The Systems K_3AlF_6—Li_3AlF_6 and Rb_3AlF_6—Li_3AlF_6

II. The Structure of the Melt

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The phase diagrams of the binary systems $K_3AlF_6 - Li_3AlF_6$ and $Rb_3AlF_6 - Li_3AlF_6$ were used to find a structural model which can explain the equilibrium "solidus-liquidus" of the molten mixtures at either side of each system. From the course of the liquidus line of the K_3AlF_6- and the Li_3AlF_6-sides of the system $K_3AlF_6 - Li_3AlF_6$ it was found that the melt can be treated as a strictly regular ionic solution. The partial molar excess free energy of mixing can be written as:

$$\Delta \overline{G}_m^E = -5900(1 - X_{K_3AlF_6})^2 \qquad \text{at the } K_3AlF_6\text{-side}$$
$$\text{and} \quad \Delta \overline{G}_m^E = -6500(1 - X_{Li_3AlF_6})^2 \qquad \text{at the } Li_3AlF_6\text{-side}$$

where X represents the mol fraction.

For the Rb_3AlF_6- and the Li_3AlF_6-sides of the system $Rb_3AlF_6 - Li_3AlF_6$ it was found that the melt can also be treated as a strictly regular ionic solution. The partial molar excess free energy of mixing can be written as:

$$\Delta \overline{G}_m^E = -5500(1 - X_{Rb_3AlF_6})^2 \qquad \text{at the } Rb_3AlF_6\text{-side}$$
$$\text{and} \quad \Delta \overline{G}_m^E = -6600(1 - X_{Li_3AlF_6})^2 \qquad \text{at the } Li_3AlF_6\text{-side}$$

In part I of this work [1] the two binary systems $K_3AlF_6 - Li_3AlF_6$ and $Rb_3AlF_6 - Li_3AlF_6$ were investigated using differential thermal analysis (DTA), low- and high-temperature X-ray diffraction, and density measurements. One intermediate incongruently melting compound was detected in each system; K_2LiAlF_6 at 780°C, and Rb_2LiAlF_6 at 700°C. In the first system, $K_3AlF_6 - Li_3AlF_6$, a peritectic point was found at 780°C and 41.5 mol % Li_3AlF_6 and a eutectic at 650°C and 75 mol % Li_3AlF_6. In the second system, $Rb_3AlF_6 - Li_3AlF_6$, a peritectic point was detected at 700°C and 44 mol % Li_3AlF_6 and a eutectic point at 605°C and 71 mol % Li_3AlF_6. The aim of this part of the work is to find a certain model which is able to explain the equilibrium "solidus-liquidus" of the molten mixtures of the investigated systems.

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This model should give the best agreement between the calculated and the experimental results.

In case of a binary mixture of two components A and B, which are completely miscible in the liquid phase and have no solid solubility in each other, the general form of Le Chatelier [2] and Schröder [3] equations holds;

$$\ln a_A = -\frac{\Delta H_A^f}{R}\left(\frac{1}{T_A} - \frac{1}{T_A^f}\right) \tag{1}$$

where a_A is the activity of A in the mixture,
      ΔH_A^f is the enthalpy of fusion of component A, (taken to be independent of temperature within the interval $T_A - T_A^f$),
      T_A^f is the melting point of component A,
      T_A is the liquidus temperature, and
      R is the gas constant.

The terms T_A^f and T_A are obtained experimentally, and therefore the activity a_A can be calculated, if ΔH_A^f is known. By knowing the activity, the activity coefficient γ_A can be obtained from the expression:

$$a_A = X_A \gamma_A \tag{2}$$

where X_A is the mol fraction of component A.

DETERMINATION OF AN UNKNOWN ENTHALPY OF FUSION

If data on the enthalpy of fusion, ΔH^f, are not available, an approximate value of it can be obtained from the experimental data of the liquidus line using any of the following methods. (a) The cryoscopic method, which was developed by Darmois [4] as well as by his co-workers Rolin [5] and Petit.[6] (b) The second method was developed and applied by Malinovský.[7] He made use of Schröder's equation in the following way:

In case of a dilute solution, the activity of the component A, a_A, will be equal to its mol fraction, X_A, which is approximately equal to unity. Schröder's equation can, therefore, be written in the following form:

$$T_A = f(X_A) = \Delta H_A / (\Delta H / T_A - R \ln X_A) \tag{3}$$

This expression represents the equation of the liquidus curve of the component A. The slope of the curve at any point can be determined by differentiating equation (3) with respect to X_A;

$$\frac{dT_A}{dX_A} = \frac{\Delta T_A}{\Delta X_A} = \frac{R\Delta H_A^f}{X_A(\Delta H_A^f/T_A^f - R \ln X_A)^2} \tag{4}$$

where $\Delta T = T_A^f - T_A$, and $\Delta X_A = 1 - X_A$.

Therefore for the slope, K_A, at the melting point of the component A, i.e. when $1 - X_A = 0$, we have:

$$K_A = \lim (dT_A/dX_A)X_A \rightarrow 1$$
$$= \lim [\Delta T_A/(1 - X_A)]X_A \rightarrow 1$$
$$= (R/\Delta H_A^f)(T_A^f)^2 \tag{5}$$

If the term $\Delta T/(1 - X_A)$ is plotted as a function of $1 - X_A$, the value of K_A is given by the intercept on the ordinate, $i.e.$ $\Delta T/(1 - X_A) \rightarrow K_A$ when $1 - X_A \rightarrow 0$.

Just as for the cryoscopic method, eqn. (5) is valid when one molecule of the added salt B yields only one foreign particle in the melt of pure A. If the number of foreign particles is r_B, then;

$$K_A = \frac{R(T_A^f)^2}{\Delta H_A^f} r_B \tag{6}$$

$$\Delta H_A^f = \frac{R(T_A^f)^2}{K_A} r_B \tag{7}$$

CALCULATION OF THE LIQUIDUS CURVE

Ideal ionic solution. In case of ionic melts, the concept "ideal ionic solution", given by Temkin,[8] is found to be very useful. It is successfully applied to different categories of molten systems. In the present investigation we deal with systems where the generally accepted dissociation scheme is as follows:

$$M_3AlF_6 \rightarrow 3\ M^+ + AlF_6^{3-}$$

where $M = Li$, K, or Rb.

According to Temkin, the activity of the compound M_3AlF_6 can be written as follows:

$$a_{M_3AlF_6} = N_{M^+}^3 N_{AlF_6^{3-}}$$

where N_{M^+} and $N_{AlF_6^{3-}}$ are the cation and anion fractions, respectively. And since

$$N_{M^+} = \frac{3X}{3X + 3Y} = X$$

and

$$N_{AlF_6^{3-}} = \frac{X + Y}{X + Y} = 1$$

we get for the activity

$$a_{M_3AlF_6} = X^3$$

and likewise

$$a_{R_3AlF_6} = Y^3$$

where X and Y are the mol fractions of M_3AlF_6 and R_3AlF_6, respectively, $(X + Y = 1)$.

Regular ionic solution. The regular ionic solution model assumes that the partial molar Gibbs free energy of mixing, $\Delta \bar{G}_{m,i}$, of component i in the mixture can be expressed as follows:[9]

$$\Delta \overline{G}_{\mathrm{m,i}} = RT \ln \gamma_{\mathrm{i}} = b(1 - X_{\mathrm{r,i}})^2 \tag{8}$$

where γ_{i} is the activity coefficient of component i in the binary mixture, and is equal to the ratio between the mol fraction of the component i, $X_{\mathrm{ideal}} = $ activity a_{i}, which is obtained from the curve of the ideal ionic model at temperature T, and the mol fraction of i, $X_{\mathrm{r,i}}$, from the experimental curve at the same temperature, b is the interaction parameter.

RESULTS AND DISCUSSION

Enthalpies of fusion

The data given by Rolin, Latreille, and Pham [10] for the enthalpy of fusion of Li_3AlF_6, $\Delta H^f{}_{Li_3AlF_6} = 21.5$ kcal/mol, was used in the present calculations.

For K_3AlF_6, the only data on the enthalpy of fusion were published by Yoshioka and Kuroda [11] on the basis of the phase diagram of the system $Na_3AlF_6 - K_3AlF_6$. Their result for $\Delta H^f{}_{K_3AlF_6}$ (44.4 − 44.7 kcal/mol) seems to be unreasonably high, however. By use of the liquidus curve of the system $Li_3AlF_6 - K_3AlF_6$ obtained in the present work, Part 1, and by following the two previously reported procedures, $\Delta H^f{}_{K_3AlF_6}$ was found to be equal to 38.0 kcal/mol.

As no data on the enthalpy of fusion of Rb_3AlF_6 were found in the literature, calculations were made to evaluate it from the present experimental data of the liquidus curve of the system $Li_3AlF_6 - Rb_3AlF_6$.[1] The two previously reported procedures were used to determine $\Delta H^f{}_{Rb_3AlF_6}$. This was found to be equal to 37.0 kcal/mol.

A model for the melt

By applying Temkin's model,[8] the calculated curves at both sides of each system were, in general, much higher than the experimental ones. However, the regular ionic solution model was successfully applied and the results can be summarized as follows:

The system $K_3AlF_6 - Li_3AlF_6$. (i) *The Li_3AlF_6-side.* The calculations, according to the regular ionic solution model, are summarized in Table 1, and

Table 1. Calculation of a regular ionic solution model for Li_3AlF_6 in the system $Li_3AlF_6 - K_3AlF_6$.

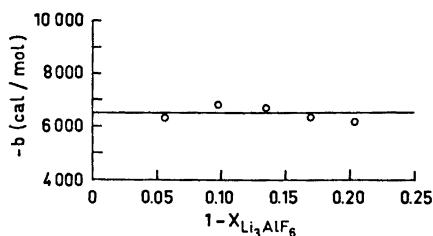| T K	X_{id}	X_{r}	$1 - X_{\mathrm{r}}$	$(1 - X_{\mathrm{r}})^2$	γ	$-RT \ln \gamma$	$-b$
953	0.698	0.798	0.202	0.0408	0.875	252.4	6186
973	0.755	0.830	0.170	0.0289	0.910	182.9	6329
993	0.813	0.865	0.135	0.0182	0.940	122.2	6714
1013	0.873	0.902	0.098	0.0096	0.968	65.8	6854
1033	0.935	0.944	0.056	0.0031	0.991	19.9	6322

Fig. 1. The interaction parameter b as a function of $1 - X_{Li_3AlF_6}$ on the basis of the phase diagram of the system $Li_3AlF_6 - K_3AlF_6$.
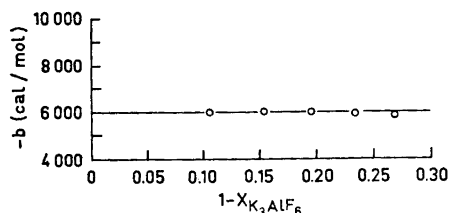
Fig. 2. The interaction parameter b as a function of $1 - X_{K_3AlF_6}$ on the basis of the phase diagram of the system $Li_3AlF_6 - K_3AlF_6$.

the interaction parameter b is presented as a function of $(1 - X_{Li_3AlF_6})$ in Fig. 1. From the figure it appears that b has a constant value of -6500 ± 400 cal/mol, and hence the mixture may be considered as a strictly regular ionic solution, $i.e.$ the partial molar excess free energy of mixing, $\Delta \bar{G}_m^E$, is equal to the partial molar enthalpy of mixing, $\Delta \bar{H}_m$;

$$\Delta \bar{G}_m^E = \Delta \bar{H}_m = -6500(1 - X_{Li_3AlF_6})^2$$

while the partial molar excess entropy of mixing, expressed as:

$$\Delta \bar{S}_m^E = \partial \Delta \bar{G}_m^E / \partial T$$

will be equal to zero.

(ii) The K_3AlF_6-$side$. The calculations are summarized in Table 2, and the interaction parameter b is presented as a function of $(1 - X_{K_3AlF_6})$ in Fig. 2. The interaction parameter b was found to be constant and equal to -5900 ± 100 cal/mol. Therefore the mixture may be considered as a strictly regular ionic solution. The partial molar excess free energy of mixing may be expressed as follows:

$$\Delta \bar{G}_m^E = \Delta \bar{H}_m = -5900 \ (1 - X_{K_3AlF_6})^2$$

and $\Delta S_m^E = 0$

Table 2. Calculation of a regular ionic solution model for K_3AlF_6 in the system $Li_3AlF_6 - K_3AlF_6$.

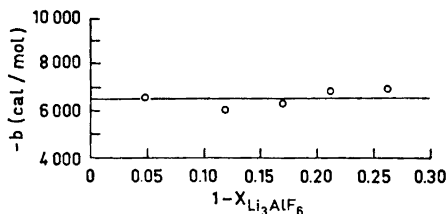| T K	X_{id}	X_r	$1 - X_r$	$(1 - X_r)^2$	γ	$-RT \ln \gamma$	$-b$
1153	0.608	0.731	0.267	0.0724	0.832	421.5	5822
1173	0.667	0.766	0.234	0.0548	0.871	322.0	5876
1193	0.730	0.804	0.196	0.0384	0.908	228.7	5956
1213	0.798	0.846	0.154	0.0237	0.943	141.6	5973
1233	0.870	0.891	0.106	0.0112	0.973	67.1	5991

Fig. 3. The interaction parameter b as a function of $1 - X_{\text{Li}_3\text{AlF}_6}$ on the basis of the phase diagram of the system $\text{Li}_3\text{AlF}_6 - \text{Rb}_3\text{AlF}_6$.
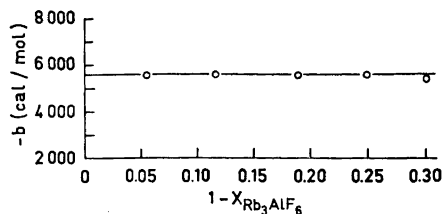
Fig. 4. The interaction parameter b as a function of $1 - X_{\text{Rb}_3\text{AlF}_6}$ on the basis of the phase diagram of the system $\text{Li}_3\text{AlF}_6 - \text{Rb}_3\text{AlF}_6$.

The system $Rb_3AlF_6 - Li_3AlF_6$. (i) *The* Li_3AlF_6-*side:* Table 3 shows the calculations according to the regular ionic solution model, and Fig. 3 shows the interaction parameter b as a function of $(1 - X_{\text{Li}_3\text{AlF}_6})$. The interaction parameter b was found to be constant and equal to -6600 ± 400 cal/mol. The mixture may, therefore, be treated as a strictly regular ionic solution. The partial molar excess free energy of mixing can be expressed as:

$$\Delta \overline{G}_m{}^E = \Delta \overline{H}_m = -6600(1 - X_{\text{Li}_3\text{AlF}_6})^2$$

and $\Delta \overline{S}_m{}^E = 0$

Table 3. Calculation of a regular ionic solution model for Li_3AlF_6 in the system $\text{Li}_3\text{AlF}_6 - \text{Rb}_3\text{AlF}_6$.

T K	X_{id}	X_r	$1 - X_r$	$(1 - X_r)^2$	γ	$- RT \ln \gamma$	$- b$
903	0.566	0.738	0.262	0.0686	0.767	475.9	6937
943	0.669	0.788	0.212	0.0449	0.849	306.8	6832
973	0.755	0.830	0.170	0.0289	0.910	182.9	6329
1003	0.844	0.881	0.119	0.0142	0.958	85.4	6028
1033	0.935	0.942	0.048	0.0023	0.993	15.1	6574

Table 4. Calculation of a regular ionic solution model for Rb_3AlF_6 in the system $\text{Li}_3\text{AlF}_6 - \text{Rb}_3\text{AlF}_6$.

T K	X_{id}	X_r	$1 - X_r$	$(1 - X_r)^2$	γ	$- RT \ln \gamma$	$- b$
1073	0.547	0.698	0.302	0.0966	0.784	518.9	5372
1103	0.641	0.751	0.249	0.0620	0.854	345.7	5577
1133	0.743	0.811	0.189	0.0357	0.918	197.5	5532
1163	0.856	0.884	0.116	0.0135	0.968	75.0	5573
1183	0.938	0.945	0.055	0.0030	0.993	16.3	5545

(ii) *The Rb_3AlF_6-side*. As in the previous cases, it seems that the mixture can be treated as a strictly regular ionic solution. The results of the calculations are presented in Table 4. Fig. 4 shows the interaction parameter as a function of $(1 - X_{Rb_3AlF_6})$. It is shown that b has a constant value of -5500 ± 200 cal/mol. The expression for the partial molar excess free energy of mixing may be written as:

$$\Delta \bar{G}_m{}^E = \Delta \bar{H}_m = -5500(1 - X_{Rb_3AlF_6})^2$$

and $\Delta \bar{S}_m{}^E = 0$

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