5150	− 0.52
$T = 998$ K	0.461	224.3	5170	5650	− 0.48
	0.492	251.9	5810	5950	− 0.14
	0.512	272.3	6280	6100	0.18
	0.532	285.7	6590	6350	0.24
	0.562	311.6	7180	6700	0.48
	0.658	394.9	9100	7800	1.30

Table 3. Thermodynamic data for the $NaCl - MnCl_2$ mixtures. Emf's for the galvanic cell

$$C,Cl_2(g) \mid NaCl - SrCl_2(l) \mid Na\text{-glass} \mid NaCl - MnCl_2(l) \mid Cl_2(g),C$$

where $X_{SrCl_2} = 0.500$, are measured. The corrected emf's, emf^{corr}, at 610°C given below are obtained by using the equation: emf^{corr} = emf + 65.5 mV. The number, 65.5 mV, is the emf for the analogous $NaCl(l) \mid Na\text{-glass} \mid NaCl - SrCl_2(l)$ ($X_{NaCl} = 0.500$) cell adjusted to 610°C.[7] The thermodynamic data for NaCl in the fused $NaCl - MnCl_2$ mixtures are calculated from the present emf values and the enthalpy of mixing data given by Papatheodorou and Kleppa.[15]

System and temperature	X_{MnCl_2}	Emf mV	Emf^{corr} mV	$- \varDelta \mu_{NaCl}$ cal/mol	$- \varDelta \overline{H}_{NaCl}$ cal/mol	$\varDelta \overline{S}_{NaCl}$ cal/mol deg.
$MnCl_2 - NaCl$	0.357	10.0	75.5	1740	1000	0.84
$T = 885$ K	0.376	17.1	82.6	1900	1200	0.79
	0.397	26.2	91.7	2110	1600	0.58
	0.409	33.0	98.5	2270	1700	0.65
	0.461	57.9	123.4	2840	2150	0.78
	0.462	56.8	122.3	2820	2150	0.76
	0.510	81.9	147.4	3400	2500	1.02
	0.562	107.7	173.2	3990	2850	1.29
	0.562	107.5	173.0	3990	2850	1.29
	0.608	131.0	196.5	4530	3000	1.73
	0.655	155.0	220.5	5080	3250	2.07
	0.656	155.7	221.2	5100	3250	2.10

Table 4. Thermodynamic data for the $KCl-MnCl_2$ mixtures. Emf's for the galvanic cell

$$C,Cl_2(g) \mid KCl-SrCl_2(l) \mid K\text{-glass} \mid KCl-MnCl_2(l) \mid Cl_2(g),C$$
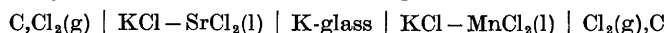
where $X_{SrCl_2} = 0.333$, are measured at 690 and 710°C. The corrected emf's, emf^{corr}, given below are obtained by adding the emf for the analogous $KCl(l) \mid K\text{-glass} \mid KCl-SrCl_2(l)$ $(X_{KCl} = 0.667)$ cell adjusted to the above temperatures.[7] The thermodynamic data for KCl in the fused $KCl-MnCl_2$ mixtures are calculated from the present emf values and the enthalpy of mixing data given by Papatheodorou and Kleppa.[15]

System and temperature	X_{MnCl_2}	Emf mV	Emf^{corr} mV	$-\Delta\mu_{KCl}$ cal/mol	$-\Delta\bar{H}_{KCl}$ cal/mol	$\Delta\bar{S}_{KCl}$ cal/mol deg.
$MnCl_2-KCl$	0.299	27.5	82.7	1900	1050	0.86
$T=983$ K	0.355	64.1	119.3	2750	2250	0.51
	0.372	82.4	137.6	3170	2800	0.38
	0.392	96.5	151.7	3500	3400	0.11
	0.408	106.8	162.0	3730	4000	−0.28
$MnCl_2-KCl$	0.387	89.4	144.1	3320	3150	0.18
$T=963$ K	0.419	116.6	171.3	3950	4300	−0.36
	0.461	149.3	204.0	4700	5000	−0.31
	0.512	187.1	241.8	5570	5500	0.07
	0.562	225.4	280.1	6460	5800	0.69
	0.658	298.5	353.2	8140	6300	1.90

In Tables 2 − 4 the experimental data are presented together with the partial enthalpies of mixing of the alkali chlorides in mixtures with manganese chloride, $\Delta\bar{H}_{MeCl}$, calculated from integral enthalpies of mixing determined by Papatheodorou and Kleppa.[15] The partial entropies of mixing presented in these tables are calculated from the present chemical potentials and the calculated partial enthalpies of mixing. In Figs. 1 and 2 $\Delta\mu_{MeCl}$, $\Delta\bar{H}_{MeCl}$ and $\Delta\bar{S}_{MeCl}$ are plotted *versus* the mol fraction of $MnCl_2$, X_{MnCl_2}.

DISCUSSION

For mixtures of fused salts containing monovalent and divalent cations most of the available experimental data indicate that the fused systems may be described as random mixtures of the two cations when the cations have ionic potentials, Z_+/R_+, of comparable magnitude. Deviations from the Temkin entropy of mixing may otherwise occur. In the $MgCl_2-MeCl$ systems where $Me = Li$, Na, K, Rb, and Cs, marked deviations from the random mixing of cations behavior were observed for the KCl, RbCl and CsCl containing systems.[6,7,13] In these mixtures the double charge and small size of the magnesium ion will make its ionic potential much greater than that of the potassium, rubidium, and cesium ions. In mixtures involving Mg^{2+} and K^+, Rb^+, or Cs^+, the Cl^- anions will undoubtedly prefer association with the Mg^{2+} cation. This preference will be limited by steric factors, but may be favored by possible covalent interactions between the ions. A lower cation-cation repulsion between unlike cations will also contribute to a preferred
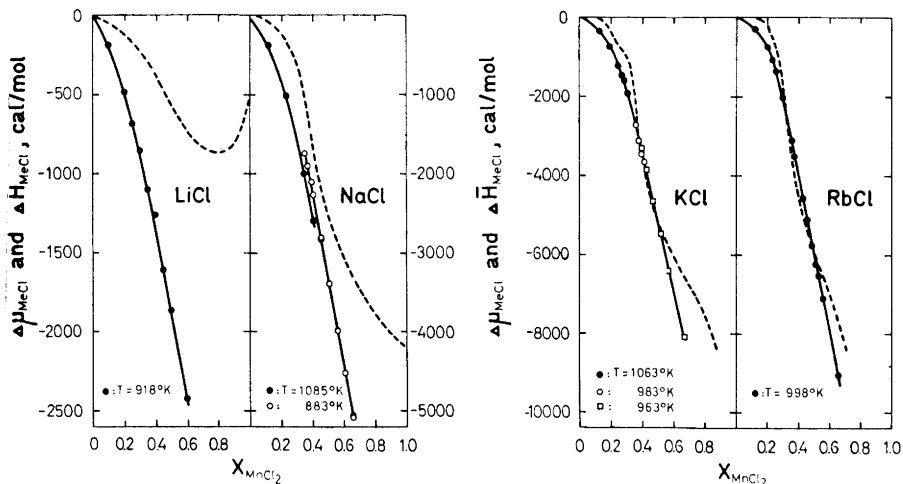
Fig. 1. Chemical potentials and partial enthalpies of mixing (dotted lines) of the alkali chlorides in mixtures with manganese chloride. The partial enthalpies, $\Delta\overline{H}_{MeCl}$, are calculated from integral enthalpies of mixing given by Papatheodorou and Kleppa.[15]
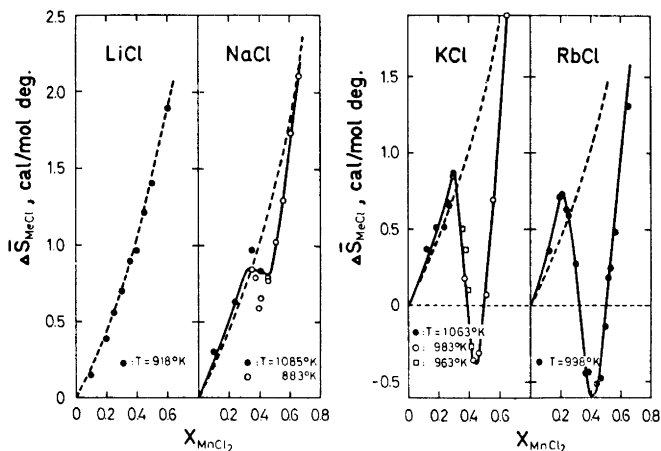

Fig. 2. Partial entropies of mixing of the alkali chlorides in mixtures with manganese chloride. The dotted lines represent the ideal entropies given by $-RT \ln X_{MeCl}$.

$Mg^{2+} - Cl^-$ association. The actual structural arrangements of the ions will be a compromise between the interactions which tend to make an ordered system, namely the polarization interactions and the Coulomb repulsion between next nearest neighbors, and the thermal movements of the ions which show a tendency towards randomization to increase the entropy of the system. In a recent paper Bredig [25] discussed the experimental evidence for "complex ions" in some binary molten salt mixtures. He concluded that the experimental

evidence of MX_3^- and MX_6^{4-} complex ions in binary molten halide systems, $MeX - MX_2$, is not satisfactory. The accurate calorimetric determinations of the integral enthalpies of mixing of Kleppa and coworkers [13-16] and the partial entropies obtained in the $MgCl_2 - MeCl$ [6,7] melts indicate a predominance of the MCl_4^{2-} species in the $MgCl_2 - MeCl$, $NiCl_2 - MeCl$, $CoCl_2 - MeCl$, $FeCl_2 -$ MeCl, $MnCl_2 - MeCl$, and $CdCl_2 - MeCl$ mixtures when $Me = K$, Rb, and Cs. When the partial entropies of the alkali chloride (KCl, RbCl, or CsCl) on mixing in the $MgCl_2 - MeCl$ mixtures are plotted *versus* concentration, S-shaped curves are obtained. These entropy functions show inflection points at $X_{MgCl_2} = 0.333$ and a sharp dependence on composition at this concentration. This may be accounted for in terms of the high degree of local order associated with this composition due to the formation of the four-coordinated magnesium chloride "complex", $MgCl_4^{2-}$ or in other words Mg^{2+} ions with K^+, Rb^+, or Cs^+ ions only as next nearest neighbors.

Østvold and Kleppa [20] have shown in their study of the $PbO - SiO_2$ system that a partial entropy curve having an S-shape is to be expected when a complex ion constituent of the molten mixture, *e.g.* the SiO_4^{4-} ion, is partly dissociated. Ikeuchi and Krohn [6] and Østvold [7] adopted the method outlined by Østvold and Kleppa [20] for calculating entropies of mixing in binary systems forming four-coordinated anion complexes. They assumed random mixing of cations, M^{2+} and Me^+, on a cation lattice and anions, MCl_4^{2-} and Cl^- on an anion lattice. The following expression for the partial entropy of mixing of the alkali chloride, MeCl, was obtained.[7]

$$\Delta \bar{S}_{MeCl} = - R\{\ln X_{Me} + X_{Cl^-} - \frac{\partial n_{MCl_4^{2-}}}{\partial n_{MCl_2}} \ln K\} \tag{5}$$

Here $n_{MCl_4^{2-}}$ is the number of moles of the "complex" ion MCl_4^{2-} and n_{MCl_2} is the total number of moles of MCl_2 in the molten mixture. K is the "dissociation quotient" of the MCl_4^{2-} ion: $K = X_{M^{2+}} X_{Cl^-}^4 / X_{MCl_4^{2-}}$. By choosing different values for K qualitative agreement between experiment and calculation was obtained for the different $MgCl_2 - MeCl$ mixtures. This is also the case for the present, $MnCl_2 - MeCl$, mixtures, and partial entropies calculated by eqn. (5) shown in Fig. 3 agree fairly well with the experimental partial entropies shown in Fig. 2. In a previous paper [7] the weaknesses of the above model, model 1, were discussed and an alternative model, model 2, taking into account the possible concentration dependence of the "dissociation quotient", was introduced.

In model 2 a second variable parameter which takes into account the change in the equilibrium

$$2MeCl + MMCl_4 = MCl_2 + Me_2MCl_4 \tag{6}$$

when one alkali ion, Me^+, is substituted by another, was introduced. In eqn. (6) the hypothetical compounds $MMCl_4$ and Me_2MCl_4 contain two kinds of cations, those M^{2+} cations which are closely surrounded by four Cl^- ions in the MCl_4^{2-} "complex" and those which are considered "normal" cations Me^+ and M^{2+}.

Using model 2 it was possible to express the entropy of mixing as a function of the mol fractions of the components, MeCl and MCl_2, constituting the
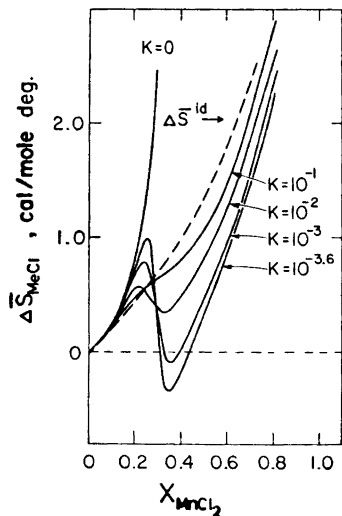
Fig. 3. Partial entropies of mixing of the alkali chlorides in mixtures with manganese chloride (eqn. (5)) calculated on the basis of random mixtures of Me^+ and Mn^{2+} on a quasi-cation-lattice and of Cl^- and $MnCl_4^{2-}$ on a quasi-anion-lattice, respectively, for different values of the dissociation quotient, K, for the equilibrium $MnCl_4^{2-} = Mn^{2+} + 4Cl^-$.

binary mixture and the fraction, α, of the divalent ion which is present in the MCl_4^{2-} "complex". The value of α which actually occurs in the expression for the partial entropy is that which minimizes the Helmholz energy of the system. Both the partial entropy and energy of the alkali chloride on mixing could be calculated. For the detailed calculations a paper by Østvold [7] should be consulted. In Figs. 4 and 5, $\Delta \bar{S}_{MeCl}$, $\Delta \bar{E}_{MeCl}$, and $\Delta E^M/X_1X_2$ calculated by this method are presented as functions of the $MnCl_2$ concentration. A fairly good agreement between calculated and experimental entropies is observed (compare Figs. 2 and 4). The partial energies of mixing calculated by the present method (see Fig. 5), however, do not compare quantitatively with the experimental enthalpies shown in Fig. 1. Because of the crude approximations introduced in the above model, it comes as no surprise that the thermodynamic data obtained by the present model-calculations deviate significantly from the experimental data, but the qualitative agreement between calculated and experimental data gives us at least some understanding of the order-disorder phenomena in the alkali chloride – manganese chloride melts.

As pointed out by Kleppa and McCarty,[13] S-shaped entropy functions could perhaps be discussed by a suitable modification of the statistical model developed by Wagner and Schottky [27] and Ölander [28] for nearly ordered solid compounds. A comparison between the Wagner – Schottky – Ölander theory and the experimental partial entropies of alkali chloride in the $MgCl_2$ – $MeCl$ mixtures was made by Østvold.[7] Qualitative agreement between experimental and theoretical data was obtained. The same comparison could be made with the present entropy data. The same qualitative agreement would be obtained.

On the basis of the present entropy data and the enthalpy of mixing data obtained by Papatheodorou and Kleppa [15] we can conclude that the alkali rich mixtures of $MnCl_2$ with KCl, RbCl, CsCl, and to some extent the $MnCl_2$ – NaCl
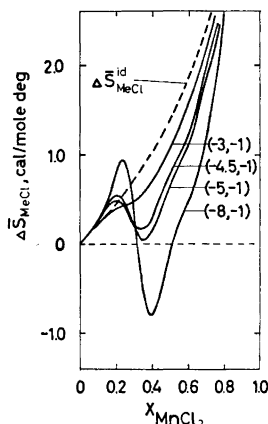
Fig. 4. Partial entropies of mixing of the alkali chlorides in mixtures with manganese chloride calculated on the basis of random mixtures of Me^+ and Mn^{2+} on a quasi-cation-lattice and of Cl^- and $MnCl_4^{2-}$ on a quasi-anion-lattice, respectively, for definite values of the energy parameters ΔE_1 and ΔE_2 which refer to the energy changes associated with the following two reactions: (1) $2MeCl + MnMnCl_4 = MnCl_2 + Me_2MnCl_4$, and (2) $2MnCl_2 = MnMnCl_4$. The first number in the parenthesis represents ΔE_1 and the second ΔE_2, both in kcal/mol.
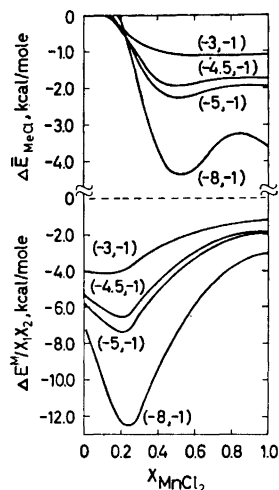
Fig. 5. The energy of mixing interaction parameter, $\Delta E^M/X_1X_2$, and the partial energy of mixing of alkali chloride in mixtures with manganese chloride, $\Delta \bar{E}_{MeCl}$, calculated on the basis of random mixtures of Me^+ and Mn^{2+} on a quasi-cation-lattice and Cl^- and $MnCl_4^{2-}$ on a quasi-anion-lattice, respectively. Nearest neighbors only are counted in the energy summation. The calculations are performed for definite values of the energy parameters ΔE_1 and ΔE_2 which refer to the energy changes associated with the following two reactions: (1) $2MeCl + MnMnCl_4 = MnCl_2 + Me_2MnCl_4$, and (2) $2MnCl_2 = MnMnCl_4$. The first number in the parenthesis represents ΔE_1 and the second ΔE_2, both in kcal/mol.

mixtures all contain the four-coordinated manganese chloride "complex", $MnCl_4^{2-}$ or in other words Mn^{2+} ions with monovalent ions *only* as next nearest neighbors.

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