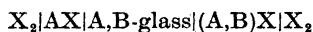


Partial Gibbs Energy for Alkali Halide Systems from Emf Measurements

LARS UNO THULIN

*Institute of Theoretical Chemistry, University of Trondheim-NTH,
Trondheim, Norway*

The chemical potentials of NaCl, in mixture with other alkali chlorides, are determined by measurements of transport numbers and emf in cells of the type



The electrodes are reversible to the anion X^- . A represents Na^+ while B in sequence is Li^+ , K^+ , Rb^+ , and Cs^+ . The membrane is not permeable for the anions.

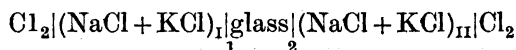
I. INTRODUCTION

Studies of the use of glass membranes in galvanic cells with molten salts showed that if the current transport through the membrane is performed exclusively by one of the ions in the glass, no change takes place in the glass and no chemical work is carried out in the junction.¹ Førland and Østvold² calculated the chemical work done in glass membranes when an electrical charge passes through the membranes. The calculations were based on the assumption of two kinds of mobile monovalent ions in the glass. It was found that the chemical work, or the liquid junction potential, depended on the transport numbers of the mobile ions in the membrane and on the activities of the corresponding silicates.

In a treatment of processes in membranes where the use of unmeasurable quantities like single ion activities, single electrode potentials, and phase-boundary potentials (Donnan potentials) were avoided, Førland and Thulin³ showed that the change in chemical potential for one of the components, in a galvanic cell with membrane, can be calculated when the transport numbers in the membrane and the emf of the cell are known as functions of the composition of the melts.

The emf Gibbs energy equations

The following type of cell may be considered:



This is a high temperature cell having fused salts as electrolyte and a silicate glass as membrane. The ions Na^+ and K^+ can migrate through the membrane.^{2,4}

In experimental series it is convenient to use pure NaCl as electrolyte I and also refer to this as the standard state for sodium chloride in electrolyte II. For a small change in the composition of electrolyte II, the change in emf of the cell is given by:³

$$F dE = \frac{t_{\text{K}^+} - \chi_{\text{KCl}}}{\chi_{\text{KCl}}} d\mu_{\text{NaCl}} \quad (1)$$

which solved with respect to $d\mu_{\text{NaCl}}$ and integrated gives:

$$\Delta\mu_{\text{NaCl}} = F \int_1^2 \frac{\chi_{\text{KCl}}}{t_{\text{K}^+} - \chi_{\text{KCl}}} dE \quad (2)$$

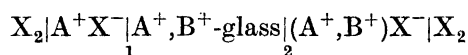
Thus for a given composition, χ_{KCl} , of electrolyte II one can measure E and the transport number, t_{K^+} , of potassium ion in a glass membrane, which is in equilibrium with an electrolyte of the same composition as electrolyte II. By plotting corresponding values of $\chi_{\text{KCl}}/(t_{\text{K}^+} - \chi_{\text{KCl}})$ and E , the chemical potential for sodium chloride, $\Delta\mu_{\text{NaCl}}$, is obtained from the area under a curve.

It should be noted that a requirement for the above integration is that the composition of the membrane is uniform, except for the cations, from 1 to 2.

The eqn. (2) may be written in the more general form:

$$\Delta\mu_{\text{AX}} = F \int_1^2 \frac{t_{\text{BX}} \chi_{\text{BX}}}{t_{\text{B}^+} - \chi_{\text{BX}}} dE \quad (3)$$

Eqn. (3) is valid for all cells of the type



where the electrodes are reversible to the anion X^- and the glass membrane is penetrable to the cations A^+ and B^+ only.

In eqn. (3) the transport number for a component may be higher or lower than the mol fraction of the same component. As an intermediate case the transport number may be equal to the mol fraction.

In order to give consistent results the measured emf have to behave in the way shown below

1. if $t_{\text{B}^+} < \chi_{\text{BX}}$ then emf > 0
2. if $t_{\text{B}^+} = \chi_{\text{BX}}$ then emf $= 0$
3. if $t_{\text{B}^+} > \chi_{\text{BX}}$ then emf < 0

The change of polarity of the emf from case 1 to case 3 is experimentally verified in this work.

In Fig. 1 is shown a graphical representation of eqn. (3). The change in chemical potential is found from the area under the curve.

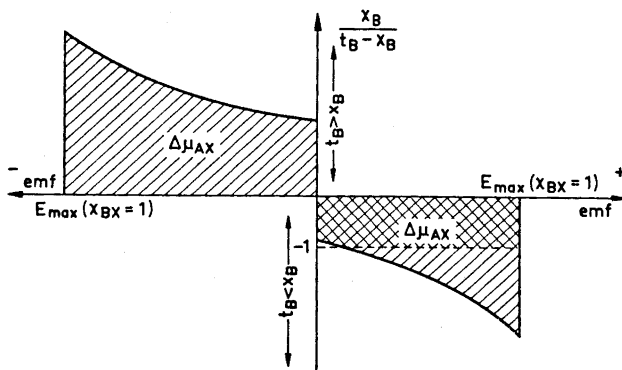
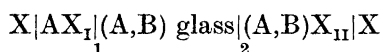


Fig. 1. Graphical representation of eqn. (3), showing the different possibilities in behaviour. The double hatched area represents $\Delta\mu_{AX}$ if $t_A = 1.0$.

II. TRANSPORT IN THE GLASS MEMBRANE

In order to calculate the chemical potential by using eqn. (2), it is necessary to know the transport number as a function of composition of the melts. Consider the galvanic cell



where X is an electrode reversible to X^- , and A^+ as well as B^+ in the mixtures I and II are interchangeable with the A^+ and B^+ in the glass membrane.

If we measure the transport number by applying an electric field, and thereby passing electric current through the membrane, we will, after a while, reach steady-state conditions with a composition as shown in Fig. 2.

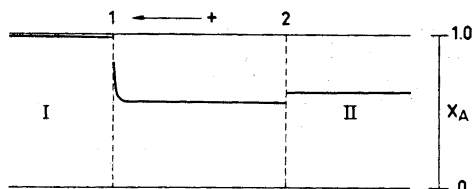


Fig. 2. Composition profile for the cell $X|AX_I|(A,B) \text{ glass} |(A,B)X_{II}|X$ for transport number measurements at steady-state conditions.

Positive ions are passed from compartment II, where we have a mixture $AX - BX$ of constant composition, into compartment I. At the interface 2 we assume equilibrium between mixture and glass-membrane. In the region of the interface 1 there will, however, be non-equilibrium conditions.

In order to have equilibrium at the interface 2 we must assume the transport in the liquid being so rapid due to stirring, that there will be no concentration gradient in the liquid. We also assume a rapid exchange reaction between glass and melt.

The mobilities of the two ions will not be equal. A change of current density may therefore produce a local change of composition in the glass, in the meaning that the relative amounts of diffusing cations will not be constant over the membrane. This change of composition will, however, not take place if the rate of ion-exchange across the membrane-solution interface is so frequent that the composition in the membrane, at the interface, will be constant as long as the composition of the melt is unchanged.

For measurements at room-temperature, in water-solution, Conti and Eisenman⁵ have demonstrated the possibility of controlling the transport numbers by current density variation. This may be the case at lower temperatures where the rate of ion exchange is quite slow, compared to the ion transfer between solution and glass, caused by the charge transfer.

For the systems treated in this work a possible dependence of the transport number on the current is tested and is not found to be of a measurable magnitude.

The transport number of sodium ions in glass membranes are determined for the glasses in equilibrium with the binary alkali halide systems NaCl – LiCl, NaCl – KCl, NaCl – RbCl, and NaCl – CsCl, as a function of the composition of the salt systems in the temperature region 800 – 900°C.

The transport number for sodium ions in the glass membrane is given by the equation

$$t_{\text{Na}^+} = \frac{n_{\text{Na}^+}}{n_{\text{tot}}} = \frac{n_{\text{Na}^+}}{\Delta Q/F}$$

where n_{Na^+} is the number of moles of sodium ions transferred and n_{tot} is the total number of moles of alkali ions transferred through the membrane, when a charge ΔQ coulombs is passed through the cell.

Experimental

The transport numbers were measured by the aid of an electrolytic cell, a modified type of the cell shown in Fig. 5. Due to the high temperatures employed in these measurements, and due to its good insulating properties, silica is chosen as cell material. The electrodes were made from pure graphite,* and connection to the electrodes was obtained by Pt-wires.

The chlorine gas, which was passed into the cell, was dried with sulfuric acid and P_2O_5 . Impurities which would attack the graphite electrodes were removed by bubbling the gas over a "dummy" graphite electrode at high temperature. The same chlorine gas was sent through both cell-compartments. The alkali chlorides** were premelted in order to remove humidity and broken into fragments before weighed out to give the wanted compositions.

The glass membrane in the cell was about 3 mm in diamter. The top of the cell was made from commercial "teflon". The upper part of the cell was furnished with copper cooling coils on the outside.

A current of about 15 mA was sent through the cell for more than 10 h. This represents an electric charge which amounts to at least two orders of magnitude more than the total charge of the mobile ions in the glass.

* GRAPHITE AGKSP, 242 × 12", from Carbon Products Div., Union Carbide, USA.

** LiCl, NaCl, and KCl, *p.a.*, RbCl and CsCl, suprapur, Merck, Germany.

After completing the charge transfer the composition of the anode solution was determined by flame photometry analysis. The temperature in the cell was measured with a Pt/Pt10Rh thermocouple.

The amount of D. C. current which was sent through the cell was determined by using a low-inertia integrating motor * with a mechanical counting unit. The motor is a permanent magnet D. C. motor in which practically all factors likely to affect the linearity of the voltage/speed curve have been eliminated. The resulting accuracy is such that the motor can be used to integrate minute currents on a time basis. The motor was calibrated against a traditional silver coulomb-meter and also against a current sent through a high precision resistance.** The potential drop was measured with a Tinsley potentiometer.***

The two different methods gave a difference amounting to 0.05 % of the measured amount of transferred charge. The glasses were made from SiO_2 ,^a Al_2O_3 ,^b and the appropriate alkalicarbonates.^c The mol % of the two kinds of alkali carbonates, e.g. Na_2CO_3 and Li_2CO_3 in sodium-lithium glass, were equal for both kinds of alkali ions in the respective glasses. The composition of the different types of glasses are given in Table 1.

Table 1.

Glass type	Composition in mol %		
	SiO_2	Al_2O_3	Alk_2CO_3
Na,Li	70	15	15
Na,K	80	10	10
Na,Rb	80	10	10
Na,Cs	80	10	10

Low content of alkali and addition of alumina, causing an even distribution of alkali, gives low alkali interaction in the glass. However, such glasses will have a very high viscosity and are difficult to melt. The composition chosen is a compromise between the two tendencies. The components of the glasses were ground together and melted. Thereafter the glasses were crushed and remelted to assure uniform composition.

Results and discussion

The results of the investigations concerning the dependence of the transport number upon the concentration of the melts in equilibrium with the glasses, and the dependence upon the temperature of the melt are shown in Tables 2–5. The results concerning the transport number dependence upon the current density are shown in Table 6. In these experiments the area of the membrane was kept constant, whereas the current, I , was varied.

Considering the cumulative effect of uncertainties in the chemical analysis and in the original composition of the melt, it seems reasonable to consider

* Low-inertia integrating motor, type No. 913. Electromethods, Herts, England.

** Sullivan and Griffiths, Non-Reactive Resistance, 0.05 % Grade, H. W. Sullivan, England

*** Tinsley Thermoelectric Free Potentiometer, Type 3589 R/AUTO, No. 171, 877.

^a SiO_2 p.a. from Riedel-de Haën, Germany.

^b Al_2O_3 from The British Drug Houses, England.

^c Li_2CO_3 from Schering, Germany. Na_2CO_3 , K_2CO_3 , Rb_2CO_3 , and Cs_2CO_3 p.a. from Merck, Germany.

Table 2. Transport numbers in Na,Li glass at constant current density.

χ_{LiCl}	T K	t_{Li^+}	χ_{LiCl}	T K	t_{Li^+}
0.17	1083	0.28	0.45	1158	0.73
0.17	1133	0.32	0.50	1103	0.82
0.25	1098	0.47	0.50	1183	0.77
0.25	1143	0.42	0.65	1108	0.86
0.32	1093	0.57	0.65	1163	0.88
0.32	1158	0.55	0.80	1088	0.95
0.45	1113	0.74	0.80	1178	0.94

Table 3. Transport numbers in Na,K glass at constant current density.

χ_{KCl}	T K	t_{K^+}	χ_{KCl}	T K	t_{K^+}
0.25	1083	0.02	0.52	1183	0.16
0.25	1083	0.03	0.55	1103	0.16
0.25	1123	0.04	0.55	1158	0.17
0.25	1183	0.04	0.65	1093	0.23
0.30	1093	0.03	0.65	1163	0.25
0.30	1163	0.03	0.75	1123	0.37
0.40	1083	0.07	0.78	1173	0.43
0.40	1143	0.08	0.80	1083	0.48
0.52	1083	0.12	0.80	1113	0.50
0.52	1113	0.16	0.80	1178	0.48
0.52	1183	0.13	0.85	1088	0.58
			0.85	1163	0.62

Table 4. Transport numbers in Na,Rb glass at constant current density.

χ_{RbCl}	T K	t_{Rb^+}	χ_{RbCl}	T K	t_{Rb^+}
0.10	1133	0.00	0.50	1133	0.01
0.20	1093	0.01	0.58	1098	0.03
0.20	1158	0.01	0.58	1163	0.02
0.35	1093	0.01	0.80	1103	0.09
0.35	1183	0.02	0.80	1163	0.10
0.50	1103	0.01			

Table 5. Transport number measurements in Na,Cs glass at constant current density.

χ_{CsCl}	T K	t_{Cs^+}	χ_{CsCl}	T K	t_{Cs^+}
0.20	1083	0.00	0.50	1178	0.00
0.20	1143	0.00	0.65	1103	0.00
0.35	1103	0.00	0.65	1173	0.00
0.35	1158	0.00	0.80	1083	0.00
0.50	1098	0.00	0.80	1148	0.01

Table 6. Transport number measurements in Na,K glass at constant temperature and with variable current density.

χ_{KCl}	$I(\text{mA})$	t_{K^+}	χ_{KCl}	$I(\text{mA})$	t_{K^+}
0.25	5	0.02	0.50	30	0.10
0.25	30	0.02	0.80	5	0.50
0.50	5	0.14	0.80	30	0.58

the transport numbers reliable within $\pm 10\%$ for the (Na,K) system whereas the uncertainty for the (Na,Li) system is likely to be about 20%. As seen from Tables 2–5 there are no significant dependence of the transport number upon the temperature.

The experimental results show that the transport number dependence upon the composition is of importance in the Na,Li and the Na,K glass, whereas it is of less importance in Na,Rb glass and of none at all in the Na,Cs glass. The results, excluding the Na,Cs glass, are shown in Fig. 3.

Conti and Eisenman have, as already mentioned, demonstrated a transport number dependence upon the current density. Such a dependence seemed unlikely under the experimental conditions in the present work. The transport

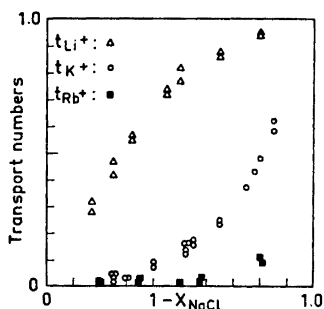


Fig. 3. Transport numbers in Na,Li glass, Na,K glass and Na,Rb glass plotted against the composition of the melts.

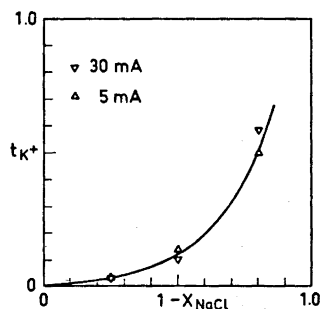
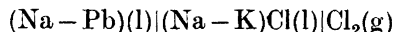


Fig. 4. Transport numbers in Na,K glass at two current densities, 30 mA and 5 mA, plotted against the composition of the melt.

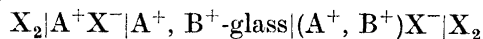
numbers were, however, measured *versus* the current density for the Na,K glass. The results are shown in Fig. 4 where the curve is taken from Fig. 3. As seen from the experimental results the transport numbers are independent of the current density within the measured range.

III. EMF MEASUREMENT

So far there have been only a few direct studies of the free energies of mixing of the alkali chlorides. Krohn and Moser⁶ used a formation cell of the type



In the present investigation the emf are measured as a function of composition for cells of the type



where X^- stands for Cl^- and A^+ for Na^+ , whereas B^+ is, in sequence, Li^+ , K^+ , Rb^+ , and Cs^+ . The cells have electrodes reversible to X^- and the glass membrane is permeable to the cations only.

Experimental

The galvanic cell used for the emf measurements is shown in Fig. 5.

The outer quartz-tube contained the molten alkali halide mixtures, while the inner quartz tube contained the molten sodium chloride, which served as reference salt. The glass membrane which was melted into a hole in the inner tube had a diameter of approx. 3 mm.

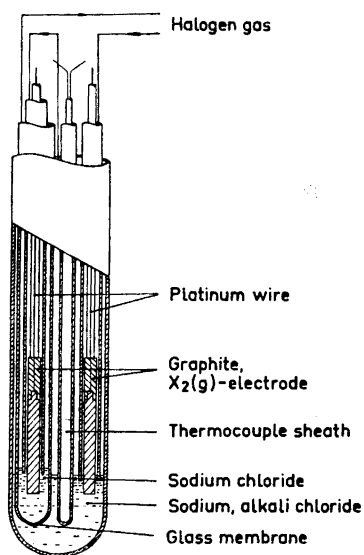


Fig. 5. The galvanic cell used for the emf measurements.

The graphite electrodes were made from graphite of the type used in the transport number measurements. Connection to the electrodes were obtained by Pt-wires, protected by quartz tubes. The top of the cell was made from teflon.

Chlorine gas of commercial quality was dried over sulfuric acid and P_2O_5 . Impurities which would attack the graphite electrodes were removed by passing the chlorine gas over a heated "dummy" graphite electrode before it was bubbled over the graphite electrode, immersed in the molten reference salt. The same gas was bubbled over the graphite electrode in the mixture compartment. The gas left the cell *via* a sulfuric acid trap.

The cell was heated in an electrical furnace, of the type described by Motzfeldt.⁷ To obtain a zone with temperature variations of approx. $0.1^\circ\text{C}/\text{cm}$ over the lower 8 cm of the cell in the temperature range $800 - 900^\circ\text{C}$, the furnace contained three resistance

windings where the current could be varied independently. Further it contained a copper tube between the heating element and the inner furnace room. The temperature was measured with a Pt/Pt10Rh thermocouple. The temperature and the emf was recorded by means of a differential voltmeter.* With this instrument the determination of the unknown potential is independent of the resistance of its source.

For all the systems investigated the emf was determined as a function of the composition of the salt mixture. The salts used in the emf measurements were all premelted to remove moisture.

The outer compartment was filled with the binary alkali halide mixture. After sealing the blown hole in the bottom of the inner silica tube with the glass membrane the inner compartment was filled with sodium chloride, the reference salt. Before the graphite electrodes were immersed in the melts, they were heated until glowing, in order to remove volatile impurities. The chlorine gas, taken from a cylinder, was first introduced into the reference compartment and from there the gas was passed into the outer, the compartment containing the mixture. The cell was left some hours for stabilization. The internal resistance of the cells were in the range 200–2000 Ω .

The composition of the binary mixture was changed by introducing a weighed amount of salt crystals, and the emf for the different compositions were determined after the potential had stabilized itself. After stabilization the potential fluctuated within ± 0.1 mV. The results are given in Table 7.

Table 7. Experimental emf (mV) as a function of composition of salt mixture for cells of the type $\text{Cl}_2|\text{NaCl}|(\text{Na},\text{B})\text{ glass}|(\text{Na},\text{B})\text{Cl}|\text{Cl}_2$ where B is, in sequence, Li, K, Rb, and Cs.

B=Li $T=1133\text{ K}$		B=K $T=1158\text{ K}$		B=Rb $T=1123\text{ K}$		B=Cs $T=1138\text{ K}$	
χ_{LiCl}	emf	χ_{KCl}	emf	χ_{RbCl}	emf	χ_{CsCl}	emf
.106	– 4.0	.045	3.7	.100	9.2	.10	8.6
.205	– 8.0	.105	9.6	.200	20.6	.21	21.8
.303	– 13.8	.145	14.0	.300	33.5	.29	32.9
.403	– 22.4	.200	20.9	.400	50.0	.38	47.5
.495	– 31.0	.233	25.6	.505	72.8	.46	63.0
.592	– 42.2	.330	36.9	.606	98.3	.57	87.6
.692	– 53.7	.415	51.4	.702	127.0	.66	112.8
.800	– 64.6	.440	53.0	.802	169.9	.75	142.6
		.500	61.6			.81	176.0
		.582	76.5				
		.704	98.4				
		.750	107.0				

IV. CALCULATION AND DISCUSSION

According to Temkin⁸ the ideal chemical potential of mixing of sodium chloride would be expressed as

$$\Delta\mu_{\text{NaCl}}^{\text{id}} = RT \ln \chi_{\text{NaCl}} \quad (4)$$

Differences between the experimentally observed quantities and quantities to be expected for a Temkin mixture are given by excess quantities.

* Model 895A DC Differential Voltmeter, John Fluke, Mfg. Co., USA.

The excess chemical potential of mixing is given by

$$\Delta\mu_{\text{NaCl}}^{\text{E}} = \Delta\mu_{\text{NaCl}}^{\text{exp}} - \Delta\mu_{\text{NaCl}}^{\text{id}} \quad (5)$$

The excess partial entropy, $\Delta\bar{S}_{\text{NaCl}}^{\text{E}}$, and the excess partial enthalpy, $\Delta\bar{H}_{\text{NaCl}}^{\text{E}}$, of mixing are defined in an analogous way.

For the excess values the following relation is valid

$$\Delta\mu_{\text{NaCl}}^{\text{E}} = \Delta\bar{H}_{\text{NaCl}}^{\text{E}} - T\Delta\bar{S}_{\text{NaCl}}^{\text{E}} \quad (6)$$

Calculation of $\Delta\mu_{\text{NaCl}}^{\text{exp}}$ is done by the use of eqn. (3).

$$\Delta\mu_{\text{AX}}^{\text{exp}} = F \int_1^2 \frac{\chi_{\text{BX}}}{t_{\text{B}} + \chi_{\text{BX}}} dE \quad (7)$$

where AX is NaCl and BX is – in sequence – LiCl, KCl, RbCl, and CsCl.

The experimentally calculated chemical potentials are shown together with the ideal (Temkin) chemical potentials in Tables 8–11.

Table 8. Experimental and ideal chemical potentials (cal/mol) of mixing of NaCl in the system (Na,Li)Cl at 1133 K.

$1 - \chi_{\text{NaCl}}$	$-\Delta\mu_{\text{NaCl}}^{\text{exp}}$	$-\Delta\mu_{\text{NaCl}}^{\text{id}} = -RT \ln \chi_{\text{NaCl}}$
.106	120	252
.205	246	518
.303	406	815
.403	705	1162
.495	1020	1542
.592	1550	2020
.692	2290	2657
.800	3390	3614

Table 9. Experimental and ideal chemical potentials (cal/mol) of mixing of NaCl in the system (Na,K)Cl at 1158 K.

$1 - \chi_{\text{NaCl}}$	$-\Delta\mu_{\text{NaCl}}^{\text{exp}}$	$-\Delta\mu_{\text{NaCl}}^{\text{id}} = -RT \ln \chi_{\text{NaCl}}$
.045	85	106
.105	227	253
.145	337	361
.200	509	516
.233	632	610
.330	939	921
.415	1283	1236
.440	1394	1335
.500	1653	1597
.582	2115	2009
.704	2909	2808
.750	3337	3194

Table 10. Experimental and ideal chemical potentials (cal/mol) of mixing of NaCl in the system (Na,Rb)Cl at 1123 K

$1 - \chi_{\text{NaCl}}$	$-\Delta\mu_{\text{NaCl}}^{\text{exp}}$	$-\Delta\mu_{\text{NaCl}}^{\text{id}} = -RT \ln \chi_{\text{NaCl}}$
.100	213	234
.200	475	498
.300	772	794
.400	1153	1140
.505	1680	1571
.606	2268	2080
.702	2929	2700
.802	3918	3615

Table 11. Experimental and ideal chemical potentials (cal/mol) of mixing of NaCl in the system (Na,Cs)Cl at 1138 K.

$1 - \chi_{\text{NaCl}}$	$-\Delta\mu_{\text{NaCl}}^{\text{exp}}$	$-\Delta\mu_{\text{NaCl}}^{\text{id}} = -RT \ln \chi_{\text{NaCl}}$
.10	198	238
.21	502	534
.29	758	778
.38	1096	1083
.46	1453	1395
.57	2021	1914
.66	2601	2457
.75	3288	3098
.81	4058	3805

As indicated earlier, the uncertainty of the values of the transport numbers is $\pm 10\%$ for the (Na,K) system and $\pm 20\%$ for the (Na,Li) system.

If the uncertainty in the transport numbers is considered to be the decisive factor concerning the reliability of the chemical potentials, the uncertainty in these values is then less than $\pm 15\%$ for the (Na,K) system and less than 25% for the (Na,Li) system, whereas the uncertainty is less than 10% for the other systems.

Excess functions

The excess chemical potential is found from eqn. (5), and in Table 12 the calculated excess chemical potentials of mixing of NaCl are given as functions of composition.

The values obtained by Hersh and Kleppa⁹ for the enthalpy of mixing, ΔH^M , for binary alkali halide systems have been used for the calculation of the partial enthalpy of mixing of NaCl in the different systems.

The heat of mixing measurements by Herch and Kleppa were performed at lower temperatures than the emf measurements presented in this work.

Table 12. Excess chemical potentials of mixing of NaCl in the systems (Na,Li)Cl, (Na,K)Cl, (Na,Rb)Cl, (Na,Cs)Cl.

(Na,Li)Cl,	1133 K	(Na,K)Cl,	1158 K
$1 - \chi_{\text{NaCl}}$	$\Delta\mu_{\text{NaCl}}^{\text{E}}(\text{cal/mol})$	$1 - \chi_{\text{NaCl}}$	$\Delta\mu_{\text{NaCl}}^{\text{E}}(\text{cal/mol})$
.106	130	.045	20
.205	270	.105	30
.303	410	.145	20
.403	460	.200	10
.495	520	.233	-20
.592	470	.330	-20
.692	370	.415	-50
.800	230	.440	-60
		.500	-60
		.582	-110
		.704	-100
		.750	-140

(Na,Rb)Cl,	1123 K	(Na,Cs)Cl,	1138 K
$1 - \chi_{\text{NaCl}}$	$\Delta\mu_{\text{NaCl}}^{\text{E}}(\text{cal/mol})$	$1 - \chi_{\text{NaCl}}$	$\Delta\mu_{\text{NaCl}}^{\text{E}}(\text{cal/mol})$
.100	20	.100	40
.200	20	.210	30
.300	20	.290	20
.400	-10	.380	-10
.505	-110	.460	-60
.606	-190	.570	-110
.702	-230	.660	-140
.802	-300	.750	-190
		.810	-250

This difference in experimental temperature does not cause any serious error — as shown in a previous investigation by Kleppa.¹⁰

In a Temkin mixture the partial enthalpy of mixing is zero. Any value of $\Delta\bar{H}_{\text{NaCl}}$ will accordingly be equal to the excess value, $\Delta\bar{H}_{\text{NaCl}}^{\text{E}}$. In Fig. 6 the values $\Delta\mu_{\text{NaCl}}^{\text{E}}$ and $\Delta\bar{H}_{\text{NaCl}}^{\text{E}}$ for the different systems are plotted *versus* composition.

In order to determine the excess partial entropy of mixing we use eqn. (6) together with the calculated values of $\Delta\mu_{\text{NaCl}}^{\text{E}}$ and $\Delta\bar{H}_{\text{NaCl}}^{\text{E}}$. The values obtained for the excess partial entropy of mixing are listed in Table 13. In Fig. 7 the values are plotted *versus* the composition of the melts. The reliability of the reported excess partial entropies is within ± 0.10 e.u. for the (Na,Li) system and within ± 0.05 e.u. for the other systems.

V. CONCLUDING REMARKS

The experimentally obtained results indicate clearly that there are very small excess entropy values to be found for the partial entropy of mixing of sodium chloride in the systems (Na,K)Cl, (Na,Rb)Cl and (Na,Cs)Cl. This is in

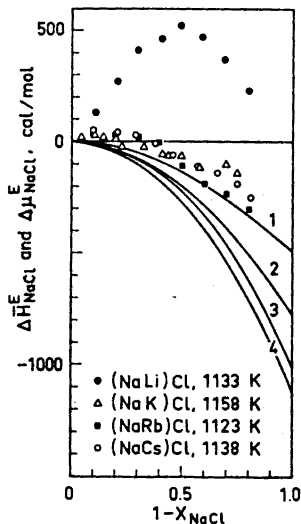


Fig. 6. Partial excess enthalpies and excess chemical potentials of mixing of NaCl. The curves 1-4 represent in sequence, $\Delta\bar{H}_{\text{NaCl}}^E$ in (Na,K)Cl, (Na,Rb)Cl, (Na,Cs)Cl, and (Na,Li)Cl.

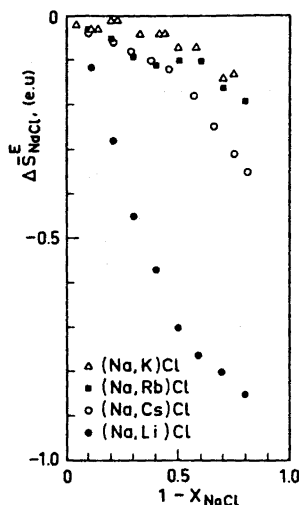


Fig. 7. Excess partial entropy of mixing of NaCl in the systems (Na,Li)Cl at 1133 K; (Na,K)Cl at 1158 K; (Na,Rb)Cl at 1123 K, and (Na,Cs)Cl at 1138 K.

Table 13. Excess partial entropy of mixing of NaCl in the systems (Na,Li)Cl, (Na,K)Cl, (Na,Rb)Cl, and (Na,Cs)Cl.

(Na,Li)Cl,	1133°K	(Na,K)Cl,	1158°K
$1 - \chi_{\text{Na}}$	$-\Delta\bar{S}_{\text{NaCl}}^E(\text{e.u.})$	$1 - \chi_{\text{Na}}$	$\Delta\bar{S}_{\text{NaCl}}^E(\text{e.u.})$
.106	.12	.045	.02
.205	.28	.105	.03
.303	.45	.145	.03
.403	.57	.200	.01
.495	.70	.233	.01
.592	.76	.330	.04
.692	.80	.415	.04
.800	.85	.440	.04
		.500	.07
		.582	.07
		.704	.14
		.750	.13
(Na,Rb)Cl,	1123 K	(Na,Cs)Cl,	1138K
$1 - \chi_{\text{NaCl}}$	$-\Delta\bar{S}_{\text{NaCl}}^E(\text{e.u.})$	$1 - \chi_{\text{NaCl}}$	$-\Delta\bar{S}_{\text{NaCl}}^E(\text{e.u.})$
.100	.03	.100	.04
.200	.05	.210	.06
.300	.09	.290	.08
.400	.11	.380	.10
.505	.10	.460	.12
.606	.10	.570	.18
.702	.16	.660	.25
.802	.19	.750	.31
		.810	.35

good agreement with the expected occurrence of small negative excess entropies both in simple mixed anion and in mixed cation systems.¹¹ The partial excess entropy of mixing of NaCl in the system (Na,K)Cl obtained in this work may be compared with the values obtained by Krohn and Moser.⁶ They obtained the values

$1 - \chi_{\text{Na}}$	$-\Delta\bar{S}_{\text{NaCl}}^{\text{E}}$ (e.u.)
0.25	0.1
0.50	0.1
0.75	0.6

which, as the potassium content increases, deviate markedly from the values given in Table 13. It seems reasonable to assume that this difference is a result of side reactions in the formation cell used by Krohn and Moser.

As seen from Table 13 the partial excess entropy of mixing of NaCl in the system (Na,Li)Cl has quite large negative values. Whether this excess entropy is to be explained by configurational or by vibrational consideration is not clear. There is, however, clearly a need for additional data in this area before a more general discussion can be given. Such data should now be quite readily obtainable, using the method elucidated in this work.

Acknowledgement. The author is indebted to *Norges Teknisk-Naturvidenskapelige Forskningsråd* and *Det Videnskapelige Forskningsfond av 1919* for financial support.

REFERENCES

1. Førland, T., Grjotheim, K., Motzfeldt, K. and Urnes, S., Eds., *Selected Topics in High Temperature Chemistry*, Universitetsforlaget, Oslo 1966, p. 27.
2. Førland, T. and Østvold, T. *Acta Chem. Scand.* **20** (1966) 2086.
3. Førland, T. and Thulin, L. U. *Acta Chem. Scand.* **22** (1968) 3023.
4. Førland, T. and Thulin, L. U. *Acta Chem. Scand.* **21** (1967) 1121.
5. Conti, F. and Eisenman, G. *Biophys. J.* **5** (1965) 511.
6. Krohn, C. H. and Moser, Z. *Kgl. Norske Videnskap. Selskabs, Skrifter* **1967** No. 9.
7. Bockris, J. O'M, White, J. L. and Mackenzie, J., Eds., *Physico-Chemical Measurements at High Temperatures*, Butterworths, London 1960.
8. Temkin, H. *Acta Physicochim. USSR* **20** (1945) 411.
9. Hersch, L. S. and Kleppa, O. J. *J. Chem. Phys.* **42** (1965) 1309.
10. Kleppa, O. J. *J. Phys. Chem.* **64** (1960) 1937.
11. Kleppa, O. J. *Ann. Rev. Phys. Chem.* **16** (1965) 187.

Received March 15, 1971.