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Enthalpy of $NaAlCl_4$, $KAlCl_4$, and Their Mixtures

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Drop calorimetric measurements between 350 and 1100 K on $NaAlCl_4$, $KAlCl_4$, the $NaAlCl_4$–$KAlCl_4$ eutectic, and the $AlCl_3$–$NaAlCl_4$–$KAlCl_4$ eutectic are reported. The enthalpies of melting were found to be 20.3 ± 0.5 kJ mol^{-1} ($NaAlCl_4$), 19.3 ± 0.6 kJ mol^{-1} ($KAlCl_4$), and 16.2 ± 0.3 kJ mol^{-1} ($0.7NaAlCl_4$–$0.3KAlCl_4$). Heat capacities have been deduced from fitted enthalpies and the enthalpies of mixing are estimated for the binary and ternary eutectics, respectively.

Molten chloroaluminates have various interesting properties such as low crystallization temperatures and good chemical and thermal stabilities (*1*-*2*). Spectroscopic studies have proved their clearly ionic character (*3*, *4*), and their utilization in high-efficiency batteries and low-temperature metallurgical processing has been proposed.

Inspection of available data for chloroaluminates (see JANAF tables (*5*)) surprisingly indicated a complete lack of enthalpy and heat-capacity data. To fill a part of this gap, we have made a drop calorimetric investigation of $NaAlCl_4$ and $KAlCl_4$ and also of the binary and ternary eutectics $NaAlCl_4$–$KAlCl_4$ and $NaAlCl_4$–$KAlCl_4$–$AlCl_3$ in the temperature range 350-1100 K. During the completion of our work, enthalpy data between 298 and 573 K were published (*6*). As discussed below, they are in poor agreement with our measurements.

Experimental Section

Apparatus. The apparatus which was set up at the laboratory is similar to that of Ginnings et al. (*7*, *8*). The main features have been described in previous works (*9*, *10*) and are shown in Figure 1. Special care has been taken for its thermal insulation. The internal Pyrex vessel is filled with distilled water and mercury and insulated by an external evacuated Pyrex vessel. To reduce heat leak during the experiments, mercury flows in a Pyrex coil maintained at 273 K in the thermostat. The heat leak does not exceed 9 J h^{-1} and is measured on a calibrated capillary (see Figure 1). The present calorimetric arrangement is able to work in controlled atmosphere. Therefore, it was possible to remove the anticondensation device which was described in our previous work (*9*). Two gates protect the calorimeter against radiation from the furnace. The cone-shaped crucible is made of platinum–rhodium 10%. Small Pt-Rh screens improve contact with the ice calorimeter after the drop and reduce the radiative effects. The hot junction of the thermocouple enters the crucible (see Figure 2). Hence, the measured temperature is that of the salt at the time of the drop. When filled with the sample, this crucible is sealed under vacuum by pinching off and flame cutting. It is held by a thin metallic wire in the isothermal zone of the furnace above the calorimeter. When thermal equilibrium is reached, the crucible is dropped by electrically cutting off its fixing wire. The crucible falls into the calorimeter in a massive copper block which fits the shape of the crucible and strongly dissipates heat content to the calorimeter. The experiment is terminated when the heat leak returns to its initial value. Before the main series of measurements, enthalpy measurements on the empty crucible are made in the same range of temperature.

Table I. Enthalpy and Heat Capacity of α-Alumina

	$H_T - H_{273}$, kJ mol^{-1}			C_p, J mol^{-1} K^{-1}		
T, K	NBS	obsd	Δ, %	NBS	calcd[a]	Δ, %
367.3	7.829	7.901	+0.92	91.56	91.66	−0.11
482.6	19.215	19.239	+0.13	104.70	104.36	−0.33
601.5	32.174	32.220	+0.14	112.63	112.57	−0.05
733.4	47.414	47.426	+0.02	118.10	118.39	+0.24
820.8	57.857	57.920	+0.11	120.71	121.02	+0.26
1004.0	80.370	80.477	+0.13	124.85	124.45	−0.32
1123.8	95.460	95.393	−0.07	127.01	125.62	−1.11
1309.0	119.254	118.780	−0.40	129.86	126.30	−2.82

[a] $C_p = 222.68 - (24.046 \times 10^{-3})T + (0.5367 \times 10^{5})T^{-2} - 2349.3T^{-1/2}$. This equation was obtained from a least-squares fit of the enthalpy data.

The mean value of the electric calibration of the calorimeter is 270.54 ± 0.10 J (g of mercury)$^{-1}$ (*11*). This value is in good agreement with and within accuracies of the other published values (J (g of Hg)$^{-1}$): 270.37 ± 0.6 (*7*), 270.46 ± 0.03 (*8*), 270.56 ± 0.13, and 270.43 ± 0.09 (*12*).

Accuracy and Precision. To assess the accuracy of our measurements, we have made some runs on α-Al_2O_3 powder with less than 200 ppm impurities (Alumine Exal-Alpha A6 from Pechiney-Ugine-Kuhlmann). The experimental results are given in Table I. Comparison of our data above 480 K with the fitted equation of the NBS suggests an accuracy better than 0.2% and 0.4% for the enthalpy and the heat capacity, respectively (*13*). The precision as given by the scatter of our results is also around 0.2%. Below 400 K our results are much less accurate (see the comparison between the enthalpies of the solid binary eutectic and that of the pure compounds $NaAlCl_4$ andd $KAlCl_4$ below).

Materials. Samples were prepared from $AlCl_3$, NaCl, and KCl. $AlCl_3$ (Prolabo) was purified in Pyrex ampules under vacuum by three distillations running at about 468 K with Al ribbons (Puriss., Johnson-Matthey). NaCl and KCl (Merck, Suprapur) were heated above their melting points for 12 h. $NaAlCl_4$ (or $KAlCl_4$) was prepared from weighed stoichiometric amounts cf NaCl (or KCl) and $AlCl_3$. The compound was purified by thermoelectrolysis at about 473 K (or 520 K for $KAlCl_4$) with Al ribbons under vacuum in a Pyrex ampule with a quartz filter. The heating was continued until a water-clear melt was produced (72 h is necessary). The melt was then filtered, allowed to solidify, and stored in a glovebox in a dry atmosphere of argon. Usually all handlings of the samples were carried out in this glovebox.

The composition of the binary eutectic $NaAlCl_4$–$KAlCl_4$ has been determined from the studies of Fischer and Simon (*14*). It has been confirmed by differential thermal analysis (DTA) at the laboratory, i.e., 30 mol % $KAlCl_4$ and 70 mol % $NaAlCl_4$ (T_m = 402 K). The mixture was prepared in the glovebox by thoroughly grinding and mixing weighed amounts of $NaAlCl_4$ and $KAlCl_4$.

The ternary eutectic $AlCl_3$–$NaAlCl_4$–$KAlCl_4$ was prepared in the same way as the binary eutectic. To ascertain its composition, we made DTA measurements on the previously reported eutectic compositions (*14*-*18*). A good agreement was found with the data of Midorikawa (*15*), i.e., 33.5 mol % $AlCl_3$,

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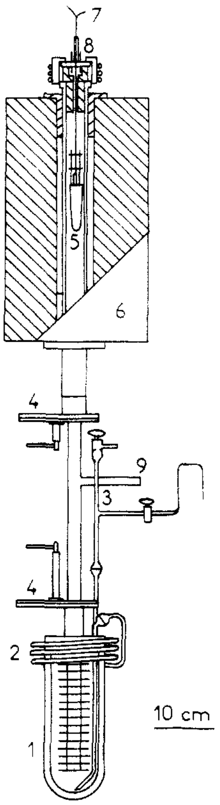

Figure 1. (1) Calorimetric vessel. (2) Glass coil for mercury flow. (3) Calibrated capillary. (4) Protection gate. (5) Pt-Rh 10% crucible. (6) Electric furnace. (7) Thermocouple. (8) Electric plugs for cutting off. (9) To argon supply or vacuum.

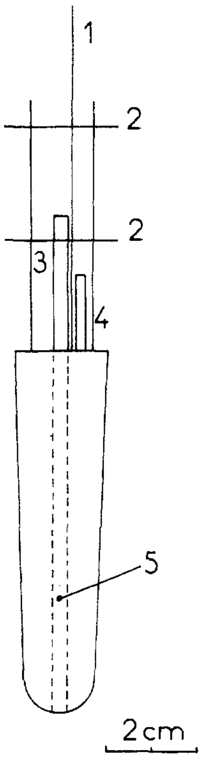

Figure 2. (1) Fixing metallic wire. (2) Pt-Rh screens. (3) Sheath. (4) Sealed tube. (5) Location of the couple before drop.

43 mol % $NaAlCl_4$, and 23.5 mol % $KAlCl_4$ (T_m = 363.5 K).

Results and Discussion

All of the experimental data are reported in Table II and were smoothed as polynomials, the coefficients of which were determined by the least-squares method. We have also defined an estimation of the variance of the smoothed values σ^2; we give here the standard deviation σ:

Table II. Experimental Measurements

T, K	ΔH_{est},[a] J mol^{-1}	$\Delta\%$[b]	C_p, J mol^{-1} K^{-1}
	$NaAlCl_4$		
273.2			145.7
325.8	7 804	−0.20	151.2
368.1	14 341	+0.24	155.6
400.6	19 375	−0.22	158.9
414.9	21 723	+0.10	160.4
426.1	25 946		
428.9	28 655		
431.3	44 547	−0.48	184.8
453.6	48 787	−0.19	184.6
467.8	51 238	−0.51	184.3
498.5	57 335	+0.32	184.0
526.2	62 280	+0.06	183.6
572.0	70 624	−0.02	183.0
575.4	71 436	+0.25	183.0
598.7	75 873	+0.47	182.7
646.7	84 862	+0.72	182.0
704.9	94 723	−0.13	181.3
785.9	108 727	−0.69	180.2
909.4	131 456	−0.14	178.6
958.1	140 399	+0.05	178.0
1017.0	150 900	+0.07	177.2
1099.8	165 526	+0.06	176.2
	$KAlCl_4$		
273.2			164.5
331.0	9 278	−2.76	164.5
379.4	17 980	+2.72	164.5
451.2	29 188	−0.44	164.5
510.7	39 052	−0.14	164.5
515.9	40 829		
521.7	47 183		
525.3	59 342		
531.8	61 538		
575.2	70 231	−0.15	187.2
615.0	77 672	−0.12	186.1
677.7	89 498	+0.14	184.2
706.3	94 872	+0.25	183.5
762.1	104 801	−0.02	181.9
822.3	115 706	−0.01	180.1
895.5	128 884	+0.04	178.0
966.5	140 984	−0.29	176.0
1057.8	157 582	+0.15	173.4
	$NaAlCl_4$-$KAlCl_4$		
346.1	10 930	+0.25	164.4
375.2	15 607	−0.52	164.4
394.7	18 987	+0.48	164.4
402.1	20 076	−0.18	164.4
413.5	38 465	−0.29	190.5
433.6	42 443	+0.10	189.9
488.3	52 998	+0.46	188.6
523.9	59 057	−0.66	187.6
556.3	65 619	+0.16	186.8
591.3	72 219	+0.26	185.8
649.5	83 045	+0.29	184.3
684.1	90 612	−0.42	183.1
717.9	95 508	+0.17	182.5
800.2	110 003	−0.25	180.3
861.6	121 571	+0.22	178.7
962.2	138 966	−0.13	176.1
1023.5	149 983	+0.07	174.4
	$AlCl_3$-$NaAlCl_4$-$KAlCl_4$		
412.4	39 003	+0.30	169.5
494.7	52 851	+0.32	165.7
525.0	57 299	−0.66	164.3
555.3	62 421	−0.34	162.9
621.3	73 471	+0.25	159.8
715.6	88 439	+0.33	155.4
809.8	102 415	−0.16	151.0

[a] $\Delta H_{est} = H_T - H_{273}$ from the least-squares fit. [b] $\Delta\% = [100(\Delta H_{est} - \Delta H_{obsd})]/\Delta H_{est}$.

$$\sigma^2 = \sum \frac{[H_i - (A + BT_i + CT_i^{\,2} + \ldots)]^2}{n(n - m)}$$

The heat capacities were determined by differentiating the respective enthalpy–temperature equations with respect to temperature. The method for estimating the precision of $\Delta H/H$ and $\Delta C_p/C_p$ has been previously reported (*9*).

The least-squares method is also used to determine the melting. In that case the actual enthalpy measurements are selected near the discontinuity between the two phases. The method consists in pointing out the variance when the first experimental data are assigned to the first phase and the others to the second phase. Then, the two first experimental data are assigned to the first phase and the others to the second and so on. Thus, for the i values which define the melting we calculate

$$\sigma_j^{\,2} = \sum_{i=1}^{i=j} [H_i - (A_1 + B_1T_i + C_1T_i^{\,2} + \ldots)]^2 + \sum_{i=j+1}^{i=i} [H_i - (A_2 + B_2T_i + C_2T_i^{\,2} + \ldots)]^2$$

where 1 and 2 represent the solid and liquid phases, respectively. The temperature for which σ_j is a minimum is taken as the melting point, $T_m = T_j$ and accordingly

$$\Delta H_m = (A_2 - A_1) + (B_2 - B_1)T_m + (C_2 - C_1)T_m^{\,2} + \ldots$$

The accuracy of the determination is of course affected not only by the error in the temperature but also by the enthalpy measurement above and under the melting point.

Pure Compounds. $NaAlCl_4$. Measurements were made on 15.620 g of salt with a crucible weighing 52.440 g. In the solid phase (σ = 25 J)

$$H_T - H_{273} = -35931 + 117.36T + (5.188 \times 10^{-2})T^2 \text{ J mol}^{-1} \qquad (\Delta H/H = 1.8\%)$$

$$C_p = 117 + (10.4 \times 10^{-2})T \text{ J mol}^{-1}\text{ K}^{-1} \ (\Delta C_p/C_p = 4\%)$$

In the liquid phase (σ = 85 J)

$$H_T - H_{273} = -36161 + 190.40T - (0.647 \times 10^{-2})T^2 \text{ J mol}^{-1} \qquad (\Delta H/H = 0.2\%)$$

$$C_p = 190.4 - (1.29 \times 10^{-2})T \text{ J mol}^{-1}\text{ K}^{-1} \ (\Delta C_p/C_p = 0.3\%)$$

$$T_m = 427 \text{ K}$$

$$\Delta H_m = 20.3 \pm 0.5 \text{ kJ mol}^{-1}$$

$KAlCl_4$. Measurements were made on 14.913 g of salt with a crucible weighing 51.430 g. In the solid phase (σ = 146 J)

$$H_T - H_{273} = -44904 + 164.52T \text{ J mol}^{-1} \qquad (\Delta H/H = 1.2\%)$$

$$C_p = 164 \pm 4 \text{ J mol}^{-1}\text{ K}^{-1} \qquad (\Delta C_p/C_p = 2\%)$$

In the liquid phase (σ = 167 J)

$$H_T - H_{273} = -42094 + 203.68T - (1.432 \times 10^{-2})T^2 \text{ J mol}^{-1} \qquad (\Delta H/H = 0.12\%)$$

$$C_p = 203.7 - (2.9 \times 10^{-2})T \text{ J mol}^{-1}\text{ K}^{-1} \ (\Delta C_p/C_p = 0.5\%)$$

$$T_m = 520 \text{ K}$$

$$\Delta H_m = 19.3 \pm 0.6 \text{ kJ mol}^{-1}$$

Mixtures. The two mixtures which we have studied are eutectics (*14*, *15*), that is to say, mechanical mixtures. Therefore, their enthalpies in the solid phase should be equal to that of the weighed sum of the enthalpies of pure compounds.

Table III. Calculated Enthalpies of Solid Binary Eutectic

T, K	ΔH_{calcd},[a] J mol^{-1}	Δ%[b]	T, K	ΔH_{calcd},[a] J mol^{-1}	Δ%[b]
346.1	11243	−2.9	402.1	20130	−0.4
375.2	15833	−1.4	273.2	9	
394.7	18942	+0.2			

[a] $\Delta\% = [100(\Delta H_{\text{calcd}} - \Delta H_{\text{obsd}})]/\Delta H_{\text{calcd}}$. $\Delta H_{\text{calcd}} = H_T - H_{273}$ from the weighed sum of pure compounds.

Binary Eutectic $NaAlCl_4$–$KAlCl_4$. Measurements were made on 15.000 g of mixture with a crucible weighing 61.780 g. In Table III the measured enthalpy values of the solid binary eutectic are compared with the weighed sum of the fitted values for the pure compounds, i.e.

$$H_T - H_{273} = -38623 + 132T + (3.632 \times 10^{-2})T^2 \text{ J mol}^{-1}$$

$$C_p = 132 + (7.3 \times 10^{-2})T \text{ J mol}^{-1}\text{ K}^{-1}$$

The agreement is good, except below 400 K, where the latter values are probably more accurate than the former ones due to the wider temperature range of measurements for the pure compounds. In the liquid phase (σ = 73 J)

$$H_T - H_{273} = -42465 + 201.42T - (1.319 \times 10^{-2})T^2 \text{ J mol}^{-1} \qquad (\Delta H/H = 0.2\%)$$

$$C_p = 201.4 - (2.6 \times 10^{-2})T \text{ J mol}^{-1}\text{ K}^{-1} \ (\Delta C_p/C_p = 0.4\%)$$

$$T_m = 402 \text{ K}$$

$$\Delta H_m = 16.2 \pm 0.3 \text{ kJ mol}^{-1}$$

Ternary Eutectic $AlCl_3$–$NaAlCl_4$–$KAlCl_4$. Measurements were made on 15.011 g of mixture with a crucible weighing 61.297 g. No measurements were made in the solid phase because the melting temperature was too low for our experimental apparatus; the enthalpy may be estimated from our experimental values for solid $NaAlCl_4$ and $KAlCl_4$ and the known enthalpy values of solid $AlCl_3$ (*19*); i.e.

$$H_T - H_{273} = -33037 + 110.9T + (0.37 \times 10^{-2})T^2 \text{ J mol}^{-1}$$

$$C_p = 110.9 + (0.74 \times 10^{-2})T \text{ J mol}^{-1}\text{ K}^{-1}$$

In the liquid phase (σ = 117 J)

$$H_T - H_{273} = -35016 + 188.7T - (2.327 \times 10^{-2})T^2 \text{ J mol}^{-1} \qquad (\Delta H/H = 0.4\%)$$

$$C_p = 188.7 - (4.7 \times 10^{-2})T \text{ J mol}^{-1}\text{ K}^{-1} \ (\Delta C_p/C_p = 0.8\%)$$

$$T_m = 363 \text{ K}$$

$$\Delta H_m = 18.370 \text{ kJ mol}^{-1}$$

The latter value seems high in view of this low melting temperature but could be expected from the high enthalpy of melting of $AlCl_3$ in excess in the ternary mixture (35.321 ± 0.84 kJ mol^{-1}) (*5*).

No more calorimetric data have been published for alkali chloroaluminates and their mixtures. Measurements on $NaAlCl_4$ by Rogers (*6*) show a systematic discrepancy of −6% with our values all along the curve $H_T - H_{273} = f(T)$. The values 9.8 and 10.5 kJ mol^{-1} have been given for the heat of melting of $NaAlCl_4$ and $KAlCl_4$, respectively; they are inconsistent with our results and those of Rogers (*20*, *21*).

It was interesting to compare the measured values of the binary eutectic with enthalpies and entropies calculated from the pure compounds. Because eutectics are mechanical mixtures in the solid phase, their enthalpy and entropy of mixing are equal to zero. Consequently, mixing enthalpies may be

Table IV. Mixing Functions for the Binary Eutectic

T, K	ΔH_{mix}, J mol^{-1}	ΔS_{mix}, J mol^{-1} K^{-1}	ΔG_{mix}, J mol^{-1}	ΔC_{mix}, J mol^{-1} K^{-1}
500	−2090	−0.15	−2020	0.1
600	−1870	0.30	−2050	−3.5
700	−1730	0.56	−2120	−6.9
800	−1680	0.66	−2210	−10.3
900	−1720	0.66	−2320	−13.7
1000	−1840	0.57	−2420	−17.1

calculated by difference between the experimental relative enthalpy of the mixture and the weighed sum of pure-compound enthalpies relative to the same temperature (here 273 K) (*22*, *23*). The mixing entropy and the Gibbs free energy may be estimated in the same way. From Table IV, the binary eutectic appears to have both an enthalpy and an entropy of mixing almost constant with temperature. This supports the validity of the heat-capacity-additivity assumption. Similarly, the smallness of the entropy of mixing results in a slight temperature dependence of the Gibbs free energy of mixing.

Assuming now the heat-capacity additivity for the ternary eutectic, the heat capacity of pure $AlCl_3$ is calculated to be

$$C_p = 176.1 - (10.3 \times 10^{-2})T \text{ J mol}^{-1} \text{ K}^{-1}$$

from the measured value of pure $NaAlCl_4$ and $KAlCl_4$ and that of the ternary eutectic. Measurements on pure liquid $AlCl_3$ have been made only between 473 and 504 K (*5*, *24*), giving C_p = 125.4 J mol^{-1} K^{-1}. This figure agrees very well with the average computed value for this temperature interval, i.e., 125.8 J mol^{-1} K^{-1}.

Finally, combining our calculated C_p for pure liquid $AlCl_3$, the enthalpy of solid $AlCl_3$, and the enthalpy of fusion of $AlCl_3$ (*5*), one can calculate the enthalpy of liquid $AlCl_3$ in the temperature interval 466–810 K; i.e.

$$H_T - H_{273} = -16746 + 176.09T - (5.17 \times 10^{-2})T^2 \text{ J mol}^{-1}$$

Within the additivity assumption for C_p, the values of the mixing enthalpy and entropy are obviously temperature independent; i.e.

$$\Delta H_{mix} = -3920 \text{ J mol}^{-1} \qquad \Delta S_{mix} = 3.19 \text{ J mol}^{-1} \text{ K}^{-1}$$

On the other hand the enthalpy of mixing of 0.43 mol of $NaAlCl_4$ and 0.235 mol of $KAlCl_4$ was calculated from the ΔH_{mix} of the binary eutectic by assuming a regular solution enthalpy of mixing, as justified by ref *25*. This value, ΔH_{mix} = −1510 J, corresponding to the ternary composition, suggests that the nonideality of the mixture strongly increases with the $AlCl_3$ content, since adding 0.30 mol of $AlCl_3$ to this mixture results in ΔH_{mix} = −2410 J mol^{-1}.

As a conclusion of these newly reported results, the most noteworthy point is the interest of using alkali chloroaluminate mixtures as liquids between 380 and 1000 K with a specific heat higher than, for example, liquid sodium (from 1.68 to 1.2 J cm^{-3} K^{-1} for the liquid eutectic $NaAlCl_4$–$KAlCl_4$ and 0.17 J cm^{-3} K^{-1} for liquid sodium). On the other hand, these results show that the heat of melting of the ternary eutectic appears to have a high value for a very low melting temperature. It would be worthwhile to confirm this point experimentally.

Acknowledgment

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Glossary

σ	standard deviation, J
A, B, C	coefficients of the polynomial function
H	measured enthalpy, J mol^{-1}
C_p	heat capacity, J mol^{-1} K^{-1}
n	number of experiments
$n - m$	degrees of freedom
T_m, ΔH_m	temperature and enthalpy of melting, K and kJ mol^{-1}
ΔH_{mix}	enthalpy of mixing, J mol^{-1}
ΔS_{mix}	entropy of mixing, J mol^{-1} K^{-1}
ΔG_{mix}	Gibbs free energy of mixing, J mol^{-1}
ΔC_{mix}	heat capacity of mixing, J mol^{-1} K^{-1}
ΔH_{obsd}	experimental data, J mol^{-1}
ΔH_{est}	$H_T - H_{273}$ from the least-squares fit, J mol^{-1}
ΔH_{calcd}	$H_T - H_{273}$ from the weighed sum of pure compounds, J mol^{-1}

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