The Molar Volumes and the Surface Tensions of Melts in the Systems $\text{CaF}_2\text{-MF}$ ($M\text{:Li, Na}$) and $\text{CaF}_2\text{-MF}_2$ ($M\text{:Mg, Sr, Ba}$)

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(Received on June 21, 1989; accepted in the final form on November 17, 1989)

Surface tension and density of molten CaF_2 -based binary system were measured. From the measurement, the following results were obtained.

(1) Molar volumes of the melts in the systems $\text{CaF}_2\text{-NaF}$, and $\text{CaF}_2\text{-BaF}_2$ are deviated positively from the additive rule, while for $\text{CaF}_2\text{-LiF}$ and $\text{CaF}_2\text{-MgF}_2$ melts negative deviation from the additive rule on volume is found, but $\text{CaF}_2\text{-SrF}_2$ melt behaves ideally on volume.

(2) Surface tensions of the melts in the binary systems can be expressed by Guggenheim's equation for regular solution, if a suitable interaction energy ω of each binary system is selected.

(3) The interaction energy ω , estimated from surface tension of binary fluoride systems, is related to the excess volume on mixing for $\text{CaF}_2\text{-M}_x\text{F}_2$ equi-molar composition ($x=1$ for divalent and $x=2$ for monovalent fluoride).

(4) Liquidus lines for the systems, calculated from the interaction energy ω in combination with the thermochemical data are fairly in good agreement with those reported, but that for $\text{CaF}_2\text{-NaF}$ system is exceptional.

(5) Surface tensions of binary fluoride melts are strongly depended on packing density of fluorine ions on the surface.

KEY WORDS: surface tension; molar volume; calcium fluoride; binary fluoride; melt; regular solution.

1. Introduction

Currently, alkaline metal and alkali-earth metal fluorides are used as additives or main components of pyrometallurgical slags and fluxes. Janz and co-workers have already published the collective works related to the physicochemical properties of pure fluorides and the mixtures.^{1,2)} However, there are not so many works on the properties of alkali-earth metal fluoride based melts, which are especially important for pyrometallurgists. In the preceding paper,³⁾ authors have reported on the densities and the surface tensions of pure fluoride melts. In the present work, the surface tensions and the densities of CaF_2 -based binary fluorides are measured. From the results, the thermodynamic properties of the melts were discussed.

2. Experimental Procedure

The measurements of the densities and the surface tensions were carried out under a purified argon atmosphere, using the Archimedean method and the maximum bubble pressure method, respectively. The experimental details are already described in the preceding paper.³⁾ Fluorides used in the present work are shown in Table 1. All of samples were provided by mixing of pure fluorides which were heated to 180°C under vacuum for the dehydration before use.

The major source of experimental errors on the density determinations and the contributions to the

error are listed below.

Factor	Error in determination	Error in density
Temperature measurement	$< \pm 2^\circ\text{C}$	$< \pm 0.04\%$
Volumes of bobs	$< \pm 2 \times 10^{-4} \text{ cm}^3$	$< \pm 0.04\%$
Composition of mixture	$< \pm 0.1 \text{ mass}\%$	$< \pm 0.05\%$
Buoyancy measurement	$< \pm 1 \text{ mg}$	$< \pm 0.08\%$
Total		$< \pm 0.21\%$

On the other hand, the errors on the measurement of the surface tension are shown in the table below.

Factor	Error in determination	Error in surface tension
Temperature measurement	$< \pm 2^\circ\text{C}$	$< \pm 0.07\%$
Capillary radius	$< \pm 0.005 \text{ mm}$	$< \pm 0.93\%$
Composition of mixture	$< \pm 0.1 \text{ mass}\%$	$< \pm 0.02\%$
Pressure measurement	$< \pm 0.12 \text{ mmAq}$	$< \pm 0.16\%$
Total		$< \pm 1.18\%$

The major error is from the determination of the radius of the capillary tube.

3. Results

The densities and the surface tensions of CaF_2 -

Table 1. Fluorides used.

Fluoride	Impurities (max. wt%)					Purity (%)
	Cl ⁻	SO ₄ ²⁻	Pb	Fe	HF	
CaF ₂	0.012	0.02	0.02	0.01		>99.0
	0.03	0.05	0.005	0.005		>98.0
MgF ₂	0.01	0.05	0.002	0.01		>98.0
BaF ₂	0.004		0.001	0.0005	Ca: 0.01	>99.5
SrF ₂	0.005	0.02	0.002	0.0010	0.005	>97.1
NaF	0.004	0.001	0.0005	0.00045	0.07	>99.2
LiF	0.002	0.02	0.002	0.0018		>98.2

Table 2. Densities of CaF₂-based binary fluoride melts.

System	$\rho = a - b \times 10^{-3} T$ (g/cm ³)		$\rho_{1823 K}$ (g/cm ³)	Temperature (K)
	a	b		
CaF ₂	3.299	0.445	2.488	1 714-1 859
CaF ₂ -10mol%MgF ₂	3.322	0.461	2.482	1 673-1 853
CaF ₂ -30mol%MgF ₂	3.273	0.446	2.460	1 672-1 853
CaF ₂ -50mol%MgF ₂	3.312	0.483	2.431	1 670-1 854
CaF ₂ -60mol%MgF ₂	3.287	0.482	2.408	1 673-1 853
CaF ₂ -80mol%MgF ₂	3.199	0.454	2.371	1 673-1 859
MgF ₂	3.057	0.400	2.328	1 673-1 853
CaF ₂ -25mol%BaF ₂	3.930	0.540	2.946*	1 579-1 774
CaF ₂ -50mol%BaF ₂	4.647	0.720	3.334*	1 373-1 573
CaF ₂ -75mol%BaF ₂	5.074	0.774	3.663*	1 465-1 677
BaF ₂	5.682	0.946	3.957	1 623-1 823
CaF ₂ -50mol%SrF ₂	3.998	0.554	2.988	1 667-1 823
SrF ₂	4.611	0.650	3.426	1 723-1 823
CaF ₂ -10mol%NaF	3.194	0.434	2.403*	1 573-1 773
CaF ₂ -30mol%NaF	3.243	0.548	2.244*	1 423-1 573
CaF ₂ -50mol%NaF	3.073	0.548	2.074*	1 323-1 503
CaF ₂ -75mol%NaF	2.941	0.606	1.836*	1 173-1 323
NaF	2.769	0.646	1.591*	1 273-1 473
CaF ₂ -50mol%LiF	3.088	0.520	2.140*	1 370-1 573
LiF	2.301	0.454	1.473*	1 171-1 375

* Extrapolated

based binary melts are listed in Tables 2 and 3, respectively. There are not so many available data on the density and the surface tension of binary fluorides. Fig. 1 shows the densities of melts in the system CaF₂-LiF at 1 077°C reported by Porter and Meaker^{4,5)} using the Archimedeian method in comparison with those obtained in the present work. Porter and Meaker measured the densities of various binary fluoride melts such as CaF₂-LiF, KF-MF₃ (M: La, Sm, Y), LiF-MF₃, NaF-MF₃, etc.^{4,5)} but their values of pure fluoride melts are lower than those accepted generally as shown in the preceding paper.³⁾ They used a single bob to measure the buoyancy, and then their results are affected by surface tension working on a suspension wire of the bob. Fig. 2 shows the densities of molten CaF₂-NaF system at 1 117°C reported by Abramov and Kozunov⁶⁾ using the same method as in the present work. The accordance is fairly good.

On the surface tension, Mellors and Senderoff⁷⁾ measured for binary alkaline metal fluoride melts, but the surface tensions of alkaline metal-alkali earth

Table 3. Surface tensions of CaF₂-based binary fluoride melts.

System	$\gamma = a - b \times 10^{-2} T$ (dyn/cm)		$\gamma_{1823 K}$ (dyn/cm)	Temperature (K)
	a	b		
CaF ₂	459.0	9.56	284.7	1 724-1 895
CaF ₂ -10mol%MgF ₂	437.1	8.61	280.1	1 681-1 848
CaF ₂ -30mol%MgF ₂	442.7	9.66	266.6	1 681-1 851
CaF ₂ -50mol%MgF ₂	389.2	7.44	253.6	1 673-1 853
CaF ₂ -60mol%MgF ₂	374.4	7.07	245.5	1 678-1 848
CaF ₂ -80mol%MgF ₂	345.9	6.05	235.6	1 681-1 854
MgF ₂	304.5	4.85	216.1	1 683-1 856
CaF ₂ -25mol%BaF ₂	433.7	9.51	260.3*	1 577-1 772
CaF ₂ -50mol%BaF ₂	407.7	9.29	238.3*	1 415-1 578
CaF ₂ -75mol%BaF ₂	399.0	9.45	226.7*	1 477-1 674
BaF ₂	372.9	8.68	214.7*	1 656-1 809
CaF ₂ -50mol%SrF ₂	424.1	8.30	272.8	1 681-1 827
SrF ₂	427.4	9.16	260.4	1 722-1 827
CaF ₂ -10mol%NaF	437.6	9.80	258.9*	1 616-1 746
CaF ₂ -30mol%NaF	377.9	9.07	212.6*	1 462-1 567
CaF ₂ -50mol%NaF	355.6	9.79	177.1*	1 327-1 484
CaF ₂ -75mol%NaF	333.9	9.97	152.1*	1 187-1 379
NaF	325.6	11.20	121.4*	1 326-1 470
CaF ₂ -50mol%LiF	398.2	9.65	222.3*	1 378-1 579
LiF	336.3	9.44	164.2*	1 193-1 389

* Extrapolated

Fig. 1. Density in the system CaF₂-LiF at 1 077°C. Fig. 2. Density in the system CaF₂-NaF at 1 117°C.

metal fluoride melts are not reported yet.

4. Discussion

4.1. The Molar Volume of Binary Fluorides

The molar volume of a binary fluoride melt is

generally defined as follows,

$$V_M = (M_1X_1 + M_2X_2)/\rho \quad \text{.....(1)}$$

where, ρ : density of the melt

X_1, X_2 : molar fractions of components 1 and 2, whose molecular weight are M_1 and M_2 , respectively.

If the melt behaves as an ideal solution, the volume change on mixing is equal to be zero. However, in the case of non-ideal solution, the volume change on mixing ΔV_M , will be observed. The excess volume ΔV_M can be calculated by the following equation.

$$\Delta V_M = V_M - (V_{M_1}^\circ X_1 + V_{M_2}^\circ X_2) \quad \text{.....(2)}$$

Suffix $^\circ$ denotes the pure component.

Fig. 3 shows the molar volumes of CaF_2 -based binary melts at 1550°C. For melts in the systems CaF_2 - Na_2F_2 and CaF_2 - BaF_2 , a positive deviation is observed, while a negative deviation is found for CaF_2 - Li_2F_2 and CaF_2 - MgF_2 systems. For the regular solution, it is known that the heat of mixing can be described by the equation as $\Delta H_M = \omega X_1 \cdot X_2$ (ω : interaction energy) and hence it is assumed that the excess volume ΔV_M on mixing can be shown by Eq. (3).

$$\Delta V_M = K \cdot X_1 \cdot X_2 \quad \text{.....(3)}$$

where, K : a constant.

On assumption of Eq. (3), best fit values of K and the excess volume ΔV_M for each CaF_2 -based binary system at 1550°C are computed and listed in Table 4.

In metallic melts,⁸⁾ the excess volume on mixing

Fig. 3. Molar volumes of CaF_2 - $M_x\text{F}_2$ melts at 1550°C.

Table 4. The value K in Eq. (3), excess molar volume ΔV_M and enthalpy change of mixing ΔH_{vol} for CaF_2 - $M_x\text{F}_2$ equimolar melts at 1550°C.

Melt	K	ΔV_M (cm ³ /mol)	ΔH_{vol} (cal/mol)
CaF_2 - MgF_2	-0.84	-0.21	-180
CaF_2 - SrF_2	0.24	0.06	60
CaF_2 - BaF_2	0.64	0.16	160
CaF_2 - Li_2F_2	-1.12	-0.28	-300
CaF_2 - Na_2F_2	0.88	0.22	200

ΔV_M is related with entropy change and enthalpy change of mixing ΔS_{vol} , and ΔH_{vol} as follows,

$$\Delta S_{\text{vol}} = (\alpha/\beta) \cdot \Delta V_M \quad \text{.....(4)}$$

$$\Delta H_{\text{vol}} = T \cdot (\alpha/\beta) \cdot \Delta V_M \quad \text{.....(5)}$$

where, α : the thermal expansivity

β : the isothermal compressibility.

On the above calculation, it is assumed that the values of α and β for equimolar melts are equal to the mean values of component fluoride melts estimated from the scaled particle theory reported in the preceding paper.³⁾ The calculated results based on Eq. (5) are listed in Table 4. With increase of cationic radius, the values K and ΔH_{vol} change from negative to positive value.

4.2. Surface Tension and Surface Concentration of Binary Fluorides

Quantitative treatment of the surface tension-composition isotherm for a binary melt was carried out by Belton and Evans,⁹⁾ and Guggenheim.¹⁰⁾ According to the theory, the surface tension of the binary melt is given by the following equation.

$$\begin{aligned} \sigma &= \sigma_1^\circ + (kT/A) \ln(a_1'/a_1) \\ &= \sigma_2^\circ + (kT/A) \ln(a_2'/a_2) \quad \text{.....(6)} \end{aligned}$$

where, σ : surface tension of binary melt

σ_i° : surface tension of pure component i

a_i, a_i' : activities of component i in the bulk and on the surface layer, respectively

A : average surface area of one molecule

k : Boltzman constant (1.3805×10^{-16} erg/K)

T : absolute temperature.

The average surface area of one molecule is computed from the molar volumes of pure components 1 and 2 as follows:

$$A = X_1'(V_{M_1}^\circ/N)^{2/3} + X_2'(V_{M_2}^\circ/N)^{2/3} \quad \text{.....(7)}$$

where, N : Avogadro's number

X_i' : molecular fraction of i component on surface layer.

Assuming that the melt behaves as an ideal solution and the activities of components on surface layer can be treated similarly as those of bulk phase, the activities, a_i and a_i' can be replaced by the molar fractions, X_i and X_i' , respectively. Since the relations of $X_1 + X_2 = 1$ and $X_1' + X_2' = 1$ are hold on the surface as well as in the bulk melt, one can get a general form of the surface tension for the ideal solution from Eq. (6) as follows:

$$\begin{aligned} \exp(-\sigma A/kT) &= X_1 \exp(-\sigma_1^\circ A/kT) \\ &+ X_2 \exp(-\sigma_2^\circ A/kT) \quad \text{.....(8)} \end{aligned}$$

The broken lines in Fig. 4 show the calculated values from Eq. (8). Measured values of CaF_2 - NaF and CaF_2 - BaF_2 binary melt at 1550°C are slight lower than those calculated from Eq. (8). Similar tendency is found for binary chloride melts^{11,12)} and also for binary nitride melts.¹³⁾ For CaF_2 - SrF_2 binary melt

Fig. 4. Surface tensions of CaF_2 -based binary melt at 1550°C.

at 1550°C, the surface tension measured in the present work agrees well with that calculated from Eq. (8). On the other hand, positive deviation of measured values from those computed from Eq. (8) is found for melts in systems CaF_2 -LiF and CaF_2 -MgF₂.

Lumsden¹⁴⁾ suggests that regular solution model can be applied for some binary melts and hence activity coefficient of each component γ_i can be written as for NX_2 - MX_2 binary system,

$$\begin{aligned} RT \ln \gamma_{\text{NX}_2} &= \omega X_{\text{MX}_2}^2 \\ RT \ln \gamma_{\text{MX}_2} &= \omega(1 - X_{\text{MX}_2})^2 \end{aligned} \quad (9)$$

and for NX_2 - MX binary system,

$$\begin{aligned} RT \ln \gamma_{\text{NX}_2} &= \omega X_{\text{MX}}^2 / (2 - X_{\text{MX}})^2 \\ RT \ln \gamma_{\text{MX}} &= 2\omega(1 - X_{\text{MX}})^2 / (2 - X_{\text{MX}})^2 \end{aligned} \quad (10)$$

where, ω : an interaction energy between N^{2+} and M^{2+} cation or $\text{N}_{0.5}^{+}$ and M^{+} cation

R : gas constant.

For the regular solution, Guggenheim proposed Eq. (11) on the assumption of a quasi-crystalline model in which each molecule is arranged on a lattice point and it is distributed randomly in both the bulk and surface layer.

$$\begin{aligned} \sigma &= \sigma_1^0 + (kT/A) \ln (X_1'/X_1) \\ &+ (X_2'^2 - X_2^2) \cdot (l\omega/A) - mX_2^2 \cdot (\omega/A) \end{aligned} \quad (11-a)$$

$$\begin{aligned} &= \sigma_2^0 + (kT/A) \ln (X_2'/X_2) \\ &+ (X_1'^2 - X_1^2) \cdot (l\omega/A) - mX_1^2 \cdot (\omega/A) \end{aligned} \quad (11-b)$$

where, l, m : fractions of nearest neighbors which oc-

cupy the same lattice plane and the next lattice plane below, respectively, and hence the relation of $l+2m=1$ should be satisfied.

The Guggenheim's equations for the regular solution can be rewritten as follows.

For NX_2 - MX_2 binary system,

$$\begin{aligned} \sigma &= \sigma_{\text{NX}_2}^0 + (kT/A) \ln (X_{\text{NX}_2}'/X_{\text{NX}_2}) \\ &+ (l\omega/A)(X_{\text{MX}_2}'^2 - X_{\text{MX}_2}^2) - (m\omega/A)X_{\text{MX}_2}^2 \\ &= \sigma_{\text{MX}_2}^0 + (kT/A) \ln (X_{\text{MX}_2}'/X_{\text{MX}_2}) \\ &+ (l\omega/A)(X_{\text{NX}_2}'^2 - X_{\text{NX}_2}^2) - (m\omega/A)X_{\text{NX}_2}^2 \end{aligned} \quad (12-a)$$

and for NX_2 - MX binary system,

$$\begin{aligned} \sigma &= \sigma_{\text{NX}_2}^0 + (kT/A) \ln (X_{\text{NX}_2}'/X_{\text{NX}_2}) \\ &+ (l\omega/A)[(X_{\text{MX}}'^2/(2 - X_{\text{MX}}')^2 - X_{\text{MX}}^2/(2 - X_{\text{MX}})^2)] \\ &- (m\omega/A)[(X_{\text{MX}}^2/(2 - X_{\text{MX}})^2)] \\ &= \sigma_{\text{MX}}^0 + (kT/A) \ln (X_{\text{MX}}'/X_{\text{MX}}) \\ &+ (2l\omega/A)[(1 - X_{\text{MX}}')^2/(2 - X_{\text{MX}}')^2] \\ &- (1 - X_{\text{MX}})^2/(2 - X_{\text{MX}})^2] \\ &- (m\omega/A)[(1 - X_{\text{MX}})^2/(2 - X_{\text{MX}})^2] \end{aligned} \quad (12-b)$$

If Eq. (12) is applicable to calculate the surface tension of binary fluoride melts at a constant temperature, informations of the interaction energy ω and the coordination parameter l or m are required.

In the preceding paper,³⁾ it is pointed out that the surface structure of each alkaline metal or alkali-earth fluoride melt is resemble to the cleavage plane of the corresponding solid crystals. Therefore, it was assumed that the value m for CaF_2 , whose cleavage plane is (111), is 1/2, for LiF and NaF (NaCl structure, whose cleavage plane is (100)) $m=1/6$, and for MgF_2 (Rutile structure, the cleavage plane (110)), $m=1/6$. It is also assumed that an additive rule on the coordination parameters can be applied for the binary systems as follows,

$$\begin{aligned} m &= m_1X_1' + m_2X_2' \\ l &= l_1X_1' + l_2X_2' \end{aligned} \quad (13)$$

In combination of Eqs. (7), (12) and (13), best fit values of the interaction energy ω for each binary melt are computed by numerical calculation from the measurements of the surface tensions at 1550°C and shown in Fig. 4. These figures suggest that surface tensions of each binary system can be reproduced by the regular solution model, if a suitable value ω for each system are chosen. From the calculation, it was found that the values of the interaction energy ω are related to the excess volumes on mixing ΔV for CaF_2 - M_xF_2 equimolar systems ($x=1$ for divalent and $x=2$ for monovalent fluorides) as shown in Fig. 5. The surface concentration of component can also be estimated from the calculation as shown in Fig. 6. It suggests that on the surface, concentration of a component having lower surface tension is higher than that in the bulk phase.

Fig. 5. Relation between interaction energy ω and excess volume for $\text{CaF}_2\text{-}M_x\text{F}_2$ equimolar melts at 1550°C.

Fig. 6. Surface and bulk concentration of component for CaF_2 -based binary melts at 1550°C.

4.3. Interaction Energy ω and Phase Diagrams for Binary Fluorides

Although the interaction energy of $\text{CaF}_2\text{-MgF}_2$ and $\text{CaF}_2\text{-BaF}_2$ binary system are not reported yet, those values can be calculated from the activity coefficient of CaF_2 in the systems, which is measured by Kojima and Masson using the cryoscopic method.¹⁵⁾ If the quasi-chemical method is applied for the binary regular solution, the interaction energy ω is given as follows:

$$\omega = RT \ln \gamma_i / (1 - X_i)^2 \quad \text{.....(14)}$$

Calculated values of ω in $\text{CaF}_2\text{-MgF}_2$ and $\text{CaF}_2\text{-BaF}_2$ binary system are -1.3 and 1.0 kcal/mol, respectively. Those values are in good agreement with those computed from the surface tensions, which are -1.3 kcal/

mol for $\text{CaF}_2\text{-MgF}_2$ system and 1.0 kcal/mol for $\text{CaF}_2\text{-BaF}_2$ system. Kleppa and Hong measured the enthalpies of mixing in liquid $\text{CaF}_2\text{-MF}$ (M : Li, Na, K) mixtures at 1081°C,¹⁶⁾ from which the interaction parameters ω are computed as -1.30 , -4.68 and -7.88 kcal/mol for $\text{CaF}_2\text{-LiF}$, $\text{CaF}_2\text{-NaF}$ and $\text{CaF}_2\text{-KF}$ binary melts, respectively. On the other hand, estimated values of ω from the surface tension measurements are -1.3 kcal/mol for $\text{CaF}_2\text{-LiF}$ and 1.0 kcal/mol for $\text{CaF}_2\text{-NaF}$ system. A remarkable difference is found for $\text{CaF}_2\text{-NaF}$ system.

Assuming that a binary melt behaves as the regular solution and the binary system has no solid solubility at the terminal composition each other, the liquidus line can be calculated from the value of the interaction energy ω . The molar Gibbs free energy of melting of a component i , $\Delta G_{m(i)}^\circ$ is defined as follows:

$$\begin{aligned} \Delta G_{m(i)}^\circ &= -RT \ln a_{i(l)} \\ &= \Delta H_{m(i)}^\circ + \int_{T_m}^T \Delta C_{P(i)} dT - T[\Delta S_{m(i)}^\circ \\ &\quad + \int_{T_m}^T (\Delta C_{P(i)}/T) dT] \quad \text{.....(15)} \end{aligned}$$

where, $\Delta C_{P(i)}$: difference between the heat capacities of the liquid and the solid, being equal to $C_{P(i)\text{liquid}} - C_{P(i)\text{solid}}$

$\Delta H_{m(i)}^\circ$: heat of fusion of the component

$\Delta S_{m(i)}^\circ$: the entropy change of fusion at the melting point, T_m which is defined by $\Delta H_{m(i)}^\circ/T_m$.

From Eqs. (9), (10) and (15), the liquidus line can be calculated in combination of the interaction parameter ω with the suitable thermal data¹⁷⁾ listed in Table 5. The calculated results are shown in Fig. 7. In the systems $\text{CaF}_2\text{-MgF}_2$, $\text{CaF}_2\text{-BaF}_2$, and $\text{CaF}_2\text{-LiF}$, the liquidus lines calculated are fairly in good agreement with those reported.^{15,18-23)} However, for $\text{CaF}_2\text{-NaF}$ system, the liquidus line calculated, using the interaction parameter from the binary surface tension, is different from that by the phase diagram,²⁴⁾ from which the parameter of -1.9 kcal/mol is computed. It is not clear why the difference occurs, but it may suggest that solid solubility of the terminal composition exists in the system, because ionic radii of Ca^{2+} cation (0.99 nm) is resemble to that of Na^+ cation (0.97 nm).

4.4. Molar Volume and Surface Tension of Binary Fluoride

In the preceding paper,³⁾ it is shown that the surface tension of pure fluoride melt is related to the packing density of fluorine ions on the surface. Assuming that structural parameter K is additive as shown in Eq. (16), similar idea is applied for the binary melts. The result is as shown in Fig. 8.

$$K_{\text{binary}} = K_1 X_1' + K_2 X_2' \quad \text{.....(16)}$$

where, K_i : structural parameter of pure component i , which are 1 for LiF and NaF (NaCl structure), $\sqrt{1+\sqrt{2}}$ for MgF_2 (Rutile structure) and $4\sqrt{3}$ for CaF_2 (Fluorite structure).

Table 5. Thermochemical data for the calculation.

Fluoride	Temperature range (K)	Specific heat C_p° (cal/K mol)
$\text{CaF}_{2(l)}$	1 691–2 807	23.88 Melting point: 1 691 K Heat of fusion: 7.10 kcal/mol
$\text{CaF}_{2(s)}$	1 424–1 691	$25.81 + 2.51 \times 10^{-3} T$ Transition temp: 1 424 K Heat of transition: 1.14 kcal/mol
$\text{CaF}_{2(s)}$	1 424–298	$12.11 + 8.80 \times 10^{-3} T + 8.41 \times 10^5 / T^2 - 2.07 \times 10^8 / T^3$
$\text{MgF}_{2(l)}$	1 536–2 536	22.69 Melting point: 1 536 K Heat of fusion: 14.03 kcal/mol
$\text{MgF}_{2(s)}$	298–1 536	$19.10 + 0.76 \times 10^{-3} T - 7.05 \times 10^5 / T^2 + 0.88 \times 10^8 / T^3$
$\text{BaF}_{2(l)}$	1 641–2 545	23.86 Melting point: 1 641 K Heat of fusion: 5.58 kcal/mol
$\text{BaF}_{2(s)}$	1 480–1 641	25.73 Transition temp: 1 480 K Heat of transition: 0.64 kcal/mol
$\text{BaF}_{2(s)}$	1 240–1 480	27.01
$\text{LiF}_{(l)}$	1 990–1 121	15.34 Melting point: 1 121 K Heat of fusion: 6.47 kcal/mol
$\text{LiF}_{(s)}$	1 121–298	$10.82 + 2.78 \times 10^{-3} T - 1.53 \times 10^5 / T^2 + 0.79 \times 10^{-6} T^2$
$\text{NaF}_{(l)}$	1 269–2 060	$15.33 - 0.03 \times 10^{-3} T - 23.83 \times 10^5 / T^2$ Melting point: 1 269 K Heat of fusion: 7.97 kcal/mol
$\text{NaF}_{(s)}$	298–1 269	$12.73 - 1.64 \times 10^{-3} T - 1.19 \times 10^5 / T^2 + 3.25 \times 10^{-6} T^2$

structure)

X_i' : molecular fraction of pure component i on the surface, which is computed from Eq. (12) and is already shown in Fig. 7.

Fig. 8 suggests that surface tension is strongly related to packing density of fluorine ions on the surface for the binary melts as well as for the pure melts.

5. Summary

From the measurement of surface tension and density of binary fluorides, the following results were obtained.

(1) Molar volume of CaF_2 – SrF_2 melt behaves ideally on mixing, but a positive and a negative excess volume from ideal mixing is observed for CaF_2 – NaF and CaF_2 – BaF_2 systems, and for CaF_2 – LiF and CaF_2 – MgF_2 system.

(2) Surface tension of binary system can be represented by Guggenheim's equation for regular solution.

(3) Interaction energy for the regular solution model, estimated from surface tension of binary melts, is related to the excess volume on mixing for CaF_2 – $M_x\text{F}_2$ equimolar melt ($x=1$ for divalent and $x=2$ for monovalent fluoride).

(4) Liquidus lines for the systems, which are cal-

Fig. 7. Liquidus curves for CaF_2 -based binary system. Fig. 8. Relation between surface tension and molar volume for CaF_2 -based binary melts at 1 550°C.

culated from the interaction parameter ω in combination with the thermochemical data are fairly in good agreement with those reported, but CaF_2 – NaF system is exceptional.

(5) Surface tension of binary fluoride system is strongly depended on packing density of fluorine ions on the surface.

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