

Thermodynamic Properties of Binary, Liquid Magnesium Chloride-Alkali Chloride Mixtures

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The emf of the formation cell



has been measured in the temperature range from 700 to 850°C, M being Na, K, and Cs, respectively, in the present investigation. From the obtained data some thermodynamic properties of the binary systems have been calculated.

For the systems MgCl_2-KCl and $\text{MgCl}_2-\text{CsCl}$, a model involving the complex ion MgCl_4^{2-} seems to be adaptable to the liquid mixture in a narrow concentration region around 33.3 mole % MgCl_2 .

The chemistry of magnesium chloride and its mixtures with the alkali chlorides is of particular interest, both theoretically and from a commercial point of view. Most of these systems form compounds in the solid state, and the possible existence of complex ions in these molten mixtures has been the topic of several papers.¹⁻³ The commercial aspect of the chemistry of such mixtures is the magnesium electrowinning process, where an electrolyte of molten magnesium chloride with the addition of mainly sodium, potassium, and calcium chloride is employed.

The purpose of the present investigation was dual: to find a reversible magnesium electrode generally applicable for measurement and control in magnesium chloride systems, and to measure the thermodynamic properties of magnesium chloride-alkali chloride mixtures, employing such an electrode.

The thermodynamic data was evaluated from emf measurements of formation cells of the following type:



M being Na, K, and Cs in the present investigation.

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Neil *et al.*² used in principle the same method as in the present work to obtain thermodynamic data for the systems $\text{MgCl}_2\text{--NaCl}$ and $\text{MgCl}_2\text{--KCl}$, but the arrangement of the cell was somewhat different.

One of the limitations for using galvanic cells of the present type for the study of molten salts at high temperature is that the fused metal of the electrodes, like magnesium and aluminium, inheres the additional difficulty that there is only a small difference in density between the metal and the salt phase which makes a proper separation of the two liquid phases problematic. In the present work, therefore, bismuth was added to the magnesium electrode in order to increase the density of the electrode and depress the solubility of magnesium in the salt phase.

EXPERIMENTAL

The arrangement of the cell, shown in Fig. 1, is the same as of the cell previously employed by Krohn and Moser⁴ for the system NaCl--KCl .

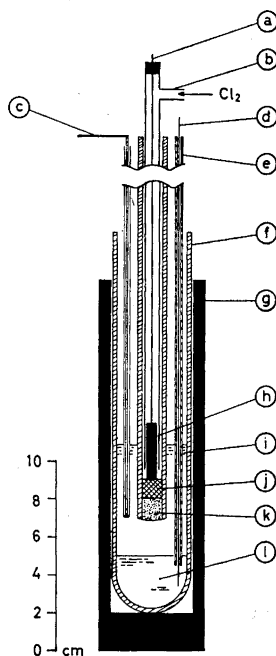


Fig. 1. Galvanic cell assembly. (a) Pt lead for Cl_2 electrode. (b) Silica glass tube. (c) Pt/Pt10Rh thermocouple in sintered alumina sheath. (d) Ta lead for Mg-Bi electrode in Pythagoras ceramic protection tube. (e) Pythagoras tube. (f) Sintered alumina crucible. (g) Graphite supporter. (h) Graphite rod Cl_2 electrode. (i) Electrolyte. (j) Silica powder held by silica wool wad. (k) Sintered alumina diaphragm. (l) Mg-Bi alloy.

An alloy composition of 14.3 mole % Bi was used for the measurements in the MgCl_2 mixtures with NaCl and KCl, and an alloy with 14.0 mole % Bi for the $\text{MgCl}_2\text{--CsCl}$ system. The Mg-Bi alloy was prepared in an alumina crucible under an atmosphere of Ar. The alumina crucible was not attacked by the liquid alloy.

The diaphragm, which is one of the most important parts of the cell, consisted of a Pythagoras ceramic tube with a sintered alundum-silica cement plug at the bottom.

The porosity of the plug was made as uniform as possible and was such as to prevent viscous mixing of the anolyte and the catholyte. Normally the diaphragm was prepared from alundum cement (100–150 μ) with 40 wt. % silica powder (100–150 μ) and sintered at 1150°C for 1 h. In order to ensure the functioning of the diaphragm, even if cracking occurred during an experimental run, a layer of silica powder held by a silica wool wad was placed on top of the sintered plug.

The chlorine electrode consisted of a spectrographic grade graphite rod (5 mm \varnothing \times 30 mm) with a Pt wire (0.5 mm \varnothing) for establishing electrical contact, and was supported vertically by concentric silica glass tubes through which the chlorine gas was passed. The Pt wire was protected from the chlorine gas by a silica glass tube.

An ordinary, vertical furnace with Kanthal resistors was used for heating, and the cell assembly was placed between ceramic radiation shields to diminish the longitudinal temperature gradient.

The cell was surrounded by a thin copper foil at earth potential to avoid influence from the electric field of the furnace on the emf measurements.

Measurements were carried out at both decreasing and increasing temperatures in the range from 700 to 850°C. The emf of the cell and the temperature was measured every 5 min by means of an ordinary potentiometer, and for part of the measurements also recorded simultaneously on a two-canal potentiometric recorder with suppressed zero point.

The composition of the mixture was determined by analysis, using the EDTA method for magnesium and the silver titration for the chloride. The accuracy of the analyses, expressed by the relative standard deviation, was 0.5 %, and the analytical results for pure magnesium chloride showed the theoretical value.

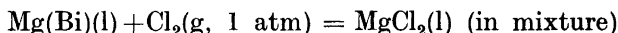
The Pt/Pt10Rh thermocouple for temperature measurement was calibrated against the melting points of pure Ag and Mg, respectively. The recorded emf values further were corrected for the thermoelectric emf which arises in the measuring circuit due to the application of Pt and Ta for the current leads to the respective electrodes.

Anhydrous magnesium chloride was prepared from the hexahydrate by passing dry, gaseous HCl through the solid in four steps: at 120°C, 240°C, and 320°C for 2 h, respectively, and at 400°C for 4 h, then melted in an argon atmosphere and filtered through a fritted silica glass filter. The pure MgCl₂ (with a maximum MgO concentration level of 0.05 %) then was sealed off under argon in silica glass ampoules. The sodium and the potassium chloride (Baker) and the cesium chloride (Hopkin & Williams) were analytical reagent grade chemicals. Pure magnesium and bismuth (99.9 %) were obtained from A/S Norsk Hydro and Merck AG., respectively.

RESULTS

The observed values of emf *versus* temperature for the systems MgCl₂–NaCl, MgCl₂–KCl, and MgCl₂–CsCl are shown in Figs. 2, 3, and 4, respectively. The reproducibility is better than ± 3 mV in all runs.

The cell reaction in the present case is:



The change in Gibbs' free energy for this reaction is:

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{MgCl}_2}}{a_{\text{Mg}} \cdot p_{\text{Cl}_2}} \quad (1)$$

Here the standard states are taken as pure, liquid magnesium chloride, pure, liquid magnesium metal, and gaseous chlorine at 1 atm. Then, in a reversible electrochemical cell:

$$E = E^\circ - \frac{RT}{2F} \ln \frac{a_{\text{MgCl}_2}}{a_{\text{Mg}}} \quad (2)$$

Fig. 2. Emf versus temperature for the system MgCl_2 - NaCl . N_{MgCl_2} =(a): 0.158; (b): 0.203; (c): 0.320; (d): 0.455; (e): 0.458; (f): 0.590; (g): 0.694; (h): 1.000.

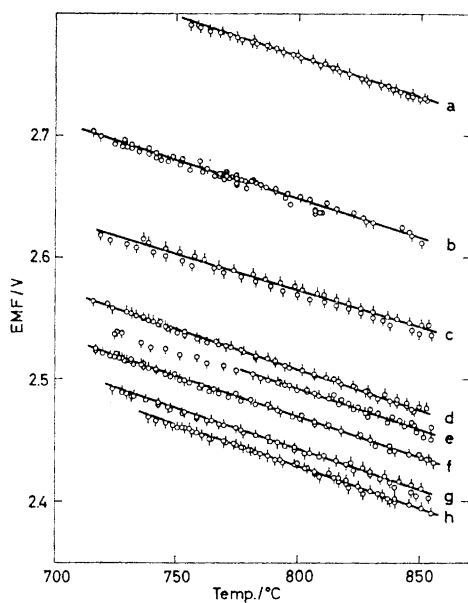
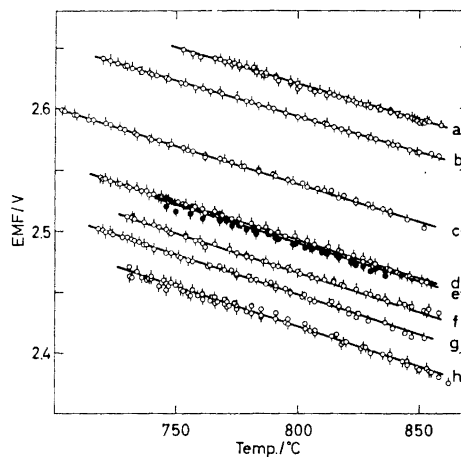


Fig. 3. Emf versus temperature for the system MgCl_2 - KCl . N_{MgCl_2} =(a): 0.130; (b): 0.295; (c): 0.391; (d): 0.495; (e): 0.559; (f): 0.672; (g): 0.810; (h): 0.912.

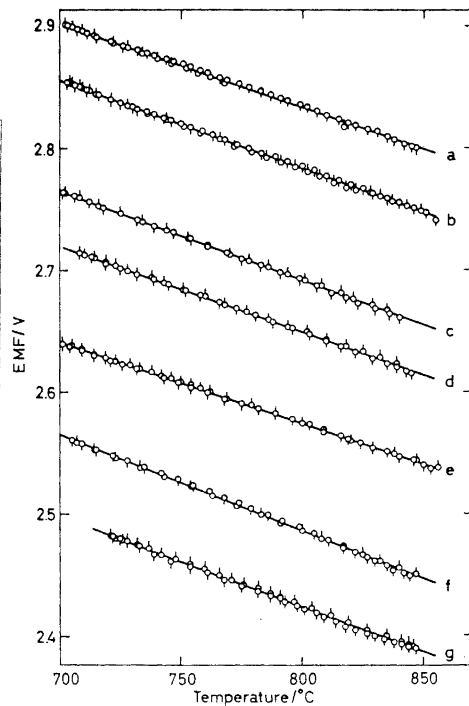


Fig. 4. Emf versus temperature for the system MgCl_2 - CsCl . N_{MgCl_2} =(a): 0.140; (b): 0.196; (c): 0.304; (d): 0.355; (e): 0.445; (f): 0.575.

where E is the observed emf of the cell. E° can be calculated from the standard Gibbs' free energy of formation of liquid magnesium chloride.⁵ The reversibility in the present case is demonstrated by the agreement of the emf values at increasing temperature with those at decreasing temperature, and the linearity of emf *versus* T (although this is not a general proof of reversibility).

The activity of pure magnesium chloride in the actual case may be taken as unity within the experimental error, since the solubility of magnesium in its chloride is small. The solubility has been measured by Rogers *et al.*⁶ to 0.3 mole % at 800°C and 0.69 mole % at 1000°C. When equilibrium is attained between the alloy and the salt phase, the actual solubility should be lower than the values reported above due to the lower magnesium activity in the alloy. When an alkali chloride is added to the magnesium chloride, the magnesium solubility is further depressed.^{7,8} This also means that the concentration of magnesium in the alloy may be taken as the weighed-in concentration. From the reproducibility of the emf values in an experimental run, it is also concluded that the magnesium activity of the alloy may be taken as constant during measurements.

The activity of magnesium in an Mg—15 mole % Bi alloy has by Egan⁹ been found to be about 0.7 at 700°C. The corresponding value according to the present data is about 0.5 at the same temperature. The discrepancy is not readily explainable. Egan reports, however, a precision in his measurements lower than 10 % at the actual concentration.

Magnesium chloride activities were in the present investigation calculated from the equation:

$$E - E^* = - \frac{RT}{2F} \ln a_{\text{MgCl}_2} \quad (3)$$

where E^* is the measured emf of a cell with pure MgCl_2 as the electrolyte and the same Mg—Bi alloy composition as in the other measurements.

The magnesium chloride activity, as calculated from eqn. (3), for the binary systems MgCl_2 —NaCl, MgCl_2 —KCl, and MgCl_2 —CsCl, is given in Figs. 5 and 6.

DISCUSSION

In Fig. 5 results from the present investigation on the MgCl_2 —NaCl system are compared with values reported by Neil *et al.*² and by Østvold.¹⁰ The latter investigator measured sodium chloride activities in MgCl_2 —NaCl mixtures by means of concentration cells with glass membrane alkali metal electrodes, and magnesium chloride activities were calculated from his data by using the Gibbs-Duhem equation. Østvold's data seems to agree fairly well with the present results on the sodium rich side of the system.

For the MgCl_2 —KCl system, the present results agree well with those reported by Neil *et al.*² (Fig. 6). The system MgCl_2 —CsCl has not previously been studied.

From the obtained data the partial molar Gibbs' free energy of magnesium chloride in the binary mixtures has been calculated, employing eqn. (3):

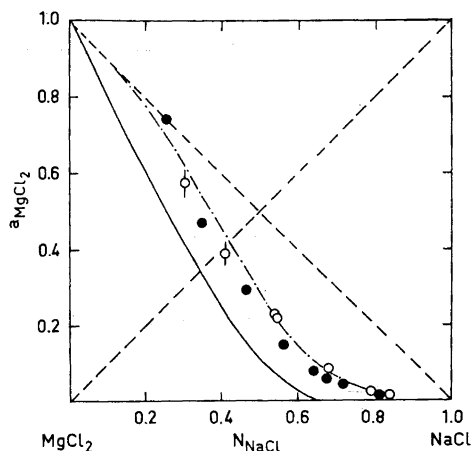


Fig. 5. Activity of MgCl_2 in MgCl_2 - NaCl mixtures. Open circles: This investigation, 810°C . Filled circles: Neil *et al.*² 825°C . Dash-dot curve: Østvold's data¹⁰ at 850°C , calculated from NaCl activities by Gibbs-Duhem's equation. Full drawn curve: Theoretical activity from Førland's¹¹ model.

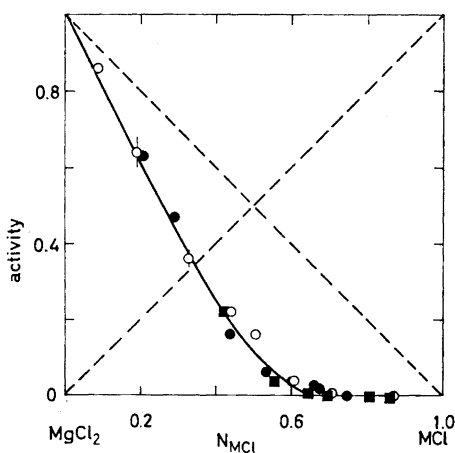


Fig. 6. Activity of MgCl_2 in MgCl_2 - KCl and MgCl_2 - CsCl mixtures. Open circles: This investigation, MgCl_2 - KCl at 800°C . Filled squares: This investigation, MgCl_2 - CsCl at 730°C . Filled circles: Neil *et al.*² Full drawn curve: Førland's model.

$$\Delta\bar{G}_{\text{MgCl}_2} = -2F(E-E^*) = RT \ln a_{\text{MgCl}_2} \quad (4)$$

Some results are given in Table 1.

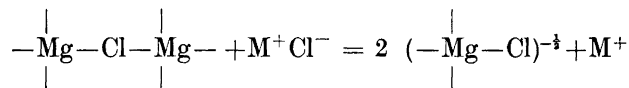
Table 1. Thermodynamic data for MgCl_2 - MCl systems (From smooth curves through experimental data).

| N_{MgCl_2} | MgCl_2 - NaCl a_{MgCl_2} | (810°C) $\Delta\bar{G}_{\text{MgCl}_2}^E$ | MgCl_2 - KCl a_{MgCl_2} | (800°C) $\Delta\bar{G}_{\text{MgCl}_2}^E$ | MgCl_2 - CsCl a_{MgCl_2} | (730°C) $\Delta\bar{G}_{\text{MgCl}_2}^E$ |
|---------------------|--|--|---|--|--|--|
| 0.80 | | | 6.3×10^{-1} | - 0.51 | | |
| 0.70 | 5.9×10^{-1} | - 0.37 | 4.3×10^{-1} | - 1.1 | | |
| 0.60 | 4.2×10^{-1} | - 0.77 | 2.7×10^{-1} | - 1.7 | 2.5×10^{-1} | - 1.8 |
| 0.50 | 2.7×10^{-1} | - 1.3 | 1.5×10^{-1} | - 2.6 | 9.3×10^{-2} | - 3.4 |
| 0.40 | 1.5×10^{-1} | - 2.0 | 4.5×10^{-2} | - 4.7 | 1.5×10^{-2} | - 6.6 |
| 0.30 | 6.9×10^{-2} | - 3.2 | 8.7×10^{-3} | - 7.6 | 1.9×10^{-3} | - 10.1 |
| 0.20 | 2.4×10^{-2} | - 4.5 | 1.8×10^{-3} | - 10.0 | 2.7×10^{-4} | - 13.1 |
| 0.10 | 6.1×10^{-3} | - 6.0 | 3.9×10^{-4} | - 11.8 | 4.0×10^{-5} | - 15.6 |

The precision in the excess Gibbs' free energy values (kcal/mole) has been evaluated to ± 0.15 kcal/mole from the experimental data.

Large, negative values for the partial Gibbs' free energy of magnesium chloride may be attributed to the formation of associated magnesium-con-

taining species in these liquid mixtures. On the magnesium rich side of the systems $\text{MgCl}_2\text{--KCl}$ and $\text{MgCl}_2\text{--CsCl}$, the experimental data may be rationalized by a model suggested by Førlund.¹¹ According to this, the liquid is considered as a mixture of two types of chloride ions; those attached to two magnesium ions to bridge them ($-\text{Cl}-$), and those connected to only one ($-\text{Cl}$). The addition of MCl to MgCl_2 could then be described by the scheme:



A melt with the composition $n\text{MgCl}_2 \cdot (1-n)\text{MCl}$ will have $(3n-1)$ ($-\text{Cl}-$)-ions and $2(1-n)$ ($-\text{Cl}$)-ions. Thus:

$$a_{\text{MgCl}_2} = N^2_{-\text{Cl}-} = \left(\frac{3n-1}{n+1} \right)^2 \quad (5)$$

In Figs. 5 and 6, theoretical values of a_{MgCl_2} , calculated from eqn. (5) are given together with the corresponding experimental values. It is seen from the figures that the model applies well for the $\text{MgCl}_2\text{--KCl}$ and $\text{MgCl}_2\text{--CsCl}$ mixtures, but apparently is not applicable to the system $\text{MgCl}_2\text{--NaCl}$.

On the alkali rich side of these binary systems various models featuring the presence of MgCl_4^{2-} -ions in the liquid mixture, have been applied. Thus Flood and Urnes¹ have shown that the liquidus line on the KCl side of the $\text{MgCl}_2\text{--KCl}$ phase diagram can be rationalized by assuming the liquid mixture to be ideal and consisting of K^+ , Cl^- , and MgCl_4^{2-} ions. A more sophisticated version of the same theory was set forth by Neil *et al.*,² who assumed that the MgCl_4^{2-} ion partly dissociated to form an ideal, liquid mixture with the constituent M^+ , Mg^{2+} , MgCl_4^{2-} , and Cl^- ions. From their emf data they calculated dissociation constants for the MgCl_4^{2-} ion in the mixtures, being 1.8×10^{-3} at 800°C in the $\text{MgCl}_2\text{--KCl}$ system. The low value of the dissociation constant is taken as an indication of the stability of the MgCl_4^{2-} ion.

These models appear to be too crude, since it was shown by Kleppa and McCarthy³ that the partial enthalpy of mixing of the alkali chlorides in magnesium chloride is not zero, these mixtures thus not being ideal. It is further difficult to follow the argument by Neil *et al.* that the value of the dissociation constant does not change with composition. Kleppa and McCarthy found, thus, the interaction parameter $\Delta H^M/N(1-N)$ to exhibit a sharp minimum around the composition corresponding to the M_2MgCl_4 compound. Some additional clues to the problem of the existence of the MgCl_4^{2-} ion in mixture may be obtained by studying the functional dependence of the partial thermodynamic quantities near the M_2MgCl_4 composition.

The partial enthalpy of magnesium chloride in the mixtures can be obtained from the interaction parameter or from the integral heat of mixing curve by graphical differentiation. Whether the intercept method is used on the former or the latter curve makes no difference to the results, except for the $\text{MgCl}_2\text{--CsCl}$ system where the precision of Kleppa and McCarthy's data apparently is lower than for the remaining systems. Here an evaluation from the interaction parameter is considered to be the more precise, since:

$$\Delta\bar{H}_{\text{MgCl}_2} = \frac{\partial \Delta H^M}{\partial n_{\text{MgCl}_2}} = (1-N)^2(\lambda(N) + N \lambda'(N)) \quad (6)$$

Thus the graphical differentiation only introduces error in part of the expression for the $\Delta\bar{H}_{\text{MgCl}_2}$. The values calculated for the actual systems are shown in Fig. 7, together with the excess partial Gibbs' free energy values from this investigation.

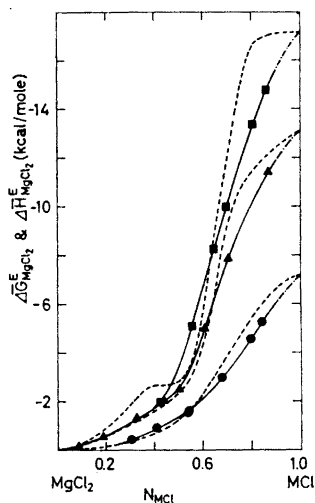


Fig. 7. Partial enthalpy and Gibbs' free energy of magnesium chloride. Full drawn curves: This investigation: circles, MgCl_2 - NaCl at 810°C ; triangles, MgCl_2 - KCl at 800°C ; squares, MgCl_2 - CsCl at 730°C . Dotted curves: Corresponding partial enthalpy data, from Kleppa and McCarty.³

Dotted curves: Corresponding partial enthalpy data, from Kleppa and McCarty.³

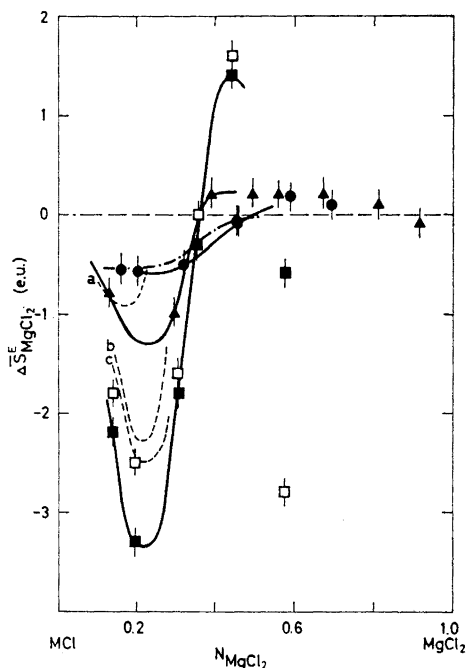


Fig. 8. Excess partial entropy of mixing. Full drawn curves: This investigation: circles, MgCl_2 - NaCl at 810°C ; triangles, MgCl_2 - KCl at 800°C ; squares, MgCl_2 - CsCl at 730°C . Estimated limits of error are ± 0.15 e.u. Dash-dot curve: Calculated from Østvold's data for the MgCl_2 - NaCl system at 850°C . Dotted curves: Calculated from complex ion model; (a) $K=10^{-2}$, (b) $K=10^{-3}$ (c) $K=2.5 \times 10^{-4}$.

Open squares: Calculated from emf versus T curve for the MgCl_2 - CsCl system in the present investigation.

Since the precision of the present data does not permit sufficiently precise entropy values to be evaluated from the slope of the emf versus T curve, partial entropy values have been calculated from the equation:

$$\Delta\bar{S}_{\text{MgCl}_2} = (\Delta\bar{H}_{\text{MgCl}_2} - \Delta\bar{G}_{\text{MgCl}_2})/T \quad (7)$$

Some results are presented in Fig. 8. Here also some values calculated from the slope of the emf *versus* T curve for the system $\text{MgCl}_2\text{--CsCl}$ are plotted for comparison.

A noticeable feature of the partial entropy curves of Fig. 8 is an increased tendency towards an S-shape when going from $M=\text{Na}$ to $M=\text{Cs}$. Further, $\Delta\bar{S}_{\text{MgCl}_2}^E$ is slightly positive or zero above $N_{\text{MgCl}_2}=0.4\text{--}0.5$, but becomes negative below this value. This corresponds to a local minimum in the integral entropy of mixing curve.

Østvold and Kleppa¹² have shown, in their study of the PbO--SiO_2 system, that a partial excess 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. The systems of the present investigation may be treated similarly, that is, to express the entropy of mixing by:

$$\Delta S^M = -R(n_{\text{Mg}^{2+}} \ln N_{\text{Mg}^{2+}} + n_{\text{M}^+} \ln N_{\text{M}^+} + n_{\text{MgCl}_4^{2-}} \ln N_{\text{MgCl}_4^{2-}} + n_{\text{Cl}^-} \ln N_{\text{Cl}^-}) \quad (8)$$

where n and N represent the molar amounts and the molar fractions, respectively, of the constituent ions. The partial entropy of mixing of magnesium chloride can be obtained from a differentiation of eqn. (8):

$$\Delta\bar{S}_{\text{MgCl}_2} = \left[\frac{\partial \Delta S^M}{\partial n_{\text{MgCl}_2}} \right] = -R(\ln N_{\text{Mg}^{2+}} N_{\text{Cl}^-}) - \left(n_{\text{MgCl}_4^{2-}} + N_{\text{MCl}} \frac{d n_{\text{MgCl}_4^{2-}}}{d N_{\text{MgCl}_2}} \right) \ln K \quad (9)$$

K is the dissociation constant of the MgCl_4^{2-} ion, and N_{MCl} and N_{MgCl_2} are the total molar fractions of alkali chloride and magnesium chloride, respectively, in the mixture. The $d n_{\text{MgCl}_4^{2-}}/d N_{\text{MgCl}_2}$ term may be evaluated from a differentiation of the expression for the dissociation constant:

$$K = \frac{N_{\text{Mg}^{2+}} N_{\text{Cl}^-}^4}{N_{\text{MgCl}_4^{2-}}} = \frac{(N_{\text{MgCl}_2} - n_{\text{MgCl}_4^{2-}})(1 + N_{\text{MgCl}_4^{2-}} - 4n_{\text{MgCl}_4^{2-}})^4}{(1 - n_{\text{MgCl}_4^{2-}})n_{\text{MgCl}_4^{2-}}(1 + N_{\text{MgCl}_2} - 3n_{\text{MgCl}_4^{2-}})^3} \quad (10)$$

Thus:

$$\frac{d n}{d N} = \frac{\frac{1}{N-n} + \frac{4}{1+N-4n} - \frac{3}{1+N-3n}}{\frac{1}{N-n} + \frac{16}{1+N-4n} + \frac{1}{n} - \frac{1}{1-n} - \frac{9}{1+N-3n}} \quad (11)$$

n and N being $n_{\text{MgCl}_4^{2-}}$ and N_{MgCl_2} , respectively. Excess partial entropy values for K chosen as 10^{-2} , 10^{-3} , and 2.5×10^{-4} are given in Fig. 8. The figure demonstrates the applicability of the model involving a partly dissociating MgCl_4^{2-} ion to the present systems. The dissociation constant should be of the order of 10^{-3} and less than 10^{-4} in the $\text{MgCl}_2\text{--KCl}$ and $\text{MgCl}_2\text{--CsCl}$ systems, respectively, whereas the constant for the $\text{MgCl}_2\text{--NaCl}$ system exceeds 10^{-2} .

The corresponding integral entropy of mixing data has been evaluated from Kleppa and McCarthy's enthalpy of mixing data and results from the present investigation. The resulting curves are given in Fig. 9, together with

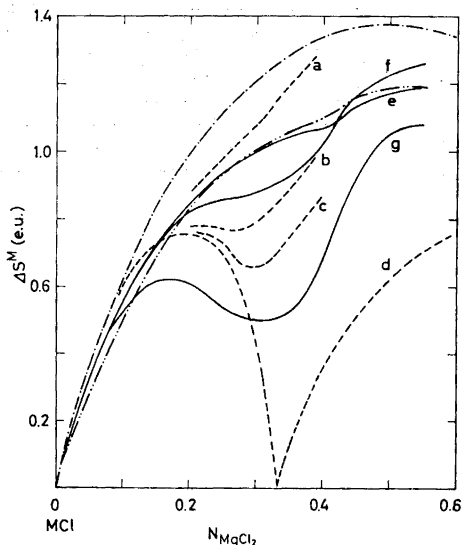


Fig. 9. Integral entropy of mixing. Full drawn curves: This investigation, (e) MgCl_2 - NaCl at 810°C , (f) MgCl_2 - KCl at 800°C , (g) MgCl_2 - CsCl at 730°C . Dotted curves: Calculated from complex ion model: (a) $K=10^{-2}$, (b) $K=10^{-3}$, (c) $K=2.5 \times 10^{-4}$, (d) $K=0$. Dash-dot curve: Ideal Temkin model.

theoretical curves calculated from the complex ion model discussed previously. The "experimental" curves exhibit local minima or shoulders in the composition range around $N_{\text{MgCl}_2}=0.33$, which again can be accounted for in terms of a high degree of local order pertaining in this composition range. There is further a good qualitative agreement between experimental and theoretical curves.

It hence must be concluded that the MgCl_4^{2-} ion is partly dissociated in these mixtures, according to:



The complex ion appears to be fairly stable in the concentration range around 33.3 mole % MgCl_2 in the MgCl_2 - KCl and MgCl_2 - CsCl mixtures, with an increased stability with a lowering of the polarizing power of the alkali metal ion in the mixture.

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