

Structure and Thermodynamics of Potassium Fluoride–Aluminium Fluoride Melts. Raman Spectroscopic and Vapour Pressure Studies

Eric Robert,^a Jørn E. Olsen,^b Bernard Gilbert^a and Terje Østvold^{b,*}

^aLaboratory of Analytical Chemistry, University of Liège, Liège, Belgium and ^bInstitute of Inorganic Chemistry, Norwegian University of Science and Technology, N-7034 Trondheim, Norway

Robert, E., Olsen, J. E., Gilbert B. and Østvold, T., 1997. Structure and Thermodynamics of Potassium Fluoride–Aluminium Fluoride Melts. Raman Spectroscopic and Vapour Pressure Studies. – Acta Chem. Scand. 51: 379–386. © Acta Chemica Scandinavica 1997.

Raman spectra and vapour pressures have been obtained as functions of temperature, $860 < T/^\circ\text{C} < 1000$, and composition, $1 < n_{\text{KF}}^\circ/n_{\text{AlF}_3}^\circ < 5$ (for pressures), 16 (for Raman spectra) for KF–AlF₃ melts. Stoichiometric equilibrium constants are calculated for the two equilibria $\text{AlF}_6^{3-} = \text{AlF}_5^{2-} + \text{F}^-$ and $\text{AlF}_5^{2-} = \text{AlF}_4^- + \text{F}^-$ established in the melt. The temperature variation of these constants is given as $\ln K' = -7698/T/\text{K} + 7.46$ and $-5894/T/\text{K} + 2.29$, respectively. These data are based on a quantitative analysis of the Raman intensities of the AlF_6^{3-} , AlF_5^{2-} and AlF_4^- vibrational frequencies. When combined with thermodynamic data, these results indicate a non-ideal mixture of the established anions.

Raman spectroscopy has shown that the structures of the two $M\text{F–AlF}_3$ ($M = \text{Na}, \text{K}$) melts are very similar, and that both binary systems can be described by the following equilibria:^{1–3}



Performing a quantitative analysis of the Raman intensities of the AlF_6^{3-} , AlF_5^{2-} and AlF_4^- vibrational frequencies, the total number of moles may be determined. From these data stoichiometric equilibrium constants, K_i' , for reactions (1) and (2) can be calculated by

$$K_1' = \frac{n_{\text{AlF}_5^{2-}} n_{\text{F}^-}}{n_{\text{AlF}_6^{3-}} N} = \frac{x_{\text{AlF}_5^{2-}} x_{\text{F}^-}}{x_{\text{AlF}_6^{3-}}} \quad (3)$$

$$K_2' = \frac{n_{\text{AlF}_4^-} n_{\text{F}^-}}{n_{\text{AlF}_5^{2-}} N} = \frac{x_{\text{AlF}_4^-} x_{\text{F}^-}}{x_{\text{AlF}_5^{2-}}} \quad (4)$$

where N is the total number of moles of anions, and n_i and x_i the number of moles and mole fractions of the i th species, respectively.

A comparison of the spectra for the three $M\text{F–AlF}_3$ systems shows that the characteristic bands of the complexes become sharper in the sequence $\text{Li} < \text{Na} < \text{K}$.⁴ This indicates a distortion of the respective anion structures in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$.

*To whom correspondence should be addressed.

From an industrial point of view the system NaF–AlF₃ is by far the most interesting and also the most studied. A study of KF–AlF₃ mixtures, however, where the interactions between the anion complexes and the cation are much weaker, may give valuable information about structure and properties of the industrial important NaF–AlF₃ melts.

The KF–AlF₃ phase diagram has been determined by several workers.^{5–7} Among all these data, the work of Holm⁷ seems to be the most reliable. Holm reported the presence of two solid compounds, K₃AlF₆ and KAlF₄, congruently melting at 1000 and 560 °C, respectively. Two eutectic points at 7 and 45 mol% AlF₃, with eutectic temperatures at 820 and 580 °C, respectively, were found.

Lee *et al.*⁸ estimated the activities of KF and AlF₃, with KF(1) and AlF₃(s) as standard states, respectively, in acidic, $n_{\text{KF}}^\circ/n_{\text{AlF}_3}^\circ < 3$, KF–AlF₃ melts. n_i° is the initial number of moles of component i . These activities were estimated using the partial enthalpies, $\Delta\bar{H}_{\text{KF}}$ and $\Delta\bar{H}_{\text{AlF}_3}$, derived from the enthalpy of mixing of liquid KF with solid AlF₃.⁹ The partial entropies of mixing, $\Delta\bar{S}_{\text{KF}}$ and $\Delta\bar{S}_{\text{AlF}_3}$, were assumed to be equal to $\Delta\bar{S}_{\text{NaF}}$ and $\Delta\bar{S}_{\text{AlF}_3}$ in the NaF–AlF₃ system.¹⁰

Zhou¹¹ determined the composition of the vapour phase above K₃AlF₆ at 1100 °C using a condensation technique. The vapour phase consisted of 12.6 mol% KF and 87.4 mol% KAlF₄. No direct measurements of activities for the KF–AlF₃ system have been found.

In the present work Raman spectra of KF–AlF₃ mixtures as a function of temperature ($860 < T/^{\circ}\text{C} < 1000$) and varying composition have been determined. Careful quantitative analysis of the Raman spectra yields $\ln K'$ as a function of $1/T$. From these data approximate enthalpy and entropy changes of reactions (1) and (2) may be evaluated. The Raman data were compared with measured total vapour pressures.

Experimental

Chemicals. KF, Merck, p.a. was recrystallised in an N₂ atmosphere. AlF₃, BDH Fibre grade, was first dried under vacuum at 400 °C and then sublimed at 1000 °C in a glassy carbon crucible for Raman and in graphite cells for vapour pressure studies.

Raman spectra. The samples were prepared in a dry box containing less than 5 ppm of water using the same method as reported earlier.^{1,2} The furnace, specially designed for Raman measurements, allows a temperature regulation of $\pm 5^{\circ}\text{C}$. Windowless graphite cells placed inside argon-filled quartz tubes were used for recording of the Raman spectra.¹² The spectra were recorded using a Spectra-Physics model 2020 argon-ion laser (800 mW, 488 nm), and a modified Cary 81 spectrometer interfaced with a microcomputer. A slit width of 5 cm^{-1} , a time constant of 0.1 s and a scan rate of 250 or $500\text{ cm}^{-1}\text{ min}^{-1}$ were used for all the spectra. In order to improve the signal-to-noise ratio, the spectra were recorded several times and averaged. This procedure was not applied if the spectra were changing with time due to evaporation and composition changes. In such a case, only the first spectrum was used for further analysis. Smoothing procedures were not applied to the spectra.

Vapour pressure measurements. The boiling point method¹³ was chosen for our measurements, since this method gives reliable data in the pressure region 10^{-2} to 1 atm and at high temperatures (i.e. 1000–1300 °C). An apparatus specially designed for measurements of corrosive gases was readily available at the Institute of Inorganic Chemistry and has been described in detail by Herstad and Motzfeldt.¹⁴ The main components of the equipment were a cold wall vacuum furnace with a vertically mounted graphite tube heater. Further descriptions of the experimental procedure are given by Gilbert *et al.*^{1,2}

Results

Raman spectra. In order to study the structure of KF–AlF₃ melts, spectra have been recorded over a wide composition range, where $n_{\text{KF}}^{\circ}/n_{\text{AlF}_3}^{\circ}$ varied from 16 to 1, in the temperature region 860–1000 °C. Data obtained for the KF–AlF₃ system at 1027 °C,³ together with the present data, were used to determine K_i' as a function of T . Some spectra are presented in Figs. 1–3. The assign-

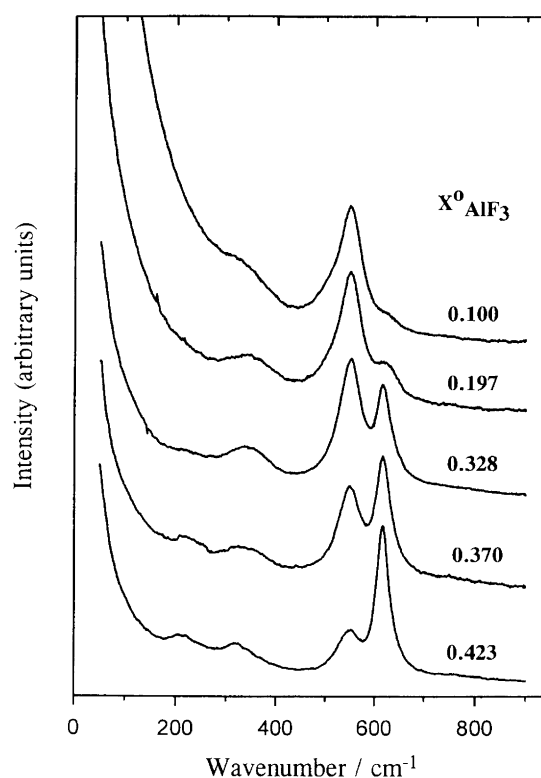


Fig. 1. Spectra of molten KF–AlF₃ mixtures at varying initial AlF₃ mole fraction, at 1000 °C.

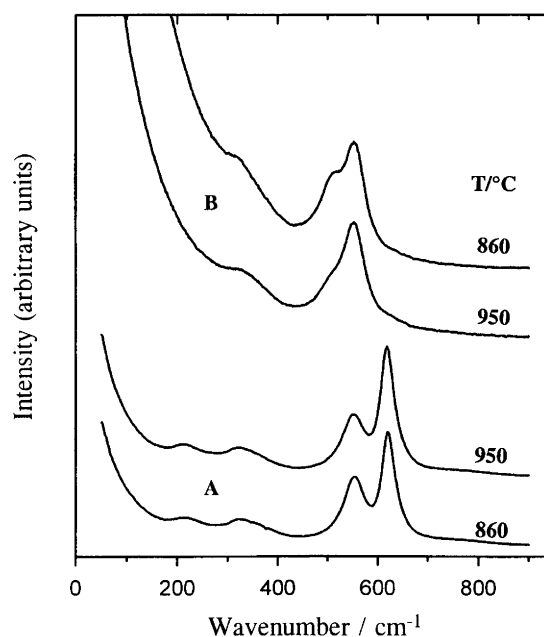


Fig. 2. Spectra of molten KF–AlF₃ mixtures at different temperatures. (A) $x_{\text{AlF}_3}^{\circ} = 0.4$, (B) $x_{\text{AlF}_3}^{\circ} = 0.15$.

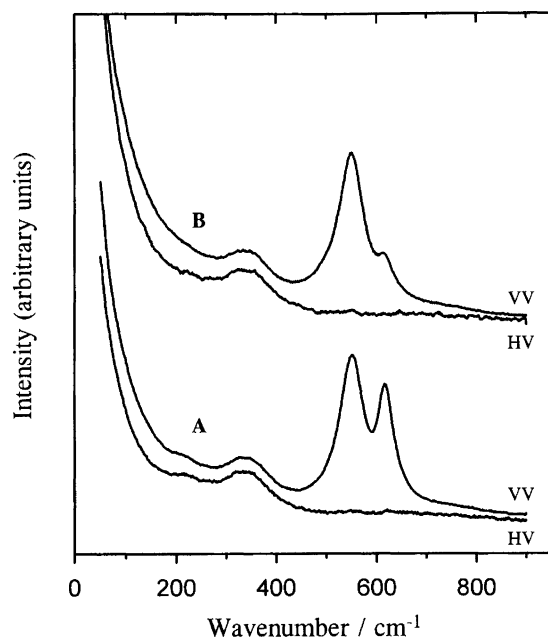


Fig. 3. VV and HV Raman spectra of molten KF-AlF₃ mixtures at 1020 °C. A: $x_{\text{AlF}_3} = 0.4$, B: $x_{\text{AlF}_3} = 0.25$.

ments and qualitative intensities of the bands were found to be:

AlF₄⁻: 622 cm⁻¹ (s,p);

760 cm⁻¹ (w,dp); 320 and 215 cm⁻¹ (m,dp)

AlF₅²⁻: 555 cm⁻¹ (s,p); 345 cm⁻¹ (m,dp)

AlF₆³⁻: 515 cm⁻¹ (s,p); 320 cm⁻¹ (m,dp)

where s, m and w mean strong, medium and weak intensity, respectively, and p and dp mean polarised and depolarised bands. The detailed interpretations of the assignments and the choice of the model have been published previously.¹⁻³

Figure 2 shows a shift in the 622 cm⁻¹ band towards lower frequency when the temperature increases. From a close examination of all the spectra, it seems that the frequencies of the three main bands decrease when the temperature is raised. For instance, at 860 °C, the ν_1 band of AlF₄⁻ is situated at 622 ± 1 cm⁻¹, and at 950 °C, this frequency is 619 ± 1 cm⁻¹. The experimental error, however, is close to the frequency shift, and no firm conclusion can be drawn.

The ionic distribution can be calculated from the intensity of the bands using the scattering coefficients characteristic of each species. These coefficients relate measured intensities to concentrations. A detailed procedure for the determination of scattering coefficients for NaF-AlF₃ melts diluted with NaCl was recently presented.¹ For the KF-AlF₃ system these coefficients have been calculated at 1027 °C, using a different method.³ This method is based on accurate measurements of the intensity ratios of the different bands (intensities meas-

ured as the area of the bands), for several different compositions and at constant temperature. A program based on a simplex procedure⁴ allows us to calculate scattering coefficients (D). Data determined at 1027 °C, $D_{\text{AlF}_6^{3-}} = 1.3$, $D_{\text{AlF}_5^{2-}} = 1.1$ and $D_{\text{AlF}_4^-} = 1$, were used by us at any temperature, since scattering coefficients are probably independent of temperature.

A general procedure for extraction of intensity ratios of Raman bands has been presented in previous papers.^{1,3} A discussion on the effect of frequency and temperature on the measured band intensities is given in the Appendix. Knowing the intensity ratios and scattering coefficients, the mole ratios of the different ions can be calculated; $n_{\text{AlF}_5^{2-}}/n_{\text{AlF}_4^-} = (I_{\text{AlF}_5^{2-}}/I_{\text{AlF}_4^-})/D_{\text{AlF}_5^{2-}}$ and $n_{\text{AlF}_6^{3-}}/n_{\text{AlF}_5^{2-}} = (I_{\text{AlF}_6^{3-}}/I_{\text{AlF}_5^{2-}})(D_{\text{AlF}_5^{2-}}/D_{\text{AlF}_6^{3-}})$. Using the mass balance of Al, $n_{\text{AlF}_3} = n_{\text{AlF}_4^-} + n_{\text{AlF}_5^{2-}} + n_{\text{AlF}_6^{3-}}$, and the two molar ratios, the number of moles of the different complexes can be calculated. The number of moles of free fluoride, n_{F^-} , is calculated using the mass balance of fluorine $n_{\text{F}^-} = n_{\text{KF}} - n_{\text{AlF}_4^-} - 2n_{\text{AlF}_5^{2-}} - 3n_{\text{AlF}_6^{3-}}$. The total number of moles of anions is given by $N = n_{\text{AlF}_4^-} + n_{\text{AlF}_5^{2-}} + n_{\text{AlF}_6^{3-}} + n_{\text{F}^-}$. The mole fraction of each species can then be expressed as $x_i = n_i/N$. The resulting mole fractions of the different species are presented in Table 1. The data in Table 1 can be used to calculate K_1' and K_2' for any composition, and within the accuracy of the method, these constants were found to be composition independent. These stoichiometric equilibrium constants, obtained directly from the Raman spectra, refer to the hypothetical pure undissociated compound standard state. This means that each compound in this hypothetical state is not dissociated according to eqns. (1) and (2), and $x_{\text{AlF}_6^{3-}} = 1$ for K₃AlF₆, etc. Using the expression for Gibbs free energy,

$$\Delta G' = \Delta H' - T\Delta S' = -RT \ln K' \quad (5)$$

enthalpy and entropy changes of reactions (1) and (2), have been obtained by plotting $\ln K_i'$ versus $1/T$. Results are given in Table 2.

Thermodynamic data for the hypothetical standard states used above are not available, and the results given in Table 2 cannot be tested. This means also that the assumption of constant activity coefficients made by us in the calculation of $\Delta H'$ and $\Delta S'$ in Table 2 cannot be evaluated.

Using eqns. (3) and (4) together with the data for $\ln K'$ in Table 2 and the mass balances for Al and F, the molar fractions of the different anions, x_i , may be calculated at any temperature and composition. We need these molar fractions to compare Raman and thermodynamic data for these melt mixtures. This comparison will be presented later.

Vapour pressures above liquid mixtures of KF-AlF₃ at different temperatures and $n_{\text{KF}}/n_{\text{AlF}_3}$ values are presented as $\log p_{\text{tot}}$ versus K/T in Fig. 4 and Table 3.

Table 1. Anion mole fractions in the KF–AlF₃ binary as obtained from Raman spectra. x_{F^-} is calculated from the fluoride mass balance.

$x_{AlF_3^0}$	$x_{AlF_4^-}$	$x_{AlF_5^{2-}}$	$x_{AlF_6^{3-}}$	$x_{F^-}^a$
<i>T</i> = 1000 °C				
0.099	0.009 ± 0.002	0.101 ± 0.007	0.019 ± 0.005	0.874 ± 0.010
0.126	0.017 ± 0.003	0.125 ± 0.010	0.029 ± 0.007	0.829 ± 0.020
0.189	0.039 ± 0.005	0.217 ± 0.015	0.039 ± 0.008	0.696 ± 0.020
0.197	0.045 ± 0.006	0.229 ± 0.015	0.038 ± 0.008	0.682 ± 0.030
0.328	0.207 ± 0.014	0.544 ± 0.025	0.038 ± 0.010	0.211 ± 0.040
0.337	0.259 ± 0.010	0.514 ± 0.025	0.026 ± 0.010	0.204 ± 0.040
0.370	0.405 ± 0.010	0.457 ± 0.020	0.025 ± 0.010	0.111 ± 0.040
0.384	0.464 ± 0.008	0.432 ± 0.019	0.020 ± 0.010	0.085 ± 0.040
0.407	0.570 ± 0.006	0.367 ± 0.013	0.000 ± 0.000	0.063 ± 0.020
0.423	0.650 ± 0.006	0.306 ± 0.009	0	0.044 ± 0.010
0.500	1	0	0	0
<i>T</i> = 950 °C				
0.102	0.000 ± 0.000	0.103 ± 0.005	0.029 ± 0.003	0.868 ± 0.008
0.139	0.009 ± 0.004	0.152 ± 0.005	0.038 ± 0.004	0.801 ± 0.010
0.356	0.332 ± 0.010	0.503 ± 0.018	0.025 ± 0.010	0.141 ± 0.040
0.373	0.405 ± 0.010	0.483 ± 0.014	0.021 ± 0.010	0.091 ± 0.030
0.403	0.561 ± 0.005	0.369 ± 0.009	0.012 ± 0.006	0.054 ± 0.020
0.424	0.654 ± 0.006	0.308 ± 0.005	0	0.039 ± 0.010
0.428	0.675 ± 0.007	0.296 ± 0.005	0	0.029 ± 0.010
0.447	0.767 ± 0.008	0.207 ± 0.003	0	0.025 ± 0.010
0.452	0.800 ± 0.008	0.189 ± 0.003	0	0.020 ± 0.010
0.500	1	0	0	0
<i>T</i> = 900 °C				
0.060	0	0.051 ± 0.001	0.018 ± 0.001	0.931 ± 0.002
0.096	0	0.090 ± 0.003	0.032 ± 0.002	0.878 ± 0.005
0.382	0.452 ± 0.010	0.452 ± 0.016	0.020 ± 0.005	0.076 ± 0.030
0.393	0.503 ± 0.007	0.422 ± 0.016	0.022 ± 0.010	0.053 ± 0.030
0.428	0.676 ± 0.007	0.292 ± 0.005	0	0.032 ± 0.010
0.436	0.712 ± 0.007	0.264 ± 0.005	0	0.023 ± 0.010
0.446	0.761 ± 0.007	0.219 ± 0.005	0	0.020 ± 0.010
0.452	0.791 ± 0.008	0.192 ± 0.004	0	0.017 ± 0.010
0.475	0.893 ± 0.003	0.100 ± 0.003	0	0.007 ± 0.010
0.500	1	0	0	0
<i>T</i> = 860 °C				
0.063	0	0.051 ± 0.003	0.023 ± 0.002	0.926 ± 0.005
0.395	0.514 ± 0.006	0.420 ± 0.020	0.021 ± 0.010	0.045 ± 0.030
0.422	0.663 ± 0.004	0.293 ± 0.010	0.023 ± 0.010	0.026 ± 0.020
0.434	0.718 ± 0.005	0.250 ± 0.005	0.018 ± 0.003	0.021 ± 0.015
0.448	0.772 ± 0.008	0.214 ± 0.005	0	0.015 ± 0.010
0.476	0.901 ± 0.008	0.094 ± 0.005	0	0.005 ± 0.010
0.500	1	0	0	0

^aCalculated from the fluoride mass balance.

Table 2. Enthalpy and entropy changes of reactions (1) and (2) assuming constant activity coefficients and hypothetical undissociated compound standard states.^a

Reaction	ΔH° / kJ	ΔS° / J K ⁻¹	$A/(T/K)$	B
1	64 ± 12	62 ± 9	-7698	7.46
2	49 ± 12	19 ± 8	-5894	2.29

^aTemperature dependence of stoichiometric equilibrium constants are given as $\ln K' = A/(T/K) + B$.

Figure 4 shows that the pressure is increasing with increasing acidity as expected. This trend is similar to what is observed for the NaF–AlF₃ system, but the pressures are higher as shown in Fig. 5.

Discussion

Thermodynamic data for molten salts are often given for pure components. Equilibrium constants for equilibria established in molten salts will therefore usually be based on pure component standard states. It is possible to use the above Raman data to calculate stoichiometric equilibrium constants for reactions (1) and (2) based on pure component standard states.

The important point is to obtain unit activity for each pure component. This can be obtained by defining the activity for, e.g. K₃AlF₆ as

$$a_{K_3AlF_6} = [x_{AlF_6^{3-}}/x_{AlF_6^{3-}}(n_{KF}^\circ/n_{AlF_3}^\circ = 3)]\gamma_{K_3AlF_6} \quad (6)$$

where $x_{AlF_6^{3-}}$ and $x_{AlF_6^{3-}}(n_{KF}^\circ/n_{AlF_3}^\circ = 3)$ are the real molefraction of AlF₆³⁻ observed by Raman at a given

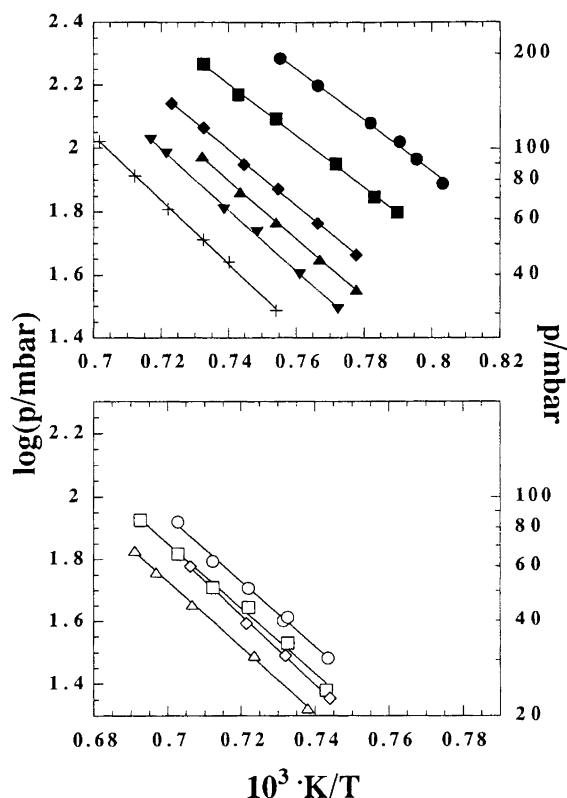


Fig. 4. Vapour pressures at varying temperature and composition ($R = n_{\text{KF}}^\circ/n_{\text{AlF}_3}^\circ$) for the KF-AIF₃ system. (●) $R = 1.0$, (■) $R = 1.4$, (◆) $R = 1.8$, (▲) $R = 2.0$, (▼) $R = 2.2$, (+) $R = 2.6$, (○) $R = 3.0$, (□) $R = 3.5$, (◇) $R = 4.0$, (△) $R = 5.0$.

Table 3. Vapour pressure data for the system KF-AIF₃, given as $\log p_{\text{tot}}/\text{mbar} = A - B/(T/K)$.

$n_{\text{KF}}^\circ/n_{\text{AlF}_3}^\circ$	A	B	Regr. coef.
1.0	8.356	8034	0.998
1.4	8.199	8104	0.999
1.8	8.480	8763	0.999
2.0	8.698	9189	0.999
2.2	8.906	9595	0.999
2.6	9.093	10 079	0.999
3.0	9.259	10 460	0.997
3.5	9.137	10 411	0.996
4.0	9.607	11 093	0.999
5.0	9.107	10 540	0.999

$n_{\text{KF}}^\circ/n_{\text{AlF}_3}^\circ$ and at $n_{\text{KF}}^\circ/n_{\text{AlF}_3}^\circ = 3$, respectively. $\gamma_{\text{K}_3\text{AlF}_6}$ is the Raoultian activity coefficient of pure K_3AlF_6 . For later use, we will define $R = n_{\text{KF}}^\circ/n_{\text{AlF}_3}^\circ$. The activity coefficient is by definition unity for pure K_3AlF_6 , which is dissociated according to eqns. (1) and (2). This implies that a_i for species i is unity at the melt composition corresponding to compound i even if this compound is dissociated. Raman spectra at $R = 1$ show only the bands characteristic of NaAlF_4 . This means that only AlF_4^- ions, as far as we can observe, are present at that composition. When this definition is used, the stoichiometric equilibrium constants based on Raman data and the thermodynamic equilibrium constants based on pure

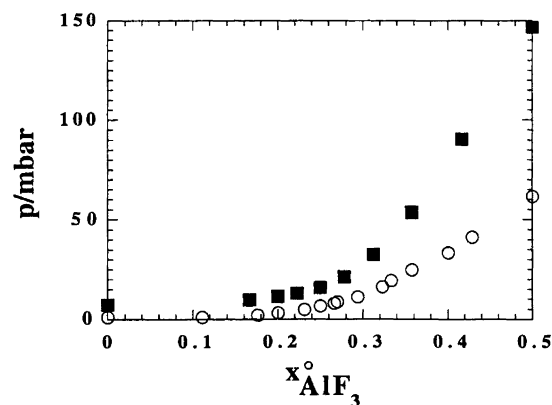


Fig. 5. Vapour pressure as a function of $x_{\text{AlF}_3}^\circ$ for the MF-AIF₃ ($M = \text{Na}, \text{K}$) systems at $T = 1027^\circ\text{C}$. (■) K, (○) Na.^{2,15}

real component standard states can be compared. The new stoichiometric equilibrium constants for eqns. (1) and (2) are given through the relations

$$K_1'' = \frac{a_{\text{K}_2\text{AlF}_5}^{\text{ideal}} a_{\text{KF}}^{\text{ideal}}}{a_{\text{K}_3\text{AlF}_6}^{\text{ideal}}} = K_1' \frac{1/x_{\text{AlF}_5}^{2-} (R=2)}{1/x_{\text{AlF}_6}^{3-} (R=3)} \quad (7)$$

and

$$K_2'' = \frac{a_{\text{KAlF}_4}^{\text{ideal}} a_{\text{KF}}^{\text{ideal}}}{a_{\text{K}_2\text{AlF}_5}^{\text{ideal}}} = K_2' \frac{1}{1/x_{\text{AlF}_5}^{2-} (R=2)} \quad (8)$$

Ideal activities are based on random mixing of the anions: AlF_6^{3-} , AlF_5^{2-} , AlF_4^- and F^- . The mole fractions of the anions at the stoichiometric compositions have to be known if we want to calculate the stoichiometric equilibrium constants K_1'' and K_2'' . For temperatures below the melting point of, e.g. K_3AlF_6 , $x_{\text{AlF}_6}^{3-}$ can not be obtained experimentally and must therefore be calculated as outlined above, using the data given in Table 2. Some data for K_1'' and K_2'' as functions of temperature are presented in Table 4.

The temperature dependence of the new stoichiometric equilibrium constants may under certain assumptions give the changes in enthalpy and entropy for reactions (1) and (2).

The connection between the thermodynamic and stoichiometric equilibrium constants, e.g. for eqn. (1), is given by

$$K_1 = K_1'' \cdot \pi(\gamma_1) \quad (9)$$

where $\pi(\gamma_1) = \gamma_{\text{K}_2\text{AlF}_5} \gamma_{\text{KF}} / \gamma_{\text{K}_3\text{AlF}_6}$. If $\pi(\gamma_1)$ and $\pi(\gamma_2)$ are temperature-independent, it is possible to compare dir-

Table 4. Stoichiometric equilibrium constants as given by eqns. (7) and (8).

$T/^\circ\text{C}$	K_1''	K_2''
1027	0.373 ± 0.011	0.055 ± 0.004
1000	0.364 ± 0.012	0.051 ± 0.006
950	0.348 ± 0.010	0.044 ± 0.005
900	0.331 ± 0.005	0.038 ± 0.002
860	0.312 ± 0.013	0.033 ± 0.004

ectly our calculated enthalpy and entropy changes for reactions (1) and (2) with thermodynamic data.

Hong and Kleppa⁹ have measured the enthalpies of mixing in the $MF-AIF_3$ ($M=Li, Na, K$) systems. From these measurements it is possible to derive the reaction enthalpies of reactions (1) and (2). If one further uses the assumption made by Lee *et al.*⁸ that the partial entropies in the $KF-AIF_3$ system are the same as those in the $NaF-AIF_3$ system, thermodynamic equilibrium constants for reactions (1) and (2) may be calculated using the reaction entropies given by Dewing.¹⁰ The results of these calculations are given in Table 5 together with the data obtained in this work. Also given in Table 5 are the products of the activity coefficients, $\pi(\gamma_i)$, for reactions (1) and (2). This product is calculated from the relation $\ln K = \ln K'' + \ln \pi(\gamma_i)$. There are large uncertainties in the calculated enthalpy and entropy data given in Table 5. This, of course, is due to the uncertainty in the Raman intensity variations with temperature. Within the uncertainty, however, agreement is observed.

To be able to compare our vapour pressure data with data calculated from the Raman spectra, activities need to be known. From vapour pressure data some information may be obtained by splitting the measured total pressures into partial pressures. Mass spectrometric studies of $KF-AIF_3$ melts by Kolosov *et al.*¹⁶ and Guzman¹⁷ showed that the main vapour species above these melts probably are $KAlF_4$, $K_2Al_2F_8$ and KF . The total pressure can then be expressed by:

$$p_{tot} = p_{KAlF_4} + p_{KF} + p_{K_2Al_2F_8} \quad (10)$$

The dimer pressure is obtained using the reaction



where the equilibrium constant, K_{11} , is given by Sidorov *et al.*¹⁸

$$\ln K_{11} = 12.733 - 17111.1(T/K) \quad (12)$$

To solve eqn. (10) one needs to know p_{KF} or the composition of the gas phase above $KF-AIF_3$ melts. Zhou¹¹ determined the composition of the gas phase above pure K_3AlF_6 at 1100 °C by a condensation experiment. The gas phase contained 12.6 mol% KF and

87.4 mol% $KAlF_4$. The amount of $K_2Al_2F_8$ in the gas phase at this composition was considered negligible.¹¹ Using the obtained data for the composition of the vapour phase, p_{KF} and p_{KAlF_4} may be calculated.

A comparison between Raman and vapour pressure data can be made by calculating pressures from the Raman data using the relation $p_i = x_i \gamma_i p_i^\circ$ where p_i is the pressure, x_i is the mole fraction, γ_i is the activity coefficient of component i in the mixture, and p_i° is the pressure above pure component i . $p_{KAlF_4}^\circ$ has been obtained by combining the total vapour pressure data above liquid $KAlF_4$, given in Table 3 with eqn. (12), since the gas phase above pure $KAlF_4$ mainly consists of $KAlF_4$ and its dimer.¹⁶ This gives

$$\log p_{KAlF_4}^\circ / \text{mbar} = 8.222 - 7958.2/(T/K) \quad (13)$$

The vapour pressure above liquid KF , p_{KF}° , is calculated using data from Ref. 19.

The stoichiometric equilibrium constants, K_i'' , are independent of composition as mentioned previously. This means that the product of the activity coefficients, $\pi(\gamma_i)$, must be constant as shown in Table 5. As expected from the data obtained for the $NaF-AIF_3$ system,¹ the activity coefficient of the major gas component, $KAlF_4$, is larger than 1. Using the data given by Zhou,¹¹ activities of KF and $KAlF_4$ equal to 0.3 and 0.13 at $R=3$ are obtained. Having activities and Raman based mole fractions of KF and $KAlF_4$ in the $KF-AIF_3$ melt at $R=3$, activity coefficients for KF and $KAlF_4$ equal to 0.6 and 1.5, respectively, are obtained. These activity coefficients are assumed to be close to temperature-independent, since they mainly reflect the deviation from random mixing of the anions of the $KF-AIF_3$ melt. A small temperature variation was, however, observed for γ_{NaAlF_4} in the $NaF-AIF_3$ system.¹ We may with some uncertainty use the above activity coefficients calculated at 1100 °C also at 1027 °C where the melt composition is known and where partial and total pressures may therefore be calculated. Using $\gamma_{KAlF_4}=1.5$ in the concentration range $0 \leq x_{AlF_3} \leq 0.3$, the partial pressure of $KAlF_4$ and its dimer can be calculated. This calculation is done with reasonable precision, since γ_{KAlF_4} will be constant for KF -rich melts. A similar situation was observed for the

Table 5. Enthalpy and entropy changes, equilibrium constants, stoichiometric equilibrium constants and product of the activity coefficients of reactions (1) and (2) at 1027 °C, with pure real compounds used as standard states.

Reaction	Thermodynamic data ⁸⁻¹⁰			Raman data			
	$\Delta H^\circ / \text{kJ}^a$	$\Delta S^\circ / \text{J K}^{-1}$	$\ln K$ (K)	$\Delta H'' / \text{kJ}^b$	$\Delta S'' / \text{kJ K}^{-1}$	$\ln K''$ (K'')	$\ln \pi(\gamma_i)$ $\pi(\gamma_i)$
1	20 ± 4	7.5 ^c	-0.893 (0.41)	13 ± 12	2 ± 3	-0.962 (0.38)	0.069 (1.07)
2	49 ± 5	12.9 ^c	-3.019 (0.049)	35 ± 12	3 ± 9	-2.877 (0.056)	-0.142 (0.87)

^aThe errors associated with ΔH_1° and ΔH_2° are based on the uncertainty in the enthalpy of fusion of $AlF_3(s)$.⁹ ^bThe large errors in the enthalpy data determined from the Raman data are due to the uncertainty in the slope of the $\ln K''$ versus $1/T$ plots. ^cReaction entropies for the $NaF-AIF_3$ system given by Dewing.¹⁰

NaF–AlF₃ system when $x_{\text{AlF}_3}^\circ < 0.28$. The activity of KF will change with composition from 1 in pure KF to ca. 0.3 in K₃AlF₆. Since the total pressure is mainly determined by the KAlF₄ pressure as soon as the melt contains a reasonable concentration of AlF₃, the KF activity will not influence the pressure calculations significantly. We have therefore kept $\gamma_{\text{KF}} = 0.6$ when calculating pressures up to $x_{\text{AlF}_3}^\circ \approx 0.3$. Results are given by the full drawn line in Fig. 6. Even at concentrations lower than $x_{\text{AlF}_3}^\circ \approx 0.3$ some deviations between calculation and measurement are observed. This is due to a too large value of γ_{KAlF_4} .

The data in Table 5 also indicate that the KF and KAlF₄ activities obtained by Zhou¹¹ at $x_{\text{AlF}_3}^\circ = 0.25$ are not correct. This can be observed by calculating the activity coefficient for K₂AlF₅ from experimental activity coefficients of KF and KAlF₄ at $x_{\text{AlF}_3}^\circ = 0.25$. At this concentration the activity coefficient products for reactions (1) and (2) give $\gamma_{\text{K}_2\text{AlF}_5}$, which varies between 1.8 and 1. This is a large difference and indicates a considerable uncertainty in the activity data. A Gibbs–Duhem integration of activity data in combination with the present vapour pressures also shows an uncertainty in the activity of KF in K₃AlF₆.

The liquidus lines for KF–AlF₃ phase diagram may be calculated using the equation

$$\frac{1}{T} = \frac{1}{T_{(f,i)}} - \frac{R \ln a_i}{\Delta H_{(f,i)}} \quad (14)$$

where T is the liquidus temperature, $T_{f,i}$ is the fusion temperature, $\Delta H_{f,i}$ is the enthalpy of fusion at T and a_i is the activity of component i . We used eqn. (14) to calculate the liquidus line for KF and K₃AlF₆. In the calculation the enthalpy of fusion of K₃AlF₆ was assumed to be independent of temperature, and the activity coefficient of KF and K₃AlF₆ as defined previously were considered unity in the actual concentration ranges. Calculated data and experimental data from Holm⁷ are presented in Fig. 7. The agreement is reason-

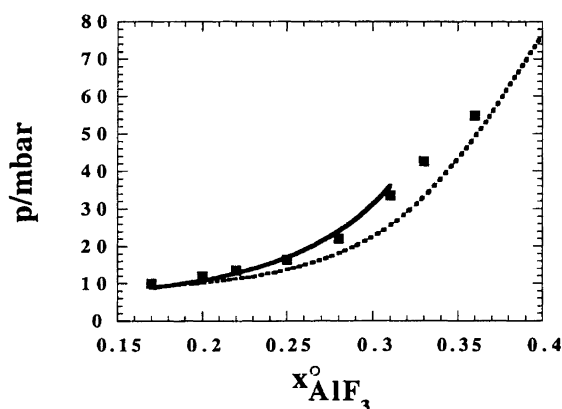


Fig. 6. Experimental and calculated vapour pressure for the KF–AlF₃ system at $T = 1027^\circ\text{C}$. (■) Experimental, (····) calculated using activity coefficients equal to unity, (—) calculated using $\gamma_{\text{KAlF}_4} = 1.5$ and $\gamma_{\text{KF}} = 0.6$.

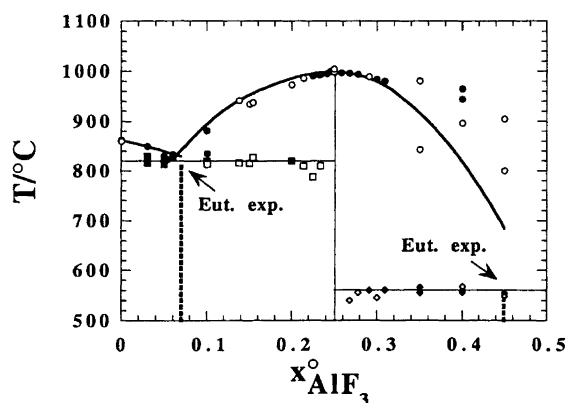


Fig. 7. The phase diagram of the system KF–AlF₃. Filled and open symbols indicate reliable and unreliable data, respectively.⁶ (—) Calculated. Expected eutectic points are indicated.

able. The calculated temperature may be a little too high when approaching the eutectic point at 7 mol% AlF₃. In our calculation $\gamma_{\text{K}_3\text{AlF}_6}$ is assumed to be unity over the concentration range $0.07 \leq x_{\text{AlF}_3}^\circ \leq 0.45$. This is obviously not correct. A value of 0.8 for $\gamma_{\text{K}_3\text{AlF}_6}$ at $x_{\text{AlF}_3}^\circ = 0.07$ would give a perfect fit with the measured eutectic temperature. The KF liquidus is calculated using $\gamma_{\text{KF}} = 1$. Using $\gamma_{\text{KF}} = 0.95$ gives a eutectic temperature in agreement with experimental data at $x_{\text{AlF}_3}^\circ = 0.07$.

Conclusions

It is evident that more experimental activity data are needed before the KF–AlF₃ binary is well characterized thermodynamically. Data of the composition of the vapour phase in combination with vapour pressure data for the KF–AlF₃ system at different AlF₃ concentrations may give valuable information on melt activities.

Appendix 1

Concerning the quantitative analysis of Raman spectra, we would like to make some comments. The intensity of a Raman spectrum depends on the frequency and the temperature. Brooker proposed to use a reduced form of the spectra for which the intensity is calculated as follows:

$$R_i = I_i \frac{\omega_i}{(\omega_0 - \omega_i)^4} B$$

where R_i is the corrected intensity, I_i is the experimental intensity, ω_0 is the wavenumber of the exciting line (in our case 20491 cm^{-1}), ω_i is the Raman shift of the i th band, in cm^{-1} , and $B = 1 - \exp(-hc\omega_i/kT) = 1 - \exp(-1.438786\omega_i/T)$ (ω_i in cm^{-1} and T in K).

This correction allows a direct comparison of the intrinsic scattering efficiency of several bands of a spectrum, since the corrected intensity no longer depends on frequency. It also allows a direct comparison of the

intensity of spectra recorded at different temperatures. However, in our case, these corrections do not affect the numbers of moles calculated from the spectra. In fact, what are measured on the spectra are intensity ratios of bands. These intensity ratios are related to the number of mole ratios through the relative scattering coefficient:

$$\frac{I_y}{I_x} = D_{y/x} \frac{n_y}{n_x} \quad (\text{A1})$$

In our case, when we calculated the relative scattering coefficients ($D_{5/4}$ and $D_{6/4}$) at 1300 K, we did not use the reduced form of the spectra. It means that, if we now want to analyse our spectra with the reduction procedure, we must first recalculate the relative scattering coefficients on the basis of this technique. We would, of course, obtain values different from those we have now. However, the measured intensity ratios of all the subsequent analysed spectra would also be different, due to the reduction process. So, finally, when the molar ratio is calculated using eqn. (A1), the result will be exactly the same. We may say that, on the basis of our data, we calculate an apparent relative scattering coefficient, related to the intrinsic relative scattering coefficient through the following equation:

$$D_{y/x}^{\text{app}} = D_{y/x}^{\text{intr}} \frac{(\omega_0 - \omega_y)^4}{\omega_y B_y} \frac{\omega_x B_x}{(\omega_0 - \omega_x)^4} \quad (\text{A2})$$

The only correction that we could have to apply to our data is thus due to a possible modification of the apparent relative scattering coefficients with the temperature. This correction can easily be obtained through the equation:

$$[D_{y/x}^{\text{app}}]_{T1} = [D_{y/x}^{\text{app}}]_{T1} \frac{(B_y)_{T1} (B_x)_{T2}}{(B_x)_{T1} (B_y)_{T2}} \quad (\text{A3})$$

In our case, we know that at 1027 °C, $(D_{6/4}^{\text{app}})_{1027} = 1.3$ and $(D_{5/4}^{\text{app}})_{1027} = 1.1$. We can calculate these coefficients at 800 °C, which is our lowest working temperature. We then obtain: $(D_{6/4}^{\text{app}})_{800} = 1.288$, i.e. 0.92% of variation, $(D_{5/4}^{\text{app}})_{800} = 1.094$, i.e. 0.55% of variation.

These variations are well below the error made in the determination of intensity ratios. We may thus use the values 1.3 and 1.1 without making any significant error. In conclusion, the reduction of the spectra does not

modify the distribution of the different species in the medium. In our case, this treatment is not necessary.

Acknowledgement. This project has benefitted scientifically and financially from our participation in a Human Capital and Mobility Network of the European Communities. Financial support from The Research Council of Norway and the Norwegian aluminium industry is also gratefully acknowledged. The FNRS of Belgium is acknowledged for financial support to one of the authors (E.R.).

References

- Gilbert, B., Robert, E., Tixhon, E., Olsen, J. E. and Østfold, T. *Inorg. Chem.* 35 (1996) 4198.
- Gilbert, B., Robert, E., Tixhon, E., Olsen, J. E. and Østfold, T. *Light Metals* (1995) 181.
- Tixhon, E., Robert, E. and Gilbert, B. *Appl. Spectrosc.* 48 (1994) 1477.
- Gilbert, B. and Materne, T. *Appl. Spectrosc.* 44 (1990) 299.
- Fedotieff, P. P. and Timofeff, K. *Z. Anorg. Allg. Chem.* 206 (1932) 263.
- Phillips, B., Warshaw, C. M. and Mockrin, I. *J. Am. Ceram. Soc.* 49 (19) 631.
- Holm, B. J. *Thesis*, Institute of Inorganic Chemistry, University of Trondheim, NTH 1969.
- Lee, M. S., Terry, B. S. and Grieverson, P. *Trans. Inst. Min. Met. C* 103 (1994) c33.
- Hong, K. C. and Kleppa, O. J. *J. Phys. Chem.* 82 (1978) 176.
- Dewing, E. W. *Met. Trans.* 21B (1990) 285.
- Zhou, H. *Thesis*, Institute of Inorganic Chemistry, University of Trondheim, NTH 1991.
- Gilbert, B., Begun, G. M. and Mamantov, G. *J. Chem. Phys.* 62 (1975) 950.
- Motzfeldt, K., Kvande, H. and Wahlbeck, P. G. *Acta Chem. Scand., Ser. A31* (1977) 444.
- Herstad, O. and Motzfeldt, K. *Rev. Haut. Temp. Refract.* 3 (1966) 291.
- Kvande, H. *Thesis*, Institute of Inorganic Chemistry, University of Trondheim, NTH 1979.
- Kolosov, E. N., Sidorov, L. N. and Voronin, G. F. *Russ. J. Phys. Chem.* 45 (1971) 1548.
- Guzman, J. *Thesis*, Institute of Inorganic Chemistry, University of Trondheim, NTH 1986.
- Sidorov, L. N., Belousov, V. I. and Scholtz, V. B. *Adv. Mass Spectrom.* 5 (1971) 394.
- JANAF Thermochemical Tables*, Vol. 14, Am. Chem. Soc., New York 1985.

Received August 16, 1996.