Enthalpies of Mixing of Some Binary Fused-Salt Mixtures Involving the Chlorides of Transition Metals, Calcium, Magnesium, and Cadmium

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Enthalpies of Mixing of Some Binary Fused-Salt Mixtures Involving the Chlorides of Transition Metals, Calcium, Magnesium, and Cadmium

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The integral enthalpies of mixing of the following binary fused-salt mixtures have been determined calorimetrically: (a) $MnCl_2$–$FeCl_2$, $MnCl_2$–$CoCl_2$, $FeCl_2$–$CoCl_2$ at 810°C; $MnCl_2$–$CdCl_2$, $FeCl_2$–$CdCl_2$ at 690°C; (b) $CaCl_2$–M_jCl_2; and (c) $MgCl_2$–M_jCl_2 with M_j=Mn, Fe, Co, at 810°C. The results are discussed with respect to the following points: (1) comparison with the binary alkaline-earth chloride systems; (2) comparison with the existing theories for the enthalpies of mixing of fused salts; and (3) effect of possible covalent or covalent-bridging interactions between the ions in the pure components and in the mixture. The results are interpreted in terms of a cyclic process which allows a separation of the enthalpy of mixing into two principal parts. One part is *negative* and is associated with ionic and dispersion interactions, as in the binary alkali halides and in some of the binary alkaline-earth chlorides. The other part is *positive* and is attributed to the effect of covalent interactions between the ions on the enthalpy of mixing.

I. INTRODUCTION

Since 1960, Kleppa and co-workers have developed precision high-temperature calorimetric techniques, by means of which they have made a systematic investigation of the heats of mixing (ΔH^M) of binary molten-salt mixtures. Among the systems studied are the binary mixtures formed by the alkali halides and by the alkali nitrates,[1,2] the mixtures of silver and thallium chloride with the alkali chlorides[3] and most recently the binary mixtures formed among $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$.[4]

In this last investigation Papatheodorou and Kleppa found that the enthalpy interaction parameter (λ^M) for the three systems $CaCl_2$–$BaCl_2$, $CaCl_2$–$SrCl_2$, and $SrCl_2$–$BaCl_2$ can be represented by the following approximate expression, which is simply related to the corresponding expression for the binary alkali halides[2]:

$$\lambda^M = \Delta H^M / X_1 X_2 = U_0^{++} - Z^2 \Omega_0 \delta_{12}^2. \quad (1)$$

Here X_1 and X_2 are the mole fractions of the two components;

$$\delta_{12} = (d_1 - d_2) / (d_1 d_2),$$

where d_1 and d_2 are the sums of the ionic radii of anion and cation in the two salts, while Z is the charge of the cation in the component salts ($Z=1$ for alkali halides, $Z=2$ for alkaline-earth chlorides). The term U_0^{++} represents an estimate of the contribution to the enthalpy of mixing which arises from the London dispersion interactions between next-nearest-neighbor cations. Ω_0 is a constant, which was found to be approximately the same for all alkali halide and nitrate binaries.[2] Recent measurements on the binary alkali fluorides,[5] and more precise data for the alkali iodides[6] show that the value of Ω_0 actually increases somewhat with increasing size of the common anion. A re-evaluation of the data for the alkali-chloride binaries yields a numerical value of Ω_0 of 440 kcal/mole·A².[7] With this value of Ω_0, Eq. (1) represents the interaction parameter both for the alkali chlorides and for the $CaCl_2$–$SrCl_2$, $CaCl_2$–$BaCl_2$, and $SrCl_2$–$BaCl_2$ binaries.

Papatheodorou and Kleppa found that the enthalpies of mixing for the $MgCl_2$–$CaCl_2$, $MgCl_2$–$SrCl_2$, and $MgCl_2$–$BaCl_2$ binaries are much less exothermic than predicted by Eq. (1). The results for these three systems were interpreted to support the view, originally advanced by Førland,[10] that pure $MgCl_2$ has a certain tendency to form covalently bonded Mg–Cl–Mg bridges. It was suggested that the breaking of these bridges gives rise to a significant endothermic contribution to the enthalpy of mixing, over and above the contributions which arise from coulombic and dispersion forces.

The present investigation was initiated in order to explore a wider range of binary liquid systems of the type M_jCl_2–M_kCl_2. It was hoped that this work would give evidence as to the possible existence of the covalent-bridging interactions in other chloride melts, and as to the influence of these interactions on the enthalpy of mixing. Apart from $MgCl_2$ and $CaCl_2$,

[1] O. J. Kleppa and L. S. Hersh, J. Chem. Phys. **34**, 351 (1961).
[2] L. S. Hersh and O. J. Kleppa, J. Chem. Phys. **42**, 1309 (1965).
[3] L. S. Hersh, A. Navrotsky, and O. J. Kleppa, J. Chem. Phys. **42**, 3752 (1965).
[4] G. N. Papatheodorou and O. J. Kleppa, J. Chem. Phys. **47**, 2014 (1967).
[5] J. L. Holm and O. J. Kleppa, J. Chem. Phys. **49**, 2425 (1968).
[6] M. E. Melnichak and O. J. Kleppa (unpublished).
[7] In this re-evaluation U_0^{++} was calculated by the method of Hersh and Kleppa,[2] with the exception that the multiplying factor of the ionization potential was increased from 0.75 to 1. This new value is still lower than that recommended by Pitzer for noble gases[8] and that argued by Stillinger for molten salts.[9]
[8] K. S. Pitzer, Advan. Chem. Phys. **2**, 59 (1959).
[9] F. H. Stillinger, *Molten Salts*, M. Blander Ed. (Interscience Publishers, Inc., New York, 1964), p. 13.
[10] T. Førland in *Fused Salts*, B. R. Sundheim Ed. (McGraw-Hill Book Co., New York, 1964), p. 145.

the chlorides studied are $MnCl_2$, $FeCl_2$, $CoCl_2$, and $CdCl_2$. In the solid state these salts all have the $CdCl_2$ structure and are isostructural with $MgCl_2$. Experimentally, the following 11 binaries have been investigated: at 690°C $CdCl_2$–$MnCl_2$ and $CdCl_2$–$FeCl_2$; at 810°C $MnCl_2$–$FeCl_2$, $MnCl_2$–$CoCl_2$, $FeCl_2$–$CoCl_2$, $CaCl_2$–$MnCl_2$, $CaCl_2$–$FeCl_2$, $CaCl_2$–$CoCl_2$, $MgCl_2$–$MnCl_2$, $MgCl_2$–$FeCl_2$, and $MgCl_2$–$CoCl_2$. The new results are compared with the theories for the enthalpies of mixing of fused salts developed by Reiss, Katz, and Kleppa (RKK)[11] and by Davis and Rice (DR)[12] as well as with the semiempirical Eq. (1).

II. EXPERIMENTAL AND RESULTS

The calorimetric equipment used in the present work and the experimental procedures adopted were the same as those reported in our previous communication.[4] The fused salt samples to be mixed were again contained in "crucible" and "breakoff" tubes made from fused silica. As before, calibrations were made by the platinum-drop method, based on the heat content equation for platinum given by Kelley.[13] Due to heat pick up by the falling Pt wire a correction of 1.3% was applied at 810°. For 690°C the corresponding correction was found to be too small to be determined. Corrections also were made for the small heat effect associated with the crushing of the tip of the breakoff tube and for any apparent heat effect associated with the displacement of the liquid levels resulting from the mixing procedures. The latter effect, which may arise in the presence of a small temperature gradient along the axis of the calorimeter, was easily determined in blank experiments.

The anhydrous chlorides of the divalent metals were prepared by removal of water from the corresponding hydrated Mallinckrodt Analytical Reagents.[14] In general the following procedure was used. First the salt was placed in a platinum container and its temperature raised to 100° in a vacuum over a period of one day. Then a dry HCl–N_2 flowing atmosphere (1:1) was introduced and the temperature gradually increased to 150°C. When no more water was given off, the temperature was raised stepwise to 250, 350, 450, 550, and 700°C over a period of 6–8 h. While the flow of the HCl–N_2 gas was maintained, the salt (except in the case of $CdCl_2$) was heated to a final temperature of 850°C for a short while. At 850°C $CaCl_2$, $MgCl_2$, $MnCl_2$, $FeCl_2$, and $CoCl_2$ (the $CdCl_2$ at 700°C) are the liquid state.

The salts were then slowly cooled to room tempera-

TABLE I. Enthalpies of mixing in binary liquid mixtures formed by $CoCl_2$, $FeCl_2$, and $MnCl_2$ at 810°C. Data in calories per mole.

X_{CoCl_2}	Total moles	ΔH^M	λ^M
	$CoCl_2$–$MnCl_2$		
0.904	0.0995	33.4	387
0.806	0.0992	49.1	315
0.700	0.1000	75.9	362
0.600	0.1000	77.1	321
0.500	0.1000	78.3	313
0.400	0.1000	79.1	329
0.300	0.1000	71.9	342
0.200	0.1002	53.0	331
0.100	0.1009	26.8	297
	$CoCl_2$–$FeCl_2$		
0.849	0.1007	21.3	167
0.750	0.1005	28.7	154
0.650	0.1002	29.6	130
0.549	0.1004	41.4	167
0.449	0.1001	46.4	187
0.349	0.1000	31.3	137
0.250	0.1003	25.1	134
0.149	0.1007	21.3	167
	$FeCl_2$–$MnCl_2$		
0.100	0.1014	−0.3	−4
0.205	0.1009	0.7	4
0.300	0.1001	0.7	3
0.502	0.1006	−0.7	−3
0.701	0.1029	0.7	3

ture over a period of 4–6 h, under a stream of dry N_2. After this treatment the solids $MgCl_2$, $MnCl_2$, $CdCl_2$, $CoCl_2$, and $FeCl_2$ consisted of an agglomeration of large, soft crystals with a layerlike texture, while $CaCl_2$ had small white crystals and was quite hard.

Aqueous solutions of the dried salts were found to be neutral with respect to phenolphthalein. The presence of valencies other than 2 in the oxidizable transition-metal chlorides was checked by passing the aqueous solution through a cation-exchange column and titrating the resulting acidic solution. The calculated amounts of divalent M^{++} cations were within 0.2% of the amounts expected from the purity of the original materials. While all these salts are quite hygroscopic in powdered form, they could readily be weighed in the form of small chunks without significant gain in weight outside a dry box.

In the course of the present work we carried out a total of 90 successful calorimetric experiments. All the experimental results are recorded in Tables I–IV. In these tables, the first column gives the mole fraction of the final mixture, the second the total number of moles used in each experiment, the third the molar enthalpy of mixing ΔH^M, and the fourth the enthalpy interaction parameter λ^M. The enthalpy changes actually observed in each experiment, i.e., the product of Columns 2 and 3, ranged from less than 0.5 cal in $MnCl_2$–$FeCl_2$

[11] H. Reiss, J. L. Katz, and O. J. Kleppa, J. Chem. Phys. **36**, 144 (1962).
[12] H. T. Davis and S. A. Rice, J. Chem. Phys. **41**, 14 (1964).
[13] K. K. Kelley, U.S. Bur Mines, Bull. No. 584 (1960).
[14] Mallinckrodt Analytical Reagents: $MnCl_2 \cdot 4H_2O$ (99.8%), $FeCl_2 \cdot 4H_2O$ (99.8%), $CoCl_2 \cdot 6H_2O$ (99.6%), $MgCl_2 \cdot 6H_2O$ (99.9%), $CdCl_2$ (99.6%), and $CaCl_2 \cdot 2H_2O$ (99.8%).

TABLE II. Enthalpies of mixing in binary liquid mixtures of $CdCl_2$ with $MnCl_2$ and $FeCl_2$ at 690°C. Data in calories per mole.

X_{CdCl_2}	Total moles	ΔH^M	λ^M
	$MnCl_2$–$CdCl_2$		
0.198	0.0503	10.06	63.15
0.300	0.0500	14.68	69.90
0.405	0.0500	15.12	62.80
0.500	0.0500	19.25	77.00
0.598	0.0501	21.06	87.70
0.700	0.0500	21.00	100.00
0.798	0.0501	16.70	104.10
	$FeCl_2$–$CdCl_2$		
0.200	0.0500	16.95	106.00
0.301	0.0501	23.98	113.90
0.398	0.0500	24.02	100.30
0.499	0.0503	19.13	76.55
0.601	0.0501	19.83	82.70
0.683	0.0512	22.11	102.30
0.896	0.1004	4.61	49.80

TABLE III. Enthalpies of mixing in binary liquid mixtures of $CaCl_2$ with $MnCl_2$, $FeCl_2$, $CoCl_2$ at 810°C. Data in kilocalories per mole.

X_{CaCl_2}	Total moles	ΔH^M	λ^M
	$CaCl_2$–$MnCl_2$		
0.101	0.1001	0.127	1.405
0.201	0.1001	0.217	1.352
0.302	0.1008	0.231	1.096
0.400	0.1002	0.214	0.894
0.503	0.1011	0.188	0.744
0.600	0.1003	0.149	0.624
0.700	0.1003	0.099	0.472
0.800	0.1002	0.055	0.347
0.901	0.1009	0.023	0.259
	$CaCl_2$–$FeCl_2$		
0.100	0.1001	0.205	2.281
0.206	0.1008	0.323	1.976
0.301	0.1016	0.363	1.700
0.400	0.1000	0.360	1.502
0.500	0.1001	0.331	1.326
0.599	0.1002	0.281	1.172
0.700	0.1009	0.218	1.040
0.800	0.1001	0.113	0.711
0.900	0.1002	0.049	0.547
	$CaCl_2$–$CoCl_2$		
0.099	0.1005	0.371	4.140
0.199	0.1002	0.592	3.704
0.298	0.1010	0.673	3.219
0.400	0.1017	0.707	2.947
0.499	0.1002	0.641	2.567
0.628	0.1030	0.510	2.187
0.759	0.1079	0.352	1.933
0.844	0.1103	0.240	1.830
0.945	0.1006	0.076	1.479

to more than 65 cal for certain compositions in the $CaCl_2$–$CoCl_2$ binary.

In Figs. 1–3 we plot the experimentally determined interaction parameters against mole fraction. The lines drawn in these figures represent least-squares curves of λ^M. The deviation of the actual experimental points from these curves averages less than 50 cal/mole. This represents from ±2 to $\pm20\%$ of λ^M, depending on its absolute magnitude.

TABLE IV. Enthalpies of mixing in binary liquid mixtures of $MgCl_2$ with $MnCl_2$, $FeCl_2$, $CoCl_2$ at 810°C. Data in calories per mole.

X_{MgCl_2}	Total moles	ΔH^M	λ^M
	$MgCl_2$–$MnCl_2$		
0.209	0.0750	43.9	265
0.296	0.0999	61.0	293
0.399	0.1004	77.0	321
0.500	0.0991	78.5	314
0.605	0.0995	79.6	334
0.698	0.1000	83.1	394
0.790	0.1072	55.6	336
0.893	0.1004	35.0	367
	$MgCl_2$–$FeCl_2$		
0.901	0.1001	25.3	283
0.798	0.1013	52.8	328
0.701	0.1006	67.5	322
0.598	0.1003	93.2	388
0.500	0.1002	99.2	397
0.399	0.1002	105.3	439
0.299	0.1002	100.6	480
0.199	0.1006	87.9	550
0.101	0.1001	66.6	736
	$MgCl_2$–$CoCl_2$		
0.895	0.0501	33.8	361
0.897	0.1004	33.8	366
0.799	0.1003	64.2	400
0.697	0.1005	88.5	419
0.599	0.1001	95.0	395
0.494	0.0991	100.0	400
0.401	0.1002	117.6	490
0.300	0.1000	107.1	510
0.201	0.1002	94.2	587
0.101	0.1005	71.6	784

III. DISCUSSION

A. General

The Reiss, Katz, and Kleppa (RKK)[11] conformal solution theory for the heats of mixing in fused salts is based on a model ionic melt in which only coulombic interactions and short-range repulsion are present between the ions. An extension of this theory to include short-range non-Coulombic interactions is made in the theory of Davis and Rice (DR).[12] For a fused-salt mixture of the type (A^{+Z_1}, X^{-Z_2})–(B^{+Z_1}, X^{-Z_2}) the

RKK–DR pair potential between unlike ions at a distance R is taken to be of the form

$$\varphi(R) = \infty, \qquad\qquad R \le d,$$

$$\varphi(R) = -(Ze^2/\kappa R) + \xi V(R), \qquad R > d. \qquad (2)$$

In this expression $Z = Z_1 \cdot Z_2$, d is the anion–cation hard-core separation and κ is an effective dielectric constant. The term $\xi V(R)$ represents a perturbation to the Coulombic potential, and is attributed to short-range dispersion-type interactions. In general the coupling parameter, ξ, will have different numerical values for different kinds of interactions, e.g., induced dipole-ion, induced dipole-induced dipole, etc., while $V(R) = -R^{-n}$ ($n = $ positive number).

For the mixing of X_2 moles of a reference salt (B^{+Z_1}, X^{-Z_2}) with X_1 moles of (A^{+Z_1}, X^{-Z_2}) the RKK–DR theory gives as a first approximation for the enthalpy of
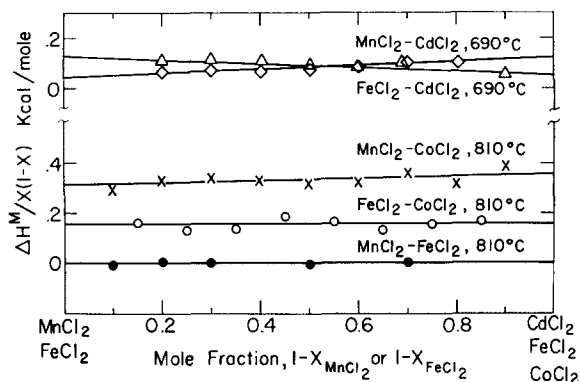

FIG. 1. Enthalpy interaction parameters $[\lambda^M = \Delta H^M / X(1-X)]$ in the binary liquid systems MnCl$_2$–CdCl$_2$ and FeCl$_2$–CdCl$_2$ at 690°C; MnCl$_2$–FeCl$_2$, MnCl$_2$–CoCl$_2$, and FeCl$_2$–CoCl$_2$ at 810°C. Least-squares curves.

mixing the following expression:

$$\Delta H^M = X_1 X_2 (U_0 + U_1 \delta_{12} + U_2 \delta_{12}^2), \qquad (3)$$

with

$$U_1 = Z(U_1^{+-} + U_1^{++} + X_1 U_{1a}^{++}),$$

$$U_2 = Z[U_2^{+-} + ZX_1 U_{2a}^{+-} + Z\Omega(T,V)], \qquad (4)$$

where the coefficients U are complicated functions of ξ. Qualitatively they may be described in terms of the types of interactions on which they depend as follows:

U_0: This coefficient is determined largely by the change in the dispersion interactions between next-nearest-neighbor cations, when the mixture is formed.

U_1^{+-}, U_1^{++}, U_{1a}^{++}, U_2^{+-}, and U_{2a}^{+-}: These quantities, as the superscripts indicate, are determined by the dispersion interaction between nearest-neighbors $(+-)$ or next-nearest-neighbor cations $(++)$ in the two pure components (1 and 2 as subscripts of ξ) and
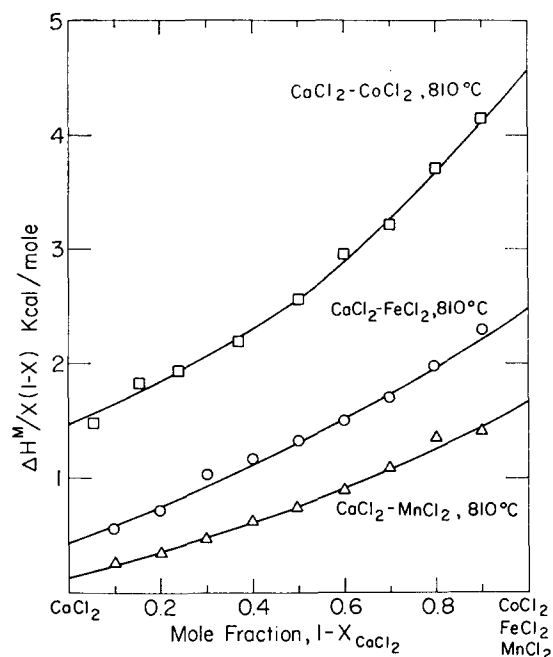

FIG. 2. Enthalpy interaction parameters, $[\lambda^M = \Delta H^M / X(1-X)]$ in the binary liquid systems CaCl$_2$–NnCl$_2$, CaCl$_2$–FeCl$_2$, and CaCl$_2$–CoCl$_2$ at 810°C. Least-squares curves.

in the mixture (12 as subscript of ξ). Thus,

$$U_0 = U_0[2\xi_{12}^{++} - (\xi_1^{++} + \xi_2^{++})], \qquad (5a)$$

$$U_1^{+-} = U_1^{+-}(\xi_2^{+-} - \xi_1^{+-}), \qquad (5b)$$

$$U_1^{++} = U_1^{++}(\xi_{12}^{+-} - \xi_2^{++}, \xi_2^{++} - \xi_1^{++}), \qquad (5c)$$

$$U_{1a}^{++} = U_{1a}^{++}[2\xi_{12}^{+-} - (\xi_1^{++} + \xi_2^{++})], \qquad (5d)$$

$$U_2^{+-} = U_2^{+-}(\xi_2^{+-} - \xi_1^{+-}, \xi_1^{+-}), \qquad (5e)$$

$$U_{2a}^{+-} = U_{2a}^{+-}(\xi_2^{+-} - \xi_1^{+-}, \xi_1^{+-}). \qquad (5f)$$

The $\Omega(T,V)$ term is a sum of complicated integrals and is independent of the perturbation potential.
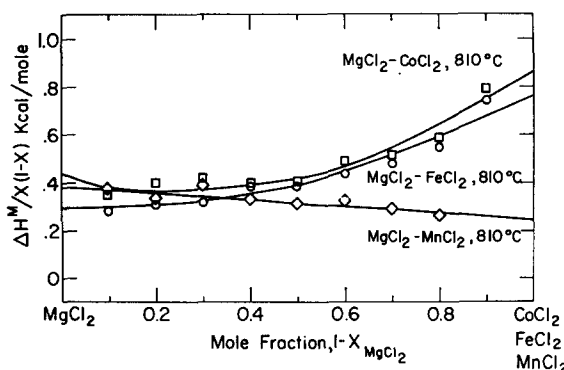

FIG. 3. Enthalpy interaction parameters, $[\lambda^M = \Delta H^M / X(1-X)]$ in the binary liquid systems MgCl$_2$–MnCl$_2$, MgCl$_2$–FeCl$_2$, and MgCl$_2$–CoCl$_2$ at 810°C. Least-squares curves.

For ions without dispersion interactions ($\xi=0$), Eq. 3 reduces to the original RKK expression modified through the charge factor Z^2:

$$\Delta H^M = X_1 X_2 Z^2 \Omega(T,V)\delta_{12}^2. \qquad (6)$$

As was emphasized by Davis and Rice,[12] Eq. (3) can be used for the comparison of a set of binary systems with a common component, which is considered as the reference salt. Therefore this equation may be used to compare the enthalpies of mixing of a family of mixtures, e.g., $CaCl_2$-$M_jCl_2(M_j=$ Mn, Fe, Co), in which $CaCl_2$ is the reference salt. On the other hand, in order to compare two or more mixtures which do not have a common component, e.g., $CaCl_2$-$MnCl_2$ and $MgCl_2$-$CoCl_2$, a more general equation is needed. Such an equation is given by Davis and Rice.[12] However, we have as yet been unable to apply this equation in any practical case of comparison.

Equation (6) is independent of the choice of reference salt and may be used to compare all charge-symmetrical binaries with completely ionized components at a given temperature and pressure. Finally, it should be noted that the coefficients U_0 and U_1^{+-} in Eq. (3) are also independent of the choice of reference salt. For the RKK case ($\xi=0$) Blander[15] has calculated higher order approximations for the enthalpy of mixing. According to his treatment the following terms should be added to Eq. (6):

$$\Delta H^{M'}| = X_1 X_2 (X_1-X_2)\pi\delta_{12}^3 + X_1 X_2 [\theta+(X_1-X_2)^2\Sigma]\delta_{12}^4. \qquad (7)$$

Again π, θ and Σ are unevaluated complicated integrals.

If we represent the experimental values of ΔH^M for symmetrical binaries by algebraic equations of the form:

$$\Delta H^M = X_1 X_2 (a+bX_1+cX_1 X_2) \qquad (8)$$

then, according to the theoretical Eqs. (6), and (7), the coefficients a, b and c should have the following dependence on δ_{12}:

(i) The quantity a represents a sum of the coulombic term, $\Omega(T,V)Z^2\delta_{12}^2$, plus U_0 and all other terms in Eqs. (4) and (7) which are independent of mole fraction.

(ii) The quantity b represents the "energetic asymmetry" in the heat of mixing curve

$$b = \lim_{x_1\to 0}(\Delta H^M/X_1 X_2) - \lim_{x_2\to 0}(\Delta H^M/X_1 X_2),$$

and depends on the terms $U_{1a}^{++}\delta_{12}$, $U_{2a}^{+-}\cdot\delta_{12}^2$ and $\pi\delta_{12}^3$.
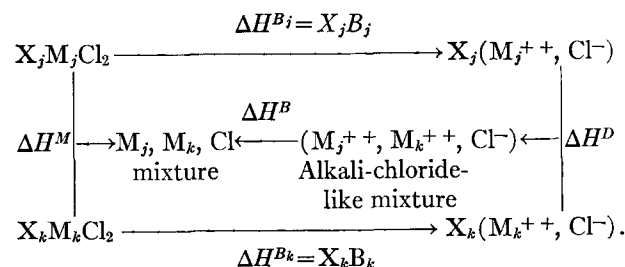
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[15] M. Blander, J. Chem. Phys. **36**, 1092 (1962).

(iii) The quantity c depends only on the higher-order term Coulombic interactions and should be proportional to $\Sigma\delta_{12}^4$ (Eq. 7).

B. The Systems $(Mn-Fe)Cl_2$, $(Mn-Co)Cl_2$, $(Fe-Co)Cl_2$, $(Mn-Cd)Cl_2$, $(Fe-Cd)Cl_2$

The enthalpies of mixing for these five systems are positive. Figure 1 shows that the interaction parameters, λ^M_{exptl}, as a function of composition, are straight lines possessing little or no energetic asymmetry. In Table V we list the experimental values of λ^M, the calculated values of the U_0^{++} dispersion interactions,[16] and the quantities $Z^2\Omega_0\delta_{12}^2(\Omega_0=440$ cal/mole A^2, $Z=2)$. The values of this quantity are negative and fall in the range -26 cal/mole (Fe–Co) to -1810 cal/mole (Cd–Fe). While the values of U_0^{++} tend to be small compared to $Z^2\Omega_0\delta_{12}^2$, the experimental interaction parameters are positive and range from ±0 cal/mole (Fe–Mn) to $+340$ cal/mole (Co–Mn). This clearly demonstrates that, in spite of the essential simplicity of the considered systems, Eq. (1) is not capable of representing the results for these binary mixtures.

Due to the similarity of the ionic radii and polarizabilities of the considered four cations, attempts to correlate the experimental and calculated values of λ by means of terms proportional to δ_{12}, δ_{12}^2 or by next-nearest-neighbor London interactions were unsuccessful. It is possible, however, to analyze the thermodynamic properties in terms of a cyclic process which allows for the assumed covalent interaction between cations and anions in these salts. We shall use the symbol B_j to denote the energy necessary to convert one mole of the molten component M_jCl_2 into a hypothetical, purely ionic alkali-chloridelike melt (M_j^{++}, Cl^-). The formation of one mole of the liquid mixture, from X_j moles of M_jCl_2 and X_k moles of M_kCl_2, can be achieved using B_j and B_k in the following way:

$$\Delta H^{B_j} = X_j B_j$$

$X_j M_j Cl_2 \xrightarrow{\hspace{3cm}} X_j(M_j^{++}, Cl^-)$

ΔH^B

$\Delta H^M \left|\begin{array}{c}\rightarrow M_j, M_k, Cl^- \longleftarrow (M_j^{++}, M_k^{++}, Cl^-)\longleftarrow\end{array}\right| \Delta H^D$
$\qquad$ mixture $\qquad$ Alkali-chloride-
$\qquad\qquad\qquad$ like mixture

$X_k M_k Cl_2 \xrightarrow{\hspace{3cm}} X_k(M_k^{++}, Cl^-).$

$$\Delta H^{B_k} = X_k B_k$$

Here ΔH^B is the enthalpy required to convert the molten mixture into an alkali-chloridelike mixture, ΔH^D is the enthalpy of mixing of the alkali-chloridelike ionic binaries, i.e., the value given by Eq. (1), and

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[16] Calculated by the method used by Hersh and Kleppa. The polarizabilities of the transition metals were taken from Ref. 17. Interionic distances were based on the ionic radii of Pauling.

[17] C. K. Jørgensen, in *Structure and Bonding* (Springer-Verlag, New York, 1966), Vol. 1, p. 236.

TABLE V. Experimental and theoretical data on charge-symmetrical chloride systems.

System	$\lambda_{0.5}{}^{M}$ (cal/mole)	$U_0{}^{++}$ (cal/mole)	$Z^2\Omega\delta_{12}{}^2$ (cal/mole)	$b_j - b_k$ (cal/mole)$^{1/2}$
Co–Fe	160	11	−36	13.6
Co–Mn	340	5	−227	23.7
Fe–Mn	0	1	−99	9.9
Mn–Cd	80	161	−1020	30.7
Fe–Cd	90	190	−1810	41.4

System	$\lambda_0{}^{M}$	$U_0{}^{++}$	$Z^2\Omega\delta_{12}{}^2$	$b_j - b_{Ca}$
Co–Ca	1480	63	−2545	62.7
Fe–Ca	410	21	−1962	48.5
Mn–Ca	142	33	−1197	36.2

System	$\lambda_0{}^{M}$	$U_0{}^{++}$	$Z^2\Omega\delta_{12}{}^2$	Range of $b_j - b_{Mg}$
Mg–Co	450	486	−217	5–20
Mg–Fe	300	351	−440	17–24
Mg–Mn	380	391	−970	24–30

ΔH^M is the observed enthalpy of mixing. For the cyclic process we can write:

$$\Delta H^M = \Delta H^D + \Delta H^{Bj} + \Delta H^{Bk} + \Delta H^B$$

$$= X_j B_j + X_k B_k + \Delta H^B - X_j X_k Z^2 440 \delta_{12}{}^2$$

$$+ X_j X_k U_0{}^{++}. \quad (9)$$

The terms ΔH^{Bj} and ΔH^B are measures of the covalent contributions to the cohesive energy (enthalpy) in the pure components and in the mixture, respectively. If we make the reasonable assumption that this covalency depends only on ions of the first and second coordination sphere, then the major contribution presumably will arise from the direct M_j–Cl covalent interactions and from the influence on this of the nature of the next-nearest-neighbor cations.

In the pure components the juxtaposition of two like cations with the same Cl⁻ anion as nearest neighbor may create an additional covalent bridging interaction, while in the mixture the two unlike next-nearest-neighbor cations will "compete" for the Cl⁻ ion. This suggests that the magnitude of ΔH^B will depend on the probability of having M_j–M_k or M_j–M_j next-nearest-neighbor cation configurations. In the random mixing approximation ΔH^B may be expressed as

$$\Delta H^B = -[X_j{}^2 B_j + X_k{}^2 B_k + 2 X_j X_k B_{jk}]. \quad (10)$$

Here $X_j{}^2$ and $2 X_j X_k$ are, respectively, the probability that in a given pair of next-nearest-neighbor cations, both are M_j, i.e., M_j–M_j, and that one is M_j and the other M_k, i.e., M_j–M_k. B_{jk} is the enthalpy required per mole to transform a molten mixture which contains only M_j–M_k pairs into an alkali-chloridelike mixture which has the same kind of pairs.

Using the combinatorial approximation:

$$B_{jk} = (B_j B_k)^{1/2} = b_j b_k, \quad (11)$$

where $b_j = B_j{}^{1/2}$, and Eqs. (9) and (10) we have

$$\Delta H^M = X_j X_k [U_0{}^{++} - Z^2 440 \delta_{12}{}^2 + (b_j - b_k)^2]. \quad (12)$$

According to this model the enthalpy of mixing, apart from the ionic and van der Waals terms considered previously, depends only on the difference between two *positive* quantities b_j and b_k, which give a measure of the covalent character of the two pure components. A numerical evaluation of $|b_j - b_k|$ can be obtained from Eq. (12), which can be rewritten:

$$|b_j - b_k| = (\lambda_{\text{exptl}}{}^M + Z^2 440 \delta_{12}{}^2 - U_0{}^{++})^{1/2}. \quad (13)$$

Using this equation and the values of $\lambda_{\text{exptl}}{}^M$, $Z^2 440 \delta_{12}{}^2$ and $U_0{}^{++}$ given in Table V we have calculated the values of $|b_j - b_k|$ in (cal/mole)$^{1/2}$ listed in the last column of this table.

A simple justification for the validity and self-consistency of this treatment can be obtained by considering the differences $|b_j - b_k|$ for three salts which form three different binary mixtures. We shall first examine the first three binaries listed in Table V, for which $|b_{Co} - b_{Fe}| = 13.6$, $|b_{Co} - b_{Mn}| = 23.7$ and $|b_{Mn} - b_{Fe}| = 9.9$ (cal/mole)$^{1/2}$. On the basis of the electronegativity differences[18] between M and Cl, and of the values of the second ionization potential of the neutral metal atoms, we conclude that the covalent character of the M^{++}–Cl⁻ bond should increase in the sequence Mn < Fe < Co. This is the same sequence which was found by Pearson and Gray[19] in their study of the co-

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[18] E. J. Little and M. M. Jones, J. Chem. Educ. **37**, 231 (1960).
[19] R. G. Pearson and H. G. Gray, Inorg. Chem. **2**, 358 (1963).

valent character of the M–Cl bonds in the corresponding MCl$_2$ gaseous molecules. Thus we should expect that

$$b_{Co} > b_{Fe} > b_{Mn}. \qquad (14)$$

Taking these inequalities into account we have

$$| b_{Co} - b_{Fe} | = | b_{Co} - b_{Mn} | - | b_{Fe} - b_{Mn} |$$

$$= 23.7 - 9.9 = 13.8 (cal/mole)^{1/2}.$$

This value, which results from a combination of the data for the CoCl$_2$–MnCl$_2$ and FeCl$_2$–MnCl$_2$ binaries, is in remarkable agreement with the value, 13.6 (cal/mole)$^{1/2}$, found for the FeCl$_2$–CoCl$_2$ binary.

We can also check the validity of the model by examining the results for the CdCl$_2$–FeCl$_2$ and CdCl$_2$–MnCl$_2$ binaries. From Refs. 18 and 19 we expect that $b_{Cd} \lesssim b_{Mn} < b_{Fe}$; thus we should have:

$$| b_{Fe} - b_{Cd} | - | b_{Mn} - b_{Cd} | = b_{Fe} - b_{Mn} = 41.4 - 30.7$$

$$= 10.7 \ (cal/mole)^{1/2}.$$

This result again is in good agreement with the value of 9.9 (cal/mole)$^{1/2}$ found from the study of the FeCl$_2$–MnCl$_2$ binary.

Using Eq. (13) and Table V, it is of course possible, from the enthalpies of mixing of two different binaries with a common component, to predict ΔH^M for an unknown binary. As an example, consider the CoCl$_2$–CdCl$_2$ system, for which we were not able to carry out calorimetric measurements, because of the high vapor pressure of CdCl$_2$ at the melting point of CoCl$_2$. A combination of the data for CoCl$_2$–FeCl$_2$ and CdCl$_2$–FeCl$_2$ and for the CoCl$_2$–MnCl$_2$ and CdCl$_2$–MnCl$_2$ systems gives

$$| b_{Co} - b_{Cd} | = | b_{Co} - b_{Mn} | + | b_{Mn} - b_{Cd} |$$

$$= 54.5 \ (cal/mole)^{1/2},$$

$$| b_{Co} - b_{Cd} | = | b_{Co} - b_{Fe} | + | b_{Fe} - b_{Cd} |$$

$$= 55 \ (cal/mole)^{1/2}.$$

The agreement again is very satisfactory. From these values of $| b_{Co} - b_{Cd} |$ we predict a positive enthalpy of mixing for CoCl$_2$–CdCl$_2$, with an interaction parameter of about 870 cal/mole.

Finally we want to examine our new covalent terms $(b_j - b_k)^2$ in the light of a possible extension of the DR theory [Eq. (3)]. This extension may be achieved as follows: We first assume that the covalent interactions between a pair of ions in the melt can be represented by a weak pair potential of the type $\xi_c V_c(R)$. The functional dependence of V_c on R is not known but is assumed to be similar to the other short-range-type potentials, while the coupling parameter ξ_c may be

considered to be a quantitative measure of the covalency contribution to the interionic potential. For weak covalent interactions we assume that ξ_c is small and that the $\xi_c V_c(R)$ potential may be treated as a perturbation to the coulombic potential, as in Eq. (2). As a result of this perturbation, the theoretical expression for the enthalpy of mixing [Eq. (3)] will include additional terms of covalent origin, which we denote by the subscript B: $U_{0(B)}$, $U_{1(B)}{}^{+-}$, $U_{1(B)}{}^{++}$, $U_{1a(B)}{}^{++}$, $U_{2(B)}{}^{+-}$ and $U_{2a(B)}{}^{+-}$. As indicated by Eq. (4) these terms will depend on the covalent interactions between like and/or unlike ions. From the procedures of the DR theory it appears that, if two or more different interactions perturb the Coulombic potential, then the U's which occur in Eq. (3) will represent a sum of two or more terms, each of which correspond to a different type of interaction. Thus, for the binary systems studied in the present section, in which we consider the London forces and the small covalent-bonding contributions, the U_o of Eq. (3) should be a sum of two terms.

$$U_0 = U_0{}^{++} + U_{0(B)}.$$

Formally the last term $U_{0(B)}$, which is independent of composition and of δ_{12}, is the only term that can be associated directly with $(b_j - b_k)^2$. It is possible, however, that in view of the small values of δ_{12} in these systems, there will also be small covalency contributions to the remaining terms ($U_1 \delta_{12}$ and $U_2 \delta_{12}{}^2$), which are not readily recognized as such, and are therefore incorporated into $(b_j - b_k)^2$. The absence of energetic asymmetry in the experimental interaction parameters indicates that the contributions to the enthalpy of mixing which arise from the asymmetric terms $U_{1a(B)}{}^{++}$ and $U_{2a(B)}{}^{+-}$ are small. The lack of energetic asymmetry does not necessarily imply the absence of anion–cation covalent interactions, because the asymmetric term $U_{2a(B)}{}^{+-}$ is determined by the difference in the anion–cation covalent interactions in the two pure components. When the nonbridging covalent interactions in the two pure components have similar magnitudes, the differences are small and the asymmetry terms may not be recognized. We believe that the covalent-bridging interactions $U_{0(B)}{}^{++}$ make the major contribution to $b_j - b_k$, but we have no certain way of ruling out the possible contributions of the nonbridging covalent interactions.

C. The CaCl$_2$ Systems: (Ca–Mn)Cl$_2$, (Ca–Fe)Cl$_2$, (Ca–Co)Cl$_2$

The experimental interaction parameters for these three systems are presented in Fig. 2. The data were fitted in the functional form of Eq. (8). The coefficients a, b and c were determined by the method of least squares and their values are given in Table VI. Note that for these systems λ^M is always positive, and has an energetic asymmetry of considerable magnitude. In

TABLE VI. Least-square coefficients for the enthalpies of mixing in mixtures of $CaCl_2$ with $MnCl_2$, $FeCl_2$, and $CoCl_2$ ($\Delta M^M = X_1 X_2 (a + b X_2 + c X_1 X_2)$, $X_1 =$ mole fraction of $CaCl_2$). Data in calories per mole.

System	a	b	c	Standard deviation
Mn–Ca	142	1520	−560	44
Fe–Ca	411	2070	−450	62
Co–Ca	1482	3210	−1800	85

all cases the value of λ^M in pure $CaCl_2$ is less positive than in the other component. In our earlier study of the binary alkaline-earth chlorides we found that $CaCl_2$ behaves in a manner consistent with that predicted from the binary alkali chlorides. On the other hand, in the present study of the binaries involving the transition-metal dichlorides and $CdCl_2$ we have found that a covalency factor b_j must be associated with each component. Since $CaCl_2$ is assumed not to include any significant covalent interactions between the ions, we would predict that the enthalpies of mixing of $CaCl_2$–M_jCl_2 systems might also be expressed by Eq. (12), with the restriction that b_{Ca} should be very small.

Let us first examine the coefficients b and c [Eq. (8)] for the considered mixtures. As we pointed out in the discussion of the RKK, DR, and Blander theories, there are at least three terms which contribute to the energetic asymmetry b:

$$b = Z U_{1a}^{+ +} \delta_{12} - Z^2 U_{2a}^{+ -} \delta_{12}^2 - 2\pi \delta_{12}^3 \quad (15)$$

while the term c is proportional to δ_{12}^4

$$c = -4\Sigma \delta_{12}^4. \quad (16)$$

The terms $\pi \delta_{12}^3$ and $\Sigma \delta_{12}^4$ are the third- and fourth-order corrections in the (RKK) conformal solution theory, and are due to long-range Coulombic interactions. From the fact that mixtures involving $CaCl_2$ and $CdCl_2$ should have Coulombic interactions of comparable magnitude ($r_{Ca}^{+ +} \simeq r_{Cd}^{+ +}$), and since the $CdCl_2$–$MnCl_2$ and $CdCl_2$–$FeCl_2$ systems show no significant asymmetry, we conclude that $\pi \delta_{12}^3$ and $\Sigma \delta_{12}^4$ terms of the RKK–Blander theory do not contribute significantly to b and c for the $CaCl_2$ binaries.

U_1 and U_2 in the Davis–Rice theory depend mainly on the differences between the anion–cation and/or cation–cation non-Coulombic interactions in each component. When the two components have cations with similar polarizabilities, ionic radii, and degrees of covalency, as is the case for the mixtures of $MnCl_2$, $FeCl_2$, $CoCl_2$ and $CdCl_2$ considered above, these differences are small and U_1 and U_2 should not contribute to the energetic asymmetry. However, since the $Ca^{+ +}$–Cl^- interaction is considered to be without significant covalent character this is not the case for the considered

$CaCl_2$ systems. In these systems the terms U_1 and U_2 are expected to reflect principally the covalent interactions in the transition-metal chloride component. The apparent linear dependence of the energetic asymmetry on δ_{12}^2 (Fig. 4) suggests that b depends mainly on U_2.

The value of c, which measures the deviation of the interaction parameter from linearity, appears to increase with increasing magnitude of λ^M. This may be attributed to short-range ordering among the next-nearest-neighbor cations in the mixture and is consistent with the earlier studies of the binary alkali nitrates and halides.[1,2]

In the light of these considerations we may express the enthalpies of mixing for the $CaCl_2$–M_jCl_2 systems as

$$\Delta H^M = X_j X_{Ca} [U_0^{+ +} - Z^2 440 \delta_{12}^2 + (b_j - b_{Ca})^2 + b X_j - c X_j X_{Ca}]. \quad (17)$$

For the limiting value of the interaction parameter at $X_j = 0$ we have:

$$\lambda_0^M = \lim_{X_j \to 0} (\Delta H^M / X_j X_{Ca}) = U_0^{+ +} - 440 Z^2 \delta_{12}^2 + (b_j - b_{Ca})^2. \quad (18)$$

Using the experimental values of λ_0^M (Table V) and the above Eq. (18) we can calculate $| b_j - b_{Ca} | = b_j - b_{Ca}$ (since $b_j > b_{Ca}$). It is worth noting that the data again are consistent with covalency increasing in the sequence $Mn < Fe < Co$. Also if our arguments presented here are valid, the values of $| b_j - b_{Ca} |$ listed in this table should allow a new evaluation of $| b_j - b_k |$ for $(Co–Fe)Cl_2$, $(Co–Mn)Cl_2$ and $(Mn–Fe)Cl_2$ through the relations

$$| b_j - b_k | = (b_j - b_{Ca}) - (b_k - b_{Ca}). \quad (19)$$
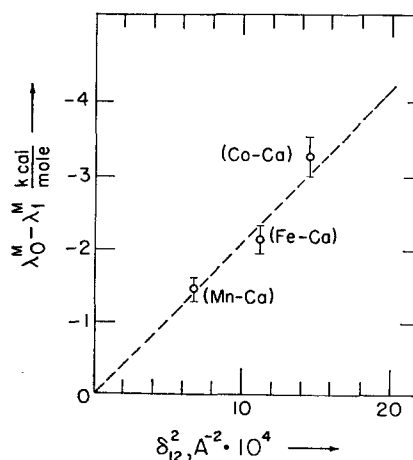
A comparison of these values with those derived pre-

FIG. 4. Plot of the energetic asymmetry parameter ($b = \lambda_0^M - \lambda_1^M$) against δ_{12}^2 for the mixture of $CaCl_2$ with $MnCl_2$, $FeCl_2$, and $CoCl_2$.

viously from the binary systems proper is given in the following:

	(Mn–Fe)	(Mn–Co)	(Fe–Co)
$\lvert b_j{-}b_k \rvert$ from the binaries proper (Table V)	9.9	23.7	13.6
$\lvert b_j{-}b_k \rvert$ from the Ca-containing system [Eq. (19)]	12.3	26.5	14.5

In view of the many uncertainties associated with the evaluations of $\lvert b_j{-}b_k \rvert$, particularly in the case of the calcium-containing systems, the agreement must be considered quite satisfactory.

D. The MgCl₂ Systems: (Mg–Mn)Cl₂, (Mg–Fe)Cl₂, (Mg–Co)Cl₂

The experimental values of the interaction parameters for the MgCl₂ binaries are given in Table IV. In the high MgCl₂ range the three interaction parameters are of very comparable magnitude, all falling in the range 300–400 cal/mole. Figure 3 shows that while λ^M for MgCl₂–MnCl₂ is essentially independent of composition, λ^M for MgCl₂–CoCl₂ and MgCl₂–FeCl₂, show increasingly positive values with increasing content of CoCl₂ and FeCl₂, respectively. These results indicate that the behavior of the MgCl₂ containing mixtures is somewhat more complex than that of the corresponding CaCl₂ systems, just as we previously found that the MgCl₂–alkaline-earth chloride systems were more complex than the corresponding binaries involving CaCl₂, SrCl₂, and BaCl₂ only.

If we use the previously estimated value of the polarizability of Mg^{++} $(\alpha_{\mathrm{Mg}^{++}}=0.4\mathrm{A}^3)$,[4] we calculate

the London–van der Waals terms $U_0{}^{++}$ for (Co–Mg)Cl₂, (Fe–Mg)Cl₂, and (Mn–Mg)Cl₂ to be 486, 351, and 391 cal/mole, respectively. Due to their strong dependence on the assumed value of $\alpha_{\mathrm{Mg}^{++}}$ these estimates are rather uncertain, and may easily be in error by $\pm$ 50% or more. On the other hand, since the negative contributions to the enthalpy due to the coulombic interactions in these systems are relatively small (Table V, Column 3), it is possible that the Coulomb and van der Waals interactions may to a first approximation fully account for the enthalpy of mixing in the (Co–Mg)Cl₂ system, but certainly not in the (Fe–Mg)Cl₂ and (Mn–Mg)Cl₂ binaries.

Let us next consider the results for the MgCl₂ systems in terms of the cyclic model advanced above, i.e., by attempting to take into account possible covalency in MgCl₂. Using Eq. (13) we have calculated the differences $b_j{-}b_{\mathrm{Mg}}$ listed in Table V. The range of values quoted principally reflects the uncertainty in $U_0{}^{++}$. While these values of $\lvert b_j{-}b_{\mathrm{Mg}} \rvert$ may not have a very quantitative significance, they nevertheless seem to indicate that b_{Mg} should have a magnitude roughly comparable to that of b_{Co}. However, the high second ionization potential of Mg would seem to place the covalency of MgCl₂ closer to that of MnCl₂ than to FeCl₂ and CoCl₂. This apparent inconsistency may possibly be resolved if we recall that the covalency parameter b_j includes contributions both from anion–cation and bridging interactions. Since the bridging interactions are very pronounced in MgCl₂,[4] the rather high value of b_{Mg} may perhaps in the main arise from these interactions.

ACKNOWLEDGMENTS