

**Determination of  $\Delta\bar{G}_{\text{KCl}}$  (Mixing) for the Systems  
BaCl<sub>2</sub>-KCl, SrCl<sub>2</sub>-KCl, and CaCl<sub>2</sub>-KCl and  $\Delta\bar{S}_{\text{KCl}}$  (Mixing)  
for the Systems BaCl<sub>2</sub>-KCl and SrCl<sub>2</sub>-KCl**

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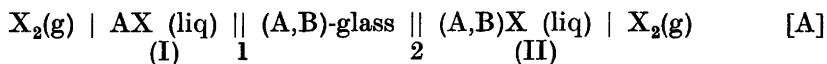
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A potassium-conducting glass membrane has been employed in cells of the type

graphite, Cl<sub>2</sub>|KCl(liquid)||K<sup>+</sup>-glass||KCl, MCl<sub>2</sub>(liquid)|Cl<sub>2</sub>, graphite  
where M = Ba, Sr, or Ca to measure emf as a function of composition. From these data excess partial molar free enthalpies of mixing of KCl in the alkaline earth-KCl mixtures are calculated and compared. Each system shows a negative deviation from the Temkin ideal mixing model in the order Ca > Sr > Ba. The partial molar entropies of mixing have been determined for M = Ba or Sr from the temperature coefficient of the emf.  $\Delta\bar{S}_{\text{KCl}}$  is ideal for the BaCl<sub>2</sub>-KCl system, while a negative  $\Delta\bar{S}_{\text{KCl}}$ <sup>28</sup> is observed in the system SrCl<sub>2</sub>-KCl. The limiting integral enthalpy of mixing has been evaluated for these two systems and compared with other alkali chloride-alkaline earth chloride mixtures on the basis of a modified conformal solution theory.

Thermodynamic properties of mixing of monovalent with divalent cations, having a common anion, have been investigated for the alkali-alkaline earth nitrates,<sup>1</sup> the alkali-magnesium chlorides,<sup>2</sup> and the alkaline earth-sodium chlorides.<sup>3,4</sup> In this investigation the thermodynamics of mixing in some potassium chloride-alkaline earth chlorides are studied. The data presented herein will permit comparison with similar systems and further test proposed correlations relating thermodynamic mixing parameters to properties of the component systems.<sup>5</sup>

Consider the following cell:



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in which X is a halogen, A<sup>+</sup> and B<sup>+</sup> are cations, and (A,B)-glass is a glass membrane in which charge is transported only by two types of mobile ions, designated A<sup>+</sup> and B<sup>+</sup>. For a cell of this kind Førland and Østvold<sup>6</sup> have shown that

$$\Delta G = \frac{\Delta Q}{F} [\bar{G}_{\text{AX(II)}} - \bar{G}_{\text{AX(I)}} - \int_1^2 t_{\text{B}} d(\bar{G}_{\text{A-sil}} - \bar{G}_{\text{B-sil}})] \quad (1)$$

where  $\Delta G$  is the change in free enthalpy (Gibbs free energy) connected with the transfer of a charge  $\Delta Q$  through the cell.  $\bar{G}_{\text{AX}}$  with subscript is the partial molar free enthalpy of AX in the respective cell compartments;  $\bar{G}_{\text{A-sil}}$  and  $\bar{G}_{\text{B-sil}}$ , the partial molar free enthalpies of the respective alkali glasses of which the glass membrane consists;  $t_{\text{B}}$ , the transport number (relative to the container walls) of the mobile B<sup>+</sup> species in the glass; and  $F$ , the Faraday number. The integration is carried out across the membrane. Eqn. (1) is based on the following additional assumptions:

1) That the diffusion of the mobile species in the glass is slow compared with their diffusion and transport by convection in the molten salt, and that equilibrium is attained for the exchange among the four species at the salt/glass interfaces.

2) That the electrostatic energy of dipole layers in the concentration gradient is not significantly affected by the passage of current.<sup>7</sup>

3) That the fluxes and forces in the membrane are related in a linear fashion.<sup>8</sup>

As Førland and Østvold have demonstrated, eqn. (1) leads to

$$\Delta G = \Delta \bar{G}_{\text{AX}} - \int_1^2 \frac{t_{\text{B}}}{\chi_{\text{B-sil}}} d\bar{G}_{\text{A-sil}} \quad (2)$$

where  $\chi$  signifies mole fraction.

If one obtains a glass in which the mobility of A<sup>+</sup> is much greater than that of B<sup>+</sup> (or  $t_{\text{B}}/\chi_{\text{B-sil}} \approx 0$ ), practically no chemical work is carried out in the membrane. The last term in eqn. (2) can then be neglected, and

$$\Delta G = \Delta \bar{G}_{\text{AX}} \quad (3)$$

Since

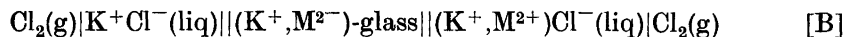
$$\Delta G = -\Delta Q \cdot E \quad (4)$$

$E$  being the equilibrium emf of the cell, the partial molar free enthalpy of mixing for one molten salt in another can be obtained from emf *vs.* composition data. In addition, the temperature dependence of the emf yields the partial molar entropy of mixing.

Østvold<sup>9</sup> has prepared a potassium glass having the following composition:

SiO <sub>2</sub> :	64.8 mole %	TiO <sub>2</sub> :	2 mole %
K <sub>2</sub> O:	15.0 mole %	ZrO <sub>2</sub> :	2 mole %
Al <sub>2</sub> O <sub>3</sub> :	15.2 mole %	Ce <sub>2</sub> O <sub>3</sub> :	1 mole %

He has measured the transport numbers of  $K^+$  and  $M^{2+}$  in cells of the type



where  $M=Ba, Sr, \text{ or } Ca$ .

The measurements were conducted in the temperature range 800–950°C and at a composition ratio of 30:70 mole % potassium chloride to alkaline earth chloride in the right side of the cell. The results were

$$\begin{array}{ll} t_{K^+} > 0.999 & t_{Ba^{2+}} < 0.001 \\ t_{K^+} = 0.992 & t_{Sr^{2+}} = 0.008 \\ t_{K^+} > 0.998 & t_{Ca^{2+}} < 0.002 \end{array}$$

Østvold demonstrated that transport numbers of this magnitude for the divalent ions result in no significant correction to eqn. (3). The chemical work carried out in his membranes was of the order of magnitude of 5 cal/mole.

In the work presented here cells of type [B] have been employed to determine emf as a function of temperature and composition in the molten salt systems  $BaCl_2-KCl$ ,  $SrCl_2-KCl$ , and  $CaCl_2-KCl$ . The glass membranes were prepared from glass of the same composition as that used by Østvold.

#### EXPERIMENTAL

*Chemicals.* The analytical-reagent grade potassium chloride was obtained from E. Merck AG, Germany, and was melted before use in order to remove moisture.

$BaCl_2 \cdot 2H_2O$  (analytical-reagent grade) was procured from the same firm and heated several days at 200°C to remove the hydrated water. The salt was then melted, and commercial quality hydrogen chloride was bubbled through the liquid for approximately one hour, or until the melt was completely clear. After cooling under nitrogen, the compound was transferred to a dry-box for handling.

$SrCl_2 \cdot 6H_2O$  (Riedel-De Haën AG, Germany) of similar quality was treated in the same manner as the barium salt.

$CaCl_2 \cdot 2H_2O$  (analytical-reagent grade, E. Merck) was heated slowly from room temperature to 450°C overnight under vacuum. Subsequent purification was similar to that for  $BaCl_2$ .

Hand picked crystals of each of the salts were used in loading the cells, the alkaline earth chlorides being handled in a dry-box and loaded under cover of a nitrogen-filled plastic bag.

Chlorine gas was obtained from Norsk Hydro, Norway and was of commercial quality.

*Apparatus.* The silica cells employed in these experiments were modified versions of those used by Østvold.<sup>9</sup> A schematic drawing of the cell arrangement is shown in Fig. 1.

The cell consisted of an outer silica tube (i.d.=3.4 cm) which served as the half cell containing pure molten potassium chloride. Chlorine gas, passed through concentrated sulfuric acid and  $P_2O_5$  and then over graphite heated to 800°C, was bubbled over a graphite electrode immersed in the potassium chloride. (The specially machined electrodes were constructed from graphite rods of the highest spectroscopic purity, National Carbon Company.) The gas then exited from a side arm of this compartment and passed through a tygon tube into the mixture compartment, where it bubbled over an identical graphite electrode before exiting in a similar manner through a sulfuric acid trap.

The mixture compartment, which dipped into the molten potassium chloride, was constructed from silica tubing of an i.d. of 1.2 cm. A hole of approximately 1–2 mm was blown in the bottom of this tube, and the potassium-glass membrane was sealed across the opening. Two small silica legs (not shown) protected the membrane from fracture from below, and a covering of finely powdered  $\alpha-Al_2O_3$  prevented adsorbable impurities in the mixture compartment from contaminating the membrane. (In later

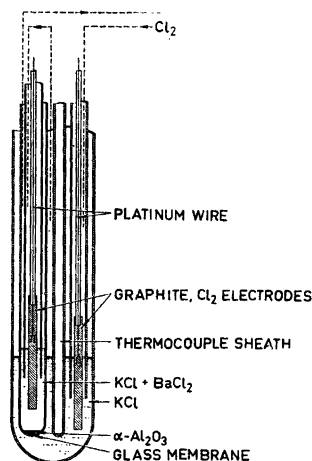


Fig. 1. Schematic drawing of silica cell.

experiments in the  $\text{SrCl}_2$ — $\text{KCl}$  and  $\text{CaCl}_2$ — $\text{KCl}$  systems it was found that the aluminum oxide powder was not necessary, and a cell consisting of two compartments positioned side by side with a connecting glass bridge was employed.)

The graphite electrodes were held in place by 0.3 cm silica tubes through which platinum wire leads made contact with the measuring instruments. The electrodes were heated to a bright orange glow in a propane-oxygen flame immediately before insertion into the cell to remove impurities on the surface of the graphite.

A teflon cap and teflon sleeves were used to introduce the tubing into the outer cell compartment. Tygon caps fastened the electrode supports into the bubbling tubes.

The lower 37 cm of the cell assembly (from the side arm down) was positioned in an upright, cylindrical furnace of the type described by Motzfeldt.<sup>10</sup> By selecting the optimum ratio of currents in the furnace windings, the temperature gradient was maintained at approximately  $0.1^\circ\text{C}/\text{cm}$  over the temperature range  $800$ — $900^\circ\text{C}$  in the lower 10 cm of the cell. However, the depth of melt in the cell was usually only about 3—4 cm.

Temperature was measured by means of a Pt/Pt—Rh(10%) thermocouple sheathed in alumina and housed in a silica tube which dipped into the fused potassium chloride. Temperature and emf were recorded on a dual channel, Philips, type PR 2212 A/00 recorder. Both were compensated by bucking potentials supplied from a thermostatically housed reference voltage supply and divider built by SINTEF, Norway. These were calibrated daily against a Tinsley, "Thermoelectric Free" potentiometer.

## RESULTS AND DISCUSSION

The results of the emf *vs.* composition experiments at  $850^\circ\text{C}$  are shown in columns 1 and 2 of Table 1. The temperature variation of the emf and the temperature range are listed in columns 3 and 4. In order to investigate the temperature dependence of the emf, for some compositions of the  $\text{BaCl}_2$ — $\text{KCl}$  and  $\text{SrCl}_2$ — $\text{KCl}$  systems the emf was measured at constant temperature for sufficient time to ascertain that no drift was occurring; the temperature was then changed and the measurement repeated. The temperature was varied in a random manner, and the emf measured at four or five temperatures, or until a reasonably straight line could be drawn through the points, from which  $\Delta\text{emf}/\Delta T$  was evaluated. The data presented in column 2 opposite entries in column 3 are the emf values at  $850^\circ$  interpolated from these linear emf *vs.*

Table 1. The systems  $MCl_2-KCl$ ,  $M=Ba, Sr, \text{ or } Ca$ .

$\chi_{BaCl_2}$	emf at 850°C (mV)	$\frac{\Delta emf}{\Delta T}$ ( $\frac{mV}{deg}$ )	Temp. range (°C)	Group
.142	16.5	.015	840-950	I
.201	26.3 <sub>5</sub>	.024	800-950	
.224	26.1 <sub>5</sub>	.021	800-940	
.292	41.8	.032	800-940	
.357	51.7	.038	800-950	
.365	59.1	.037	820-950	
.432	69.6	.050	790-950	
.508	82.8	.059	830-930	
.553	101.7	.072	800-940	
.645	140.6 <sup>a</sup>	.107	860-950	
.650	141.0 <sup>a</sup>	.089	850-960	
.767	175.1 <sub>5</sub>	.117	890-950	
.580	105.5 <sup>b</sup>	—	900	
.627	125.6 <sup>b</sup>	—	900	
.700	151.2 <sup>b</sup>	—	900	
.807	197.1 <sup>b</sup>	—	900	
$\chi_{SrCl_2}$				
.156	21.4	.012	840-930	II
.231	35.7	.015	830-950	
.319	55.8	.027	820-950	
.419	91.4	.039	820-970	
.620	143.8	.050	810-950	
.720	185.2	.062	850-950	
.813	245.2	—	850	
.328	57.5	.019	800-900	
.411	79.2 <sub>5</sub>	.033	790-900	
.496	103.4	—	850	
.211	29.6 <sub>5</sub>	—	850	III
.300	50.9	—	850	
.373	63.8	—	850	
.449	88.8	—	850	
.525	111.9 <sub>5</sub>	—	850	
.612	140.8	—	850	
.703	176.8	—	850	
.792	219.8 <sub>5</sub>	—	850	
.874	272.5	—	850	
.929	322.7	—	850	IV
$\chi_{CaCl_2}$				
.097	11.3	—	850	V
.199	30.8	—	850	
.330	66.3	—	850	
.420	107.1	—	850	
.535	152.2	—	850	VI
.618	191.2	—	850	
.695	231.8	—	850	
.801	297.5	—	850	
.900	383.8	—	850	

<sup>a</sup> Extrapolated to 850°C for comparison.<sup>b</sup> Calculated at 850°C from data at 900° assuming an ideal  $\Delta \bar{S}_{KCl}$ .

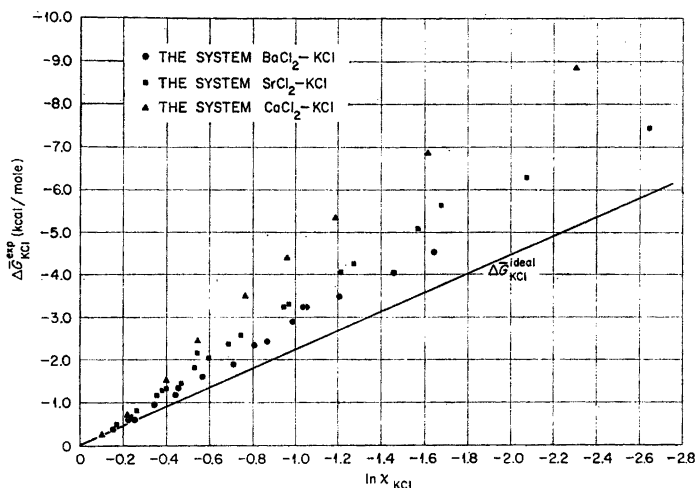


Fig. 2.  $\Delta\bar{G}_{\text{KCl}}^{\text{exp}}$  vs.  $\ln \chi_{\text{KCl}}$ . The systems  $\text{BaCl}_2\text{--KCl}$ ,  $\text{SrCl}_2\text{--KCl}$ , and  $\text{CaCl}_2\text{--KCl}$ .

temperature plots. The other emf data for the  $\text{SrCl}_2\text{--KCl}$  and  $\text{CaCl}_2\text{--KCl}$  systems were obtained at  $850^\circ\text{C}$ . The last four entries in column 2 for the  $\text{BaCl}_2\text{--KCl}$  system were calculated from emf data at  $900^\circ\text{C}$ , assuming an ideal partial molar entropy of mixing. Several widely divergent values have been omitted.

Individual analyses were obtained for each composition in Group I. We believe these to be accurate to about 1 mole %. Compositions of the remainder of the melts (Groups II–VI) were calculated from the weights of components added. Each of the groups II–VI represents a separate set of starting materials.

The experimental partial molar free enthalpies of mixing for the three systems are shown in Fig. 2. They are plotted against the natural logarithm of the mole fraction of KCl to demonstrate the deviation from the Temkin ideal mixing model, which relates the ideal partial molar free enthalpy of mixing,  $\Delta\bar{G}_{\text{KCl}}^{\text{id}}$ , to composition by the expression

$$\Delta\bar{G}_{\text{KCl}}^{\text{id}} = RT \ln \chi_{\text{KCl}} \quad (6)$$

The ideal partial molar entropy of mixing,  $\Delta\bar{S}_{\text{KCl}}^{\text{id}}$ , defined as

$$\Delta\bar{S}_{\text{KCl}}^{\text{id}} = -\frac{\partial \Delta\bar{G}_{\text{KCl}}^{\text{id}}}{\partial T} = -R \ln \chi_{\text{KCl}} \quad (7)$$

is a close approximation to the experimental data for the  $\text{BaCl}_2\text{--KCl}$  system, as shown in Fig. 3. Thus the computation of several data in column 2 of Table I assuming an ideal partial molar entropy of mixing appears reasonable.

Although the data for the partial molar entropy of mixing in the  $\text{SrCl}_2\text{--KCl}$  system show more scatter than the data for the system  $\text{BaCl}_2\text{--KCl}$ , Fig. 3 demonstrates that it is clearly negative.

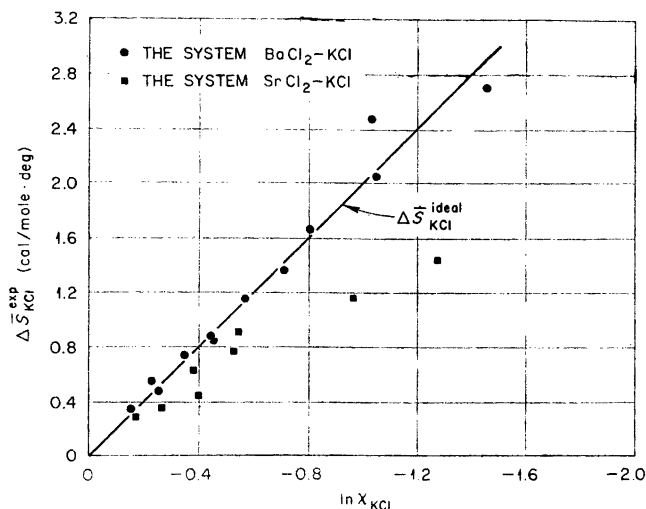


Fig. 3.  $\Delta\bar{S}_{\text{KCl}}^{\text{exp}}$  vs.  $\ln \chi_{\text{KCl}}$ . The systems  $\text{BaCl}_2\text{-KCl}$  and  $\text{SrCl}_2\text{-KCl}$ .

The excess partial molar free enthalpies, defined by the relation

$$\Delta\bar{G}_{\text{KCl}}^{\text{xs}} = \Delta\bar{G}_{\text{KCl}}^{\text{exp}} - \Delta\bar{G}_{\text{KCl}}^{\text{id}} \quad (8)$$

where  $\Delta\bar{G}_{\text{KCl}}^{\text{exp}}$  is the experimentally determined value, are represented in Fig. 4. According to the theory of regular solutions<sup>11</sup>

$$\Delta\bar{F}_{\text{KCl}} = b_{\text{K-M}} \chi_{\text{MCl}_2}^2 + RT \ln \chi_{\text{KCl}} \quad (9)$$

where  $\Delta\bar{F}_{\text{KCl}}$  is the partial molar free energy of mixing and  $b_{\text{K-M}}$  is a constant related to the cation-cation energy of mixing. Neglecting the work due to changes in volume on mixing at constant pressure

$$\Delta\bar{G}_{\text{KCl}} = \Delta\bar{F}_{\text{KCl}} \quad (10)$$

and since

$$\Delta\bar{G}_{\text{KCl}}^{\text{id}} = RT \ln \chi_{\text{KCl}} \quad (11)$$

$$\Delta\bar{G}_{\text{KCl}}^{\text{xs}} = b_{\text{K-M}} \chi_{\text{MCl}_2}^2 \quad (12)$$

As can be seen from Fig. 4, a linear variation of  $\Delta\bar{G}_{\text{KCl}}^{\text{xs}}$  with the square of mole fraction of the other component is not observed.

The curves shown in Fig. 4 are least squares plots in which the equation

$$\Delta\bar{G}_{\text{KCl}}^{\text{xs}} = b_{\text{K-M}} \chi_{\text{MCl}_2}^2 + c \chi_{\text{MCl}_2}^3 \quad (13)$$

has been fitted to the data with the aid of a computer.<sup>12</sup> Table 2 lists the values of these constants for the three systems. The last two columns are measures of the "goodness of fit" of eqn. (13) to the data (for perfect fit, both columns would be zero). The two sets of numbers in parentheses after each entry in the last two columns are "goodness of fit" values for the equations

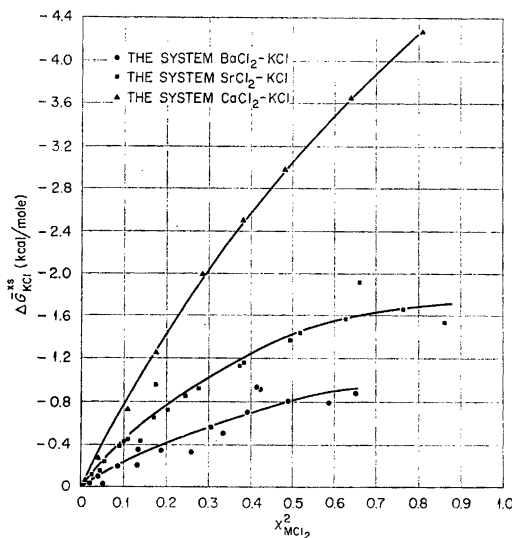


Fig. 4.  $\Delta\bar{G}_{\text{KCl}}^{\text{xs}}$  vs.  $\chi^2_{\text{MCl}_2}$ . The systems  $\text{BaCl}_2\text{-KCl}$ ,  $\text{SrCl}_2\text{-KCl}$ , and  $\text{CaCl}_2\text{-KCl}$ .

$$\Delta\bar{G}_{\text{KCl}}^{\text{xs}} = b_{\text{K-M}} \chi^2_{\text{MCl}_2} \quad (14)$$

and

$$\Delta\bar{G}_{\text{KCl}}^{\text{xs}} = b_{\text{K-M}} \chi^2_{\text{MCl}_2} + c \chi^3_{\text{MCl}_2} + d \chi^4_{\text{MCl}_2} \quad (15)$$

respectively. As can be seen, the addition of an extra term in the equation representing the data does not appreciably improve the fit.

Østvold<sup>3,4</sup> has investigated the systems  $\text{BaCl}_2\text{-NaCl}$ ,  $\text{SrCl}_2\text{-NaCl}$ , and  $\text{CaCl}_2\text{-NaCl}$  by a method analogous to that described here. He found that both the partial molar enthalpies of mixing,  $\Delta\bar{H}_{\text{NaCl}}$ , and the partial molar free enthalpies of mixing for these three systems were described by expressions of the form

$$\frac{\Delta\bar{G}_{\text{NaCl}}^{\text{xs}} \text{ (or } \Delta\bar{H}_{\text{NaCl}})}{(1-\chi_{\text{NaCl}})^2} = a + 2b \chi_{\text{NaCl}} \quad (16)$$

Converting eqn. (16) to the form of eqn. (13)

$$\Delta\bar{G}_{\text{NaCl}}^{\text{xs}} = (a + 2b) \chi^2_{\text{MCl}_2} - 2b \chi^3_{\text{MCl}_2} \quad (17)$$

Thus we may compare the potassium chloride to the corresponding sodium chloride systems by examining the coefficients in eqns. (13) and (17). The last entries in Table 2 show Østvold's values.

As has been demonstrated, the partial molar entropy of mixing in the  $\text{BaCl}_2\text{-KCl}$  system is ideal. Thus for this system

$$\Delta\bar{H}_{\text{KCl}} = b_{\text{K-M}} \chi^2_{\text{MCl}_2} + c \chi^3_{\text{MCl}_2} \quad (18)$$

When the entropy data for the  $\text{SrCl}_2\text{-KCl}$  system (Fig. 3) are combined with the  $\Delta\bar{G}_{\text{KCl}}^{\text{xs}}$  data in the form



Table 2.  $\Delta G^{xs} = b \chi^2_{\text{MCl}_2} + c \chi^3_{\text{MCl}_2}$ .

System	$b_{\text{K-M}}$ (kcal/mole)	$c$ (kcal/mole)	$\sum(Y_{\text{exp}} - Y_{\text{cal}})^2$ <sup>a</sup>	$\frac{\sum(Y_{\text{exp}} - Y_{\text{cal}})^2}{n_{\text{exp}} - n_v}$ <sup>b</sup>
CaCl <sub>2</sub> -KCl	-9.0	4.1	0.019(.473, .010)	0.052(.243, .040)
SrCl <sub>2</sub> -KCl	-5.5	3.8	0.235(1.20, .217)	0.114(.251, .113)
BaCl <sub>2</sub> -KCl	-2.7	1.6	0.159(.134, .219)	0.107(.121, .101)
	$a + 2b$ (kcal/mole)	$-b$ (kcal/mole)		
CaCl <sub>2</sub> -NaCl <sup>c</sup>	-6.6	4.4		
SrCl <sub>2</sub> -NaCl <sup>c</sup>	-1.5	0.4		
BaCl <sub>2</sub> -NaCl <sup>c</sup>	0.5	0.0		

<sup>a</sup>  $Y_{\text{exp}}$  is  $\Delta \bar{G}_{\text{KCl}}^{xs}$ ;  $Y_{\text{cal}}$  is that value of  $\Delta \bar{G}_{\text{KCl}}^{xs}$  which satisfies eqn. (13) at each experimental composition.

<sup>b</sup>  $n_{\text{exp}}$  is the number of experimental points,  $n_v$  is the number of variables.

<sup>c</sup> Østvold, T. Refs. 3 and 4.

$$\Delta \bar{H}_{\text{KCl}} = \Delta \bar{G}_{\text{KCl}}^{xs} - T \Delta \bar{S}_{\text{KCl}}^{xs} \quad (19)$$

a somewhat uniform set of data is obtained. Fig. 5 shows these data fitted to eqn. (18). The coefficients in eqn. (18) for the SrCl<sub>2</sub>-KCl and BaCl<sub>2</sub>-KCl systems are compared with Østvold's data in Table 3.

If the partial molar enthalpy of mixing has the form of eqn. (18), the integral enthalpy of mixing,  $\Delta \bar{H}_{\text{mix}}$ , is

$$\Delta H_{\text{mix}} = (1 - \chi_{\text{MCl}_2}) \chi_{\text{MCl}_2} (b_{\text{K-M}} + \frac{c}{2} + \frac{c}{2} \chi_{\text{MCl}_2}) \quad (20)$$

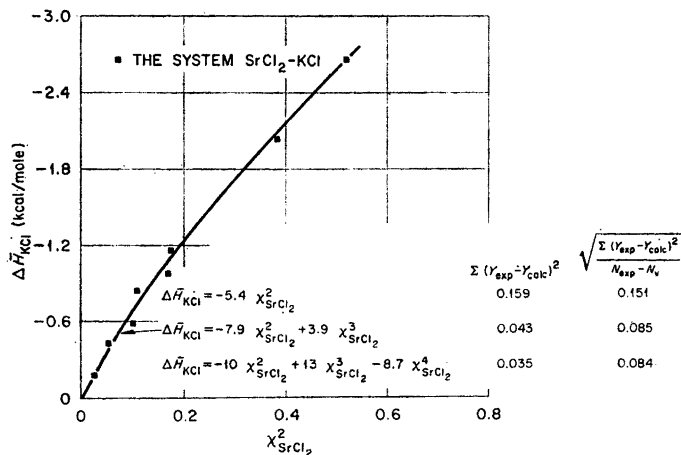


Fig. 5.  $\Delta \bar{H}_{\text{KCl}}$  vs.  $\chi^2_{\text{MCl}_2}$ . The system SrCl<sub>2</sub>-KCl.

Table 3.  $\overline{\Delta H} = b \chi^2_{MCl_2} + c \chi^3_{MCl_2}$ .

System	$b_{K-M}$ (kcal/mole)	$c$ (kcal/mole)
BaCl <sub>2</sub> -KCl	-2.7	1.6
SrCl <sub>2</sub> -KCl	-7.9	3.9
	$a + 2b$ (kcal/mole)	$-b$ (kcal/mole)
BaCl <sub>2</sub> -NaCl <sup>a</sup>	1.2	-0.6
SrCl <sub>2</sub> -NaCl <sup>a</sup>	-1.7	0.4

<sup>a</sup> Østvold, T. Refs. 3 and 4.

and

$$\frac{\Delta H_{mix}}{\chi_{MCl_2}} = b + \frac{c}{2} - b \chi_{MCl_2} - \frac{c}{2} \chi_{MCl_2}^2 \quad (21)$$

McCarty, Hersh, and Kleppa<sup>1</sup> have shown that the alkali nitrate-alkaline earth nitrate systems are described experimentally by the expression

$$\lim[\chi_{M(NO_3)_2} \rightarrow 0] \left( \frac{\Delta H_{mix}}{\chi_{M(NO_3)_2}} \right) = B + C \delta_{12} \quad (22)$$

where

$$\delta_{12} = \frac{d_1 - d_2}{d_1 d_2} \quad (23)$$

$d_1$  is the interionic distance for the monovalent nitrate; and  $d_2$ , the corresponding divalent compound distance. These values are calculated from crystal radii.

Davis<sup>5</sup> has developed a modified conformal solution theory which, as a first approximation, predicts this behavior for mixtures of monovalent and divalent cations with a common anion. From eqn. (21) it is seen that

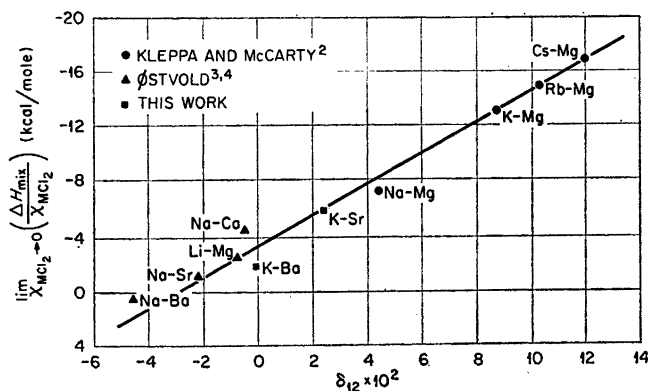


Fig. 6.  $\lim[\chi_{MCl_2} \rightarrow 0] (\Delta H_{mix} / \chi_{MCl_2})$  vs.  $\delta_{12}$ .

$$\lim[\chi_{\text{MCl}_1} \rightarrow 0] \left( \frac{\Delta H_{\text{mix}}}{\chi_{\text{MCl}_1}} \right) = b + \frac{c}{2} \quad (24)$$

Fig. 6 shows this quantity plotted as a function of  $\delta_{12}$  according to eqn. (22) for the systems magnesium chloride-alkali chlorides<sup>2</sup> (Kleppa and McCarty), alkaline earth chloride-sodium chloride<sup>3,4</sup> (Østvold), and  $\text{BaCl}_2$ -KCl and  $\text{SrCl}_2$ -KCl presented here. It is readily seen that the potassium chloride-barium chloride and potassium chloride-strontium chloride systems are also described by eqn. (22). A test of the conformity of the  $\text{CaCl}_2$ -KCl system to this relation must await determination of its partial molar or integral enthalpy of mixing.

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*Addendum:* After this work was completed, it came to our attention that Dr. J. J. Egan at Brookhaven National Laboratory had investigated these systems employing an analogous method.<sup>13</sup> Dr. Egan's results are in rather good agreement with the data reported here.

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