

## Theoretical Interpretation of Excess Molar Volumes of Mixing in Binary Alkaline Earth Chloride Mixtures and in the Binary Alkali Chloride-Magnesium Chloride Mixtures

BJØRN BERGE, JAN LÜTZOW HOLM and BJØRN LILLEBUEN

*Institute of Inorganic Chemistry, The Technical University of Norway,  
N-7034 Trondheim-NTH, Norway*

Excess volumes of mixing in the charge symmetrical systems  $\text{CaCl}_2\text{-MgCl}_2$ ,  $\text{SrCl}_2\text{-MgCl}_2$ , and  $\text{BaCl}_2\text{-MgCl}_2$  have been measured. The excess volumes have been fitted to the polynomial expansion

$$V^E = X(1-X)(a+bX)$$

( $X$  is the mol fraction of  $\text{MgCl}_2$ ), and the constants  $a$  and  $b$  have been compared with the corresponding constants in the excess enthalpy equation given by Papatheodorou and Kleppa. Since the  $a$ -terms both are negative in the two equations and proportional to  $\delta_{12}^2$ , it is assumed that the  $a$ -terms are due to changes in the *nearest neighbour* interaction on mixing. The  $b$ -terms have opposite signs and are proportional to  $\delta_{12}$ . It is assumed that this term is due to changes in the *next-nearest neighbour* interaction. Both effects have been accounted for in the so-called Davis-Rice perturbation theory for mixtures of molten salts. Finally a summary of the corresponding volume-enthalpy effects in the charge unsymmetrical systems  $\text{AlkCl-MgCl}_2$  is given.

In a recent publication from this Institute<sup>1</sup> densities and volumes of mixing for the binary mixtures of alkali chlorides and magnesium chloride were reported.

Excess volumes were calculated from the observed density data. Both negative and positive excess volumes were observed. Negative excess volumes were found on the  $\text{MgCl}_2$ -side for all systems. On addition of  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{RbCl}$ , or  $\text{CsCl}$  the deviation changed gradually from negative to positive. The excess volumes showed pronounced maxima near the composition 33 mol %  $\text{MgCl}_2$  in the systems containing  $\text{KCl}$ ,  $\text{RbCl}$ , and  $\text{CsCl}$ . The negative excess volumes, which are rather unusual in molten salt mixtures, were attributed to the breaking of the chlorine bridges of molten  $\text{MgCl}_2$  when an alkali chloride was added.

The volume data were fitted to the polynomial expansion

$$V^E = X(1-X)(a + bX + cX^2 + dX^3)$$

by a least squares treatment. Here X is the mol fraction of  $\text{MgCl}_2$ . The volume data were compared with the corresponding enthalpy of mixing data, given by Kleppa and McCarty.<sup>2</sup> These results are summarized in Tables 1 and 2. We

Table 1. Summary of excess volume of mixing data for  $\text{AlkCl}-\text{MgCl}_2$ .

$$V^E = X(1-X)(a + bX + cX^2 + dX^3) \text{ (cm}^3 \text{ mol}^{-1}\text{)}$$

X: mol fraction  $\text{MgCl}_2$ .

System	a	b	c	d
Mg-Li	-2.78	-1.54	-6.50	0
Mg-Na	-0.24	2.04	-22.50	10.00
Mg-K	2.38	23.20	-75.40	37.90
Mg-Rb	7.13	41.60	-114.00	56.70
Mg-Cs	16.4	57.0	-165.0	90.0

Table 2. Summary of enthalpy of mixing data<sup>2</sup> for  $\text{AlkCl}-\text{MgCl}_2$ .

$$H^E = X(1-X)(a + bX + cX^2 + dX^3) \text{ (kcal mol}^{-1}\text{)}$$

X: mol fraction  $\text{MgCl}_2$ .

System	a	b	c	d
Mg-Li	-2.49	0.86	1.27	0
Mg-Na	-6.97	-9.42	23.54	-12.72
Mg-K	-13.07	-29.84	69.05	-41.15
Mg-Rb	-13.79	-34.26	74.95	-44.69
Mg-Cs	-15.02	-52.64	122.17	-77.57

will return to these data later in the discussion. In the present work volumes of mixing of the charge symmetrical systems  $\text{SrCl}_2-\text{MgCl}_2$ ,  $\text{BaCl}_2-\text{MgCl}_2$ , and  $\text{SrCl}_2-\text{CaCl}_2$  will be reported.

## EXPERIMENTAL

1. *Method.* The thermo-balance and method used for the density measurements have been described in a previous paper.<sup>1</sup>

2. *Chemicals.*  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , Merck, Germany, *p.a.* min. 99.0 %;  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , Merck, Germany, *p.a.* min. 99.9 %;  $\text{SrCl}_2$ , Merck, Germany, E. L. quality;  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , Riedel de Haën, Germany. The process of purification of  $\text{MgCl}_2$  has been described in a recent paper.<sup>1</sup> Anhydrous  $\text{CaCl}_2$ ,  $\text{SrCl}_2$  and  $\text{BaCl}_2$  were made by dehydration at 400°C in a hydrogen chloride atmosphere. Filtration was not necessary in this case.

Table 3. Densities, in g/cm<sup>3</sup>, for molten mixtures of SrCl<sub>2</sub> and MgCl<sub>2</sub> at 900°C.

Composition, mol fraction MgCl <sub>2</sub>	$\rho_{900}^{\circ}$ , g/cm <sup>3</sup>
0.000	2.712
0.043	2.675
0.121	2.599
0.203	2.546
0.352	2.415
0.495	2.265
0.596	2.149
0.692	2.026
0.798	1.901
0.900	1.770
0.951	1.701
1.000	1.631

Table 4. Densities, in g/cm<sup>3</sup>, for molten mixtures of BaCl<sub>2</sub> and MgCl<sub>2</sub> at 900°C.

Composition, mol fraction MgCl <sub>2</sub>	$\rho_{900}^{\circ}$ , g/cm <sup>3</sup>
0.000	3.189 <sup>a</sup>
0.523	2.574
1.000	1.631

<sup>a</sup> From Reding: *J. Chem. Eng. Data* **10** (1965) 1.

Table 5. Densities, in g/cm<sup>3</sup>, for molten mixtures of SrCl<sub>2</sub> and CaCl<sub>2</sub> at 900°C.

Composition, mol fraction CaCl <sub>2</sub>	$\rho_{900}^{\circ}$ , g/cm <sup>3</sup>
0.000	2.712
0.349	2.484
0.457	2.411
0.531	2.362
0.553	2.345
0.560	2.342
0.760	2.203
1.000	2.032

## RESULTS

The densities of the binary mixtures were measured at 900°C. These are given in Tables 3, 4, and 5. The excess volumes have been calculated from eqn. (1)

$$V_{12}^E = V_{12} - (V_1^{\circ}X_1 + V_2^{\circ}X_2) \quad (1)$$

where  $V_{12}$  is the experimental volume given by

$$V_{12} = \frac{X_1 M_1 + X_2 M_2}{\rho_0} \quad (2)$$

$X_1$  and  $X_2$  are the mol fractions of the two components,  $\rho_0$  is the density of the liquid mixture, while  $M_1$  and  $M_2$  are the corresponding molar weights of the two components.

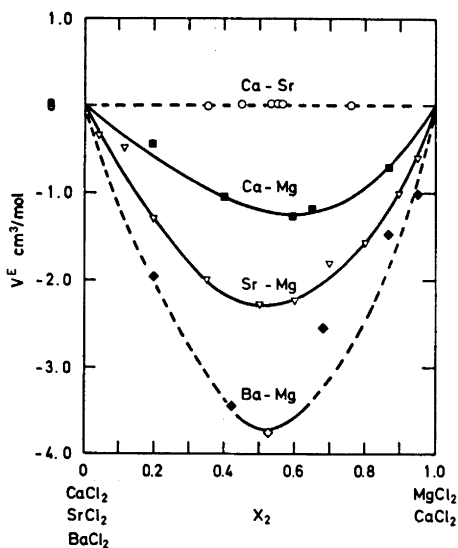


Fig. 1. Excess molar volumes of mixing ( $V^E$ ) at 900°C in some liquid mixtures of alkaline earth chlorides. In the Ba-Mg system:  $\diamond$ , this work,  $\blacklozenge$ , from Reding.

The excess volumes for the three systems are plotted in Fig. 1. This figure also contains the excess volumes of  $\text{CaCl}_2$ - $\text{MgCl}_2$  mixtures as reported by Grjotheim, Holm, Lillebuen and Øye,<sup>1</sup> and the excess volumes of  $\text{BaCl}_2$ - $\text{MgCl}_2$  mixtures calculated from the densities given by Reding.<sup>3</sup>

#### DISCUSSION

We have treated our excess volume data in the same way as was done for the  $\text{AlkCl}$ - $\text{MgCl}_2$  systems, by fitting the data to the polynomial expression

$$V^E = X(1-X)(a+bX) \quad (3a)$$

The results are summarized in Table 6. This table also includes the constants  $a$  and  $b$  in the enthalpy equation as they have been reported by Papatheodorou and Kleppa<sup>4</sup>

$$H^E = X(1-X)(a+bX + \dots) \quad (3b)$$

When it comes to the relation between volume expansion or contraction and enthalpy of mixing, the following four cases have to be taken into consideration:

1. Changes in the *nearest* neighbour interactions, which result in volume *expansion*, give rise to *endothermic* enthalpies of mixing.

2. Changes in the *nearest* neighbour interactions, which result in volume *contraction*, give rise to *exothermic* enthalpies of mixing.

3. Changes in the *next-nearest* neighbour interactions, which result in volume *expansion*, give rise to *exothermic* enthalpies of mixing.

4. Changes in the *next-nearest* neighbour interactions, which result in volume *contraction*, give rise to *endothermic* enthalpies of mixing.

Table 6. Summary of excess volume and enthalpy of mixing data for alkaline earth chloride-magnesium chloride mixtures.

$$H^E = X(1-X)(a + bX + \dots) \text{ (kcal mol}^{-1}\text{)}$$

$$V^E = X(1-X)(a + bX) \text{ (cm}^3 \text{ mol}^{-1}\text{)}$$

$X$ : mol fraction  $\text{MgCl}_2$

	System	$a$	$b$	Stand. deviation
$V^E$	(Ca - Mg) $\text{Cl}_2$	-2.08	-4.92	0.35
$H^E$	(Ca - Mg) $\text{Cl}_2$	-0.06	+1.0	-
$V^E$	(Sr - Mg) $\text{Cl}_2$	-6.16	-5.40	1.2
$H^E$	(Sr - Mg) $\text{Cl}_2$	-1.75	+6.16	-
$V^E$	(Ba - Mg) $\text{Cl}_2$	-10.16	-7.19	3.9
$H^E$	(Ba - Mg) $\text{Cl}_2$	-5.60	+18.3	-
$V^E$	(Sr - Ca) $\text{Cl}_2$	+0.08	+0.06	0.07
$H^E$	(Sr - Ca) $\text{Cl}_2$	-0.48	-	-

Next we consider the Davis Rice (DR) theory<sup>5</sup> for the enthalpy of mixing. They give the following expression, modified by Papatheodorou and Kleppa<sup>4</sup> by introduction of the charges  $Z_1$  and  $Z_2$

$$\Delta H^M = Z_1 Z_2 X_1 X_2 (U_0 + U_1 \delta_{12} + U_2 \delta_{12}^2) \quad (4)$$

$U_0$ . This quantity is determined largely by the change in the dispersion interaction between *next-nearest* neighbour cations.

$U_2$  consists of two terms, namely

$$U_2 = U_2' + U_2'' \quad (5)$$

$U_1$ ,  $U_2'$ ,  $U_2''$ . These coefficients all include a term which arises from the difference in cation-anion dispersion interaction in the two pure components and in the mixture. In addition  $U_1$  depends on the interaction between next-nearest neighbour cations in the mixture and in the pure components. The term  $U_2''$  is largely of Coulombic origin. It is principally represented by the coefficient  $\Omega(T, P, \lambda)$  of the Reiss, Katz and Kleppa (RKK) theory,<sup>6</sup> where  $\Omega(T, P, \lambda)$  is a negative function of temperature  $T$ , pressure  $P$  and  $\lambda$ , where  $\lambda$  is the length parameter for a reference salt. This term also includes contributions from nearest neighbour anion-cation dispersion interactions. These terms also contribute to the  $U_2'$  term.

If we assume that the excess volume will follow a similar expression as the enthalpy of mixing, we can simply set

$$V^E = Z_1 Z_2 X_1 X_2 (U_0 + U_1 \delta_{12} + U_2 \delta_{12}^2) \quad (6)$$

In Fig. 2 the constants  $a$  and  $b$  in the volume expansion equation as well as in the enthalpy equation have been plotted *vs.* the conformal solution parameter

$$\delta_{12} = \left( \frac{d_1 - d_2}{d_1 d_2} \right)$$

for charge symmetrical mixtures.<sup>6</sup>

It is seen that  $a$ -terms are linear functions of  $\delta_{12}^2$  while the  $b$ -terms are linear functions of  $\delta_{12}$ .

We discover very easily from Table 6 that the two  $a$ 's in eqn. (3a) and in eqn. (3b) both are negative for the three systems  $\text{CaCl}_2 - \text{MgCl}_2$ ,  $\text{SrCl}_2 - \text{MgCl}_2$ , and  $\text{BaCl}_2 - \text{MgCl}_2$ . This is equivalent to case 2, a contraction in volume and an exothermic enthalpy of mixing.

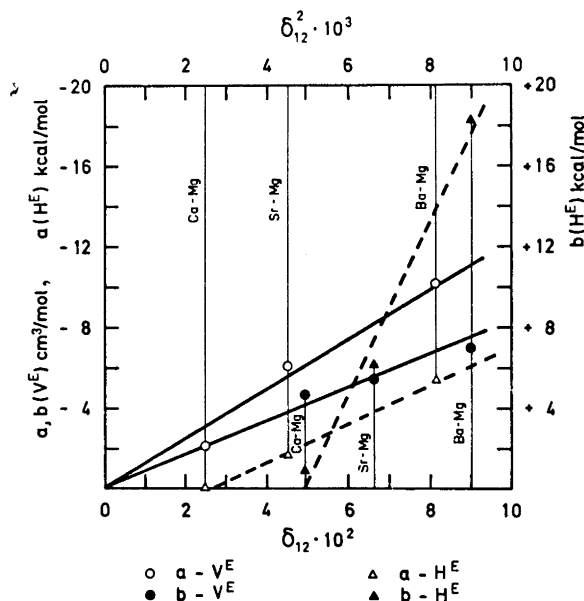


Fig. 2. Plot of  $a(H^E)$  and  $b(H^E)$ , in kcal/mol, and  $a(V^E)$  and  $b(V^E)$ , in  $\text{cm}^3/\text{mol}$ , *vs.*  $\delta_{12}$  or  $\delta_{12}^2$  for binary mixtures of  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ , and  $\text{BaCl}_2$  with  $\text{MgCl}_2$ .

Since the equations for the lines connecting the  $a$ -terms of the different systems considered in Fig. 2 contain  $\delta_{12}^2$  as the only variable they should be included in the  $U_2$  term in eqns. (4) and (6). The two constants  $b$  have opposite signs,  $b$  in eqn. (3a) being negative while  $b$  in eqn. (3b) is positive. This is equivalent to case 4. The equations for the lines connecting the constants  $b$  in Fig. 2 have to be included in the  $U_1$  term, since they contain  $\delta_{12}$  as the only variable.

In the system  $\text{SrCl}_2\text{-CaCl}_2$  the volume change is slightly positive. This mixture shows a similar behaviour as the simple  $\text{AX-BX}$  mixtures.<sup>7</sup> There is little change in the nearest neighbour cation-anion interaction. The negative enthalpy of mixing which is observed in this system is mainly due to changes in next-nearest neighbour Coulomb interaction.

When considering the charge unsymmetrical systems  $\text{AlkCl-MgCl}_2$  in Tables 1 and 2, we see that the constants  $b$ ,  $c$ , and  $d$  in the volume and enthalpy expressions have opposite signs. This means that the excess enthalpy and volume observed in these mixtures are due mainly to changes in the next-nearest neighbour interactions (cases 3 and 4).

The two constants  $a$  (volume and enthalpy) are both negative in the  $\text{LiCl-MgCl}_2$  system and in the  $\text{NaCl-MgCl}_2$  system (somewhat uncertain for the latter) while they are opposite in sign for the other three mixtures.

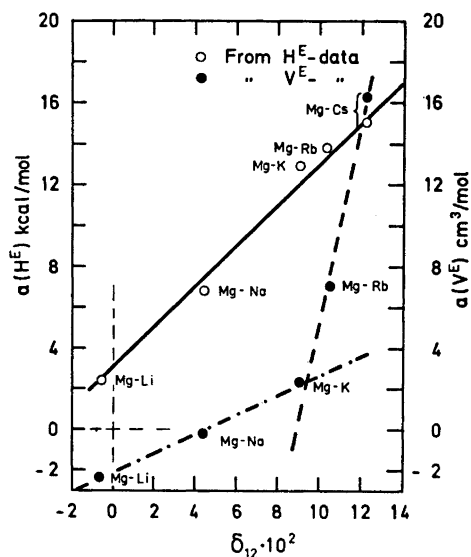


Fig. 3. Plot of  $a(H^E)$ , in kcal/mol, and  $a(V^E)$ , in cm<sup>3</sup>/mol, vs.  $\delta_{12}$  for binary  $\text{AlkCl-MgCl}_2$  mixtures.

This means that in the  $\text{LiCl-MgCl}_2$  system one also has to deal with important contributions from changes in nearest neighbour interactions, *i.e.* the  $\text{Mg}^{2+}\text{-Cl}^-$  or the  $\text{Li}^+\text{-Cl}^-$  interaction. The constants  $a$ ,  $b$ ,  $c$ , and  $d$  have been plotted vs. the conformal solution parameter

$$\delta_{12} = \frac{d_1 - d_2}{d_1 d_2}$$

in Figs. 3–5. This parameter has its justification in the Davis theory<sup>8</sup> of charge unsymmetrical mixtures of fused salts of the type  $\text{ACl-BCl}_2$ . In its first order approximation, this theory predicts for the enthalpy of mixing that

$$\lim_{x_2 \rightarrow 0} (\Delta H^M/X_2) = B + C\delta_{12}$$

where  $B$  and  $C$  are unevaluated complicated integrals containing temperature and pressure dependence.

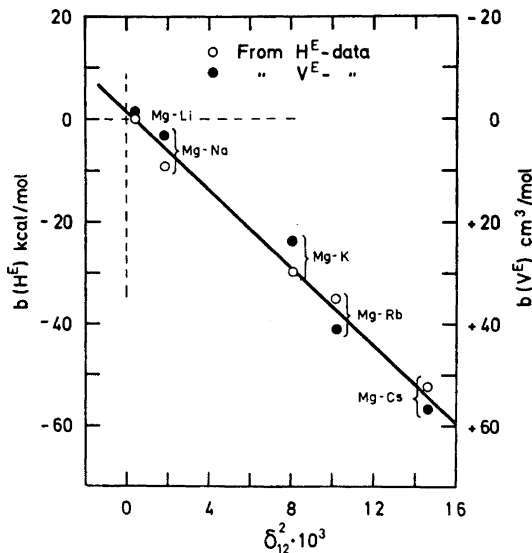


Fig. 4. Plot of  $b(H^E)$ , in kcal/mol, and  $b(V^E)$ , in cm<sup>3</sup>/mol, vs.  $\delta_{12}^2$  for binary AlkCl–MgCl<sub>2</sub> mixtures.

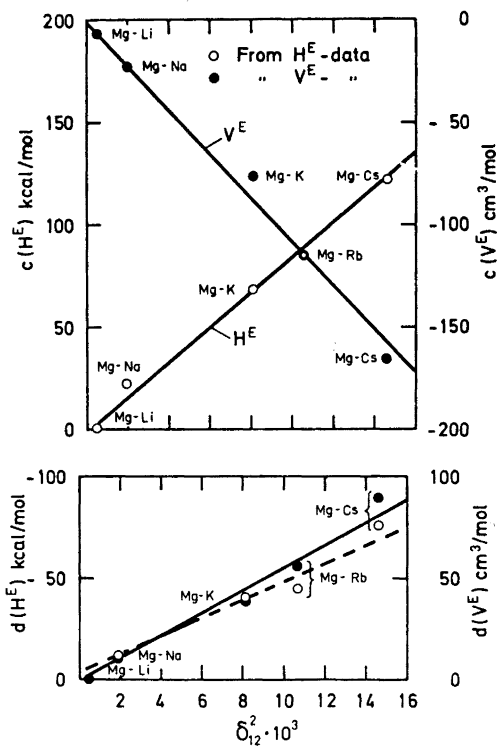


Fig. 5. Plot of  $c(H^E)$  and  $d(H^E)$ , in kcal/mol, and  $c(V^E)$  and  $d(V^E)$ , in cm<sup>3</sup>/mol, vs.  $\delta_{12}^2$  for binary AlkCl–MgCl<sub>2</sub> mixtures.



This is also the empirical relation obtained by Kleppa<sup>9</sup> for mixtures of alkali nitrates and alkaline earth nitrates.

As shown in Fig. 3 the constant  $a(H^E)$  shows a linear dependence on the parameter  $\delta_{12}$ , as predicted from the theory. However, the  $a(V^E)$  term shows a somewhat different behaviour. Here only three of the five mixtures show a similar linear dependence on  $\delta_{12}$ .

From the plots in Figs. 4 and 5 it can be seen that the three constants  $b$ ,  $c$ , and  $d$  seem to depend on  $\delta_{12}^2$  instead of  $\delta_{12}$ . Thus, these terms correspond to the second order term in the Davis theory,<sup>8</sup> and are equivalent to the RKK second order expression<sup>6</sup>

$$\Delta H^M = X_1 X_2 \delta_{12}^2 \Omega(T, P, \lambda) \quad (7)$$

Such higher order terms should therefore be included in the theory of complex mixtures of the same type as  $\text{AlkCl} - \text{MgCl}_2$ , and the enthalpy of mixing should be given the general form

$$\Delta H^M = X_1 X_2 (B + C \delta_{12} + D \delta_{12}^2) \quad (8)$$

where  $B$  and  $C$  are functions of temperature  $T$ , pressure  $P$ , and the length parameter  $\lambda$ , and  $D$  is a function of temperature  $T$ , pressure  $P$ , the length parameter  $\lambda$ , and composition  $X$ .

As mentioned in the paper by Grjotheim, Holm, Lillebuen and Øye,<sup>1</sup> the  $c$ -constants are of particular interest because the  $c(H^E)$  term is the only positive term in the enthalpy equation (eqn. (3b)). This positive term was attributed to the "breaking" of the covalent chlorine-bridges which are present in pure molten  $\text{MgCl}_2$ . This process results in a volume contraction and thereby in an increase in the next-nearest neighbour repulsion  $\text{Mg}^{2+} - \text{Mg}^{2+}$ . This positive term, however, is overwhelmed by the large negative contributions in the  $a$  and  $b$ -term, and the total enthalpy of mixing will therefore be negative.

*Acknowledgements.* Thanks are expressed to Professor K. Grjotheim for laboratory facilities and to Ing. H. Sagen for preparation of the anhydrous chemicals. Financial support from *Norges Tekniske Høgskoles Fond* (B. Berge) and from the *Royal Norwegian Council for Scientific Research* (J. L. Holm) is gratefully acknowledged.

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Received March 4, 1971.