# Determination of Partial Gibbs Energies of Mixing of LiCl in the Alk.Cl—LiCl Mixtures from Concentration Cell Measurements

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The partial Gibbs energies of mixing of LiCl in the liquid mixtures with KCl, RbCl, and CsCl have been determined by emf measurements of the following cell:

$$C(s),Cl_2(g)|LiCl(l)|Li\text{-glass}|(Li-M)Cl(l)|$$
$$Cl_2(g),C(s)$$
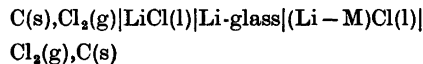
where M = K, Rb, and Cs, respectively, and by measurements of transport numbers of the Li^+ ion in the Li-glass membranes used to separate the two half cells in the above concentration cells. The partial Gibbs energies and entropies are calculated.

The results indicate relatively large deviations from regular solution behaviour. The partial excess entropies of mixing are proportional to $(1-X_{LiCl})^2$, indicating that these excess entropies are of vibrational nature.

In the present work the change in the chemical potentials of mixing of LiCl in molten LiCl— MCl mixtures were obtained using a concentration cell with Li-glass membranes, the metal ion M^+ being K^+, Rb^+ or Cs^+, respectively. The emf of this cell depends on the transport properties of the membrane, i.e. "the liquid junction potential".

The following galvanic cell was studied:

$$C(s),Cl_2(g)|LiCl(l)|Li\text{-glass}|(Li-M)Cl(l)|$$
$$Cl_2(g),C(s)$$
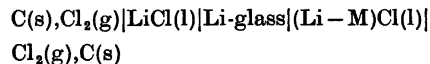
The electrolyte consisted of a fused mixture of LiCl and MCl on the right hand side, and pure fused LiCl on the left hand side of the glass membrane. The membrane is a cation

exchange membrane and it contains the mobile Li^+ ion. The chlorine over graphite electrodes are reversible to the Cl^- ions only.

By determining the transport numbers of the Li^+ ion in the glass membranes together with the cell potentials for the above cells, both as functions of composition of the LiCl—MCl liquid mixtures, one is able to determine the difference in Gibbs energy for LiCl in the mixed and the pure fused state.

The transport number of Li^+ ions in glass membranes very similar to the one used in the present work has been determined previously.[1,2] When the galvanic cell contained NaCl and LiCl it turned out that the membrane conducted Na^+ and Li^+ ions over the whole concentration range. For the KCl—LiCl, RbCl—LiCl and CsCl—LiCl systems $t_{Li^+} > 0.9$ for $X_{LiCl} > 0.5$, $X_{LiCl} > 0.3$, and $X_{LiCl} > 0.1$, respectively. When the partial Gibbs energy of sodium chloride obtained from the emf measurements is combined with enthalpy of mixing data to calculate the partial entropies of NaCl in the NaCl—LiCl system it turns out that the calculated entropies are very different from the ones observed in the present LiCl—Alk.Cl mixtures. We believe that this is due to some inaccuracy in the determination of transport numbers for the Li^+ ion in the glass membrane separating NaCl and the NaCl—LiCl mixtures. To obtain a reasonable accuracy in the thermodynamic data calculated from the galvanic cell measurement, we therefore decided to operate in concentration ranges where we could assume $t_{Li^+} \simeq 1$.

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EXPERIMENTAL

The cell used in the present investigation is similar to the one described in previous papers.[1,3,4] The composition of the glass was: 80 mol % SiO_2, 7.5 mol % Al_2O_3, 7.5 mol % Li_2O, 5 mol % La_2O_3.

All the components of the glass, obtained from E. Merck, Germany, were ground together, pressed to a pill and melted. To assure homogeneity the glass was crushed and remelted. The emf of the above cell was investigated over a concentration range $X_{LiCl} = 0.2$ to $X_{LiCl} = 1.0$ at 995, 925, and 895 K for the KCl − LiCl, RbCl − LiCl, and CsCl − LiCl mixtures, respectively. The emf and temperature were recorded on a dual channel Watanabe recorder, both compensated by bucking potentials supplied from a Fluke 895A Differentialvoltmeter. The analytical reagent grade salts, LiCl, KCl, RbCl,

and CsCl from E. Merck, Germany were dried, melted and slowly crystallized under dry nitrogen atmosphere to remove moisture and impurities. Handling of salts was performed in a drybox at max. 4 ppm water content.

The course of a typical experiment was as follows. The anode compartment, containing the glass membrane at the bottom, was filled with about 5 g of lithium − alkali chloride mixture and then immersed in the pure fused LiCl. Chlorine gas was bubbled over the graphite electrodes and the potential and temperature curves recorded. By adding small crystals of LiCl or the other alkali chloride in the anode compartment the composition of the mixture could be changed. The internal resistance of the cell was in the range 700 − 10 000 Ω. Transport numbers were determined by a modified Hittorf Method described previously.[1]

Table 1. Thermodynamic functions of mixing of liquid LiCl in mixture with KCl from calorimetric measurements of mixing at 1013 K by Hersh and Kleppa and emf measurements at 995 K.

Mol-fraction	Emf	Chemical potentials	Partial enthalpies	Partial entropies	Partial excess entropies
X_{LiCl}	E (mv)	$\Delta\mu_{LiCl}$ (kJ mol^{-1})	$\Delta\bar{H}_{LiCl}$ (kJ mol^{-1})	$\Delta\bar{S}_{LiCl}$ (J mol^{-1}K^{-1})	$\Delta\bar{S}^{E}_{LiCl}$ (J mol^{-1}K^{-1})
0.899	10.6 ± 0.5	− 1.02	− 0.19	0.84	− 0.04
0.801	24.7 ± 0.4	− 2.38	− 0.72	1.67	− 0.17
0.700	42.7 ± 0.9	− 4.12	− 1.63	2.51	− 0.46
0.600	64.9 ± 2	− 6.27	− 2.89	3.40	− 0.85
0.500	90.6 ± 2	− 8.75	− 4.49	4.28	− 1.49

Table 2. Thermodynamic functions of mixing of liquid LiCl in mixture with RbCl from calorimetric measurements of mixing at 1013 K by Hersh and Kleppa and emf measurements at 925 K.

Mol-fraction	Emf	Chemical potentials	Partial enthalpies	Partial entropies	Partial excess entropies
X_{LiCl}	E (mv)	$\Delta\mu_{LiCl}$ (kJ mol^{-1})	$\Delta\bar{H}_{LiCl}$ (kJ mol^{-1})	$\Delta\bar{S}_{LiCl}$ (J mol^{-1}K^{-1})	$\Delta\bar{S}^{E}_{LiCl}$ (J mol^{-1}K^{-1})
0.921	7.9	− 0.76	− 0.15	0.66	− 0.02
0.900	10.6	− 1.02	− 0.24	0.85	− 0.03
0.837	19.3	− 1.86	− 0.65	1.32	− 0.16
0.800	25.3	− 2.44	− 0.97	1.59	− 0.27
0.756	33.9	− 3.27	− 1.45	1.97	− 0.36
0.699	44.8	− 4.33	− 2.20	2.29	− 0.69
0.676	51.2	− 4.94	− 2.55	2.58	− 0.68
0.604	68.6 ± 0.8	− 6.62	− 3.79	3.07	− 1.13
0.531	89.2	− 8.61	− 5.25	3.64	− 1.63
0.501	98.1 ± 0.8	− 9.47	− 5.90	3.86	− 1.89
0.400	132.6 ± 1	− 12.80	− 8.26	4.91	− 2.71
0.324	163.3	− 15.73	− 10.20	5.99	− 3.39
0.300	174.4	− 16.84	− 10.82	6.51	− 3.51
0.199	224.8	− 21.70	− 13.41	8.96	− 4.47

Table 3. Thermodynamic functions of mixing of liquid LiCl in mixture with CsCl from calorimetric measurements of mixing at 943 K by Hersh and Kleppa and emf measurements at 895 K.

Mol-fraction	Emf	Chemical potentials	Partial enthalpies	Partial entropies	Partial excess entropies
X_{LiCl}	E (mv)	$\Delta\mu_{LiCl}$ (kJ mol^{-1})	$\Delta\bar{H}_{LiCl}$ (kJ mol^{-1})	$\Delta\bar{S}_{LiCl}$ (J mol^{-1}K^{-1})	$\Delta\bar{S}^{E}_{LiCl}$ (J mol^{-1}K^{-1})
0.896	10.9	− 1.05	− 0.29	0.85	− 0.07
0.799	25.8	− 2.49	− 1.15	1.50	− 0.37
0.762	32.4	− 3.13	− 1.63	1.67	− 0.59
0.699	46.0	− 4.44	− 2.65	2.00	− 0.98
0.601	70.0 ± 0.7	− 6.76	− 4.70	2.30	− 1.93
0.594	71.4	− 6.89	− 4.86	2.27	− 2.07
0.500	100.2 ± 0.8	− 9.67	− 7.30	2.66	− 3.11
0.415	128.4	− 12.39	− 9.75	2.95	− 4.37
0.398	136.0 ± 0.3	− 13.13	− 10.26	3.20	− 4.46
0.357	151.5	− 14.62	− 11.50	3.50	− 5.07
0.308	172.5	− 16.65	− 12.96	4.12	− 5.67
0.254	199.0	− 19.21	− 14.53	5.23	− 6.17
0.212	221.5	− 21.38	− 15.68	6.37	− 6.53
0.200	227.1	− 21.92	− 15.99	6.63	− 6.76
0.173	245.3	− 23.68	− 16.67	7.83	− 6.76

RESULTS AND DISCUSSION

The emf as function of composition of the galvanic cell

C(s), Cl$_2$(g)|LiCl(l)|Li-glass|LiCl − MCl(l)|

Cl$_2$(g), C(s)
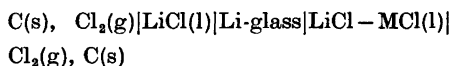
is given in Tables 1 − 3. The emf is related to the change in Gibbs energy of the cell reaction by eqn. (1).[5]

$$\Delta G = -EF = \Delta\mu_{LiCl} - \int_{\substack{over \\ membrane}} t_{M^+} d(\mu_{Li-sil} - \mu_{M-sil}) \quad (1)$$

Only results for which $t_{M^+} \approx 0$ are recorded in Tables 1 − 3 and eqn. (1) may then be simplified to eqn. (2).

$$\Delta\mu_{LiCl} = -EF \quad (2)$$

$\Delta\mu_{LiCl} = \mu_{LiCl} - \mu^{\circ}_{LiCl}$ which is the change in chemical potential of LiCl on mixing is recorded in Tables 1 − 3 together with the partial enthalpies [6] and entropies of mixing of LiCl.

When calculating the entropy of mixing for a system containing a mixture of fused salts it is common to consider the configurational entropy only. The significant entropy changes observed for reactions of the type (3),[7,8]

$$\tfrac{1}{n}MCl_n(l) + MeBr(l) = \tfrac{1}{n}MBr_n(l) + MeCl(l) \quad (3)$$

however, indicate that other contributions to the entropy of mixing have to be taken into account in a more thorough calculation. Førland [9] has proposed a model for describing the excess entropy change on mixing in systems where ΔH_{mix} is small. He assumes that the excess entropy can be attributed to changes in the environment of the ions by the mixing process. The vibrational entropy can be expressed as a sum of terms assigned to pairs of ions. For a binary mixture of LiCl and CsCl the vibrational entropy of mixing should accordingly be [eqn. (4)]

$$\Delta S_{vibr.} = \tfrac{1}{2}\{(n_{Li} + n_{Cs})(X_{Li}{}^2 S_{Li-Li} + 2X_{Li}X_{Cs}S_{Li-Cs} + X_{Cs}{}^2 S_{Cs-Cs}) - n_{Li}S_{Li-Li} - n_{Cs}S_{Cs-Cs}\} \quad (4)$$

where S_{Li-Li} is the contribution to the vibrational entropy from Li$^+$ − Li$^+$ interactions. The partial molar vibrational entropy of mixing of LiCl is then given by

$$\Delta\bar{S}_{LiCl}{}^{vibr.} = const. \ X^2_{CsCl} \quad (5)$$

In a previous paper this model was tested on the experimental excess entropies in the NaCl − NaBr and KCl − KBr systems.[10] For

these mixtures the enthalpy of mixing is very small and one would assume no deviation from random mixing of anions. The observed partial entropies, however, deviated significantly from the random mixing model and showed good agreement with eqn. (5). For the present systems one might expect deviation from random mixing of cations since the enthalpy of mixing is relatively large. This should, however, result in a positive excess partial entropy of LiCl in the LiCl-rich melts and a negative partial excess entropy at lower LiCl content.[11] The partial excess entropies are all negative, however, and agree with eqn. (5) over the whole concentration range except for very low LiCl content in the LiCl − CsCl system.

In Fig. 1 $\Delta \bar{S}^{E}_{MCl}$ is plotted *versus* $(1 - X_{MCl})^2$ for MCl = NaCl in the NaCl − KCl and NaCl − CsCl systems measured by Thulin[1] and for MCl = LiCl in the LiCl − KCl, LiCl − RbCl, and LiCl − CsCl systems. From the experimental data the maximum error in the partial entropies is estimated to be 0.2 J mol^{-1} K^{-1}. The experimental entropies in the NaCl − RbCl system also obtained by Thulin[1] seems to be less accurate and we decided there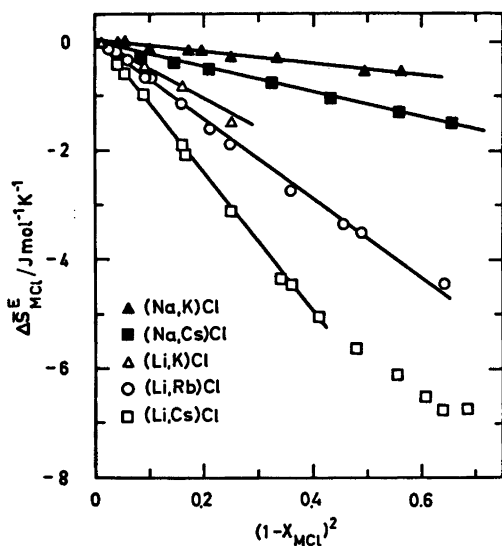fore not to use these entropies in the present figure. It is evident from Fig. 1 that there is an increase in the vibrational contribution to the entropy of mixing with an increasing mass ratio of the mixing ions.

This increasing excess partial entropy is negative over the whole concentration range determined. It is thus unlikely that this excess entropy is due to deviation from random mixing of the ions on mixing or that it is due to volume changes on mixing since these are positive for the above systems.[12] In systems where there is even larger difference in electric field strength (Z/r^2) between the mixing cations than in the present systems, deviation from random mixing will occur. In binary mixtures of MgCl$_2$ with KCl, RbCl, and CsCl a positive excess partial entropy of the alkali chloride is observed at low MgCl$_2$ content. At higher MgCl$_2$ content the partial entropy is negative.[3]

A gradual change from predominant vibrational contributions over to configurational contributions to the excess partial entropy is thus observed.

Fig. 1. Partial excess entropies of mixing of MCl as function of $(1 - X_{MCl})^2$ in liquid mixtures with KCl, RbCl and CsCl. M = Na or Li. The temperatures of the systems are given in Tables 1 − 3.

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