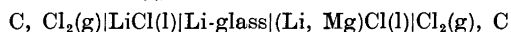


Determination of the Thermodynamic Functions of Lithium Chloride in LiCl—MgCl₂ Mixtures from Concentration Cell Measurements

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The transport number of lithium in a lithium containing silicate is determined. The result shows that the lithium ions carry practically all current through the silicate. This lithium glass is used in a concentration cell of the type:

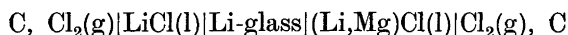


and the change in chemical potential of lithium chloride on mixing is determined. The deviation from regular solution behavior for the LiCl—MgCl₂ mixture is small.

In the present work chemical potentials of LiCl in fused mixtures of LiCl and MgCl₂ are measured by concentration cells without introducing any significant liquid junction potential.

Enthalpies of mixing for this system have been measured by Kleppa and McCarty.¹ With the present chemical potentials of mixing of LiCl, the partial entropy of mixing of LiCl can be calculated.

The following galvanic cell was studied:



The electrolyte consisted of a fused mixture of LiCl and MgCl₂ on the right hand side, and pure fused LiCl on the left hand side of the glass membrane. The membrane contains only one kind of mobile ions, namely Li⁺ ions. The chlorine over graphite electrodes are reversible to the Cl⁻ ions only and the membrane functions as an electrode reversible to Li⁺ ions.

EXPERIMENTAL

The cell used in the present investigation is similar to the one described in previous papers.^{2,3} The composition of the glass membrane was: 70 mol % SiO₂, 10 mol % Al₂O₃, 20 mol % Li₂O.

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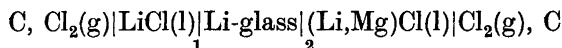
The emf for the above cell was investigated over a concentration range $X_{\text{LiCl}} = 0.9$ to $X_{\text{LiCl}} = 0.25$ at 1000°K. The concentration range was covered in two runs. The first run was started from an LiCl rich mixture and MgCl_2 was added. The second run was started from an MgCl_2 rich mixture and LiCl was added.

The temperature and emf were recorded on a dual channel Philips recorder (type PR 2212 A/00). Both were compensated by bucking potentials supplied from a thermostatically housed reference voltage supply and divider built by SINTEF, Norway. These were calibrated daily against a Tinsley "Thermoelectric Free" potentiometer. The anhydrous magnesium chloride was prepared in the following way. The salt was placed in a vertical silica tube on top of a silica frit. The salt was first heated to 70°C in vacuum for about 10 h and then heated very slowly up to 400°C in a stream of anhydrous HCl gas. Finally the melt was filtered by evacuating the silica apparatus below the silica frit. The anhydrous MgCl_2 crystals in the form of small lumps could be handled outside the drybox for a short time without noticeable increase in weight.

The above cell was also used for the determination of the transport numbers of Li^+ and Mg^{2+} ions in the glass membrane. The course of a typical experiment was as follows. The cathode compartment containing the glass membrane at the bottom was filled with 10 g of pure lithium chloride and then immersed in the fused magnesium chloride-lithium chloride mixture. Chlorine gas was bubbled over the graphite electrodes and a positive current of 10 mA was passed through the cell from the mixture to the pure salt for 20 h. The amount of charge passing through the cell was measured with a digital coulombmeter. The amount of magnesium which had migrated into the cathode compartment through the glass membrane was determined by spectroscopic analysis.

RESULTS AND DISCUSSION

The emf, E , of the galvanic cell



is connected to the change in Gibbs energy for the cell reaction by the equation ⁴

$$\Delta G = -F E = \Delta \bar{G}_{\text{LiCl}} - \int_1^2 \frac{t_{\text{Mg}^{2+}}}{X'_{\text{Mg-sil}}} d\bar{G}_{\text{Li-sil}} \quad (1)$$

over
membrane

Here $t_{\text{Mg}^{2+}}$ is the transport number of Mg^{2+} ions in the glass membrane and $X'_{\text{Mg-sil}}$ is the equivalent fraction of Mg^{2+} ions in the glass defined by the following equation

$$X'_{\text{Mg}} = \frac{2n_{\text{Mg}}}{2n_{\text{Mg}} + n_{\text{Li}}}$$

Here n_{Mg} and n_{Li} are the number of moles of Mg^{2+} and Li^+ ions in the silicate, respectively.

Since the emf and the Gibbs energy change for the cell reaction is dependent on the transport properties of the ions in the glass membrane separating the two half cells, one has to know the value of the integral in eqn. 1 before the partial quantities of mixing can be calculated. For this reason the transport number of the magnesium ion in the glass membrane was measured at 1000°K.

From the concentration of MgCl_2 in the "pure" LiCl melt after electrolysis the transport number of Mg^{2+} in the glass membrane can be calculated from the following equation:

$$t_{\text{Mg}^{2+}} = \frac{2n_{\text{MgCl}_2}}{\Delta Q/F} \quad (2)$$

Here n_{MgCl_2} is the number of moles of MgCl_2 found in the "pure" LiCl melt after electrolysis and ΔQ is the amount of charge transferred through the cell, measured in Faradays.

The transport number of Mg^{2+} in the glass membrane was found to be less than 0.01, which means that the current through the membrane is carried mainly by Li^+ ions. The integral in eqn. 1 is therefore very small and can be neglected. The change in Gibbs energy for the cell reaction



is thus given by

$$\Delta G = \Delta \bar{G}_{\text{LiCl}} = -F E \quad (4)$$

The experimental emf can be related directly to the change in chemical potential of lithium chloride on mixing.

From the integral enthalpies of mixing for the mixture $\text{LiCl}-\text{MgCl}_2$, measured by Kleppa and McCarty,¹ the partial enthalpies of mixing of LiCl can be calculated. From the data given by Kleppa and McCarty, the following equation for the molar enthalpies of mixing in the liquid mixture of magnesium chloride and lithium chloride was fitted by least squares treatment to

$$\Delta H^M = -X(1-X)(2493 - 863X - 1263X^2) \quad (5)$$

Here X is the mole fraction of MgCl_2 .

The partial enthalpy was calculated by derivation

$$\Delta \bar{H}_{\text{LiCl}} = \Delta H^M - X \frac{d\Delta H^M}{dX} = -X^2(3356 + 800X - 3790X^2) \quad (6)$$

Table 1. Experimental emf's and thermodynamic data for the $\text{MgCl}_2-\text{LiCl}$ mixtures. The emf's are measured for the galvanic cell C, $\text{Cl}_2(\text{g})|\text{LiCl(l)}|\text{Li-glass}(\text{Li, Mg})\text{Cl(l)}|\text{Cl}_2(\text{g})$, C. The thermodynamic data for LiCl in the fused $\text{MgCl}_2-\text{LiCl}$ mixtures are calculated from the present emf values and the enthalpy of mixing data by Kleppa and McCarty.¹

System and temperature	X_{LiCl}	emf, mv	$-\Delta \bar{G}_{\text{LiCl}}$ cal/mol	$-\Delta \bar{H}_{\text{LiCl}}$ cal/mol	$\Delta \bar{S}_{\text{LiCl}}$ cal/mol deg
$\text{MgCl}_2-\text{LiCl}$ $T = 1000^\circ\text{K}$	0.897	11.8	270	30	0.24
	0.818	23.2	540	110	0.43
	0.757	33.3	770	250	0.57
	0.749	33.6	780	250	0.57
	0.702	43.9	1010	330	0.72
	0.649	55.7	1280	400	0.89
	0.649	56.0	1290	400	0.90
	0.606	64.9	1500	470	1.02
	0.550	79.5	1830	540	1.23
	0.450	110.0	2540	800	1.74
	0.350	142.5	3290	950	2.33
	0.250	173.8	4010	1030	2.98

The partial Gibbs energy of mixing of LiCl was calculated from eqn. (4) and the partial entropy of mixing of LiCl was then calculated from eqn. (7)

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

The results of these calculations and the experimental emf's are given in Table 1.

In Figs. 1 and 2 graphs of the partial thermodynamic functions of LiCl

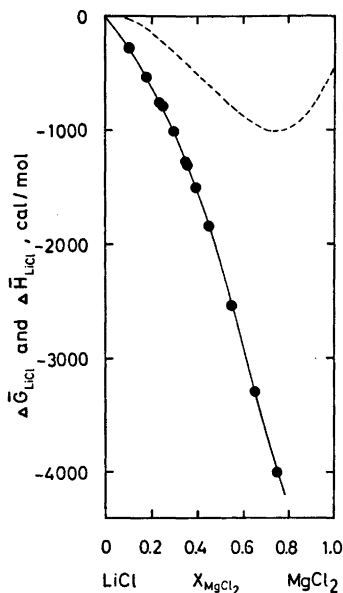


Fig. 1. Partial enthalpies of LiCl (---) on mixing in the binary mixtures of LiCl and MgCl_2 calculated from integral enthalpies of mixing by Kleppa and McCarty.¹ Chemical potentials of LiCl (●) on mixing in the binary mixtures of LiCl and MgCl_2 at 1000°K.

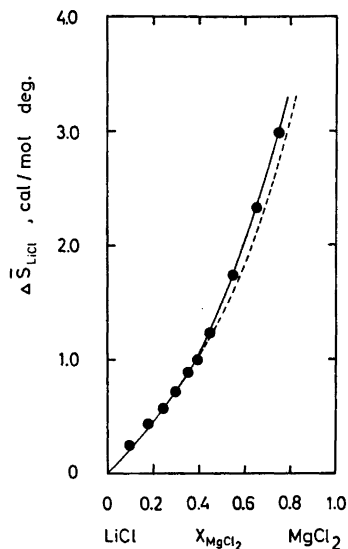


Fig. 2. Partial entropies of mixing of LiCl (●) in the binary mixtures of LiCl and MgCl_2 . $-R \ln X_{\text{LiCl}}$ (---).

on mixing *versus* composition are presented.

It can be observed from these graphs that the binary LiCl– MgCl_2 mixtures show close to regular behavior. The entropy of mixing is described very well by the Temkin⁵ entropy of mixing. The partial enthalpy of mixing follows closely the equation for symmetrical regular mixtures.

$$\Delta H_{\text{LiCl}} = X_{\text{MgCl}_2}^2 b \quad (8)$$

where b is a constant.

At high MgCl_2 contents some deviation from these expressions is observed, however. This may be due to a change in the co-ordination around the ions in the high MgCl_2 range.

In the other alkali chloride-magnesium chloride melts considerable deviations from the regular solution model are observed.^{2,6} This is due to the stabilization of the four co-ordinated MgCl_4^{2-} "complex" ion in MgCl_2 -melts where there is a considerable difference in polarizing strength between the two cations.

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