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Journal of Alloys and Compounds 321 (2001) 267–275

Journal of ALLOYS AND COMPOUNDS

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Analysis of the enthalpy of mixing data of binary and ternary [rare earth (Nd, La, Y, Yb), Al–alkali metal]–fluoride systems

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Received 5 September 2000; accepted 5 December 2000

Abstract

We analyzed the enthalpy of mixing data of several liquid [rare earth and aluminum–alkali metal] fluoride systems using the Hoch–Arpshofen solution model. We investigated the binary systems AlF_3–MF (M is Li, Na, K), (LaF_3, YF_3, YbF_3)–MF (M is Li, Na, K, Rb, Cs) and NdF_3–MF (M is Li, Na, K) and the ternary LaF_3–NaF–LiF system. We also analyzed the $LaBr_3$–MBr (M is Li, Na, K, Rb, Cs) system, to show the difference to fluoride systems. In the fluoride systems the experimental data is carried out with solid MeF_3 and thus the analysis depends on the enthalpy of fusion of the MeF_3 much below the normal melting point. In the fluoride systems the enthalpy of mixing can be represented by a regular solution; in other systems the enthalpy of mixing leans toward the alkali metal. There is a linear relationship between the maximum enthalpy of mixing and the radius of the alkali metal cation, and also the halide anion radius. In the ternary system LaF_3–NaF–LiF the enthalpy of mixing could be computed from the binary systems. The relationship between the maximum of the enthalpy of mixing and the radii of the three valent cations, the alkali cations and the halide anions is:
(a) only fluorides:

$$H_{\mathrm{m,max}}\,(\mathrm{kK}) = -(7.714\pm0.876) + (10.293\pm0.709)*r_{\mathrm{M}^{3+}} - (4.285\pm0.537)*r_{\mathrm{M}^{+}}$$
$$R = 0.9803$$

(b) all [Al, rare earth–alkali metal]–halides analyzed:

$$H_{\mathrm{m,max}}\,(\mathrm{kK}) = -(10.814\pm0.605) + (10.017\pm0.622)*r_{\mathrm{M}^{3+}} - (3.001\pm0.267)*r_{\mathrm{M}^{+}} + (1.592\pm0.337)*r_{\mathrm{L}^{-}}$$
$$R = 0.9643$$

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Keywords: Model; Enthalpy of mixing; Binary halides; Ternary halides

1. Introduction

In an earlier paper [1] we analyzed the enthalpy of mixing of several [rare earth–alkali metal]–halides (Cl, Br, J) binary systems and the NdF_3–MF system. In the fluoride system the measurements we carried out by introducing solid NdF_3 into liquid MeF and computing the enthalpy of fusion and energy used to heat the NdF_3 from room temperature to the experimental temperature. This may have introduced some uncertainty into the final enthalpy of mixing data of liquid NdF_3 and MeF. We found that the enthalpy of mixing in the binary systems (Nd,Pr,Dy,Tb)L_3–MeL the maximum of the enthalpy of mixing is given by the equation:

$$H_{\mathrm{m,max}}\,(\text{in kK}) = -(2.543\pm0.117)*r_{\mathrm{M}^{+}} + (0.855\pm0.077)*r_{\mathrm{L}^{-}}$$

where $r_{\mathrm{M}^{+}}$ is the radius of the alkali metal ion, and $r_{\mathrm{L}^{-}}$ is the radius of the halide ion. In the present paper we check the enthalpy of fusion by calculating it from the original solid–liquid data and by a general method. Hong and Kleppa [2] measured the enthalpy of mixing of aluminium fluoride with alkali fluorides and with zinc fluorides. Hatem and Gaune-Escard [3,4] measured the enthalpy of

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PII: S0925-8388(01)00962-8

mixing in the NdF_3–MF systems. Hong and Kleppa [5] measured the enthalpy of mixing of alkali fluorides with LaF_3, YF_3 and YbF_3. Abdoun et al. [6] investigated the LaF_3–MF binary systems and Abdoun [7] measured the enthalpy of mixing in the ternary system LaF_3–LiF–NaF. To show the difference between fluorides and other halide systems, we also show the $LaBr_3$–MBr systems [8].

2. The Hoch–Arpshofen model

In an earlier paper Hoch and Arpshofen [9] derived a model for binary solutions. In a subsequent paper Hoch [10] derived the model for ternary, quaternary, and larger systems. The binary model is merely a special case of the ternary model. The model is an extension of Guggenheim's [11] treatment of solutions, combined with an adaptation of Pauling's [12] ideas of the metallic bond.

Guggenheim [11], when treating regular solutions and superlattices, speaks of 'treatment of quadruplets of sites, forming regular tetrahedra' and 'triplets of sites, forming equilateral triangles.' Guggenheim [11], however, always treats the strength of the A–B bond in the same way, regardless of what other atoms are present in the complex. In our model the strength of the A–B bond depends on the number of B atoms to which the A atom bonds, or vice versa. In Pauling's [12] description of a metallic bond, the bond number is defined as the number of bonding electrons divided by the number of neighbors to which the specific atom bonds. In metallic copper, which consists of one bonding electron and 12 neighbors, the bond number is 1/12. This is a one-electron bond, which moves from one neighbor to another. In our model this idea is applied to ionic materials (ceramic) and van der Waals-type forces, in both an attractive and a repulsive mode. This idea is not extravagant because all bonds are caused by the behavior of electrons.

In a multicomponent system with the components A, B, C, D, etc. and their mole-fractions x, y, z, u, etc. the effect of the mixing function F_m (H_m, enthalpy of mixing, $G_{m_{ex}}$, excess Gibbs energy of mixing, $S_{m_{ex}}$, excess entropy of mixing) of the binary system A–B (mole-fraction x and y) in the multicomponent is

$$F_m = Wnx\left[1-(1-y)^{\{n-1\}}\right] \tag{1}$$

$$F_x = Wn\left[1-(1-y)^{\{n-1\}} - xy(n-1)(1-y)^{\{n-2\}}\right] \tag{2}$$

$$F_y = Wnx(n-1)(1-y)^{\{n-1\}} \tag{3}$$

$$F_z = F_u = -Wnxy(n-1)(1-y)^{\{n-2\}} \tag{4}$$

W is the interaction parameter; and n, the size of the complex, is an integer (2, 3, 4, etc). The term x is the mole-fraction of the component so that in Eq. (1) F_m is maximum (positive or negative) at $x>0.5$.

The excess Gibbs energy of mixing, $G_{m_{ex}}$, is a combination of H_m and $S_{m_{ex}}$. Eq. (1) can be applied to $G_{m_{ex}}$ only if $S_{m_{ex}}$ has the same n and x as H_m, or if $S_{m_{ex}}$ is zero.

Eq. (1) also applies to binary systems: In a binary system

$$x + y = 1 \tag{5}$$

In our nomenclature 3,(Al) means that n is equal to 3, and x is Al.

In the multicomponent system (A–B–C–D–etc.) the other binary systems (A–C, A–D, A–etc., B–C, B–D, B–etc., C–D, C–etc., and D–etc.) contribute similarly to the thermodynamic properties of the multicomponent system.

The partial quantities derived from Eq. (1) do not change sign in a binary system when the composition changes from $x=0$ to $x=1$ or in a large system when x changes from $x=0$ to $x=1$ and y changes from $y=0$ to $y=1$.

One major advantage of our method is that by using regression analysis, we can calculate the binary interactions from the large systems and can compare them with the values calculated from binary data.

Though we talk about 'complexes', the ideal Gibbs energy of mixing is, as in Guggenheim [3]

$$G_m^{id} = RT(x_1 \ln x_1 + x_2 \ln x_2 + x_3 \ln x_3 + \ldots) \tag{6}$$

The model was applied earlier to various binary and ternary systems [13–27]; the method of evaluation of binary phase diagrams was also shown [15–17]. To describe solid compounds that are very stable and have a wide homogeneity range, we use the Schottky–Wagner model [26] combined with activity coefficients derived by dividing the binary system into two binaries A–AB and AB–B. We refer the reader to the above publications for derivation of the model and the method of application. A great advantage of our model is, that we have never needed ternary interaction parameters. More important, we can obtain the binary interaction parameters from ternary or quaternary data by regression analysis; the latter must agree with data obtained from binary data.

The interaction parameters are designated depending on what experimental data they were calculated from: W_h from H_m enthalpy of mixing, W_s from $S_{m_{ex}}$, excess entropy of mixing, and W_g from $G_{m_{ex}}$, excess Gibbs energy of mixing.

In all of our calculations the thermodynamic quantities are divided by R, the gas constant. Thus the enthalpy H and the Gibbs energy G are expressed in kK (kiloKelvin); the entropy S and the heat capacity C_p are dimensionless.

The model always mixes metal atoms or cations, i.e. B_2O_3 is always treated as $BO_{1.5}$ and Na_2O as $NaO_{0.5}$. This obviously requires a change in composition, before the model can be applied.

In binary systems, which follow Eq. (1), the maximum (positive or negative) of G_m is at $x=(n-1)/n$, and of H_m at $x=(1/n)^{(1/(n-1))}$.

3. Difference in heat capacity between liquid and solid $C_p(L-s)$

The Gibbs energy of fusion $G(L-s)$ at temperatures below and above the melting point, and thus the calculated phase diagram is greatly influenced by the difference in heat capacity between liquid and solid $C_p(L-s)$.

The heat capacity data of solids $C_p(s)$ and liquids $C_p(L)$ of elements and compounds, where accurate data are available, can be represented by [27,28]

$$C_p(s)/R = 3F(\theta_D(s)/T) + bT + dT^3 \tag{7}$$

$$C_p(L)/R = 3F(\theta_D(L)/T) + bT + hT^{-2} \tag{8}$$

where $F(\theta_D/T)$ is the Debye function; b is the electronic contribution; and d and h are the anharmonic contributions.

In our calculations we assume that at the elevated temperatures $3F(\theta_D(s)/T)$ and $3F(\theta_D(L)/T)$ are equal.

We calculated $C_p(L-s)$ [27,28] for various materials where heat capacity or heat content data for solid and liquid are available, using Eqs. (6)–(7). Twenty-five elements and compounds, were investigated ranging from low melting Pb to high melting UO_2. For each material T_{glass}, the theoretical glass transition temperature was calculated, with $S(L-s)$ becoming zero below the melting point. At temperatures below T_{glass} this point, the glass has a somewhat higher heat capacity than the solid. The derived equation for T_{glass} provided very good agreement of calculated theoretical glass transition temperatures with experimental values where available. We also found [8], that $C_p(L-s)$ in all these cases can be represented by a linear equation over a large temperature range, and we derived equations for $G(L-s)$, the difference in Gibbs energy between liquid and solid. The equation for $G(L-s)$ depends only on the enthalpy and temperature of fusion of the material. $G(L-s)$ also passes zero once below, and once above the melting point. If one assumes that the heat capacity of the liquid is constant, or decreases with increasing temperature, and the heat capacity of the solid increases with increasing temperature, each solid will have a glass transition and a jelly transition temperature, at which the entropy of the liquid becomes less than that of the solid. We applied our method to describe the Al–Ca and Ca–Pb phase diagrams [22]. The equation for $G(L-s)$ showed that in the Al–Ca phase diagram on the Ca side a repulsive term had to be included in the thermodynamic description.

The equation for $C_p(L-s)$ was found to be [29]:

$$C_p(L-s)/R = e + fT; \text{ per atom, with}$$

$$e/T_{mp} = (7\pm3) \text{ and } (e/T_{mp})/f = -(1.081\pm0.186),$$

T_{mp}, the standard melting point, in kK (kiloKelvin).

The uncertainty in the two terms is large: however we have a check because at T_{glass} the value of $G(L-s)$ is a maximum [27]. Thus we use the equations

$$e/T_{mp} = (7\pm p^*3) \tag{9}$$

$$(e/T_{mp})/f = -(1.081\pm p^*0.186) \tag{10}$$

and we adjust p so that the above condition is met. T_{glass} is given by [27]

$$(T_{glass}/T_{mp}) = 0.4018 + 0.0853^*T_{mp} \tag{11}$$

4. Results

In treating the rare earth chlorides, bromides and iodides [8], the rare earth compound was added in liquid form to the halide solution. Thus the interaction parameter was obtained directly from the measured enthalpy values. In the case of the fluorides, the rare earth compounds are added to the liquid halides in solid form. Thus the enthalpy of fusion of the rare earth fluoride at the temperature of the experiment is required, if the rare earth fluoride is preheated to the experimental temperature. This process is the ‘indirect method’. In the direct method the rare earth compound is added at room temperature and thus in addition to the enthalpy of fusion the enthalpy difference between room temperature and the experimental temperature is needed. In either case, the enthalpy of mixing of liquid rare earth and alkali metal fluoride is obtained by the difference of two large numbers, giving a relatively small number, with large uncertainty. If the experiment is carried out at 1200 K, the enthalpy increment between 300 and 1200 K is estimated by taking $C_p/(R^*\text{atom})=3$ the high temperature Debye value as $(H_{1200}-H_{300})/\mathrm{R}=10.8$ kK, the enthalpy of fusion, e.g. LaF_3 (see Table 2) 6.8 kK. The maximum enthalpy of mixing is -5 kK at $x,MF_3=0.5$. Thus one measures $8.8-5=3.8$ kK, from which one must subtract 8.8 kK to obtain the required enthalpy of mixing. Thus the uncertainty in H_{mix}, the enthalpy of mixing is great. To avoid these uncertainties, we first looked at the H_{mix} values obtained by the authors. All data could be represented by $n=2$ in our formulas (Eqs. (2)–(4)). To avoid using the enthalpy of fusion and the heat up data we use the following equation:

$$H_{m,meas} = x\mathrm{MeF}_3^*H_{corr} + H_m(L-L) \tag{12}$$

$$H_{m,meas} = x\mathrm{MeF}_3^*H_{corr} + Wnx\left[1-(1-y)^{\{n-1\}}\right] \tag{13}$$

$$H_{m,meas} = x\mathrm{MeF}_3^*H_{corr} + W2x[1-x] \tag{14}$$

$H_{m,meas}$ is the solid–liquid enthalpy of mixing measured, if the original solid–liquid data are available [2,5]. H_{corr} is then the enthalpy of fusion at the experimental temperature. Thus we avoid using data from other sources. If only the calculated liquid–liquid data are available [3,4,6], H_{corr} is the correction term to obtain W, the interaction parameter

Table 1
Temperature, enthalpy and entropy of fusion and temperature of transformation of rare earth fluorides

Compound	Kubaschewski et al. [30]			Spedding et al. [33,34]			
	T (K)	H (kK)	S/atom	T (K)	H (kK)	±	S/atom
LaF_3				950			
LaF_3	1766	6.038	0.855	1766	6.004	0.050	0.850
NdF_3	1650	6.591	0.999	1650	6.580	0.050	0.997
YF_3	1350	3.897	0.722	1350	3.900	0.050	0.722
	1428	3.356	0.587	1428	3.364	0.050	0.589
Sum		7.253	1.308		7.265		1.311
YbF_3				1259	2.964	0.050	0.589
				1435	3.576	0.050	0.623
Sum					6.540		1.212

with the smallest uncertainty. Eq. (14) is solved by regression analysis.

Table 1 contains the the thermodynamic data of the rare earth fluorides. Barin [31] gives the same values as Kubaschewski et al. [30]. Spedding and Henderson [33] show two equations for the enthalpy of solid LaF_3, but the data does not show even a break in the $(H_T - H_{298})$ curve. The enthalpy of fusion of LaF_3 seems too low, as S_{fus}/(R*atom) should be equal to 1 or somewhat higher.

Fig. 1 shows the enthalpy of mixing in the binary systems $LaBr_3$–MBr from Gaune-Escard [8]. Here in the original measurements liquid $LaBr_3$ is introduced into liquid MBr. The data squatter somewhat, but the model for all system is 3,(MBr).

Fig. 2 shows the interaction parameters W and the maximum (in absolute terms) of the enthalpy of mixing, $H_{m,max}$ as a function of the radii of the alkali ions from Fig. 2. In spite of the scatter of the data in Fig. 1, W and $H_{m,max}$ fall on straight lines. The equation for W and the relation between W and $H_{m,max}$ is given at the bottom of Fig. 3. If no H_{fus} and $(H_T - H_{300})$/R are needed, the resulting data are much more reliable. The radii of the ions was taken from the Handbook [32].

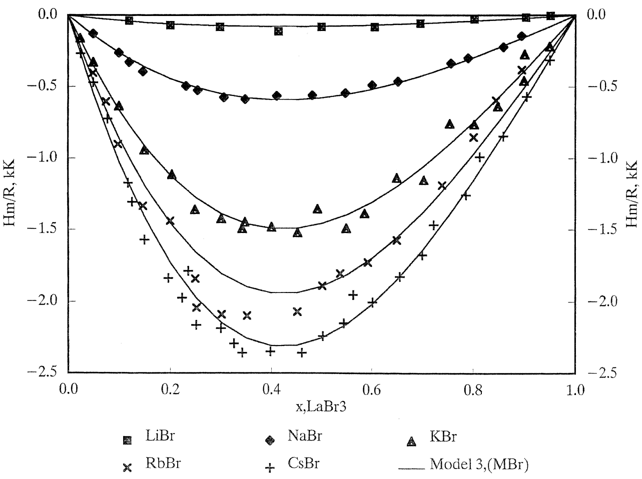


Fig. 1. Enthalpy of mixing in the binary liquid $LaBr_3$–MBr systems. Exp. data [8]. ■, LiBr; ♦, NaBr; △, KBr; ×, RbBr; +, CsBr; and —, Model 3,(MBr).

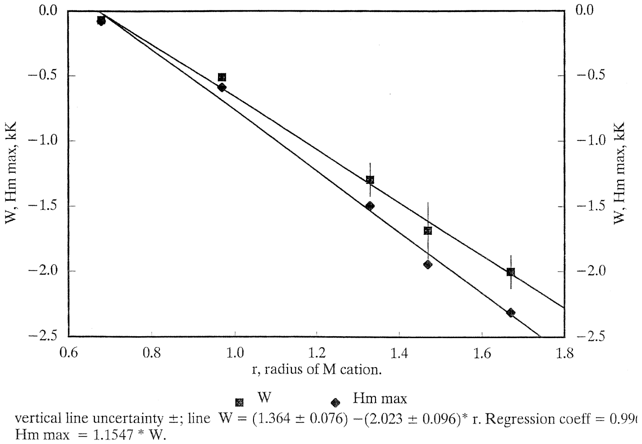


Fig. 2. Interaction parameters W and maximum enthalpy of mixing $H_{m,max}$ in the liquid binary system $LaBr_3$–MBr. ■, W; ♦, $H_{m,max}$; ±, vertical line uncertainty; line $W = (1.364 \pm 0.076) - (2.023 \pm 0.096)*r$. Regression coeff = 0.99; $H_{m,max} = 1.1547*W$.

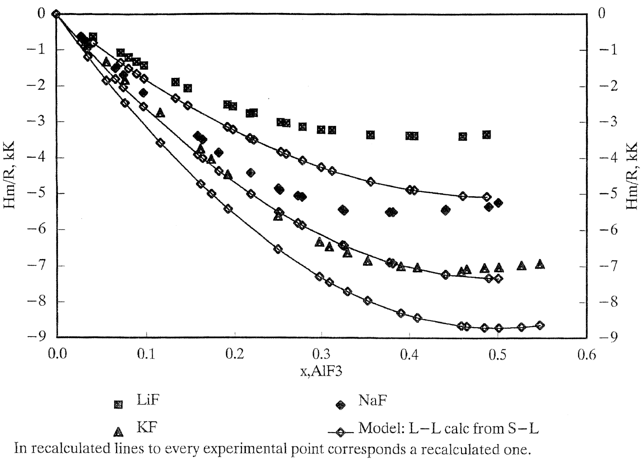


Fig. 3. Enthalpy of mixing in the binary systems AlF_3–MF. L–L data [2] with H_{fus} 13.976 kK. Model: L–L and H_{fus} calculated from S–L data. ■, LiF; ♦, NaF; ▲, KF; and –◇–, Model: L–L calculated from S–L. In recalculated lines to every experimental point corresponds a recalculated one.

Fig. 3 presents the enthalpy of mixing in the AlF_3–MF binary systems [2]. Hong and Kleppa [2] evaluated the enthalpy of fusion of AlF_3 at 1298 K as 13.976 kK. We went back to the original $S-L$ (solid–liquid) measurements and reevaluated the data with Eq. (14). Our enthalpy of fusion of AlF_3 is significantly larger than the value of Hong and Kleppa [2], but the uncertainty in W is smaller, as given in Table 2.

Fig. 4 shows the NdF_3–MF binary systems [3,4]. As one can see, the original and recalculated data coincide. The NdF_3–KF experiment were carried out at different temperatures (Table 2, 1.197–1.430 kK). Both the original and recalculated values of W change in a random fashion with temperature but the average values are the same. It is suprising, that the H_{corr} values vary so much (from -1.050 to 1.447 kK), indicating a relatively large scatter in the experimental data.

Fig. 5 presents the YF_3–MF binary data [5]. The reevaluated data are in good agreement with the original liquid–liquid data; one has to keep in mind that the original S–L data are presented only in the form of an equation. The graphs in our figures only go to the composition to which the experimental data extend. The enthalpy of fusion calcuted using Eqs. (7)–(11) agree with the original and recalculated values.

Fig. 6 presents the YbF_3–MF binary data [5]. The reevaluated data are in less good agreement compared to the YF_3–MF systems in Fig. 5.

Table 2
Interaction parameters W and enthalpy of fusion H_{fus} of liquid [Rare earth–Alkali metal]–Fluoride binary systems studied[a]

Binary system	W (kK)	±	H_{fus} (kK)	±	Refs.	This research			
						W (kK)	±	H_{fus} (kK)	±
AlF_3–LiF	-7.760	0.474	13.974	0.126	[2]	-10.154	0.311	17.494	0.392
AlF_3–NaF	-12.105	0.753				-14.649	0.322		
AlF_3–KF	-14.113	0.830				-17.434	0.347		
YF_3–LiF	-1.791	0.017	3.316	0.126	[5]	-1.803	0.000	3.185	0.000
YF_3–NaF	-4.190	0.289				-3.890	0.211	3.280	0.125
YF_3–KF	-7.240	0.288				-8.118	0.220	4.003	0.157
Average								3.489	0.094
Calc Eqs. (7)–(11)								3.151	
YbF_3–LiF	-2.261	0.008	3.573	0.010	[5]	-2.271	0.000	4.567	0.000
YbF_3–NaF	-4.781	0.233				-5.089	0.156	3.979	0.149
YbF_3–KF	-7.720	0.482				-8.820	0.260	4.703	0.249
Average								4.416	0.133
Calc Eqs. (7)–(11)								3.337	
LaF_3–LiF	-0.708	0.000	6.880	0.120	[5]	-0.709	0.000	6.702	0.000
LaF_3–NaF	-2.424	0.158				-2.797	0.002	7.064	0.002
LaF_3–KF	-3.470	0.558				-4.063	0.031	6.521	0.031
Average								6.762	0.226
Calc Eqs. (7)–(11)								4.005	
			T (kK)					H_{corr}	
NdF_3–LiF	-1.028	0.118	1.223		[3]	-1.024	0.044	0.005	0.065
NdF_3–NaF	-2.956	0.170	1.323			-3.128	0.304	0.558	0.499
NdF_3–KF	-4.619	0.266	1.197			-4.036	0.206	-1.050	0.290
NdF_3–KF	-4.798	0.170	1.223			-5.630	0.663	1.447	1.087
NdF_3–KF	-4.716	0.079	1.415			-4.550	0.242	-0.178	0.259
NdF_3–KF	-4.937	0.215	1.430			-4.898	0.412	-0.037	0.427
Average KF	-4.768	0.117				-4.779	0.579		
Average								0.124	0.438
LaF_3–LiF	-0.703	0.032	1.143		[6]	-0.562	0.464	-0.255	0.797
LaF_3–LiF	-0.707	0.028	1.183			-0.521	0.459	-0.329	0.757
LaF_3–LiF	Ternary regression					-0.564	0.014		
LaF_3–NaF	-2.520	0.095	1.183			-2.762	0.180	0.379	0.263
LaF_3–NaF	-3.482	0.958	1.089			Partial NaF measurements			
LaF_3–NaF	-2.148	0.105	1.089			Partial LaF_3 measurements			
LaF_3–NaF	Ternary regression					-2.600	0.031		
LaF_3–KF									
LaF_3–RbF	-4.408	0.177	1.098			-3.371	0.100	-1.497	0.137
LaF_3–CsF	-4.378	0.103	1.046			-4.937	0.471	0.940	0.805
Average								-0.154	
NaF–LiF	-0.489	0.022			[9]	Binary measurements			
NaF–LiF	-0.445	0.004			[31]	Phase diagram			
NaF–LiF	-0.485	0.007			[9]	Ternary regression			

[a] $n=2$ in all systems, $H_{m,max}=0.5*W$. Regression coefficient in the ternary regression $R=0.9978$.

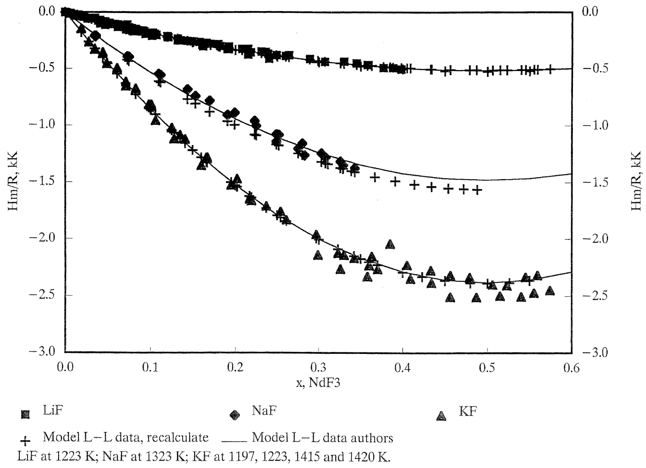


Fig. 4. Enthalpy of mixing of the liquid binary systems NdF$_3$–MF. Exp data [3,4]. ■, LiF; ♦, NaF; ▲, KF; +, Model *L–L* data, recalculate; —, Model *L–L* data authors. LiF at 1223 K; NaF at 1323 K; KF at 1197, 1223, 1415 and 1420 K.

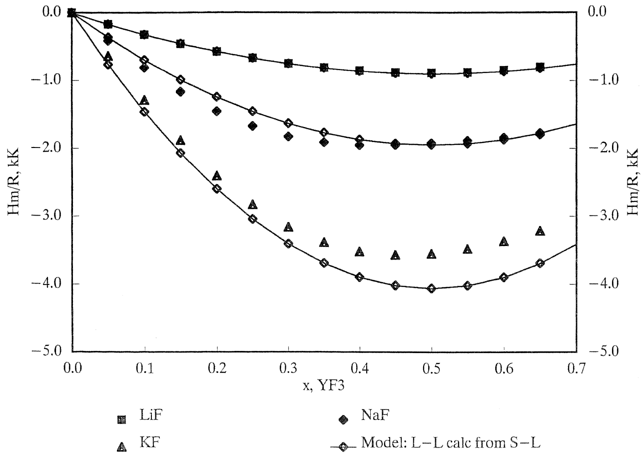


Fig. 5. Enthalpy of mixing in the liquid binary systems YF$_3$–MeF. (*L–L*) data [5]. Model: *L–L* and H_{fus} calculated from *S–L* data. ■, LiF; ♦, NaF; ▲, KF; and – ◇ –, Model *L–L* calc. from *S–L*.

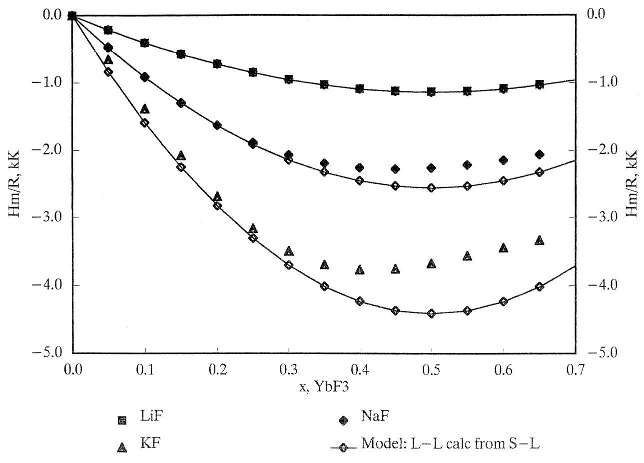


Fig. 6. Enthalpy of mixing in the binary liquid systems YbF$_3$–MF. *L–L* data [5]. Model: *L–L* calc. from *S–L* data with H_{fus} calculated. ■, LiF; ♦, NaF; ▲, and – ◇ –, Model *L–L* calc. from *S–L*.

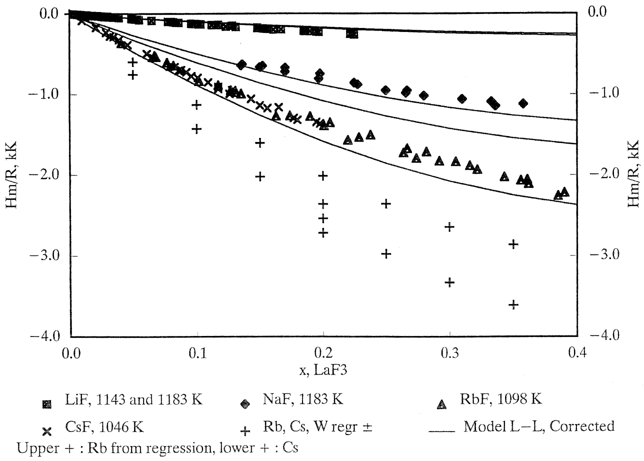


Fig. 7. Enthalpy of mixing of LaF$_3$–MF liquid systems. Liquid–liquid data from [6]. Model: using liquid–liquid data from authors, and calculate *L–L* data and H_{corr}. ■, LiF, 1143 and 1183 K; ♦, NaF, 1183 K; ▲, RbF, 1098 K; ×, CsF, 1046 K; +, Rb, Cs, W regr.±; —, Model *L–L*, corrected. Upper +: Rb from regression, lower +: Cs.

Fig. 7 shows the enthalpy of mixing data in the LaF$_3$–MF system of Hong and Kleppa [5]. There is no great difference between the original and recalculated data. Hong and Kleppa [5] mentioned that the KF used was less pure than LiF and NaF. This may explain the larger difference between the two *W*'s, keeping in mind that in the LaF$_3$ systems the interaction parameters are much smaller that in the YF$_3$ and YbF$_3$ systems.

The enthalpy of fusion at 1360 K calculated using Eqs. (7)–(11) is much too small, due to the small entropy of fusion of LaF$_3$ in Table 1, and mentioned above.

Fig. 8 presents the data of Abdoun et al. [6] of the LaF$_3$–MF binary systems. The original data with RbF and CsF coincide. The recalculated data separates these two sets. We cannot understand the large difference between the original and recalculated values.

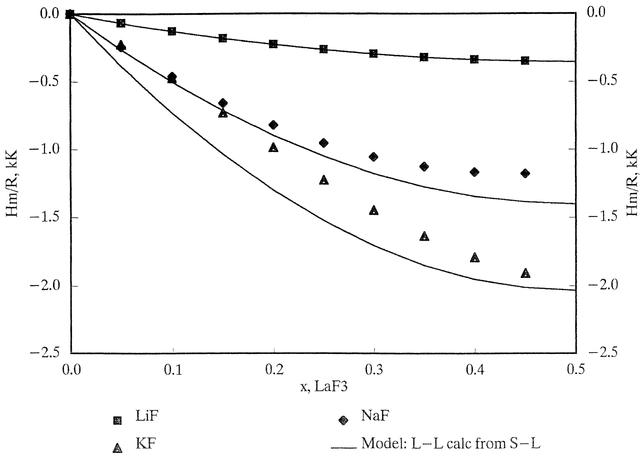


Fig. 8. Enthalpy of mixing in the liquid binary systems LaF$_3$–MF. Liquid–liquid data from [5]. Model: *L–L* and H_{fus} calculated from *S–L* data. ■, LiF; ♦, NaF; ▲, KF; and —, Model *L–L* calc. from *S–L*.

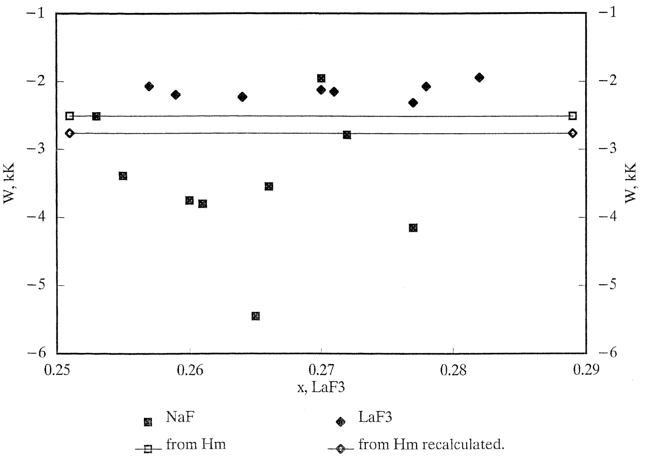


Fig. 9. Interaction parameter in liquid NaF–LaF_3 solutions at 1183 K calculated from partial enthalpies of NaF and LaF_3 and enthalpies of mixing [6]. ■, NaF; ♦, LaF_3; –□–, from H_m; and –◇–, from H_m recalc.

Fig. 9 gives the interaction parameter W in the binary system LaF_3–NaF calculated from the partial enthalpies of LaF_3 and NaF at 1183 K [6]. The composition range is very narrow, and close to pure NaF, thus the partial data of NaF are very small. The NaF data scatter significantly, the LaF_3 data are practically constant. The graph also shows the value of W obtained from the integral enthalpy measurements (Fig. 8) and also from the recalculated values.

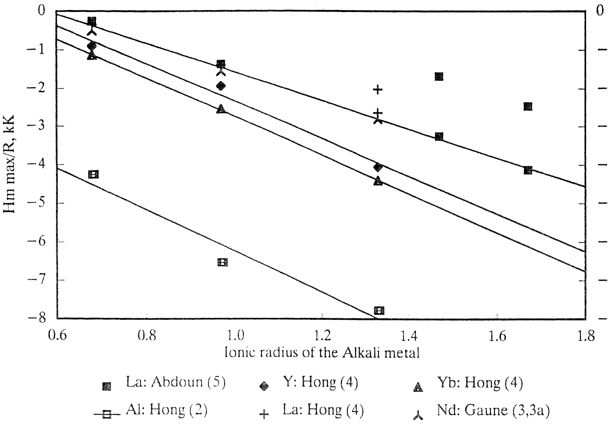
Fig. 10 shows the maximum enthalpies of mixing as a function of r_{M^+}, the alkali metal cation radius for all systems studied. The AlF_3, YF_3 and YbF_3 lines are for practical purposes parallel. The LaF_3 and NdF_3 lines have a smaller slope. The La^{3+} and Nd^{3+} radii are larger than the other three, the Al^{3+} being the smallest. The LaF_3–KF data of Hong and Kleppa [5] and the LaF_3–RbF and LaF_3–CsF data of Abdoun et al. [6] upper points are too small. The lower, more negative points are from the equation described below using fluorides only. As mentioned earlier the radii of the ions was taken from the Handbook [32].

Fig. 11 presents the data maximum enthalpies of mixing as a function of r_{L^-}, the halide anion radius for all systems studied. We have only one point each for RbF and CsF. The LiF, NaF and KF points all fall on straight lines, which are almost parallel. The types of lines are described in detail later.

Fig. 12 gives the enthalpy of mixing for the liquid LiF–NaF binary system from direct measurements [6], and from the phase diagram of Sangster and Pelton [35]. The values of W agree. In the ternary calculation in Fig. 13, we use the results from the direct measurements.

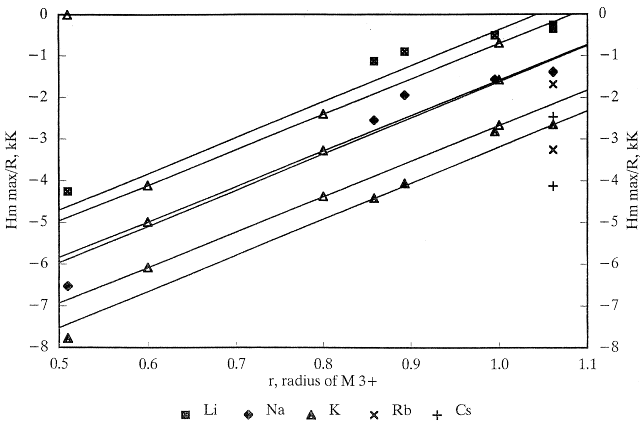
Fig. 13 presents ternary enthalpy of mixing measurements from Abdoun [7] and calculated curves from the binary data summarized in Table 2. In this evaluation we used W calculated from the original data. The agreement between measured and calculated data is excellent. Looking closer to the data with fixed LiF/NaF ratio, we see that the calculated curves fall below the experimental points close to $x,LaF_3 = 0$. We put in two points very close to $x,LaF_3 = 0$ using the recalculated value of W for the binary system LaF_3–LiF. The experimental points seem to reach these values. A regression analysis of the ternary data also gives binary values of W which are in agreement with the recalculated values for the LaF_3–MF systems and agree extremely well with the measurement of the binary LiF–NaF system. The regression coefficient for the ternary analysis is $R = 0.9978$.

Table 2 presents the interaction parameters in the liquid



With two values For LaF3 at K, Rb, Cs upper values are the original ones the lower ones calculated from the fluoride equation.

Fig. 10. Maximum enthalpy of mixing in the liquid systems [rare earth–alkali]–fluorides. AlF_3, LaF_3, YF_3, YbF_3, NdF_3. ■, La: Abdoun [6]; ♦, Y: Hong [5]; ▲, Yb: Hong [5]; –□–, Al: Hong [2]; +, La: Hong [5]; and an upside down Y, Nd: Gaune [3,4]. With two values for LaF_3 at K, Rb, Cs upper values are the original ones the lower ones are calculated from the fluoride equation.



The lower points for Rb and Cs are from the regression analysis.
Smooth lines regression data fluorides only. Lines with triangles at 0.6, 0.8 and 1 all halide data.

Fig. 11. Maximum enthalpy of mixing in the binary systems MF_3–LF. M^{3+} is Al, La, Nd, Y, Yb. ■, Li; ♦, Na; △, K; ×, Rb; and +, Cs. The lower points for Rb and Cs are from the regression analysis. Smooth lines regression data fluorides only. Lines with triangles at 0.6, 0.8 and 1 all halide data.

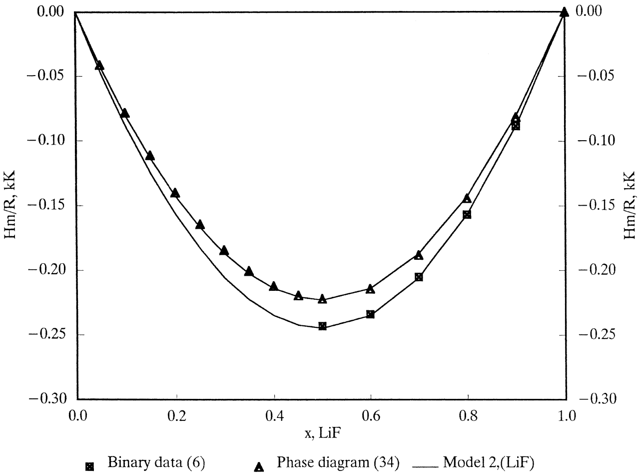


Fig. 12. Enthalpy of mixing in the ternary system LiF–LaF_3–NaF at 1186 K. Exp data [6]. Parameter is the x,LiF/x, NaF resp. the x,LiF/x,LaF_3 ratio.

binary systems MF_3–MF calculated from the liquid–liquid data of the original authors and the recalculated data.

For the data of Hong and Kleppa [2,5], the first two columns contain the trivalent and alkali metal, the third and fourth the interaction parameters obtained from the liquid–liquid data of the authors, the fifth and sixth the enthalpy of fusion used at the experimental temperature the seventh the reference, the eigth to eleventh the recalculated values of W and H_{fus} using Eq. (14).

For the data of Hatem and Gaune-Escard [3,4] and Abdoun et al. [6] the first two columns contain the trivalent and alkali metal, the third and fourth the interaction parameters obtained from the liquid–liquid data of the authors, the fifth the temperature of measurements the sixth the reference the seventh to tenth the recalculated values of W and H_{corr} using Eq. (14). In some cases the original and recalculated values agree, in others there is a significant difference.

Table 3 gives the equations for the maximum enthalpy of mixing calculated from (a) the fluorides studied in this paper, and (b) from the fluorides and the other [rare earth–alkali metal]–halides. $r_{M^{3+}}$ is the radius of the rare earth and Al cation, $r_{M^{+}}$ is the radius of the alkali cation, and $r_{L^{-}}$ is the radius of the halide anion. The regression coefficients R are acceptable. The two equations are represented in Fig. 11. The agreement between the two equations is good.

Table 3
Equations for $H_{m,max}$, maximum enthalpy of mixing, in [Al, rare earth–alkali metal]–halides studied

Fluorides only

$$H_{m,max}\ (\mathrm{kK}) = -(7.714\pm0.876) + (10.293\pm0.709)*r_{M^{3+}} - (4.285\pm0.537)*r_{M^{+}}$$

$R = 0.9803$

Al [rare earth–alkali metal]–halides studied

$$H_{m,max}\ (\mathrm{kK}) = -(10.814\pm0.605) + (10.017\pm0.622)*r_{M^{3+}} - (3.001\pm0.267)*r_{M^{+}} + (1.592\pm0.337)*r_{L^{-}}$$

$R = 0.9643$

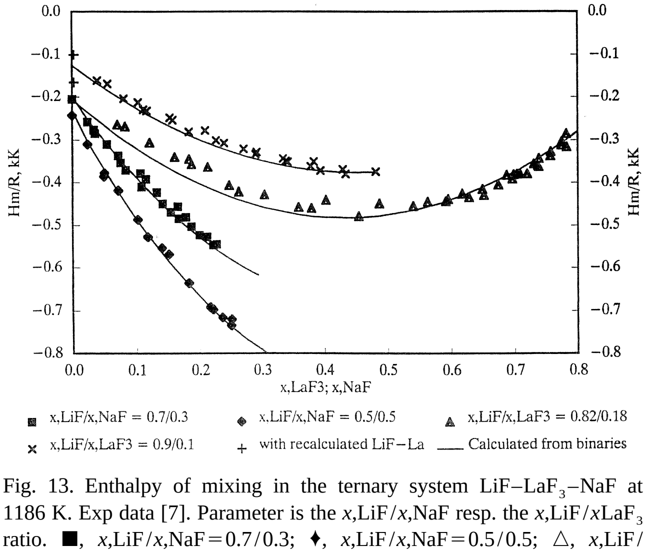


Fig. 13. Enthalpy of mixing in the ternary system LiF–LaF_3–NaF at 1186 K. Exp data [7]. Parameter is the x,LiF/x,NaF resp. the x,LiF/$x$$LaF_3$ ratio. ■, x,LiF/x,NaF = 0.7/0.3; ♦, x,LiF/x,NaF = 0.5/0.5; △, x,LiF/x,LaF_3 = 0.82/0.18; ×, x,LiF/x,LaF_3 = 0.9/0.1; +, with recalculated LiF–La; and —, calculated from binaries.

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