# Thermodynamic Properties and Decomposition of Lithium Hexafluoroarsenate, LiAsF<sub>6</sub>

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**Abstract**—The heat capacity of lithium hexafluoroarsenate is determined in the temperature range 50–750 K by adiabatic and differential scanning calorimetry techniques. The thermodynamic properties of  $LiAsF_6$  under

standard conditions are evaluated:  $C_p^0$  (298.15 K) = 162.5 ± 0.3 J/(K mol),  $S^0$ (298.15 K) = 173.4 ± 0.4 J/(K mol),  $\Phi^0$ (298.15 K) = 81.69 ± 0.20 J/(K mol), and  $H^0$ (298.15 K) –  $H^0$ (0) = 27340 ± 60 J/mol. The  $C_p(T)$  curve is found to contain a lambda-type anomaly with a peak at 535.0 ± 0.5 K, which is due to the structural transformation from the low-temperature, rhombohedral phase to the high-temperature, cubic phase. The enthalpy and entropy of this transformation are  $5.29 \pm 0.27$  kJ/mol and  $10.30 \pm 0.53$  J/(K mol), respectively. The thermal decomposition of LiAsF<sub>6</sub> is studied. It is found that LiAsF<sub>6</sub> decomposes in the range 715–820 K. The heat of decomposition, determined in the range 765–820 K using a sealed crucible and equal to the internal energy change  $\Delta U_r(T)$ , is  $31.64 \pm 0.08$  kJ/mol.

## INTRODUCTION

Given that lithium hexafluoroarsenate,  $\text{LiAsF}_6$ , is a promising material for lithium batteries, its thermodynamic properties are of considerable interest. This work continues our studies of the thermodynamic properties of alkali hexafluoroarsenates. Earlier, we investigated the heat capacity of rubidium and cesium hexafluoroarsenates in a wide temperature range [1–3].

# SAMPLE PREPARATION

Lithium hexafluoroarsenate was prepared by reacting lithium metaarsenate and a 70% aqueous HF solution, with rapid water removal. The reaction product was then purified by recrystallization from anhydrous HF. According to analytical data, the sample contained 99.7 wt % LiAsF<sub>6</sub>, 0.19 wt % hydroxylated species (in particular, LiAsF<sub>5</sub>OH and LiAsF<sub>4</sub>(OH)<sub>2</sub>), 0.07 wt % HF, and 0.04 wt % water. No insoluble arsenates were detected. The pH of aqueous LiAsF<sub>6</sub> solutions was 3.2. The sample was stored in a sealed silica tube. All manipulations, including the loading of crucibles and calorimetric cells, were carried out in a dry nitrogen atmosphere.

#### LOW-TEMPERATURE MEASUREMENTS

The low-temperature heat capacity of a 2.7895-g lithium hexafluoroarsenate sample was measured in a vacuum adiabatic calorimeter with a 2-cm<sup>3</sup> caloric cell [4]. To improve heat exchange in the calorimeter, we used helium gas (p = 3 kPa). The heat capacity data for LiAsF<sub>6</sub> in the range 51–331 K (72 data points) are sum-





<i>Т</i> , К	$C_p$	<i>Т</i> , К	$C_p$	<i>Т</i> , К	$C_p$
51.61	32.40	123.07	83.44	219.84	135.9
54.43	34.59	126.98	86.07	224.00	137.5
57.67	37.01	130.92	88.71	228.17	139.4
60.85	39.29	134.85	91.26	232.34	140.9
63.88	41.50	138.82	93.75	236.58	142.6
66.86	43.63	142.78	96.42	240.80	144.1
69.84	45.69	146.68	98.68	245.51	145.9
72.78	47.69	150.65	101.0	250.71	147.7
75.70	49.81	154.63	103.3	255.92	149.4
78.57	51.85	158.63	105.6	261.13	151.1
81.44	53.89	162.63	107.9	266.37	152.9
84.23	55.88	166.69	110.1	271.61	154.6
86.28	57.30	170.76	112.3	276.84	156.3
89.26	59.59	174.87	114.6	282.10	157.9
92.21	61.71	178.97	116.7	287.31	159.4
95.14	63.78	183.04	118.9	292.50	160.9
98.11	65.89	187.11	120.9	296.77	162.0
101.07	68.03	191.17	122.9	299.40	162.9
104.02	70.13	195.27	124.9	304.66	164.4
106.97	72.20	199.39	126.8	309.94	165.7
109.98	74.62	203.52	128.6	315.20	167.2
112.94	76.53	207.53	130.5	320.47	168.8
115.91	78.55	211.55	132.3	325.75	170.4
119.27	80.78	215.69	134.1	331.03	171.3

Table 1. Low-temperature heat capacity, J/(K mol), of  ${\rm LiAsF}_6$ 

marized in Table 1 and Fig. 1 (the molecular weight of LiAsF<sub>6</sub> was taken to be 195.853). No anomalies were detected in the  $C_p(T)$  curve in the temperature range studied. The  $C_p(T)$  data were smoothed using an application program incorporated in the IVTANTERMO Database [5]. The discrepancy between the measured and smoothed data in the range 50–330 K was no greater than 0.2%.

To extrapolate the data to absolute zero, we used a technique which takes into account that compounds similar in the structure of the complex anion and crystal structure have similar temperature dependences of the fractal dimension [6]. Lithium hexafluorophosphate and lithium hexafluoroarsenate have an LiSbF<sub>6</sub>-type rhombohedral structure ( $R_1$ ) and are close in lattice parameters [7]. In view of this, the temperature dependences of heat capacity for LiAsF<sub>6</sub> and LiPF<sub>6</sub> [8] were

converted into those of the fractal dimension (Fig. 2) by the procedure described earlier [9].

The smoothed heat capacity data and thermodynamic functions of lithium hexafluoroarsenate are summarized in Table 2. The thermodynamic properties at standard conditions are

$$C_p^0$$
(298.15 K) = 162.5 ± 0.3 J/(K mol),  
 $S^0$ (298.15 K) = 173.4 ± 0.4 J/(K mol),  
 $\Phi^0$ (298.15 K) = 81.69 ± 0.20 J/(K mol),  
 $H^0$ (298.15 K) –  $H^0$ (0) = 27340 ± 60 J/mol.

In evaluating the error, we assumed (based on earlier experimental  $C_p$  data for lithium compounds with complex anions [10–14]) that lithium hexafluoroarsenate undergoes no structural phase transitions below 50 K.

#### HIGH-TEMPERATURE MEASUREMENTS

The thermal properties of lithium hexafluoroarsenate were studied using a SETARAM DSC 111 differential scanning calorimeter (precision in temperature measurements,  $\pm 1$  K; uncertainty in temperature scale,  $\pm 1$  K; maximum sensitivity, 15  $\mu$ W). Since LiAsF<sub>6</sub> is very hygroscopic, we used Ni-sealed stainless steel crucibles (0.15-cm<sup>3</sup> volume).

First, several LiAsF<sub>6</sub> samples were subjected to the following temperature program: heating from 290 to 623–673 K at a rate of 3 K/min, isothermal hold for 10 min, and cooling at 3 or 5 K/min (Fig. 3). Thermal effects were evaluated using a SETARAM program for the graphic integration of DSC peaks. The integration error was 0.5–2%. As the peak temperature we took either the temperature at which the auxiliary line through the ascending peak slope intersected the linearly extrapolated initial baseline ( $T_e$ ) or the maximum peak temperature ( $T_p$ ).

The heating curves of LiAsF<sub>6</sub> show an endotherm at 495–560 K, which is obviously due to the structural transformation of LiAsF<sub>6</sub> [15, 16]. The enthalpy of this transformation is  $\Delta_{\rm tr} H$ (endo) = 3.728 ± 0.075 kJ/mol;  $T_{\rm e} = 534.6 \pm 0.3$  K,  $T_{\rm p} = 538.7 \pm 0.4$  K (average of four scans).

The cooling curves of LiAsF<sub>6</sub> show an exotherm in the range 540–485 K, with an enthalpy of transformation  $-\Delta_{tr}H(exo) = 3.742 \pm 0.056$  kJ/mol;  $T_e$  531.4 ± 0.8 K,  $T_p = 526.1 \pm 0.2$  K (average of three scans). The estimated uncertainty in  $\Delta_{tr}H$  includes the errors relating to peak integration and  $\Delta_{tr}H$  averaging over different samples. Our results demonstrate that the structural transformation of LiAsF<sub>6</sub> is reversible and involves no



**Fig. 2.** Fractal dimension of (1) LiPF<sub>6</sub> and (2) LiAsF<sub>6</sub> extracted from heat capacity data.

thermal hysteresis. No other thermal events were detected between 290 and 673 K.

# Thermal Decomposition of Lithium Hexafluoroarsenate

As shown earlier, experimental conditions have a significant effect on  $\text{LiAsF}_6$  decomposition. According to pyrolytic mass spectrometry data, the decomposition process begins at 553 K in vacuum and near 623 K in a sealed glass tube filled with dry air [15]. Ippolitov *et al.* [16] reported that  $\text{LiAsF}_6$  dissociates into LiF and  $\text{AsF}_4$  at 623 K, without melting.

In our studies of  $\text{LiAsF}_6$  decomposition, we used sealed steel cells and special calorimetric containers ensuring the removal of gaseous decomposition products. The measuring technique was described in detail in a previous report, dealing with LiPF<sub>6</sub> [17]. All of the thermal effects in DSC curves were reduced to the same sample weight in order to provide a comparison of processes occurring in the same temperature range under different conditions.

LiAsF<sub>6</sub> decomposition with the removal of gaseous decomposition products. As pointed out above, the heating curves of the samples contained in sealed tubes in a dry nitrogen atmosphere show no thermal events other than the phase transition up to 673 K. To ascertain that this event is indeed a phase transformation, rather than decomposition, the sample was heated in a container ensuring the removal of gaseous reaction products. To this end, the pressure in the system was slightly reduced, to 200 Pa; that is, the experiment was performed at an almost normal pressure.

Figure 4 shows the first scan of an LiAsF<sub>6</sub> sample (0.1004 g), which includes heating from 298 to 723 K at 5 K/min, isothermal hold for 30 min, and cooling from 723 K at 5 K/min. The small peak in the heating curve at 330–390 K may be due to the melting of LiAsF<sub>6</sub> · 3H<sub>2</sub>O and LiAsF<sub>6</sub> · H<sub>2</sub>O impurities (probably,



**Fig. 3.** Heating–cooling cycle around the structural phase transition of  $\text{LiAsF}_{6}$ .

the sample took up some water while it was transferred to the container).

In the range 440–570 K, the heating curve shows two endothermic peaks and a weak exothermic peak at  $T_p = 620.9$  K. The temperature of the first endotherm is 493.1 K. The parameters of the main endothermic peak (512–570 K) are  $T_e = 535.3$  K,  $T_p = 541.3$  K, and  $\Delta_t H(\text{endo}) = 3.648 \pm 0.045$  kJ/mol. The cooling curve shows one exotherm in the range 530–455 K, with  $-\Delta_t H(\text{exo}) = 3.773 \pm 0.101$  kJ/mol,  $T_e = 526.1$  K, and  $T_p = 521.1$  K. These findings provide conclusive evidence that the endothermic peak in the range 512– 570 K is not due to the decomposition process

$$LiAsF_6(cr) = LiF(cr) + AsF_5(g),$$

because, under the conditions of that experiment, at least part of the  $AsF_5$  released would be removed, and the exotherm in the cooling curve would be smaller in magnitude than the endotherm in the heating curve, which was not the case.



**Fig. 4.** First heating–cooling cycle of  $\text{LiAsF}_6$  with the removal of gaseous decomposition products.

 $C_p^0(T)$  $S^0(T)$  $\Phi^0(T)$  $H^0(T) - H^0(0)$ *T*, K J/(K mol) J/mol 1.708 0.569 0.1420 6.405 15 20 4.669 1.458 0.3485 22.19 8.822 2.922 0.7069 55.39 25 4.955 1.239 30 13.63 111.5 35 18.32 7.411 1.941 191.5 40 22.81 10.15 2.793 294.4 419.2 45 27.06 13.09 3.773 50 31.06 16.15 4.857 564.6 913.2 60 38.57 22.48 7.263 70 45.72 28.97 9.900 1335 80 52.86 35.54 12.69 1828 2392 90 60.09 42.1815.60 100 48.89 18.59 3029 67.31 110 74.43 21.65 3738 55.64 24.77 120 81.36 62.41 4517 130 88.06 69.19 27.92 5365 140 94.51 75.96 31.11 6278 150 100.6 82.69 34.33 7254 160 106.5 89.37 37.56 8290 170 112.0 95.99 40.80 9382 180 117.3 102.5 44.05 10530 122.3 190 109.0 47.30 11730 200 127.1 50.55 12970 115.4 131.6 53.79 14270 210 121.7 220 136.0 128.0 57.02 15610 230 140.0 134.1 60.23 16990 140.1 240 143.8 63.44 18410 250 147.5 146.1 66.62 19860 260 150.9 151.9 69.79 21350 154.1 72.94 270 157.7 22880 280 157.2 163.3 76.07 24440 160.2 168.9 79.18 290 26020 162.5 298.15 173.4 81.69 27340 300 163.0 174.4 82.26 27640 310 165.9 179.8 85.32 29280 320 168.6 185.1 88.35 30960 330 171.2 190.3 91.36 32660

**Table 2.** Low-temperature thermodynamic properties of  $\text{LiAsF}_6$ 

Note: The data in the range 15–50 K were obtained be extrapolating the experimental  $C_p(T)$  data to absolute zero.

Next, the same sample, without intermediate weighing, was heated again from 323 to 793 K at a rate of 10 K/min. The heating curve showed a peak due to the phase transition (525–560 K) with  $T_e = 533.0$  K and  $T_p = 540.9$  K. Decomposition began at about 720 K and did not reach completion at 793 K. At this temperature, the experiment was ceased because the container material would not withstand higher temperatures. Unfortunately, the weight loss due to sample decomposition could not be determined since the gaseous decomposition products attacked the container.

LiAsF<sub>6</sub> decomposition in a sealed crucible. In the first run, an LiAsF<sub>6</sub> sample (0.030 g) sealed in a crucible was subjected to the following temperature program: heating from 298 to 693 K at 10 K/min, isothermal hold for 10 min, heating from 693 to 873 K at 5 K/min, and cooling from 873 K at 5 K/min (Fig. 5).

As in the case of the removal of gaseous reaction products, the heating curve recorded between 298 and 693 K at a rate of 10 K/min shows two endothermic peaks. The first, small endotherm (460–510 K,  $T_p$  = 482.5 K) differs in magnitude from the exotherm in the range 605–640 K ( $T_p$  = 621.2 K) by no more than 5%. The parameters of the main peak (512–575 K), related to the phase transition, are  $T_e$  = 532.3 K,  $T_p$  = 540.6 K, and  $\Delta_{\rm tr} H$ (endo) = 3.640 ± 0.018 kJ/mol.

The heating curve recorded between 693 and 873 K at 5 K/min shows an endothermic peak due to  $LiAsF_6$ decomposition. At this heating rate, thermal decomposition occurs in the range 765-820 K, and the endotherm comprises two unresolved peaks with  $T_{\rm p}(I)$  = 775.3 K and  $T_p(II) = 796.8$  K, with a shoulder on the high-temperature side (800.6 K) of the latter peak. As the temperature of decomposition onset, we took  $T_{\rm e}(I) = 760.5$  K. Since the AsF<sub>5</sub> released during LiAsF<sub>6</sub> decomposition in a sealed crucible was not removed from the reaction zone, the thermal effect of decomposition was determined at a constant volume and varying (rising) pressure. Consequently, the measured heat of reaction is equal to the internal energy change  $\Delta U_r(T)$ . Unfortunately, the  $\Delta U_r(T)$  data cannot be converted into  $\Delta H_{\rm r}(T)$  since the AsF<sub>5</sub> pressure in the sealed crucible is unknown. The experimentally determined value of  $\Delta U_{\rm r}(T)$  is 31.64 ± 0.08 kJ/mol.

In the range 805–700 K, the cooling curve shows an exotherm due to the reverse reaction,  $\text{LiAsF}_6$  formation, with  $\Delta U_r = 31.65 \pm 0.09$  kJ/mol. The main peak is observed at 796.4 K, with a shoulder at 781.0 K.  $T_e = 799.9$  K can be taken as the onset of the reverse reaction.

The parameters of the exotherm due to the reverse transformation (530–500 K) are  $T_e = 528.7$  K,  $T_p = 525.6$  K, and  $-\Delta_{tr}H(exo) = 2.563 \pm 0.010$  kJ/mol.

Thus, lithium hexafluoroarsenate decomposes at notably higher temperatures than does lithium hexafluorophosphate [17]. As in the case of  $\text{LiPF}_6$ , the reverse

reaction (LiAsF<sub>6</sub> formation) reaches completion in a sealed crucible. Figure 6 compares the DSC curves of the processes run in a sealed crucible and with the removal of gaseous reaction products.

Comparison of the present and earlier results demonstrates that the parameters of the thermal decomposition of lithium hexafluoroarsenate depend significantly on both the process conditions and sample quality.

# Heat Capacity of LiAsF<sub>6</sub> at Elevated Temperatures

The heat capacity  $C_{p,\text{step}}(T)$  of a 0.1725-g sample (the crucible almost entirely filled with the substance) was measured from 298 to 748 K in the course of intermittent heating: each cycle included heating at a rate of 1.5 K/min for 200 s and isothermal hold for 400 s. Thus, the temperature was raised by 5 K per cycle. Each series of measurements consisted of 20–40 cycles (data points), and its temperature range overlapped with those of the preceding and subsequent series. After each series of measurements, the sample was cooled in the calorimeter at 10–20 K/min and stored at room temperature until the subsequent series. Heating to the set temperature was carried out at 5–10 K/min.

Previous work showed that, in the case of thickwalled steel cells, the measured heat capacity should be corrected using heat capacity data for a references substance (e.g., corundum). In connection with this, we also measured the heat capacity of powdered synthetic corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) crystals using the same tubes and analogous series of steplike heating. The procedure used to correct heat capacity data was described previously [8].

The corrected heat capacity data for LiAsF<sub>6</sub> in the range 298–748 K (3 series of measurements, 95 data points) are displayed in Table 3. With a rare exception, the discrepancy between the measured and smoothed values within a series does not exceed 0.5% (standard deviation of 0.15–0.23%). For the convenience of thermodynamic computations, the  $C_p$  values in Table 3 are given with one extra significant digit. In the temperature range 300–330 K, the heat capacity determined by DSC is systematically lower compared to the adiabatic calorimetry data (Table 1). For this reason, prior to the optimization and simultaneous processing of the low-and high-temperature heat capacity data, the DSC values were increased by 4.1 J/(K mol).

The  $C_p(T)$  curve in Fig. 7 shows a lambda-type anomaly (350–600 K) due to the transition from the  $\alpha$ phase (rhombohedrally distorted NaCl structure) [7] to the  $\beta$  phase (cubic NaCl structure). The most drastic changes in  $C_p$  occur in the range 480–550 K. To more accurately determine the transition temperature, we carried out two additional series of measurements (IV and V) in the range 510–550 K at a heating rate of 0.6 K/min, raising the temperature by 2 K per cycle. (The data obtained in series IV and V are not included in Table 3 because they were not used in assessing the



**Fig. 5.** Heating–cooling cycle of  $LiAsF_6$  in a sealed crucible.



**Fig. 6.** Heating curves of lithium hexafluoroarsenate in (1) a container ensuring the removal of gaseous decomposition products and (2) a sealed crucible.

thermodynamic properties of LiAsF<sub>6</sub>.) Quasi-equilibrium conditions near 530–540 K were only reached in series V (heating for 200 s and holding for 1800 s in each measurement cycle). The transition temperature was determined as the average over three measurements (series II, IV, and V) in which the highest anomalous heat capacity was obtained:  $T_{tr}(\alpha \rightarrow \beta) =$ 535.0 ± 0.5 K. In series V, the heat capacity at 535 K was 1720 J/(K mol), whereas that in series II was 722 J/(K mol).

In evaluating the thermodynamic properties of lithium hexafluoroarsenate, the temperature range 0– 748 K was divided into three portions:

0–350 K ( $\alpha$ -LiAsF<sub>6</sub>); 350–600 K ( $\alpha \longrightarrow \beta$  transition; 600–748 K ( $\beta$ -LiAsF<sub>6</sub>.

<i>Т</i> , К	$C_p$	<i>Т</i> , К	$C_p$	<i>Т</i> , К	$C_p$	<i>Т</i> , К	$C_p$
Series I		419.8	9.8 192.6		259.9	Series III	
299.8	159.0	424.8	192.4	534.9	722.1*	635.1	208.9
304.8	160.4	429.8	195.5	539.9	233.0*	639.9	208.2
309.8	161.7	434.8	195.5	545.0	205.0	644.9	208.2
314.8	163.0	439.9	197.3	549.9	201.6	649.9	208.5
319.7	164.4	444.8	199.0	554.9	202.4	654.9	209.8
324.7	165.7	449.8	201.1	559.9	202.5	659.9	209.7
329.8	167.1	454.8	203.1	564.9	203.6	664.8	210.0
334.8	168.9	459.8	204.3	569.9	204.4	669.8	211.2
339.8	169.4	464.8	205.2	574.9	204.3	674.8	211.5
344.8	171.3	Series II		579.9	205.2	679.8	211.8
349.8	171.3	460.0	204.2	584.9	204.1	684.8	213.2
354.8	173.4	465.0	205.7	589.9	204.8	689.8	213.5
359.9	175.3	470.0	205.9	594.9	204.1	694.7	213.6
364.8	176.3	475.0	207.3	599.9	204.2	699.7	214.0
369.8	177.2	480.0	209.1	604.9	204.4	704.9	213.7
374.9	180.3	485.0	209.1	609.8	204.7	709.8	215.4
379.9	179.8	490.0	212.2	614.8	205.5	714.8	216.3
384.9	182.7	495.0	215.0	619.9	206.7	719.9	217.6
389.9	182.9	500.0	216.4	624.8	205.9	724.8	218.3
394.9	184.9	505.0	221.1	629.8	206.9	729.8	219.1
399.9	185.1	510.0	223.6	634.8	207.0	734.9	218.9
404.8	187.1	515.0	226.8	639.8	208.3	739.9	221.1
409.8	187.9	519.9	234.7	644.8	208.3		

Table 3. Heat capacity, J/(K mol), of LiAsF<sub>6</sub> at elevated temperatures

\* Obtained under nonequilibrium experimental conditions.

The low- and high-temperature heat capacity data were smoothed jointly using programs described previously [18]. For the range 0–350 K, smoothed heat capacity data for  $\alpha$ -LiAsF<sub>6</sub> were obtained by the DEK equation,

 $C_p(T) = 7.40 \text{D}(211 \text{ K}) + 7.25 \text{D}(810 \text{ K})$ 

$$+ 8.00D(1884 \text{ K}) + 1.00E(503 \text{ K})$$

+ 1.25K(490, 567 K),

where D, E, and K are the Debye, Einstein, and Kiffer functions, respectively. The thermodynamic properties of  $\alpha$ -LiAsF<sub>6</sub> under standard conditions determined using this equation and the jointly processed DSC and adiabatic calorimetry data coincide with those above,

derived from the adiabatic calorimetry data, to within  ${\simeq}0.5\%$  .

The heat capacity data for  $\beta$ -LiAsF<sub>6</sub> in the range 600–715 K were smoothed using the DE equation:

 $C_p(T) = 8.304 \text{D}(287 \text{ K}) + 7.250 \text{D}(1364 \text{ K})$ 

+ 8.000D(1364 K) + 2.250E(1215 K).

The thermodynamic properties of  $LiAsF_6$  in the range 300–715 K evaluated by the above equations are summarized in Table 4. As follows from the heat capacity data for  $\beta$ -LiAsF<sub>6</sub>, this compound begins to decompose above 715 K.

The enthalpy and entropy of transformation were evaluated by graphically integrating the  $C_{p,an}(T)$  and  $C_{p,an}(T)/T$  plots in the range 350–600 K. The anomalous

INORGANIC MATERIALS Vol. 39 No. 2 2003



Fig. 7. Heat capacity of  $LiAsF_6$  at elevated temperatures: (1) adiabatic calorimetry data, (2) DSC data, (3) normal component in the region of the transformation.

heat capacity was found as  $C_{p,an}(T) = C_{p,meas}(T) - C_{p,n}(T)$ . To determine the normal component of heat capacity, the low- and high-temperature portions of the  $C_p(T)$  curve lying beyond the transformation region were extrapolated to  $T_{tr} = 535$  K. In this way, we obtained  $\Delta_{tr}H(\alpha \longrightarrow \beta, \text{step}) = 5.29 \pm 0.27$  kJ/mol and  $\Delta_{tr}S(\alpha \longrightarrow \beta, \text{step}) = 10.30 \pm 0.53$  J/(K mol)  $\approx R \ln 3$ . The indicated uncertainties arise from the scatter in experimental data.

Since, in evaluating  $\Delta_{tr} H(\alpha \longrightarrow \beta, \text{ step})$  and  $\Delta_{tr}S(\alpha \longrightarrow \beta, step)$ , we used the data points at 534.9 and 539.9 K (series II), which were obtained under nonequilibrium experimental conditions, we also measured heat capacity  $C_{p,\text{scan}}(T)$  during continuous heating from 453 to 573 K at a rate of 1 K/min. The enthalpy of transformation,  $\Delta_{tr} H'(\alpha \longrightarrow \beta, scan) = 3.98 \pm 0.06 \text{ kJ/mol},$ was evaluated by graphically integrating (SETARAM program) the endothermic peak between 485 and 547 K. For comparison,  $\Delta_{tr} H'(\alpha \longrightarrow \beta, scan)$  was corrected for the anomalous enthalpy in the ranges 350-485 and 547–600 K.  $\Delta_{tr}H(\alpha \rightarrow \beta, \text{ step})$  and  $\Delta_{tr} H''(\alpha \longrightarrow \beta, scan)$  coincide to within the experimental error (5.29  $\pm$  0.27 and 5.03  $\pm$  0.24 kJ/mol, respectively), indicating that the  $\alpha \longrightarrow \beta$  phase transition is accompanied by no isothermal contribution and is, therefore, second-order. Note that the enthalpy of transformation evaluated by integrating the peak in heating curves is substantially lower. The reason is that the anomalous enthalpy increment in the early stage of the very broad transformation is included in the baseline of the DSC curve (see, e.g., [19]).

INORGANIC MATERIALS Vol. 39 No. 2 2003

The fact that the enthalpy of transformation is close to  $R \ln 3$  suggests that the  $\alpha \longrightarrow \beta$  structural phase transition of lithium hexafluoroarsenate involves order–disorder processes which increase the number of possible equilibrium orientations of the AsF<sup>6–</sup> ion in going from the low-temperature, ordered phase to the high-temperature, disordered phase by a factor of three.

**Table 4.** Thermodynamic properties of  $\text{LiAsF}_6$  from 300 to 715 K

<i>Т</i> , К	$C_p^0(T)$	S <sup>0</sup> (T)	$\Phi^0(T)$	$H^0(T) - H^0(0)$
,		J/mol		
300	163.2	173.1	81.07	27600
350	175.8	199.2	96.11	36080
400	186.0	223.4	110.5	45140
450	194.4	245.8	124.3	54650
500	201.2	266.6	137.5	64550
535(α)	205.3	280.3	146.4	71660
535(β)	198.7	290.7	146.4	76950
550	201.1	296.2	150.9	79950
600	207.8	314.0	163.7	90180
650	213.4	341.2	178.1	106000
700	218.1	357.2	190.3	116800
715	219.3	361.8	193.9	120100

# CONCLUSION

Heat capacity measurements were used to evaluate the thermodynamic properties of lithium hexafluoroarsenate from liquid helium temperatures to the decomposition onset and to assess the characteristics of the structural phase transition in this compound. By studying the high-temperature thermal properties of  $\text{LiAsF}_6$ , we determined the parameters of its decomposition, which were found to depend significantly on both the experimental conditions and sample quality.

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