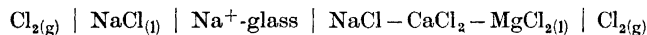


Determination of the Change in Chemical Potential of Sodium Chloride of Mixing in the Ternary System MgCl_2 — NaCl — CaCl_2 by EMF Measurements

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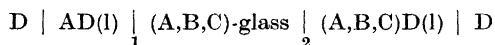
The chemical potential of NaCl on mixing is measured by an emf technique using the following concentration cell:



The composition was changed from the pure NaCl—CaCl₂ binaries to the pure NaCl—MgCl₂ binaries covering the ternary system with 48 composition points. The results show that at constant sodium chloride concentration the excess chemical potential of NaCl deviates slightly from the linear combination of the chemical potential of NaCl in the two binaries NaCl—CaCl₂ and NaCl—MgCl₂. An integration of the excess chemical potential of NaCl in the ternary system gives an excess Gibbs energy of mixing in the MgCl₂—CaCl₂ binaries which agrees very well with phase diagram and calorimetric data.

In a paper by the present author¹ on the application of glass membranes as alkali electrodes at elevated temperatures an expression was given for the emf of a galvanic cell containing a binary charge-unsymmetrical fused salt mixture on one side of the glass membrane separating the two half-cells of the concentration cell and pure fused alkali halide on the other side. The situation is slightly more complicated when we have more than two ions that can migrate through the glass membrane.

Consider the following galvanic cell:



where the electrolyte consists of a fused mixture of three salts AD, BD₂, and CD₂ (A⁺, B²⁺, C²⁺, and D⁻) on the right side and pure fused salt AD on the left side of the glass membrane. 1 and 2 denote the interfaces between the two solutions and the membrane. The electrodes, D, are reversible to the anion, D⁻, only. The change in Gibbs energy by a charge transfer of one Faraday is given by the following equation:

$$\begin{aligned}
 \Delta G &= -nFE \\
 &= -\mu_{AD}^{\circ} + \mu_{AD}t_A(2) + \frac{1}{2}\mu_{BD}t_{B^{2+}}(2) + \frac{1}{2}\mu_{CD}t_{C^{2+}}(2) \\
 &\quad - \int_1^2 \text{over membrane} (\mu_{A\text{-sil}}dt_{A^+} + \frac{1}{2}\mu_{B\text{-sil}}dt_{B^{2+}} + \frac{1}{2}\mu_{C\text{-sil}}dt_{C^{2+}}) \quad (1)
 \end{aligned}$$

where t_{A^+} , $t_{B^{2+}}$, and $t_{C^{2+}}$ refer to the transport numbers in the glass membrane of A^+ , B^{2+} , and C^{2+} ions, respectively, and $t_{A^+}(2)$, $t_{B^{2+}}(2)$, and $t_{C^{2+}}(2)$ refer to the values of these transport numbers in the glass membrane at the interface between glass and salt mixture.

Introducing the equations for the equilibria between ions in solution and ions in glass at the contact between the two phases, and integrating eqn. (1) by parts we obtain:

$$\begin{aligned}
 \Delta G &= -nFE \\
 &= \mu_{AD} - \mu_{AD}^{\circ} + \mu_{A\text{-sil}}(1) - \mu_{A\text{-sil}}(2) \\
 &\quad + \int_1^2 \text{over membrane} (t_{A^+}d\mu_{A\text{-sil}} + \frac{1}{2}t_{B^{2+}}d\mu_{B\text{-sil}} + \frac{1}{2}t_{C^{2+}}d\mu_{C\text{-sil}}) \quad (2)
 \end{aligned}$$

We cannot simplify eqn. (2) further without introducing assumptions regarding the transport properties of the ions of the glass membrane.

On the basis of the results presented in a previous paper¹ where the transport numbers of the alkaline earth ions were found to be negligible in certain glass membranes, we can use a galvanic cell of the above type to measure the activity of an alkali salt in a three- or multicomponent mixture of the alkali salt and the alkaline earth salts. The change in chemical potential of the alkali salt on mixing when $t_{A^+} = 1$, is given by the equation:

$$-nFE = \Delta\mu_{AD} = \mu_{AD} - \mu_{AD}^{\circ} \quad (3)$$

By this method we have a possibility to investigate all the ternary mixtures of one alkali halide with two alkaline earth halides. This is, however, an extensive task, and the idea behind the present work is therefore rather to check the possibility of describing the ternary alkali-alkaline earth halide mixtures by the binary halide mixtures. The system $MgCl_2 - CaCl_2 - NaCl$ was selected for that purpose. The chemical potentials of the alkali chloride in the binary mixtures $MgCl_2 - NaCl$ and $CaCl_2 - NaCl$ are known,² and the phase diagram³ and the enthalpy of mixing are known for the binary system $MgCl_2 - CaCl_2$.⁴

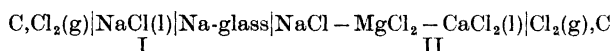
We will in the discussion compare the experimental ternary chemical potentials with the chemical potentials calculated from the binary mixtures. Guion, Blander, Hengstenberg and Hagemark⁵ studied the two ternary systems $AgCl - NaCl - KCl$ and $AgCl - NaCl - CsCl$ by an electromotive force technique using the reversible cell $Ag|AgCl + \text{alkali chloride}|Cl_2, \text{graphite}$. They introduced a thermodynamic formalism for ternary systems in which the excess Gibbs energy was related to weighted sums of the excess Gibbs energies of the three binary systems and a ternary term. This ternary term

calculated from experiments was consistent with calculations of the same term from the quasi-lattice theory.

In the present paper the thermodynamic formalism of Guion *et al.*⁵ will be adopted to describe the MgCl_2 – CaCl_2 – NaCl ternary system. A quasi-lattice calculation of the type outlined by Hagemark⁶ and used by Guion *et al.* for the above systems cannot be justified for the present mixture since the cations have different charges.

EXPERIMENTAL

The apparatus is described and the purification of the chemicals is discussed in a previous paper.² The following galvanic cell made of silica was used for the present investigation:



The concentration in compartment II was changed by adding sodium chloride crystals keeping the ratio $y = X_{\text{MgCl}_2} / (X_{\text{MgCl}_2} + X_{\text{CaCl}_2})$ constant. The cell emf was measured for varying sodium chloride concentrations with y equal to 0, 0.129, 0.344, 0.517, 0.718, 0.796, and 1.

The composition of the mixture was checked at the end of each series with constant y by taking out a small sample of the liquid mixture. The sample was analyzed by EDTA titration together with a potentiometric titration to determine the chloride content. This was done due to a slight evaporation of magnesium chloride during the experiment. The difference between the weighed in mol fractions and the analyzed mol fractions was within ± 1 mol %.

RESULTS

In the course of the present investigation the change in chemical potential of sodium chloride on mixing was determined for 117 compositions in the system MgCl_2 – CaCl_2 – NaCl counting the binary systems MgCl_2 – NaCl and CaCl_2 – NaCl . Among these compositions 48 were from the ternary system and 69 from the two binaries. All the experimental results are recorded in Tables 1–3. In these tables, the first column gives the magnesium-calcium ratio, $y = X_{\text{MgCl}_2} / (X_{\text{MgCl}_2} + X_{\text{CaCl}_2})$, in the mixture, the second the mol fraction of sodium chloride, the third the measured potential and the fourth the change in chemical potential of sodium chloride on mixing. The chemical potential of sodium chloride is getting more negative as magnesium chloride is substituted for calcium chloride. This is well illustrated by Fig. 1, where the change in chemical potential of sodium chloride on mixing divided by $(1 - X_{\text{NaCl}})^2$ is plotted *versus* composition, keeping y constant. In Fig. 2 the excess chemical potential interaction parameter, $\Delta\mu_{\text{NaCl}}^E / (1 - X_{\text{NaCl}})^2$, is plotted *versus* concentration of sodium chloride. The excess chemical potential of mixing of sodium chloride is defined by

$$\Delta\mu_{\text{NaCl}}^E = \mu_{\text{NaCl}} - \mu_{\text{NaCl}}^\circ - RT \ln X_{\text{NaCl}}$$

where $\mu_{\text{NaCl}} - \mu_{\text{NaCl}}^\circ$ is the chemical potential of solution of sodium chloride and X_{NaCl} is the mol fraction of sodium chloride in the ternary mixture. Fig. 2 is constructed from the experimental data in Fig. 1 by taking the values of $(\Delta\mu_{\text{NaCl}} - RT \ln X_{\text{NaCl}}) / (1 - X_{\text{NaCl}})^2$ at $X_{\text{NaCl}} = 0.1, 0.15, 0.20, \dots, 0.85$ and 0.9 .

Table 1. Experimental emf and corresponding change in chemical potential of sodium chloride on mixing for the binary mixture CaCl_2 – NaCl at 850°C .

$\frac{X_{\text{MgCl}_2}}{X_{\text{MgCl}_2} + X_{\text{CaCl}_2}}$	X_{NaCl}	E , mV	$-\Delta\mu_{\text{NaCl}}$ cal/mol
0	0.0791	334.5	7710
	0.082	329.7	7600
	0.114	294.1	6780
	0.133	276.8	6380
	0.150	262.9	6060
	0.188	231.7	5340
	0.222	215.6	4970
	0.241	205.2	4730
	0.291	180.5	4160
	0.307	173.1	3990
	0.342	157.9	3640
	0.395	137.1	3160
	0.459	115.4	2660
	0.465	113.2	2610
	0.483	108.—	2490
	0.484	107.6	2480
	0.519	97.2	2240
	0.566	82.9	1910
	0.580	79.—	1820
	0.607	72.5	1670
	0.644	62.—	1430
	0.652	60.3	1390
	0.683	53.4	1230
	0.698	49.5	1140
	0.704	48.4	1115
	0.724	43.8	1010
	0.731	42.2	973
	0.745	39.2	904
	0.761	36.—	830
	0.782	32.1	740
	0.831	22.8	525
	0.870	16.5	380
	0.939	6.5	150
	0.981	1.7	40

The uncertainty in the change in chemical potential interaction parameter shown in Fig. 2 is mainly due to uncertainty in the determination of the ternary concentrations. During a set of experiments with same cell set up we want to keep the ratio y constant. Since there is a slight evaporation of magnesium chloride, y will decrease slowly. The change in y , however, does not influence the measured potential significantly. The potential is much more sensitive to changes in the sodium chloride concentration following the evaporation of magnesium chloride. The ternary composition is determined by the weighed in mol fractions and the composition was only checked at the end of a set of experiments with constant y . This means that the error in composition will increase from the first to the last experiment in the series. Since the sodium chloride content determined by analysis is calculated from the difference between total chloride and total alkaline earth in the mixture, the relative

Table 2. Experimental emf and corresponding change in chemical potential of sodium chloride on mixing for the ternary system MgCl_2 - CaCl_2 - NaCl at 850°C .

$\frac{X_{\text{MgCl}_2}}{X_{\text{MgCl}_2} + X_{\text{CaCl}_2}}$	X_{NaCl}	E , mV	$-\Delta\mu_{\text{NaCl}}$ cal/mol
0.129	0.095	334.—	7700
	0.105	323.9	7470
	0.127	300.3	6920
	0.154	276.3	6370
	0.189	250.6	5780
	0.238	219.9	5070
	0.319	178.4	4110
	0.431	132.—	3040
	0.549	92.1	2120
	0.625	70.6—69.8	1628—1610
	0.659	61.7	1420
	0.712	47.8	1100
	0.344	0.278	223.5
0.370		176.4	4070
0.452		139.8	3220
0.563		97.7	2250
0.639		72.9	1680
0.689		57.9	1330
0.731		46.7	1080
0.5168	0.099	384.—	8550
	0.142	339.—	7810
	0.187	300.—	6920
	0.242	261.9	6040
	0.311	220.6	5090
	0.375	186.—	4290
	0.439	155.4	3580
	0.500	128.7	2970
0.5170	0.500	131.5	3030
	0.590	95.1	2190
	0.646	75.—	1730
	0.677	65.1	1500
	0.717	52.3	1220
	0.767	39.2	900
	0.796	32.1	740
0.717	0.116	381.22	8800
	0.205	303.7	7000
	0.270	262.8	6060
	0.347	218.7	5040
	0.422	179.9	4150
0.719	0.449	168.2	3880
	0.538	126.6	2920
	0.607	96.6	2230
	0.672	71.9	1660
0.7960	0.694	65.8	1520
	0.750	47.0	1080
	0.782	37.3	860

Table 3. Experimental emf and change in chemical potential of sodium chloride on mixing for the binary system MgCl_2 – NaCl at 850°C .

$\frac{X_{\text{MgCl}_2}}{X_{\text{MgCl}_2} + X_{\text{CaCl}_2}}$	X_{NaCl}	E , mV	$-\Delta\mu_{\text{NaCl}}$ cal/mol
1.0	0.114	396.1	9130
	0.144	396.6	8520
	0.176	346.2	7980
	0.201	328.0	7560
	0.243	299.8	6910
	0.256	292.8	6750
	0.292	272.0	6270
	0.301	265.9	6130
	0.347	241.6	5570
	0.372	234.3	5400
	0.384	220.8	5090
	0.387	230.8	5320
	0.393	222.6	5130
	0.432	200.0	4610
	0.449	189.6	4370
	0.469	183.9	4240
	0.473	178.3	4110
	0.496	161.4	3720
	0.508	160.1	3690
	0.526	148.4	3420
	0.581	117.6	2710
	0.638	91.1	2100
	0.663	79.8	1840
	0.681	72.0	1660
	0.698	65.9	1520
	0.720	57.3	1320
	0.744	51.2	1180
0.780	38.2	880	
0.784	37.7	870	
0.819	27.8	640	
0.853	20.4	470	
0.862	15.6	360	

uncertainty in the sodium chloride content is higher at higher concentrations of alkaline earth in the mixture. By estimating the maximum uncertainty to 0.5 mol % when $X_{\text{NaCl}} < 0.5$ and 1.0 mol % when $X_{\text{NaCl}} > 0.5$, the error limits of the excess chemical potential shown in Fig. 2 appear.

DISCUSSION

We will first briefly discuss the thermodynamic theory necessary for describing ternary systems in which there is only one phase region, that of the single phase solution.

The present discussion is closely related to the thermodynamic theory developed for ternary systems by Guion *et al.*⁵ For an isobaric single phase ternary solution Darken⁷ showed that it is possible to calculate the molar Gibbs energy and the chemical potential of two of the components when

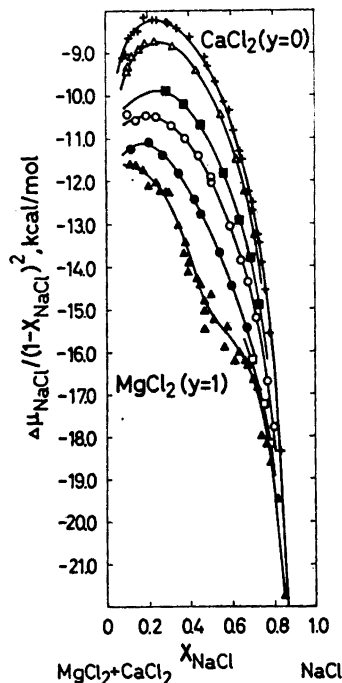


Fig. 1. Chemical potential of NaCl divided by $(1 - X_{\text{NaCl}})^2$ in the ternary mixture NaCl-CaCl₂-MgCl₂ at 850°C.

▲, $y = X_{\text{MgCl}_2} / (X_{\text{MgCl}_2} + X_{\text{CaCl}_2}) = 1$;
 □, $y = 0.796$; ●, $y = 0.718$; ○, $y = 0.517$;
 ■, $y = 0.344$; △, $y = 0.129$ and +, $y = 0$.

the chemical potential of the third component is known at all compositions. The composition of a ternary system is normally described by the three variables n_A , n_B , and n_C which represent the number of moles of the components A, B, and C, respectively. We will, however, adopt the variables previously used by Wagner⁸ to describe the ternary system

$$X_A = \frac{n_A}{n_A + n_B + n_C}$$

$$y = \frac{n_C}{n_B + n_C}$$

$$n = n_A + n_B + n_C$$

The excess chemical potential of mixing of component i is defined by

$$\Delta\mu_i^E = RT \ln \gamma_i = \mu_i - \mu_i^\circ - RT \ln X_i$$

Here γ_i is the activity coefficient of component i in solution, $\mu_i - \mu_i^\circ$ is the chemical potential of solution of component i and X_i is the mol fraction of the component i . The excess molar Gibbs energy of solution is defined by

$$\Delta G^E = \sum_i X_i \Delta\mu_i^E$$

From the above definition of the excess Gibbs energy of solution we can obtain a relation between the excess chemical potential of solution of one component and the excess molar Gibbs energy of solution for our ternary system

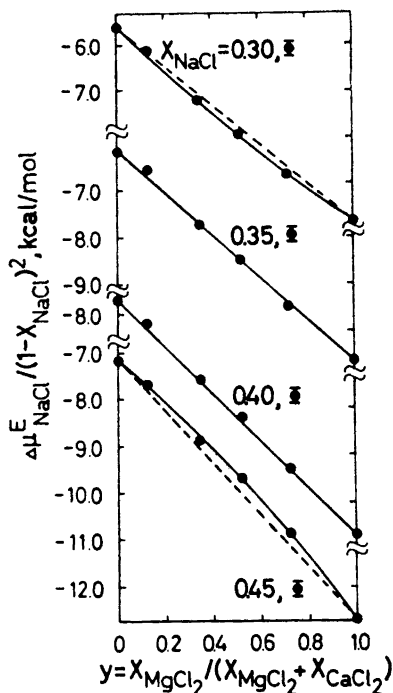
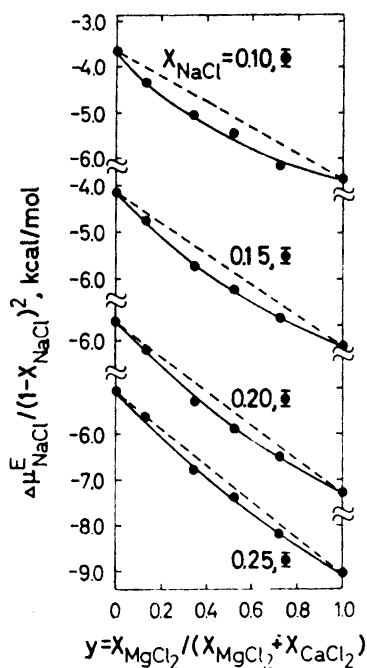
$$\Delta\mu_{\text{A}}^{\text{E}} = \left[\frac{\partial n\Delta G^{\text{E}}}{\partial n_{\text{A}}} \right]_{n_{\text{B}}, n_{\text{C}}} = \Delta G^{\text{E}} + (1 - X_{\text{A}}) \left[\frac{\partial \Delta G^{\text{E}}}{\partial X_{\text{A}}} \right]_{y, n} \quad (4)$$

By rearranging terms and dividing by $(1 - X_{\text{A}})^2$, this expression may also be written

$$\left[\frac{\partial \{\Delta G^{\text{E}}/(1 - x_{\text{A}})\}}{\partial x_{\text{A}}} \right]_{y, n} = \frac{\Delta\mu_{\text{A}}^{\text{E}}}{(1 - X_{\text{A}})^2} \quad (5)$$

Two integration paths can be used to solve this equation with respect to ΔG^{E} .

By integrating X_{A} from 1 to X_{A} keeping y and n constant, we need high accuracy in the experimentally determined excess chemical potential of solution, $\mu_{\text{A}}^{\text{E}}$, near $X_{\text{A}} = 1$ to obtain accurate values of the term $\Delta\mu_{\text{A}}^{\text{E}}/(1 - X_{\text{A}})^2$ and thus the excess Gibbs energy of solution, ΔG^{E} . By integrating from 0 to X_{A} , however, we avoid this problem, but in this case we need to know the excess Gibbs energy of solution for the binary BC. Choosing the second integration path we obtain



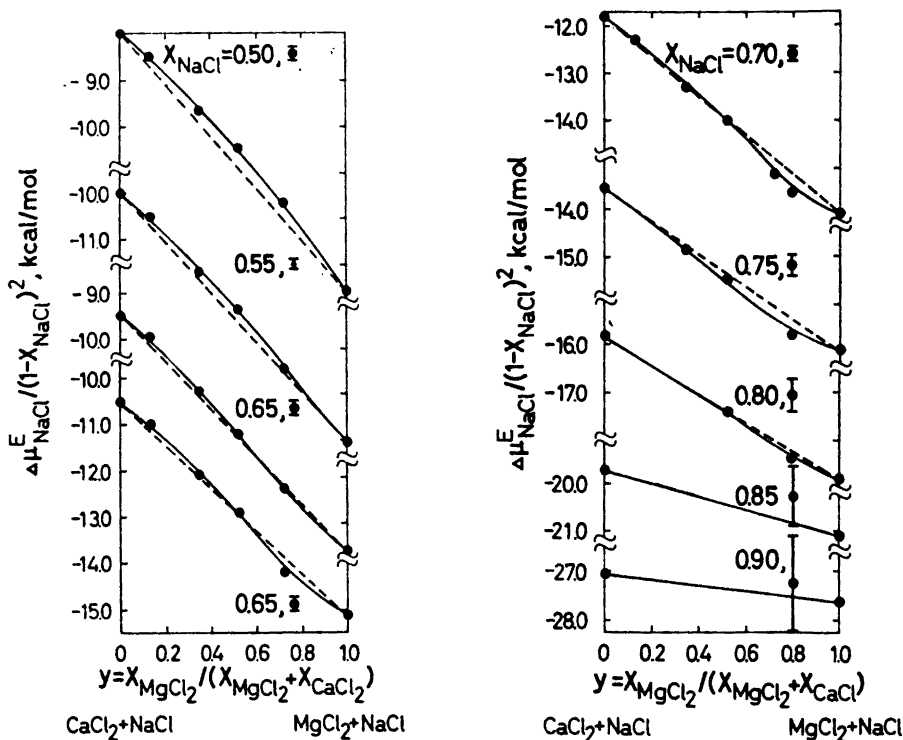


Fig. 2. Excess chemical potential interaction parameter of NaCl, $\Delta\mu_{\text{NaCl}}^E/(1-X_{\text{NaCl}})^2$, as a function of X_{NaCl} and $y = X_{\text{MgCl}_2}/(X_{\text{MgCl}_2} + X_{\text{CaCl}_2})$ in the ternary mixture NaCl - CaCl₂ - MgCl₂.

$$\Delta G^E = (1 - X_A) \left[\Delta G^E(\text{BC}) + \int_0^{X_A} \frac{\Delta\mu_A^E}{(1 - X_A)^2} dX_A \right]_{y = \text{const.}} \quad (6)$$

Here $\Delta G^E(\text{BC})$ is the excess Gibbs energy of solution for the binary BC at $y = n_c/(n_b + n_c)$.

From Fig. 3 it is readily seen that the ternary excess chemical potential of solution of component A, $\Delta\mu_A^E$, can be described by the two binary systems AB and AC and a contribution due to the properties of the ternary mixture. Keeping X_A constant we obtain from Fig. 3

$$\Delta\mu_A^E = (1 - y)\Delta\mu_A^E(\text{AB}) + y\Delta\mu_A^E(\text{AC}) + y(1 - y)(1 - X_A)^2 f(X_A = \text{const.}, y) \quad (7)$$

$\Delta\mu_A^E(\text{AB})$ and $\Delta\mu_A^E(\text{AC})$ are the excess chemical potentials of solutions of A in the two binary solutions AB and AC, respectively.

The last term in eqn. (7) gives the deviation from linearity of $\Delta\mu_A^E$ as a function of y at constant X_A . The factor $(1 - X_A)^2$ is chosen to get a simplified integration when eqn. (7) is introduced into eqn. (6). For $y = 0$ or 1 the third

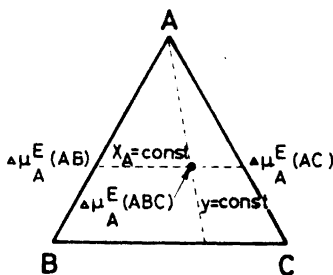


Fig. 3. Definition and location of terms used in the ternary composition diagram.

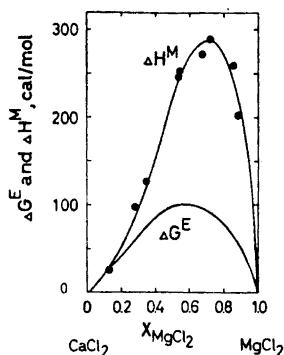


Fig. 4. Gibbs excess energy and enthalpy of mixing in the mixture $\text{CaCl}_2\text{-MgCl}_2$.

term in eqn. (7) should be zero. This is taken care of by the factor $y(1-y)$. When substituting for $\Delta\mu_A^E$ in eqn. 6, we obtain

$$\begin{aligned} \Delta G^E = & (1-y)\Delta G^E(\text{AB}) + y\Delta G^E(\text{AC}) + (1-X_A)\Delta G^E(\text{BC}) \\ & + (1-X_A)y(1-y) \int_0^{X_A} f(X_A, y) dX_A \end{aligned} \quad (8)$$

The last term is the only term which cannot be evaluated from the binary data.

The limiting case $X_A = 1$ gives us the excess molar Gibbs energy of solution for pure A.

Eqn. (8) takes the form

$$\lim_{X_A \rightarrow 1} (1-X_A)\Delta G^E(\text{BC}) = - \lim_{X_A \rightarrow 1} (1-X_A)y(1-y) \int_0^1 f(X_A, y) dX_A$$

which gives

$$\Delta G^E(\text{BC}) = -y(1-y) \int_0^1 f(X_A, y) dX_A \quad (9)$$

This constraint on the function $f(X_A, y)$ has been applied by Darken in another form to obtain the excess functions of the binary system BC, and was later introduced by Guion *et al.*⁵ in their treatment of ternary systems.

By introducing $A = \text{NaCl}$, $C = \text{MgCl}_2$ and $B = \text{CaCl}_2$ in eqn. (7) and dividing by $(1-X_{\text{NaCl}})^2$ we obtain

$$\begin{aligned} \frac{\Delta\mu_{\text{NaCl}}^E}{(1-X_{\text{NaCl}})^2} = & (1-y) \frac{\Delta\mu_{\text{NaCl}}^E(\text{Na}-\text{Ca})}{(1-X_{\text{NaCl}})^2} + y \frac{\Delta\mu_{\text{NaCl}}^E(\text{Na}-\text{Mg})}{(1-X_{\text{NaCl}})^2} \\ & + y(1-y)f(X_{\text{NaCl}}, y) \end{aligned} \quad (10)$$

In Fig. 2 $\Delta\mu_{\text{NaCl}}^E/(1-X_{\text{NaCl}})^2$ is plotted *versus* the parameter y . It can be observed from this plot that the function $f(X_{\text{NaCl}}, y)$ at some sodium chloride concentrations varies from positive through zero to negative values as y changes from zero to one.

In a paper by Hagemark⁶ the quasi-chemical approximation has been applied to ternary metal solutions. The same treatment can also be applied to ionic salt systems provided that the cations (anions) have the same charge. This was done by Guion, Blander, Hengstenberg and Hagemark⁵ and Guion⁹ to explain the variation of the term $y(1-y)f(X_{Ag},y)$ with X_{Ag} and y in the fused salt systems $AgX-NaX-KX$ and $AgX-NaX-CsX$, X being Cl or NO_3 . Good agreement between theory and experiment was obtained.

In Fig. 4 the molar excess Gibbs energy and the enthalpy of mixing for the binary $MgCl_2-CaCl_2$ are given. The molar excess Gibbs energy is obtained by a procedure outlined by Darken.⁷ This procedure calls for an integration of the function $f(X_A,y)$ over the entire range of X_{NaCl} from zero to one using eqn. (9).

The values of this function close to $X_{NaCl}=1$ was determined by extrapolation from values at lower sodium chloride concentrations. The values obtained for the Gibbs energy can be compared with the enthalpy of mixing data for the $MgCl_2-CaCl_2$ system obtained by Papatheodorou and Kleppa.⁴ The enthalpy data are obtained at $800^\circ C$ while the present chemical potentials are measured at $850^\circ C$. It is reasonable to assume small variations of the enthalpy of mixing with temperature and we can thus estimate the excess entropy of mixing for this binary to vary between 0 and $0.18 \text{ cal deg}^{-1}\text{mol}^{-1}$, which is quite possible in view of the similar properties of the calcium and magnesium ions.

The present values of the molar Gibbs energy of solution for the binary $CaCl_2-MgCl_2$ agree fairly well with the phase diagram data obtained for the same system by Grjotheim *et al.*³

By adding and subtracting the excess molar Gibbs energy of solution for the binary $CaCl_2-MgCl_2$ in eqn. (10) we obtain the following equation

$$\begin{aligned} \Delta\mu_{NaCl}^E = & (1-y)\Delta\mu_{NaCl}^E(Na-Ca) + y\Delta\mu_{NaCl}^E(Na-Mg) \\ & - (1-X_{NaCl})^2\Delta G^E(Ca-Mg) \\ & + (1-X_{NaCl})^2y(1-y)f(X_{NaCl},y) + \Delta G^E(Ca-Mg) \end{aligned} \quad (11)$$

If the last term in this equation were negligible compared to the three first terms, the equation would be the same as the one used by Toop, Olson and Toop, Alcock and Richardson, Orani and Alcock and others¹⁰ in their discussion of thermodynamic properties of ternary systems.

It is apparent from the preceding discussion, however, that the three first terms in eqn. (11) are not sufficient to describe the present ternary system. This is also true for the ternary silver-alkali chloride mixture investigated by Guion *et al.*, the ternary lead-alkali chloride melts studied by Hagemark, Hengstenberg and Blander¹¹ and the silver-alkali nitrates studied by Guion.⁹ Meschel and Kleppa¹² studied some of the ternary melts formed among the lithium-alkali and silver-alkali nitrates by a calorimetric technique obtaining the molar ternary enthalpies of mixing. In the ternary alkali nitrate systems the observed ternary enthalpies of mixing could to a good approximation be calculated from data on the binary systems using an equation of the same form as eqn. (11), neglecting the fourth term. For the silver-alkali nitrate

systems, however, significant differences between calculated and measured enthalpies were obtained. It was argued by Meschel and Kleppa that these differences could be explained by changes in the van der Waals-London interaction associated with formation of the ternary mixture or by the influence of the other cations on the covalent character of the $\text{Ag}^+ - \text{NO}_3^-$ bond.

For a few ternary chloride systems investigated in detail the excess ternary term in eqn. (11) is listed below. At $X_A=0.5$ and $y=0.5$ the function $y(1-y)f(X_A, y) + \Delta G^E(\text{BC})$ gives

A	-B	-C	$0.25f(0.5, 0.5) + \Delta G^E(\text{BC})$	
AgCl	-NaCl	-KCl	-50	cal/mol
AgCl	-NaCl	-CsCl	30	»
PbCl ₂	-NaCl	-KCl	-420	»
NaCl	-CaCl ₂	-MgCl ₂	450	»

The higher numerical value of this function for the charge unsymmetrical systems compared with the charge symmetrical ones indicates a possible influence of charge asymmetry. Since the coordination around a certain ion should not be altered significantly during a substitution of $\text{CaCl}_2(\text{MgCl}_2)$ for $\text{MgCl}_2(\text{CaCl}_2)$ in the fused mixture, the difference between the present experimental data and the values that could be calculated from data on the binary systems involved, is probably mainly due to changes in Coulomb and polarization interactions between the ions following the substitution.

Since only relatively small rare gas ions are involved, the contribution from changes in van der Waals-London interactions associated with this substitution or changes in the covalent character of the $\text{Na}^+ - \text{Cl}^-$ bond are not very likely to cause the observed deviation from linearity.

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