

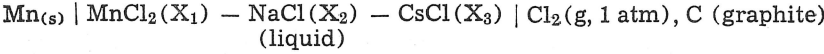
Charge Asymmetrical Ternary Molten Salt Systems: Theory of Dilute Solutions

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ABSTRACT

The thermodynamic properties of dilute solutions of MnCl_2 in the ternary system $\text{MnCl}_2\text{-NaCl-CsCl}$ have been investigated by the measurement of the reversible emf of the formation cell



The partial molar properties of MnCl_2 have been found to be in good agreement with values predicted by the complex-ion model reported in previous publications from this laboratory (1-3). In the present paper it is shown that these rather involved expressions reduce to useful, simple equations of the form

$$(\Delta Z)_{123} = (1 - t) (\Delta Z)_{12} + t(\Delta Z)_{13}$$

where Z represents either an integral or a partial molar property. The ternary solution is denoted by the subscripts 1,2,3, while the two binaries, each containing the reactive-metal chloride, are denoted by 1,2 and 1,3; t is a concentration variable. It is also shown that the following expression applies to the activity of the reactive-metal chloride (component 1) in solution

$$(a_1)_{123} = (a_1)_{12}^{1-t} \cdot (a_1)_{13}^t$$

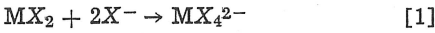
For dilute solutions obeying Henry's law, the activity coefficients are given by

$$(\gamma_1)_{123} = (\gamma_1^0)_{12}^{X_2} \cdot (\gamma_1^0)_{13}^{X_3}$$

where $(\gamma^0)_{i,k}$ is the Henrian activity coefficient in the binary i,k and X_k is the mole fraction of k present in the ternary solution, providing that X_1 in the ternary 1,2,3 is the same as that in the two binary solutions 1,2 and 1,3.

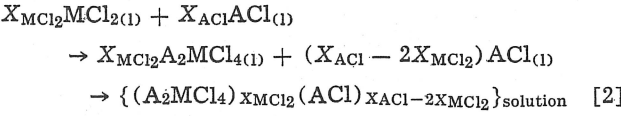
Previous work in this laboratory has shown that the thermodynamic (1-3) and transport (4) properties of molten salt solutions consisting of a divalent-metal chloride and an alkali-metal chloride may be explained by a thermodynamic model which is based on the existence of tetrahedrally coordinated complex ions.

The complex ions are thought to form by reactions of the type



The present treatment of complexing in fused salts follows postulates previously cited (1-4).

The process of mixing X_{MCl_2} moles of MCl_2 with X_{ACl} moles of ACl in a binary system $\text{MCl}_2\text{-ACl}$, where $X_{\text{MCl}_2} + X_{\text{ACl}} = 1$ and $0.33 > X_{\text{MCl}_2} > 0$, may be represented by the following two-step mechanism



The first of these reactions represents the formation of the pure complex compound, while the second represents the mixing process.

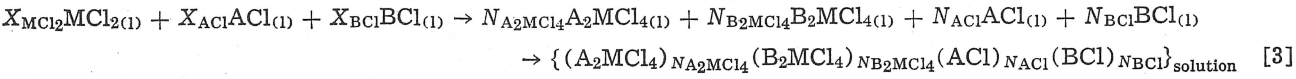
The detailed derivation of the expressions which describe the concentration dependence of the enthalpy of mixing and of the entropy of mixing in the $\text{MCl}_2\text{-ACl}$ binary systems has been given elsewhere (2). The

expressions have been found to represent to a high degree of accuracy the concentration dependence of the calorimetrically determined enthalpies of mixing reported by Papatheodorou and Kleppa (5-7) and by McCarty and Kleppa (8) in the reactive-metal chlorides $\text{MnCl}_2\text{-ACl}$, $\text{FeCl}_2\text{-ACl}$, $\text{CoCl}_2\text{-ACl}$, $\text{NiCl}_2\text{-ACl}$, $\text{MgCl}_2\text{-ACl}$, and $\text{CdCl}_2\text{-ACl}$, where A represents Li , Na , K , Rb , and Cs .

The corresponding mixing reactions and the relevant expressions for the concentration range $1.0 > X_{\text{MCl}_2} > 0.33$ also may be found elsewhere (1-3). These equations are not required for the purposes of the present study.

The partial molar properties of the $\text{MnCl}_2\text{-ACl}$ systems were investigated in this laboratory (2) by an emf method, and their concentration dependence was found to be in excellent agreement with that predicted by the model. The expressions include a number of interaction parameters which have been shown (1,2) to depend on the ionic radii of the species present in the various systems.

Further development of the model (3) has shown that the expressions for two binary systems such as $\text{MCl}_2\text{-ACl}$ and $\text{MCl}_2\text{-BCl}$, where A and B are two different alkali-metal cations, may be expanded to predict the enthalpy of mixing of the combined ternary system $\text{MCl}_2\text{-ACl-BCl}$. In this case the process of mixing X_{MCl_2} moles of MCl_2 with X_{ACl} moles of ACl and X_{BCl} moles of BCl , where $0.33 > X_{\text{MCl}_2} > 0$ and $X_{\text{MCl}_2} + X_{\text{ACl}} + X_{\text{BCl}} = 1$, may also be represented by a two-step mechanism



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The important thing to note is that the over-all solution reaction is split into two steps. The first involves the formation of pure complex species, while the second represents the mixing process.

In the Appendix the expressions which describe the concentration dependence of the integral enthalpy and entropy of mixing are given. It should be noted that the interaction parameters which appear in these equations are those representing the constituent binary systems $\text{MnCl}_2\text{-ACl}$ and $\text{MnCl}_2\text{-BCl}$.

The model for ternary solutions, so far, has been tested with respect to only a few available calorimetric data on integral enthalpies of mixing (3) for concentrated solutions.

In the present investigation the partial molar properties of dilute solutions composed of MnCl_2 and various proportions of NaCl and CsCl have been investigated by an emf method involving the use of manganese chloride formation cells.

The mathematical expressions which describe the concentration dependence of the partial molar properties, and, particularly, their behavior in dilute solutions have been derived. The experimental results for partial molar enthalpies of mixing and activities of MnCl_2 are in excellent agreement with the theory even in the dilute concentration range where all the partial molar properties acquire limiting values. The ternary system $\text{MnCl}_2\text{-NaCl-CsCl}$ was chosen as a test system because the $\text{MnCl}_2\text{-NaCl}$ binary system shows only moderate deviations from ideality, while the $\text{MnCl}_2\text{-CsCl}$ system is a highly reactive system with pronounced negative deviations from ideality. For example, the minimum integral molar enthalpy of mixing in the former is -1.8 kcal, compared to -5.3 kcal in the latter (5). Accordingly, the prediction of the behavior of such a ternary system should represent a severe test of any significant thermodynamic model.

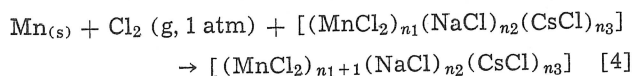
Experimental

The electromotive force was measured for the cell represented schematically as



In order both to establish electrical contact and to prevent the diffusion of chlorine gas to the manganese electrode, the cell consisted of two compartments joined by an asbestos diaphragm. Its fabrication is described elsewhere (15).

The cell reaction may be written as



where the n 's denote mole number.

The cell emf is related to the activity of manganese dichloride by the Nernst equation

$$E = E^\circ - \frac{RT}{2F} \ln a_{\text{MnCl}_2} \quad [5]$$

where R is the ideal gas constant, equal to 1.987 cal/mole $^\circ\text{K}$, T is the temperature in Kelvins, F is the Faraday constant, equal to $23,060$ cal/volt-equivalent, and E° is the standard formation cell potential of pure liquid MnCl_2 in volts at the same temperature T . The values of E° used in this study were previously determined in this laboratory (2).

The preparation of materials and cell design have been described elsewhere (2). The main improvement in the present apparatus was the use of vacuum-cast manganese rods as electrodes. These were 40 mm long and 6 mm in diameter connected to either platinum or tungsten leads. All emf's reported in the present work have been corrected for thermoelectric voltages determined experimentally.

The tube furnace used was wound with Kanthal wire. It had a 2 in. zone over which the temperature varied by 1°K . Melt depths never exceeded 1 in. Actually, temperature profiles were measured in several melts, and variations of the order of only 0.5°K were

found. A grounded Inconel sheath was placed between the cell wall and the furnace tube to eliminate induced emf's from the a-c field of the furnace windings. Cell potential did not vary as power to the furnace was switched on and off.

In order to test for reversibility, all cells were subjected to a polarization test using an external dry cell. About 1 mA was passed through the experimental cell for approximately 60 sec. Cell voltages returned to within 0.5 mV of their values before perturbation less than 15 sec after the external dry cell had been disconnected. This observation was the same regardless of the polarity of the applied voltage.

The fact that voltages were reproducible over a period of 24 hr was also a demonstration of the cell's reversibility.

Results

Table I displays measured cell emf's which have been expressed as least squares lines of the form $E = a - bt$, where E is the cell potential in volts and T is temperature in Kelvins. Melt compositions are expressed in terms of both principal mole fractions, X_i , and the corresponding ternary concentration variables, y and t , defined as

$$t = X_{\text{CsCl}} / (X_{\text{NaCl}} + X_{\text{CsCl}}) \quad [6]$$

$$y = X_{\text{NaCl}} + X_{\text{CsCl}} = 1 - X_{\text{MnCl}_2} \quad [7]$$

Plots of cell potential vs. temperature are shown in Fig. 1 a-c. The concentrations of the solutions studied are shown on the inset composition triangle. An increase in the value of t from zero to unity at constant y represents a change in the composition of the solvent from NaCl -rich to CsCl -rich. The plots are linear and demonstrate that at a given concentration level of

MnCl_2 , as the CsCl concentration of the melt increases, the cell potential also increases.

Figure 2 shows emf isotherms at 810°C displayed on a plot of cell potential vs. $\log_{10} X_{\text{MnCl}_2}$ at various values of t . Experimental data are plotted, and the lines drawn through these points represent the best straight lines having a "two-electron" slope of $-RT/2F$. Also included in the figure are measurements performed previously in this laboratory (2) on concentrated binary solutions of $\text{MnCl}_2\text{-NaCl}$ and $\text{MnCl}_2\text{-CsCl}$. It may be seen that the results of the present study are consistent with those of Kucharski and Flengas (2) and reveal the anticipated extension to dilute solutions.

Table II displays partial molar enthalpies of mixing, partial molar entropies of mixing, activities, and activity coefficients of MnCl_2 calculated from the experimental results. The pertinent formulas are also given in the table.

Discussion

The Appendix traces the method by which the previously derived expressions [1]-[3], which describe the concentration dependence of an integral or a partial molar property in binary and ternary fused salt systems, may be reduced to useful simple equations of the form

$$(\Delta Z)_{123} = (1 - t)(\Delta Z)_{12} + t(\Delta Z)_{13} \quad [8]$$

where Z represents any such property. The ternary solution is denoted by the subscripts 1, 2, 3, while the two constituent binary solutions are denoted by the subscripts 1, 2 and 1, 3. Component 1 is always the divalent metal chloride, and t is the concentration variable defined by Eq. [6].

It is worth noting that although the general expression, Eq. [8], was derived on the assumption of tetrahedrally coordinated complexes of the type

Table I. Summary of experimental results

X_{MnCl_2}	X_{NaCl}	X_{CsCl}	y	t	$E = a - bT$ (V)		
					a (V)	b ($\times 10^3$ V/ $^\circ\text{K}$)	$\sigma_{E,T}^{**}$ ($\times 10^3$ V)
0.01	0.99	0.00	0.99	0.00	2.4102	0.2244	0.5
0.0293*	0.9707	0.00	0.9707	0.00	2.4057	0.2720	0.7
0.0981*	0.9019	0.00	0.9019	0.00	2.4078	0.3309	0.4
0.01	0.7425	0.2475	0.99	0.25	2.4694	0.2421	0.2
0.03	0.7275	0.2425	0.97	0.25	2.4560	0.2713	0.6
0.05	0.7125	0.2375	0.95	0.25	2.4823	0.3310	0.6
0.01	0.485	0.485	0.99	0.50	2.5288	0.2473	0.4
0.03	0.485	0.485	0.97	0.50	2.5095	0.2771	1.4
0.05	0.475	0.475	0.95	0.50	2.5381	0.3327	0.3
0.01	0.2475	0.7425	0.99	0.75	2.5808	0.2600	0.4
0.03	0.2425	0.7275	0.97	0.75	2.6036	0.3354	0.8
0.05	0.2375	0.7125	0.95	0.75	2.5982	0.3568	1.3
0.01	0.00	0.99	0.99	1.00	2.6435	0.2697	0.4
0.0319*	0.00	0.9681	0.9681	1.00	2.6428	0.3198	0.7
0.0981*	0.00	0.9019	0.9019	1.00	2.6193	0.3662	0.8

* $E^\circ = 2391.7 + 0.4043T \log_{10} T - 0.3729 \times 10^{-4} T^2 - 1.138 \times 10^3 T^{-1} - 1.7308T$ mV where $923^\circ\text{K} < T < 990^\circ\text{K}$.

* $E^\circ = 2376.6 + 0.2721T \log_{10} T - 0.78 \times 10^{-5} T^2 + 7.32 \times 10^2 T^{-1} - 1.3510T$ mV where $990^\circ\text{K} < T < 1200^\circ\text{K}$.

* Reference (2).

** Standard error of estimate.

A_2MCl_4 , the corresponding treatment for complexes of the type AMCl_2 and A_2MCl_6 yields Eq. [8]. The compounds $\text{KAg}(\text{CN})_2$ (9) and K_2ZrCl_6 (10) are examples of nontetrahedrally coordinated complexes. In addition, similar treatment of the previously derived thermodynamic relationships in the concentration range $1.0 > X_{\text{MCl}_2} > 0.33$ also yields Eq. [8]. Hence, Eq. [8] appears to be of general applicability in expressing the relationship between the thermodynamic properties of binary and ternary fused salt systems containing a reactive component.

If Z is taken to represent the partial molar enthalpy and entropy of component 1, \bar{H}_1 and \bar{S}_1 , the relationship $RT \ln a_1 = \Delta \bar{H}_1 - T \Delta \bar{S}_1$ and Eq. 8 yield the following expression for the activity of MCl_2 in a ternary system

$$(a_{\text{MCl}_2})_{123} = (a_{\text{MCl}_2})_{12}^{(1-t)} (a_{\text{MCl}_2})_{13}^t \quad [9]$$

Equation [9] is valid when X_{MCl_2} has the same value in the ternary solution 1, 2, 3, as in the binary solutions 1, 2 and 1, 3. Equation [9] may be written in terms of activity coefficients as

$$(\gamma_{\text{MCl}_2})_{123} = (\gamma_{\text{MCl}_2})_{12}^{(1-t)} (\gamma_{\text{MCl}_2})_{13}^t \quad [10]$$

In very dilute solutions γ_{MCl_2} becomes independent of composition. As X_{MCl_2} approaches zero in a ternary

solution, $(1-t) \rightarrow X_{\text{ACl}}$, $t \rightarrow X_{\text{BCl}}$ and Eq. [10] may be written as

$$(\gamma_{\text{MCl}_2})_{123} = (\gamma^\circ_{\text{MCl}_2})_{12}^{X_{\text{ACl}}} \cdot (\gamma^\circ_{\text{MCl}_2})_{13}^{X_{\text{BCl}}} \quad [11]$$

where $(\gamma^\circ_{\text{MCl}_2})_{12}$ and $(\gamma^\circ_{\text{MCl}_2})_{13}$ represent the limiting values of γ_{MCl_2} at infinite dilution in the MCl_2 - ACl and MCl_2 - BCl binary systems, respectively, and X_{ACl} and X_{BCl} represent the mole fraction of ACl and BCl , respectively, in the ternary solution. Thus, with values of only the Henrian activity coefficient of MCl_2 in the two appropriate binary systems, Eq. [11] is able to estimate values of the activity coefficient of MCl_2 anywhere in the dilute region of the ternary system.

Table II shows a comparison between values of γ_{MCl_2} determined experimentally in the present study and values of γ_{MCl_2} calculated by Eq. [11]. For these calculations the values of γ_{MCl_2} at $X_{\text{MCl}_2} = 0.01$ in the appropriate binary solutions served as values for $(\gamma^\circ_{\text{MCl}_2})_{ik}$. Good agreement is obtained between observed and predicted values.

Figures 3a and b show plots of $\log \gamma_{\text{MCl}_2}$ vs. t in the systems NiCl_2 - NaCl - KCl (12) and CoCl_2 - NaCl - KCl (13), studied by Hamby and Scott, and MnCl_2 - NaCl - CsCl , studied in the present investigation. The linear-

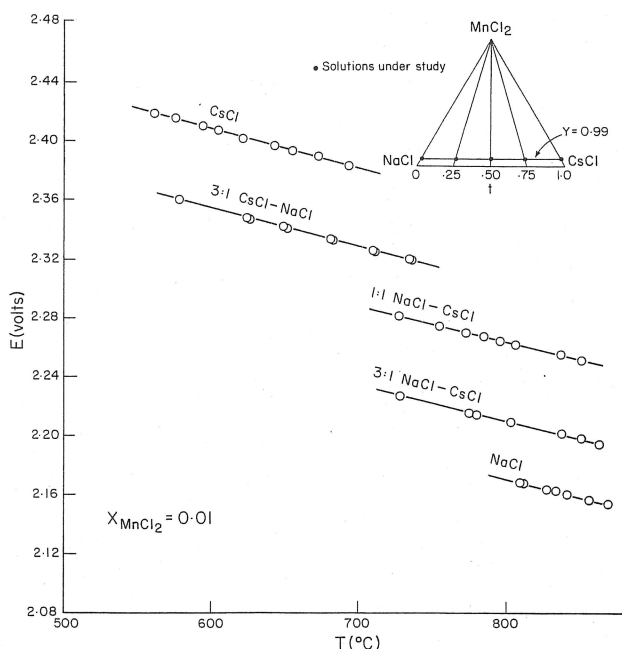


Fig. 1a. Temperature dependence of emf in the system MnCl_2 - NaCl - CsCl at $X_{\text{MnCl}_2} = 0.01$.

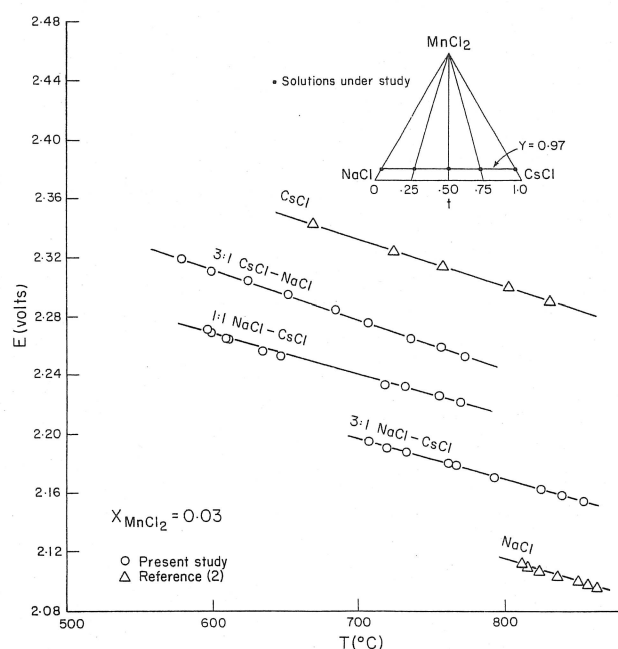


Fig. 1b. Temperature dependence of emf in the system MnCl_2 - NaCl - CsCl at $X_{\text{MnCl}_2} = 0.03$.

Table II. Partial molar properties of MnCl_2 in the ternary system $\text{MnCl}_2\text{-NaCl-CsCl}$

X_{MnCl_2}	t	$\Delta\bar{H}_{\text{MnCl}_2}^*$ (kcal) (observed)	$\Delta\bar{H}_{\text{MnCl}_2}$ (kcal) (calculated Eq. [A-6])	$\Delta\bar{S}_{\text{MnCl}_2}^{**}$ (cal/mole-°K) (observed)	$a_{\text{MnCl}_2}^{***}$ (observed)	a_{MnCl_2} (calculated Eq. [9])	$\gamma_{\text{MnCl}_2}^{***}$ (observed)	$\gamma_{\text{MnCl}_2}(\sim)$ (calculated Eq. [11])
0.01	0.00	-7.2	-7.0	9.06	3.99×10^{-4}	3.76×10^{-4}	3.99×10^{-2}	—
0.0293(x)	0.00	-6.9	-7.0	6.87	1.25×10^{-3}	1.26×10^{-3}	4.25×10^{-2}	—
0.0981(x)	0.00	-6.9	-6.7	4.27	4.70×10^{-3}	4.72×10^{-3}	4.79×10^{-2}	—
0.01	0.25	-9.6	-9.6	8.47	1.48×10^{-4}	1.60×10^{-4}	1.48×10^{-2}	1.54×10^{-2}
0.03	0.25	-9.2	-9.6	7.13	5.00×10^{-4}	3.86×10^{-4}	1.67×10^{-2}	1.68×10^{-2}
0.05	0.25	-10.3	-9.5	4.35	9.48×10^{-4}	9.54×10^{-4}	1.90×10^{-2}	1.83×10^{-2}
0.01	0.50	-12.3	-12.3	8.26	5.47×10^{-5}	5.06×10^{-5}	5.47×10^{-3}	5.78×10^{-3}
0.03	0.50	-11.4	-12.2	6.93	1.87×10^{-4}	1.53×10^{-4}	6.23×10^{-3}	6.42×10^{-3}
0.05	0.50	-12.7	-12.1	4.39	3.60×10^{-4}	3.00×10^{-4}	7.20×10^{-3}	7.12×10^{-3}
0.01	0.75	-14.8	-14.9	7.65	2.04×10^{-5}	2.24×10^{-5}	2.04×10^{-3}	2.17×10^{-3}
0.03	0.75	-15.7	-14.8	4.25	7.03×10^{-5}	7.86×10^{-5}	2.34×10^{-3}	2.45×10^{-3}
0.05	0.75	-15.5	-14.6	3.30	1.37×10^{-4}	1.45×10^{-4}	2.74×10^{-3}	2.77×10^{-3}
0.01	1.00	-17.6	-17.5	7.24	7.55×10^{-6}	7.30×10^{-6}	7.55×10^{-4}	—
0.0319(x)	1.00	-17.5	-17.4	4.99	2.37×10^{-5}	2.37×10^{-5}	7.42×10^{-4}	—
0.09871(x)	1.00	-16.4	-16.7	2.88	1.15×10^{-4}	1.15×10^{-4}	1.17×10^{-3}	—

$$^* \Delta\bar{H}_{\text{MnCl}_2} = -2F \left(\frac{\partial(E - E^*)}{\partial T} \right)_{P, n_{\text{NaCl}}, n_{\text{CsCl}}}$$

$$^{**} \Delta\bar{S}_{\text{MnCl}_2} = 2F \left(\frac{\partial(E - E^*)}{\partial T} \right)_{P, n_{\text{NaCl}}, n_{\text{CsCl}}}$$

$$^{***} \ln a_{\text{MnCl}_2} = - \frac{2F}{RT} (E - E^*), \text{ where } a_{\text{MnCl}_2} = \gamma_{\text{MnCl}_2} X_{\text{MnCl}_2}$$

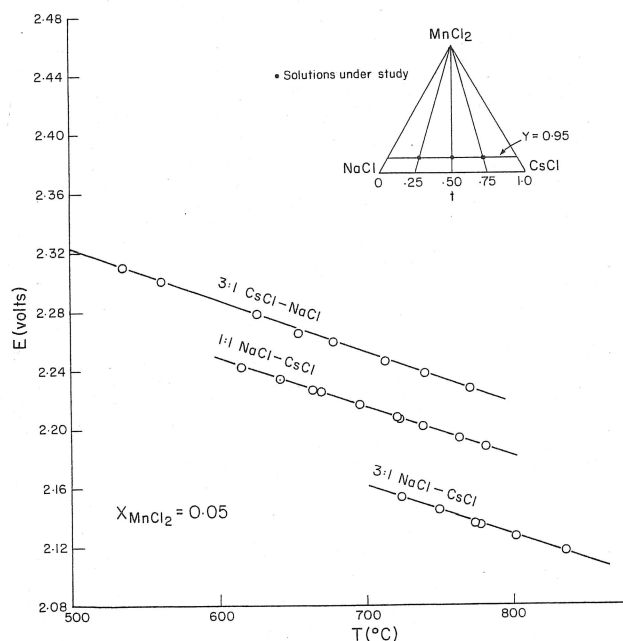
(x) Reference (2).

(∼) Values of γ_{MnCl_2} in the two binary systems: $(\gamma_{\text{MnCl}_2})_{12} = 3.99 \times 10^{-2}$; $(\gamma_{\text{MnCl}_2})_{13} = 7.55 \times 10^{-4}$.

ity of these curves demonstrates the validity of Eq. [10] even for concentrated solutions. Figure 3b also includes data from the study by Pelton and Flengas (14) of the AgCl-NaCl-RbCl system. As expected, Eq. [10] is obeyed in this system, although AgCl is not a divalent transition-metal chloride and is not known to form tetrahedrally coordinated complexes.

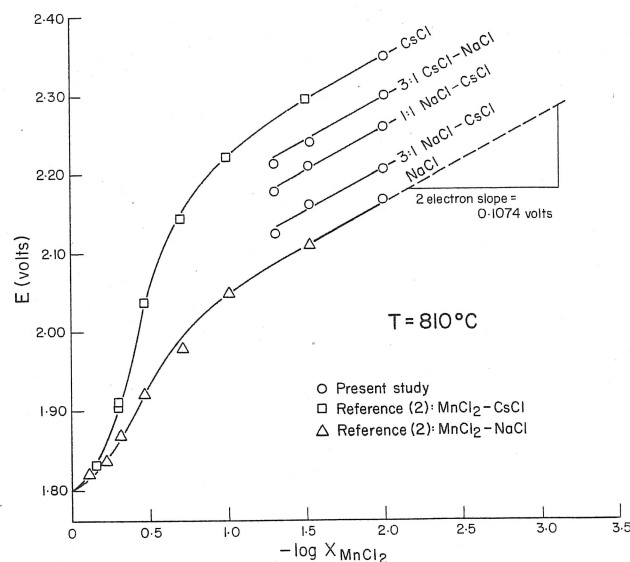
The integral enthalpies of mixing in the binary systems, $\text{MnCl}_2\text{-NaCl}$ and $\text{MnCl}_2\text{-CsCl}$, as well as those in the ternary system, $\text{MnCl}_2\text{-NaCl-CsCl}$, have been measured calorimetrically in this laboratory (12). Figure 4 shows plots of $\Delta H_{\text{mix}}^{\text{int}}$ vs. t at various fixed concentrations of MnCl_2 . The linearity of these curves demonstrates the validity of the "t-fraction average" rule proposed herein.

The least squares analysis of these data revealed linearity to 99.9% confidence limits. It should be noted that Eq. [A-5] is observed in solutions highly concentrated in MnCl_2 .

Fig. 1c. Temperature dependence of emf in the system $\text{MnCl}_2\text{-NaCl-CsCl}$ at $X_{\text{MnCl}_2} = 0.05$.

The partial molar enthalpies of MnCl_2 in the binary systems $\text{MnCl}_2\text{-NaCl}$ and $\text{MnCl}_2\text{-CsCl}$ have been measured in this laboratory by an emf method (2). In the present study $\Delta\bar{H}_{\text{MnCl}_2}$ has been determined for dilute solutions in the ternary system, $\text{MnCl}_2\text{-NaCl-CsCl}$. Figure 5 shows a plot of $\Delta\bar{H}_{\text{MnCl}_2}$ vs. t for $X_{\text{MnCl}_2} = 0.01$. By statistical analysis this curve is found to be linear within 99.9% confidence limits, as expected from the theoretical treatment.

Thus, by the use of Eq. [A-5], [A-6], [10], and [11] the thermodynamic behavior of MCl_2 in the ternary solution, $\text{MCl}_2\text{-ACl-BCl}$, is completely characterized by expressions which contain thermodynamic quantities representing only the binary solutions, $\text{MCl}_2\text{-ACl}$ and $\text{MCl}_2\text{-BCl}$. Table II also includes partial molar enthalpies and activities predicted by the theory. The binary data used for these calculations, with the exception of values for ΔS_R , were those determined by Kucharski and Flengas (2) in their emf study of the binary systems, $\text{MnCl}_2\text{-NaCl}$ and $\text{MnCl}_2\text{-CsCl}$. Values for ΔS_R in the present study were determined from

Fig. 2. Concentration dependence of emf in the system $\text{MnCl}_2\text{-NaCl-CsCl}$ at 810°C .

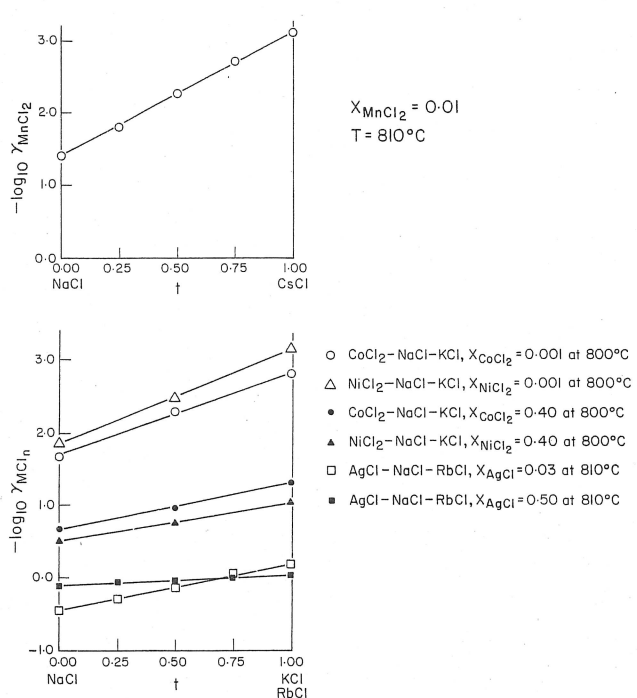


Fig. 3. Concentration dependence of activity coefficient in some ternary systems: (a, top) MnCl_2 - NaCl - CsCl and (b, bottom) CoCl_2 - NaCl - KCl ; NiCl_2 - NaCl - KCl ; AgCl - NaCl - RbCl .

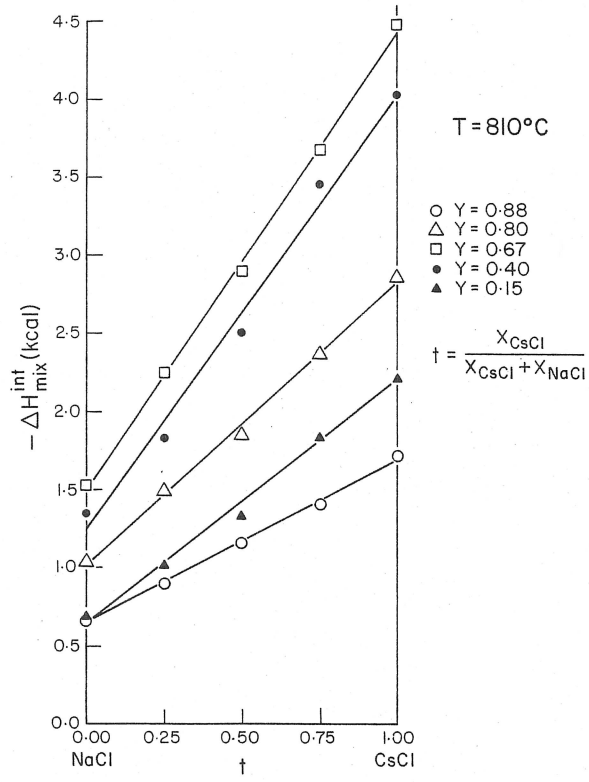


Fig. 4. Concentration dependence of the integral enthalpy of mixing in the system MnCl_2 - NaCl - CsCl at 810°C .

the slope of a plot of $\log \gamma_{\text{MnCl}_2}$ vs. $1/T$ in the appropriate binary systems.

Conclusions

The treatment of binary and ternary fused salt solutions in terms of a thermodynamic model has led to the derivation of simple expressions which relate the thermodynamic properties of ternary fused salt solu-

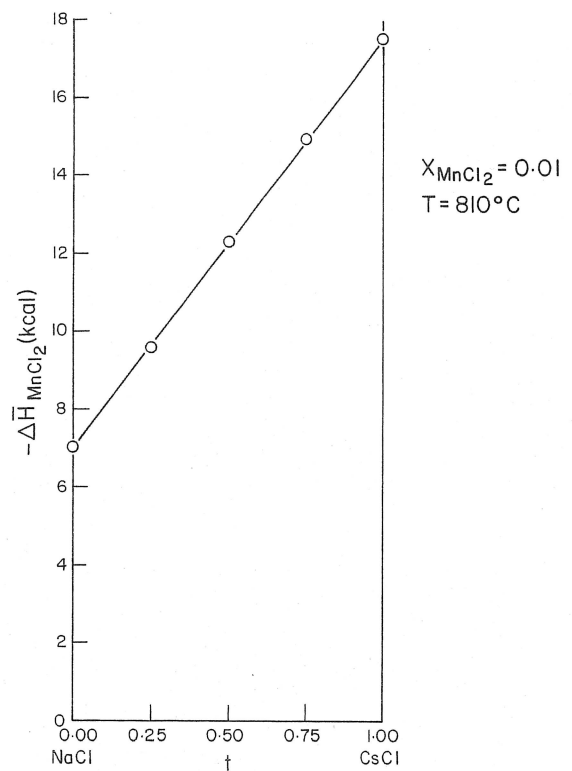


Fig. 5. Concentration dependence of the partial molar enthalpy of mixing of MnCl_2 in the system MnCl_2 - NaCl - CsCl at 810°C .

tions to the properties of constituent binary solutions. The relationship in generalized form is summarized by Eq. [8] which contains only experimentally determinable quantities and which may be used without detailed knowledge of the thermodynamic model.

Limiting laws for dilute solutions have also been derived. The expressions have been verified by the results of the present investigation of the system MnCl_2 - NaCl - CsCl , as well as by the results of several other ternary systems in the literature. The applicability of these expressions to a range of systems suggests that the structural model on which the derivations are based is physically meaningful.

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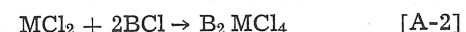
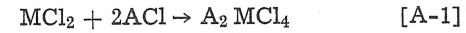
Any discussion of this paper will appear in a Discussion Section to be published in the December 1975 JOURNAL. All discussions for the December 1975 Discussion Section should be submitted by Aug. 1, 1975.

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APPENDIX

Expressions for the Thermodynamic Properties of Ternary Solutions of the Type MCl_2 - ACl - BCl Derived from the Complex Ion Model (3)

For a melt having the primary composition X_{MCl_2} , X_{ACl} , and X_{BCl} , where $0 < X_{\text{MCl}_2} < 0.33$, the reactions



produce new species.

The expression which describes the concentration dependence of the enthalpy of mixing in the ternary system MCl_2 - ACl - BCl has been derived elsewhere (3).

For a solution of composition $0 < X_{\text{MCl}_2} < 0.33$ the molar integral enthalpy of mixing is given by

$$\begin{aligned} \Delta H_{\text{mix}}^{\text{int}} = & (1-y)[(1-t)(b_R)_{12} + t(b_R)_{13}] \\ & + \frac{(1-y)^2(2-3y)}{(2y-1)^2} [(1-t)(2b_1 + b_2)_{12} \\ & + t(2b_1 + b_2)_{13}] + \frac{2(3y-2)^2(1-y)}{(2y-1)^2} \\ & [(1-t)(2b_1 + b_2)_{12} + t(2b_1 + b_2)_{13}] \\ & - \frac{(1-y)(3y-2)^2}{(2y-1)^2} [(1-t)(3b_1 + b_2)_{12} \\ & + t(3b_1 + b_2)_{13}] + \frac{2(1-y)^2(3y-2)}{(2y-1)^2} \\ & [(1-t)(b_1 + b_2)_{12} + t(b_1 + b_2)_{13}] \quad [\text{A-3}] \end{aligned}$$

By a rearrangement of terms Eq. [A-3] is further reduced to

$$\begin{aligned} \Delta H_{\text{mix}}^{\text{int}} = & (1-y)[(1-t)(b_R)_{12} + t(b_R)_{13}] \\ & + \frac{(3y-2)(1-y)}{(2y-1)^2} \{ (3y-2)[(1-t)(b_1)_{12} \\ & + t(b_1)_{13}] + (2y-1)[(1-t)(b_2)_{12} + t(b_2)_{13}] \} \quad [\text{A-4}] \end{aligned}$$

where the interaction parameters b_R , b_1 , and b_2 are defined by equations 14 and 18 of Ref. (2) and have values determined in the appropriate binary system.

The substitution of y by its equivalent, $1 - X_{\text{MCl}_2}$, in Eq. [A-4] followed by factoring and comparison of the resulting expression with the corresponding expressions for the binary systems yields the much simpler relationship

$$\{\Delta H_{\text{mix}}^{\text{int}}(X_{\text{MCl}_2}, t)\}_{123} = (1-t)\{\Delta H_{\text{mix}}^{\text{int}}(X_{\text{MCl}_2})\}_{12} + t\{\Delta H_{\text{mix}}^{\text{int}}(X_{\text{MCl}_2})\}_{13} \quad [\text{A-5}]$$

which is valid when the concentration of MCl_2 in the ternary solution 1, 2, 3 is the same as that of the two constituent binary solutions, 1, 2 and 1, 3. The expressions for $\Delta H_{\text{mix}}^{\text{int}}{}_{12}$ and $\Delta H_{\text{mix}}^{\text{int}}{}_{13}$ are given by equation 19 of Ref. (2).

Partial differentiation of Eq. [A-4] followed by rearrangement of terms yields the result

$$\{\Delta \bar{H}_{\text{MCl}_2}(X_{\text{MCl}_2}, t)\}_{123} = (1-t)\{\Delta \bar{H}_{\text{MCl}_2}(X_{\text{MCl}_2})\}_{12} + t\{\Delta \bar{H}_{\text{MCl}_2}(X_{\text{MCl}_2})\}_{13} \quad [\text{A-6}]$$

The integral entropy of mixing may also be treated as the sum of two terms: an internal entropy change associated with reactions [A-1] and [A-2] and a configurational entropy change due to the mixing of the products of these reactions. Since it is assumed that there is no interaction between A_2MCl_4 and B_2MCl_4 , the internal entropy change is given by

$$\Delta S^{\text{internal}} = (1-y)[(1-t)(\Delta S_R)_{12} + t(\Delta S_R)_{13}] \quad [\text{A-7}]$$

where $(\Delta S_R)_{12}$ and $(\Delta S_R)_{13}$ are the molar entropies of formation of pure A_2MCl_4 and B_2MCl_4 , respectively. The configurational term is given by

$$\Delta S^{\text{configurational}} = -R[N_i \sum \ln N_i] \quad [\text{A-8}]$$

where N_i is the ionic fraction of species i and the summation is extended over all ionic species present in the reacted system.

Accordingly, the molar integral entropy of mixing in the ternary system $\text{MCl}_2\text{-ACl-BCl}$ for the composition range $0.33 > X_{\text{MCl}_2} > 0.0$ is given by

$$\begin{aligned} \Delta S_{\text{mix}}^{\text{int}} = & (1-y)[(1-t)(\Delta S_R)_{12} + t(\Delta S_R)_{13}] \\ & - R[(1-t) \ln(1-t) + t \ln t \\ & + \frac{(1-y)}{(2y-1)} \ln \frac{(1-y)}{(2y-1)} + \frac{(3y-2)}{(2y-1)} \ln \frac{(3y-2)}{(2y-1)}] \quad [\text{A-9}] \end{aligned}$$

Rearrangement of terms, substitution of $y = 1 - X_{\text{MCl}_2}$, and comparison of the expression for the binary systems yields the much simpler expression

$$\{\Delta S_{\text{mix}}^{\text{int}}(X_{\text{MCl}_2}, t)\}_{123} = (1-t)\{\Delta S_{\text{mix}}^{\text{int}}(X_{\text{MCl}_2})\}_{12} + t\{\Delta S_{\text{mix}}^{\text{int}}(X_{\text{MCl}_2})\}_{13} \quad [\text{A-10}]$$

Partial differentiation of Eq. [A-10] followed by substitution of $y = 1 - X_{\text{MCl}_2}$ gives

$$\begin{aligned} \Delta \bar{S}_{\text{MCl}_2} = & (1-t)(\Delta S_R)_{12} + t(\Delta S_R)_{13} \\ & - R \ln \frac{X_{\text{MCl}_2}(1-2X_{\text{MCl}_2})}{1-3X_{\text{MCl}_2}} \quad [\text{A-11}] \end{aligned}$$

The logarithmic term may be factored to give

$$\begin{aligned} \Delta \bar{S}_{\text{MCl}_2} = & (1-t) \left[(\Delta S_R)_{12} - R \ln \frac{X_{\text{MCl}_2}(1-2X_{\text{MCl}_2})}{(1-3X_{\text{MCl}_2})^2} \right] \\ & + t \left[(\Delta S_R)_{13} - R \ln \frac{X_{\text{MCl}_2}(1-2X_{\text{MCl}_2})}{(1-3X_{\text{MCl}_2})^2} \right] \quad [\text{A-12}] \end{aligned}$$

Comparison of Eq. [A-12] with equation 47 of Ref. (2) gives

$$\begin{aligned} \{\Delta \bar{S}_{\text{MCl}_2}(X_{\text{MCl}_2}, t)\}_{123} = & (1-t)\{\Delta \bar{S}_{\text{MCl}_2}(X_{\text{MCl}_2})\}_{12} \\ & + t\{\Delta \bar{S}_{\text{MCl}_2}(X_{\text{MCl}_2})\}_{13} \quad [\text{A-13}] \end{aligned}$$

These equations demonstrate that the values of the integral and partial molar enthalpies and the integral and partial molar entropies of mixing in a ternary solution are the "t-fraction average" of the corresponding properties in the two constituent binary solutions having the same MCl_2 concentration as the ternary solution.

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