

## Emf Measurements for the Determination of Partial Gibbs Energies and Entropies of Mixing of the Alkali Chlorides in Liquid Mixtures with $\text{CoCl}_2$

YAG DUTT<sup>a</sup> and TERJE ØSTVOLD<sup>b</sup>

<sup>a</sup>*Institute of Physical Chemistry, NTH, The University of Trondheim, Trondheim, Norway and*  
<sup>b</sup>*Department of Chemistry, NLHT, The University of Trondheim, Trondheim, Norway*

The partial Gibbs energies of mixing of alkali chlorides in liquid mixtures with cobalt chloride have been determined by emf measurements. Galvanic cells of the type

$\text{C(s), Cl}_2(\text{g}) \mid \text{Alk. Cl(l)} \mid \text{Alkali glass} \mid \text{CoCl}_2(\text{l})\text{-Alk. Cl(l)} \mid \text{Cl}_2(\text{g}), \text{C(s)}$   
 were used.

In the  $\text{NaCl-CoCl}_2$  and  $\text{KCl-CoCl}_2$  systems, the volatility of  $\text{CoCl}_2$  was appreciable at the melting points of these alkali chlorides. To minimise error due to evaporation, lower melting binary mixtures  $\text{NaCl-SrCl}_2$  ( $X_{\text{NaCl}}=0.500$ ) and  $\text{KCl-SrCl}_2$  ( $X_{\text{KCl}}=0.667$ ) have been employed as reference melts.

The data obtained were combined with enthalpy of mixing data reported by Papatheodorou and Kleppa to get the partial entropies of mixing of the alkali chlorides in these systems. The results of the present investigation suggest that all systems except  $\text{LiCl-CoCl}_2$ , contain the divalent cobalt ion in the tetrahedral configuration,  $\text{CoCl}_4^{2-}$ . The tendency for "complex" formation increases with increasing size of the alkali metal ion. The entropies of mixing for these binary melts except for the  $\text{LiCl-CoCl}_2$  system, are much smaller than entropies calculated by assuming random mixtures of  $\text{Cl}^-$  and  $\text{CoCl}_4^{2-}$  ions at high alkali chloride contents. This is probably due to entropy contributions in addition to the pure configurational entropy of mixing.

Recently the partial Gibbs energies of mixing of the alkali chlorides in mixtures with the alkaline earth chlorides<sup>1,2</sup> and manganese chloride<sup>3</sup> have been measured. By combining partial Gibbs energies with partial enthalpies calculated from integral enthalpies of mixing for the same systems reported by Kleppa and coworkers<sup>4,5</sup> partial entropies could be obtained. The partial entropies of mixing of the alkali chlorides  $\text{KCl}$  and  $\text{RbCl}$  in the binary mixtures with  $\text{MgCl}_2$  and  $\text{MnCl}_2$  show inflexion points at  $X_{\text{MCl}}=0.33$

\* Present address: Department of Chemistry, Delhi University, Delhi-7, India.

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 and supports the view originally advanced by Flood and Urnes<sup>6</sup> for the alkali chloride–magnesium chloride mixtures, that the mixtures are stabilized by a preferred coordination of four anions around the divalent cation,  $MCl_4^{2-}$ . The concentration dependence of the enthalpy interaction parameter,  $\lambda = \Delta H/X_1X_2$  (where  $X_i$  is the mol fraction of the  $i$ th component), for the mixtures also supports this view.

In the present communication we report an extension of this work to the solutions of LiCl, NaCl, KCl, and RbCl in  $CoCl_2$ .

Complexation of cobalt(II) by chloride ions is well known in aqueous solutions and in organic solvents. Enthalpy of mixing measurements of cobalt chloride with alkali chlorides in the fused state have been carried out by Papatheodorou and Kleppa<sup>5</sup> who reported the presence of  $CoCl_4^{2-}$  species in all systems except LiCl– $CoCl_2$ . Emf studies over a low concentration range of cobalt chloride have been done by Trzebiatowski and Kiszka<sup>7</sup> who assumed that the deviation from random mixing in these melts was due to the formation of the complex ion,  $CoCl_4^{2-}$ .

The purpose of the present investigation is to determine the partial Gibbs energies and entropies of mixing of the alkali chlorides in liquid mixtures with cobalt chloride. For this purpose concentration cells with alkali conducting glass separating the two half cells were used. The chemical work carried out in the junction between the two half cells during a measurement is thus 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 cobalt chloride concentrations we were unable to study melts richer in cobalt chloride than  $X_{CoCl_2} = 0.6$ .

## EXPERIMENTAL

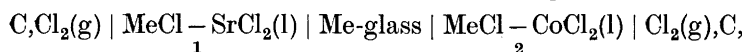
Analytical reagent grade chemicals were used in the present study and were obtained from E. Merck AG, Germany. For the treatment of the salts, the experimental set-up and composition of the glasses used in the present galvanic cell previous papers should be consulted.<sup>2,3,8</sup>

In the NaCl– $CoCl_2$  system, the volatility of  $CoCl_2$  was appreciable in mixtures containing a high mol fraction of  $CoCl_2$ . To minimise errors due to evaporation these mixtures were studied at lower temperatures employing a NaCl– $SrCl_2$  (liquid mixture:  $X_{NaCl} = 0.5$ ) mixture as a reference melt. The activity of NaCl is known in these mixtures from an earlier communication.<sup>2</sup> Similarly a KCl– $SrCl_2$  (liquid mixture:  $X_{KCl} = 0.667$ )<sup>2,8</sup> mixture was used as a reference melt in the KCl– $CoCl_2$  system in mixtures containing a higher mol fraction of  $CoCl_2$ .

Measurements of the transport number of the  $Co^{2+}$  ion in the glass membranes were carried out in the following manner: A little piece of the alkali-glass was melted into a small hole in the bottom of the quartz tube forming the cathode compartment. The cathode compartment was filled with 9–10 g of alkali chloride and the anode compartment (the outer silica tube) with molten mixture of alkali chloride and  $CoCl_2$ . A current of  $\sim 10$  mA was passed through the cell for 10 h. The amount of charge passed through the cell was measured. The amount of  $CoCl_2$  which by charge transfer had migrated into the cathode compartment was measured colorimetrically.

## RESULTS

The transport number of the  $\text{Co}^{2+}$  ion was found to be  $< 0.001$  for all the alkali glasses. There is therefore practically no chemical work carried out in the membrane between the two half cells in the galvanic cell when an emf measurement is performed. The cell reaction for the galvanic cell,



will accordingly be

$$\text{MeCl}(1) = \text{MeCl}(2) \quad (1)$$

where  $\text{MeCl}(1)$  is  $\text{MeCl}(1)$  in mixtures with  $\text{SrCl}_2(1)$ ,  
and  $\text{MeCl}(2)$  is  $\text{MeCl}(1)$  in mixtures with  $\text{CoCl}_2(1)$ .

The Gibbs energy change for reaction (1) is given by

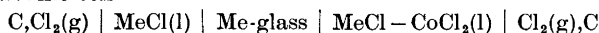
$$\Delta G = \Delta\mu_{\text{MeCl}(2)} - \Delta\mu_{\text{MeCl}(1)} = -FE \quad (2)$$

where  $\Delta\mu_{\text{MeCl}} = \mu_{\text{MeCl}} - \mu_{\text{MeCl}}^\circ$  ( $\mu_{\text{MeCl}}^\circ$  is the chemical potential of pure liquid  $\text{MeCl}$ ).

Since the chemical potentials of mixing of the alkali chlorides in mixtures with strontium chloride,  $\Delta\mu_{\text{MeCl}(1)}$ , are known,<sup>2,8</sup> we can calculate the chemical potential of mixing of the alkali chlorides in mixtures with cobalt chloride,  $\Delta\mu_{\text{MeCl}(2)}$ , from eqn. (2). When pure alkali chloride is used as a reference melt, eqn. (2) takes the form

$$\Delta G = \Delta\mu_{\text{MeCl}(2)} = -FE \quad (3)$$

Table 1. Thermodynamic data for the  $\text{CoCl}_2 - \text{MeCl}$  mixtures. Me = Li, Na, K, and Rb. Emf's for the galvanic cell

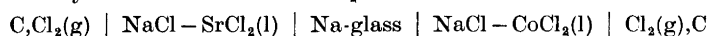


are measured. The thermodynamic data for  $\text{MeCl}$  in the fused  $\text{MeCl} - \text{CoCl}_2$  mixtures are calculated from the present emf values and the enthalpy of mixing data reported by Papatheodorou and Kleppa.<sup>5</sup>

System and temperature	$X_{\text{CoCl}_2}$	Emf mV	$-\Delta\mu_{\text{MeCl}}$ cal/mol	$-\Delta\bar{H}_{\text{MeCl}}$ cal/mol	$\Delta\bar{S}_{\text{MeCl}}$ cal/mol deg.
$\text{CoCl}_2 - \text{LiCl}$ $T = 913 \text{ K}$	0.103	10.5	240	40	0.22
	0.150	17.2	400	80	0.35
	0.181	21.1	490	110	0.42
	0.200	24.1	555	130	0.47.
$T = 969 \text{ K}$	0.249	33.8	780	210	0.59
	0.279	42.8	985	260	0.75
	0.300	47.5	1095	340	0.78
	0.330	56.0	1290	430	0.89
	0.350	61.5	1420	460	0.99
$T = 898 \text{ K}$	0.399	69.8	1610	560	1.17
	0.452	82.8	1910	620	1.44
	0.499	92.9	2140	670	1.64

Table 1. Continued.

CoCl <sub>2</sub> - NaCl	0.117	16.4	380	100	0.25	
	0.205	35.9	830	250	0.53	
	<i>T</i> = 1089 K	0.297	70.7	1630	900	0.67
CoCl <sub>2</sub> - KCl	0.099	13.3	310	50	0.24	
<i>T</i> = 1063 K						
CoCl <sub>2</sub> - RbCl	0.102	14.6	340	150	0.19	
	<i>T</i> = 1003 K	0.151	22.0	510	200	0.31
CoCl <sub>2</sub> - RbCl	0.181	31.2	720	300	0.42	
	0.202	38.6	890	400	0.49	
	<i>T</i> = 1003 K	0.232	51.2	1180	900	0.28
	0.252	60.8	1400	1100	0.30	
	0.300	94.7	2180	2200	-0.02	
	0.330	123.4	2840	3000	-0.15	
	0.350	145.0	3340	3700	-0.33	
	0.380	175.0	4030	4600	-0.57	
	<i>T</i> = 1013 K	0.409	200.0	4610	6700	-2.08
0.429	222.1	5120	7400	-2.26		
0.458	255.1	5880	8400	-2.50		
0.487	287.1	6630	8500	-1.85		
0.515	318.0	7330	8600	-1.26		
0.554	358.0	8250	8800	-0.55		
0.601	405.0	9340	9000	0.33		

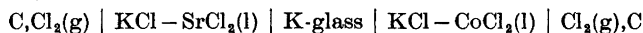
Table 2. Thermodynamic data for the CoCl<sub>2</sub> - NaCl mixtures. Emf's for the galvanic cell

where  $X_{\text{SrCl}_2} = 0.500$  are measured at 998 K, 983 K, and 883 K. The corrected emf's,  $\text{emf}^{\text{corr}}$ , given below are obtained by adding the emf for the analogous NaCl(l)/Na-glass/NaCl - SrCl<sub>2</sub>(l) ( $X_{\text{NaCl}} = 0.5$ ) cell adjusted to the above temperatures.<sup>2</sup> The thermodynamic data for NaCl in the NaCl - CoCl<sub>2</sub> mixtures are calculated from the present emf values and the enthalpy of mixing data reported by Papatheodorou and Kleppa.<sup>5</sup>

System and temperature	$X_{\text{CoCl}_2}$	Emf mV	Emf <sup>corr</sup> mV	$-\Delta\mu_{\text{NaCl}}$ cal/mol	$-\Delta\bar{H}_{\text{NaCl}}$ cal/mol	$\Delta\bar{S}_{\text{NaCl}}$ cal/mol deg.	
CoCl <sub>2</sub> - NaCl	0.150	-50.8	21.3	490	100	0.39	
	0.180	-45.2	26.9	620	200	0.42	
	<i>T</i> = 998 K	0.220	-34.2	37.9	870	350	0.53
	0.240	-28.0	44.1	1010	450	0.56	
	0.271	-16.9	55.2	1270	650	0.62	
<i>T</i> = 983 K	0.201	-39.2	32.9	760	250	0.52	
	0.249	-24.5	46.6	1070	500	0.58	
	0.299	-3.7	67.4	1550	900	0.66	
	0.320	7.1	78.2	1800	1100	0.73	
	0.350	22.2	93.3	2150	1600	0.62	

Table 2. Continued.

$T = 883 \text{ K}$	0.300	- 0.2	65.3	1510	900	0.68
	0.321	9.6	75.1	1730	1100	0.72
	0.349	24.4	89.9	2070	1600	0.55
	0.400	54.0	119.5	2750	2400	0.40
	0.420	63.5	128.5	2960	2600	0.40
	0.440	80.0	145.5	3350	2900	0.46
$\text{CoCl}_2 - \text{NaCl}$	0.460	91.0	156.5	3610	3100	0.52
	0.480	101.2	166.7	3840	3300	0.55
$T = 883 \text{ K}$	0.500	110.9	176.4	4070	3500	0.64
	0.520	121.0	186.5	4300	3600	0.71
	0.545	133.0	198.5	4580	3700	0.99
	0.600	160.5	226.0	5210	3900	1.48

Table 3. Thermodynamic data for the  $\text{CoCl}_2 - \text{KCl}$  mixtures. Emf's for the galvanic cells

where  $X_{\text{SrCl}_2} = 0.333$  are measured at 990 K and 982 K. The corrected emf's,  $\text{emf}^{\text{corr}}$ , given below are obtained by adding the emf for the analogous  $\text{KCl}(\text{l})/\text{K-glass}/\text{KCl} - \text{SrCl}_2(\text{l})$  ( $X_{\text{SrCl}_2} = 0.333$ ) cell adjusted to the above temperatures.<sup>3,8</sup> The thermodynamic data for KCl in the  $\text{KCl} - \text{CoCl}_2$  mixtures are calculated from the present emf values and the enthalpy of mixing data reported by Papatheodorou and Kleppa.<sup>5</sup>

System and temperature	$X_{\text{CoCl}_2}$	Emf mV	$\text{Emf}^{\text{corr}}$ mV	$-\Delta\mu_{\text{KCl}}$ cal/mol	$-\Delta\bar{H}_{\text{KCl}}$ cal/mol	$\Delta\bar{S}_{\text{KCl}}$ cal/mol deg
$\text{CoCl}_2 - \text{KCl}$	0.236	- 4.9	50.3	1160	900	0.26
	0.261	8.7	63.9	1470	1300	0.17
$T = 990 \text{ K}$	0.300	35.7	90.9	2100	1900	0.20
	0.336	63.5	118.7	2740	2600	0.15
	0.356	81.8	137.0	3160	3200	- 0.04
	0.380	116.9	172.1	3970	4100	- 0.13
	0.400	138.4	193.6	4460	4800	- 0.36
	0.430	167.3	222.5	5130	6100	- 0.96
	0.451	186.2	241.4	5560	6600	- 1.03
	0.471	203.4	258.6	5960	6900	- 0.92
$T = 982 \text{ K}$	0.159	- 31.4	23.4	540	200	0.34
	0.181	- 25.4	29.4	680	250	0.44
	0.201	- 19.6	35.6	820	400	0.43
	0.500	231.5	286.5	6600	7100	- 0.49
	0.530	257	312	7190	7300	- 0.11
	0.600	315	370	8530	7600	0.92

In Tables 1 - 3 the experimental data are presented together with partial enthalpies of mixing of the alkali chlorides,  $\Delta\bar{H}_{\text{MCl}}$ , in mixtures with cobalt chloride calculated by the method of intercepts from integral enthalpies of mixing determined by Papatheodorou and Kleppa.<sup>5</sup>

The partial enthalpy data are not very reliable in the concentration range  $0.25 < X_{\text{CoCl}_2} < 0.45$  where the slope of the integral enthalpies changes significantly with slight changes in composition.

For the system  $\text{NaCl}-\text{CoCl}_2$  it is in addition difficult to draw a smooth curve through the experimental points in this concentration region as the data reported appears to be a little uncertain.

The uncertainty in the  $\Delta\bar{H}_{\text{MeCl}}$  values for the present systems in this concentration range may for these reasons be as great as  $\pm 200$  cal/mol. The partial enthalpy data determined in the above mentioned way were then combined with the partial Gibbs energy data to get the partial entropy values of the alkali chlorides also given in Tables 1-3. In Figs. 1 and 2  $\Delta\mu_{\text{MeCl}}$ ,  $\Delta\bar{H}_{\text{MeCl}}$ , and  $\Delta\bar{S}_{\text{MeCl}}$  are plotted versus  $X_{\text{CoCl}_2}$ .

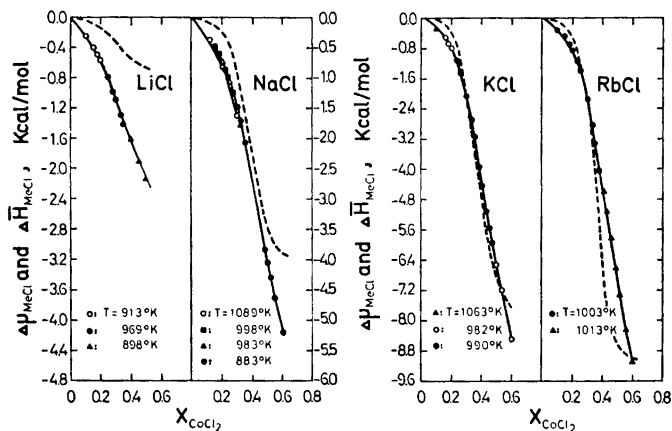


Fig. 1. Chemical potentials and partial enthalpies of mixing (dotted lines) of the alkali chlorides in mixtures with cobalt chloride. The partial enthalpies,  $\Delta\bar{H}_{\text{MeCl}}$ , are calculated from integral enthalpies of mixing given by Papatheodorou and Kleppa.<sup>5</sup>

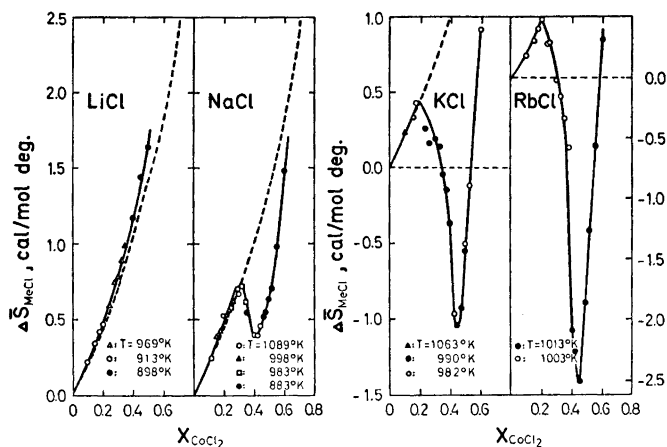


Fig. 2. Partial entropies of mixing of the alkali chlorides in mixtures with cobalt chloride. The dotted lines represent the ideal entropies given by  $-\bar{R} \ln X_{\text{MeCl}}$ .

## 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 these ions have ionic potentials,  $Z_+/R_+$ , of comparable magnitude. Deviations from the Temkin entropy of mixing may otherwise occur. In the  $\text{MgCl}_2\text{-MeCl}$  and  $\text{MnCl}_2\text{-MeCl}$  systems where  $\text{Me} = \text{Li, Na, K, Rb, and Cs}$ , marked deviations from the random mixing of cations behavior were observed for the  $\text{KCl, RbCl}$  and  $\text{CsCl}$  containing systems.<sup>1-3</sup>

In the present  $\text{CoCl}_2\text{-MeCl}$  mixtures considerable deviation from the Temkin entropy of mixing occurs in the mixtures of  $\text{NaCl, KCl}$  and  $\text{RbCl}$  with  $\text{CoCl}_2$ . This can be observed from Fig. 2. The deviation from the Temkin entropy is, however, of a different kind in these mixtures than the deviations observed in the  $\text{MgCl}_2$  and  $\text{MnCl}_2$  containing melts.

For the latter systems deviations from the Temkin entropy were explained in terms of the formation of complex ions like  $\text{MgCl}_4^{2-}$  and  $\text{MnCl}_4^{2-}$  or in other words  $\text{Mg}^{2+}$  and  $\text{Mn}^{2+}$  ions with  $\text{K}^+, \text{Rb}^+, \text{or Cs}^+$  ions *only* as next nearest neighbors. By assuming random distribution of ions and by allowing the complex to dissociate to some extent the partial entropies calculated on this basis compared very well with the observed entropies.<sup>2,3</sup>

In Fig. 3 the integral entropies of mixing for the  $\text{MgCl}_2\text{-MeCl}$  and  $\text{MnCl}_2\text{-MeCl}$  systems (the integral entropies are derived from the partials obtained previously) are compared with values calculated for the two idealized models given below.

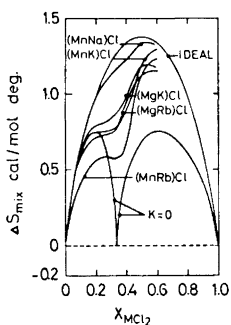


Fig. 3. Integral entropies of mixing for the  $\text{MgCl}_2\text{-MeCl}$  and  $\text{MnCl}_2\text{-MeCl}$  systems.  $\text{Me} = \text{Na, K, and Rb}$ . The integral entropies for the  $\text{MCl}_2\text{-MeCl}$  systems are obtained from partial entropies reported previously.<sup>2,3</sup> Ideal: random mixing of  $\text{MeCl}$  and  $\text{MCl}_2$ .  $\text{K} = 0$ : random mixing of  $\text{MeCl}$  and  $\text{Me}_2\text{MCl}_4$  at  $X_{\text{MCl}_2} < 0.33$  and of  $\text{MCl}_2$  and  $\text{Me}_2\text{MCl}_4$  at  $X_{\text{MCl}_2} > 0.33$  with no dissociation of the complex ion  $\text{MCl}_4^{2-}$ .

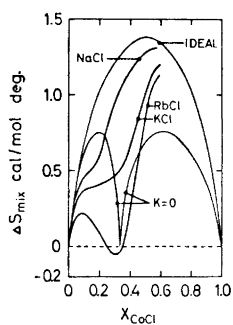


Fig. 4. Integral entropies of mixing for the  $\text{CoCl}_2\text{-MeCl}$  systems.  $\text{Me} = \text{Na, K, and Rb}$ . The "Ideal" and " $\text{K} = 0$ " entropies are the same as referred to in Fig. 3.

- (1) Random mixing of MeCl and  $MCl_2$  (or of  $Me^+$  and  $M^{2+}$ ).
- (2) Random mixing of MeCl and  $Me_2MCl_4$  (or of  $Cl^-$  and  $MCl_4^{2-}$ ) at  $X_{MCl_2} < 0.33$  and of  $MCl_2$  and  $Me_2MCl_4$  (or of  $Me^+$  and  $M^{2+}$ ) at  $X_{MCl_2} > 0.33$  with no dissociation of the complex ion  $MCl_4^{2-}$ .

Since the  $MCl_4^{2-}$  anion was assumed undissociated ( $K=0$ ), model (2) would give rise to an entropy of mixing curve which consists of two separate positive parts which join with a sharp cusp at  $X_{MCl_2}=0.33$ . The integral entropies calculated from the experimental partial entropies of mixing are given to  $X_{MCl_2}=0.6$  only. Inaccurate experimental entropies at high concentration of the divalent salts made the calculated integral entropies unreliable in this concentration region. The experimental entropies of mixing curves fall roughly in between the curves for the two idealized models. It is therefore reasonable to believe that the main contribution to the deviations observed from the Temkin entropy in these mixtures is of configurational origin.

In Fig. 4 the integral entropies of mixing derived from the partial entropies of mixing given in Fig. 2, are plotted *versus* composition together with the entropy curves obtained from the two above mentioned models. The negative entropy of mixing observed for the  $CoCl_2-RbCl$  system around  $X_{CoCl_2} \approx 0.3$  may be within experimental error.

The entropies observed for these mixtures in the alkali chloride rich melts are much lower than the entropies observed in the  $MgCl_2-MeCl$  and  $MnCl_2-MeCl$  mixtures in the same concentration range.

Trutia<sup>9,10</sup> and coworkers have reported the visible spectra of some divalent cobalt chloride-alkali chloride samples measured at liquid nitrogen temperature. The alkali chloride rich systems were dominated by the octahedral symmetry band in the  $LiCl$  containing systems and in the normally cooled  $NaCl$  containing systems. The tetrahedral symmetry band was observed in quenched  $NaCl$  containing mixtures and in the mixtures of well controlled composition made from  $KCl$ ,  $RbCl$ , and  $CsCl$  and  $CoCl_2$ . By investigating spectroscopically the  $CoCl_2$  doped alkali chloride melts Gruen and Øye<sup>11</sup> observed the tetrahedral symmetry band only. Trutia and Musa<sup>12</sup> observed a change from octahedral to tetrahedral symmetry during melting of pure cobalt chloride.

A predominance of the  $CoCl_4^{2-}$  configuration in the alkali chloride-cobalt chloride melts is therefore reasonable. The observed negative deviations of the entropy of mixing from model (2) in the present liquid binary melts are thus probably due to other than pure configurational entropy contributions. Possible volume changes on mixing may influence the entropy of mixing and change the entropy curves. We are, however, not at the present stage ready to give a satisfactory explanation for the observed discrepancies between calculated and measured partial entropies in these systems.

*Acknowledgement.* One of the authors, Yag Dutt, is grateful to *The Norwegian Agency for International Development* for economic support. The authors are indebted to Dr. techn. Harald Øye for comments on the manuscript of this paper.



## REFERENCES

1. Ikeuchi, H. and Krohn, C. *Acta Chem. Scand.* **23** (1969) 2230.
2. Østvold, T. *High Temp. Sci.* **4** (1972) 51.
3. Østvold, T. *Acta Chem. Scand.* **26** (1972) 2788.
4. Kleppa, O. J. and McCarty, F. G. *J. Phys. Chem.* **70** (1966) 1249.
5. Papatheodorou, G. N. and Kleppa, O. J. *J. Inorg. Nucl. Chem.* **33** (1971) 1249.
6. Flood, H. and Urnes, S. *Z. Elektrochem.* **59** (1955) 834.
7. Trzebiatowski, W. and Kiszka, A. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **9** (1961) 605.
8. Robbins, G. D., Førland, T. and Østvold, T. *Acta Chem. Scand.* **22** (1968) 3002.
9. Trutia, Ath. and Voda, M. *Rev. Roum. Chim.* **12** (1967) 191.
10. Trutia, Ath., Voda, M. and Vasile, A. *Rev. Roum. Phys.* **12** (1967) 101.
11. Gruen, D. M. and Øye, H. *Private communication.*
12. Trutia, Ath. and Musa, M. *Phys. Status Solidi* **8** (1965) 663.

Received November 13, 1971.