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CALORIMETRIC STUDY OF THERMAL DECOMPOSITION OF LITHIUM HEXAFLUOROPHOSPHATE

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Abstract

Enthalpy of formation of lithium hexafluorophosphate was calculated based on the differential scanning calorimetry study of heat capacity and thermal decomposition. It was found that thermal decomposition of $LiPF_6$ proceeds at normal pressure in the temperature range 450–550 K. Enthalpy of $LiPF_6$ decomposition is $\Delta_d H$($LiPF_6$, *c*, 298.15 K)= 84.27±1.34 kJ mole^{-1}. Enthalpy of formation of lithium hexafluorophosphate from elements in standard state is $\Delta_f H^0$($LiPF_6$, *c*, 298.15 K) = –2296±3 kJ mol^{-1}.

Keywords: DSC, enthalpy of formation, heat capacity, thermal decomposition

Introduction

Study of thermodynamic properties of lithium hexafluorophosphate is governed by its application in the process of lithium batteries and accumulator production. Available in literature data on the results of experimental study of formation enthalpy of alkali metal hexafluorophosphates contain only $\Delta_f H$ values for sodium, potassium, rubidium and cesium salts [1]. No information about the study of $LiPF_6$ enthalpy of formation was found in the literature. Calculation of $LiPF_6$ formation enthalpy based on the known models gives a very rough quantity results.

In this work the enthalpy of $LiPF_6$ formation was calculated based on experimental value of enthalpy of decomposition of $LiPF_6$ studied by differential scanning calorimetry (DSC) as DSC is the effective tool for the study of decomposition with the formation of gaseous products [2].

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Experimental

Sample

Crystalline lithium hexafluorophosphate was synthesized at the SGChE by the direct reaction of lithium fluoride with phosphoric pentafluoride in the HF medium. Analysis of prepared sample showed that it contains 99.7–99.8 wt.% $LiPF_6$. Content of impurities is: LiF–(0.1÷0.2 wt.%), HF–(0.02÷0.07 wt.%), H_2O–(0.001÷0.009 wt.%). Molecular mass of $LiPF_6$ is equal to 151.905.

Method

The thermal decomposition of lithium hexafluorophosphate has been studied using a SETARAM DSC 111 instrument (temperature reproducibility, ±0.1 K; uncertainty in the temperature scale, ±0.5 K; DSC measuring sensitivity, 15 μW). At temperatures below 500 K the error of thermal effects determination is within 1%.

Two different experimental ways were used to study the decomposition of lithium hexafluorophosphate according to the reaction $LiPF_6(c) \rightarrow LiF(c) + PF_5(g)$:

a) in hermetically sealed calorimetric crucible
b) in calorimetric crucible with the remove of gaseous products of decomposition.

Because the gaseous phosphoric pentafluoride forms at the decomposition of $LiPF_6$, these two ways differ radically. In the first case the thermal effect is determined at constant volume and variable (increasing) pressure, i.e. measured heat of reaction relates to the internal energy change $\Delta_r U(T)$. In the second case pressure is near to constant and equal to standard conditions, so the enthalpy of reaction $\Delta_r H(T)$ is measured.

To carry out the experiments we used stainless steel calorimetric crucibles with the nickel seal. Schemes of two used types of calorimetric crucibles are given in Fig. 1.

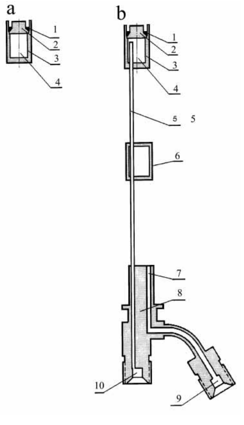

Fig. 1 Schemes of stainless steel calorimetric crucibles used in the study of thermal decomposition of $LiPF_6$ A – sealed crucible, B – crucible with remove of gaseous products of decomposition. 1 – nickel seal, 2 – cap, 3 - crucible body, 4 - sample, 5 – tube for gas remove, 6 – heat buffer, 7 – tube for argon blowing, 8 – crucible holder, 9 – argon input, 10 – gaseous products output

Testing experiment in the temperature range 300–600 K showed that no reaction of lithium hexafluorophosphate and decomposition products with crucible occurs. Experimental setup based on SETARAM DSC 111 was built up to carry out the study of $LiPF_6$ decomposition at normal pressure. To pump out all formed gaseous products the system was evacuated to bring the pressure a little down (200 Pa) the normal value. Scheme of experimental setup is plotted in Fig. 2.

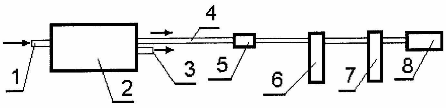

Fig. 2 Scheme of experimental setup. 1 – argon input, 2 – DSC 111 measuring block, 3 – argon output, 4 – gaseous products output, 5 – cartridge with active carbon, 6 – liquid nitrogen trap, 7 – liquid nitrogen trap with active carbon, 8 – pump

Since lithium hexafluorophosphate is extremely hygroscopic substance, all manipulations with sample (including filling of calorimetric crucibles, preliminary and intermediate operations at crucible weighing before and after $LiPF_6$ decomposition) were carried out in glove box with dried nitrogen atmosphere. Tightness of sealed calorimetric crucibles was controlled by weighing during the day after sealing a calorimetric crucible.

Values of thermal effects ($\Delta_r U$ or $\Delta_r H$) were calculated by graphic integration of peaks in the DSC curves using the SETARAM software. The error of integration varied from 0.1 to 3% depending on peak shape and area. Temperatures of thermal effects were determined as extrapolated peak onset temperature T_e and as maximum peak temperature T_p.

Results and discussion

Study of $LiPF_6$ decomposition in sealed crucible

Thermal behavior of lithium hexafluorophosphate in sealed stainless steel crucible (V=0.15 cm^3) was studied in the temperature range 298–513 K. Stainless steel crucibles with the nickel seal can stand a pressure up to 35 MPa at 573 K.

DSC curves were recorded following the regime: heating in the range 298–513 K (rate 2 K min^{-1}) – isothermal stage (10 min) - cooling from 513 to 343 K (rate 2 K min^{-1}).

Results of decomposition investigation of $LiPF_6$ samples for four different batches are presented in Table 1. The heating-cooling cycle for sample 3 is shown in Fig. 3.

From Table 1 one can see that decomposition of $LiPF_6$ in sealed crucible proceeds in the temperature range 410(425)–480 K. The endothermic peaks were fixed at T_e= 467.2±0.1 K and T_p= 470.1±0.2 K (from four runs). Heating up to 550 K showed that no thermal effects appear above the decomposition event.

Inasmuch evolved gaseous phosphoric pentafluoride formed at $LiPF_6$ decomposition does not remove from the reaction zone, the exothermic effect connected with the reverse reaction is observed at cooling in the range 468–420 K with T_e = 462.4±0.1 K and T_p = 459.8±0.3 K (from four runs).

Table 1 Parameters of thermal effects in DSC curves for lithium hexafluorophosphate (sealed calorimetric crucibles)

No., mass scanning rate	Endothermic effect in heating curve				Exothermic effect in cooling curve			
	Integrating range/ K	T_e/ K	T_p/ K	Δ_rU/ J g^{-1}	Integrating range/ K	T_e/ K	T_p/ K	– Δ_rU/ J g^{-1}
No. 1, 0.0722 g 2 K min^{-1}	408–483	467.2	469.8	25.92±0.06	468–418	462.5	460.1	17.70±0.31
No. 2, 0.0856 g 2 K min^{-1}	408–483	466.9	470.0	20.62±0.07	468–418	462.5	460.1	18.73±0.94
No. 3 0.0979 g 2 K min^{-1}	423–482	467.5	470.4	20.41±0.15	468–413	462.4	459.5	20.06±0.04
No. 4, 0.0948 g 2 K min^{-1}	423–482	467.2	470.2	19.67±0.06	468–413	462.3	459.5	19.66±0.01

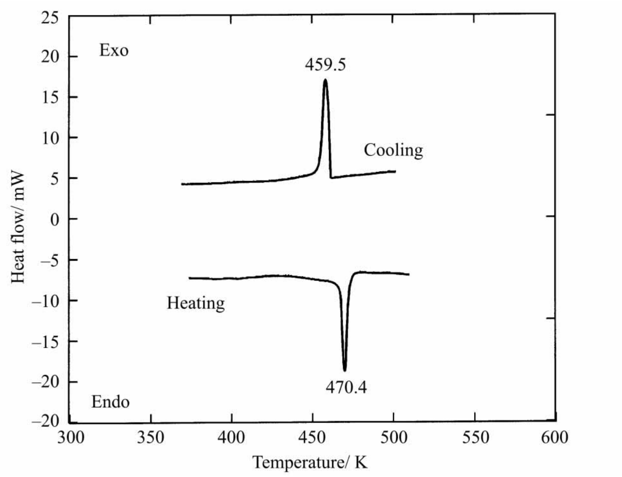

Fig. 3 DSC curves of heating and cooling for sample 3 $LiPF_6$ in sealed crucible

Values of thermal effects of forward (decomposition) and reverse (formation) reactions for $LiPF_6$ are very near (Table 1). It confirms that decomposition process in the sealed crucible is suppressed by the pressure influence of forming gaseous PF_5 and that the reverse reaction of lithium hexafluorophosphate synthesis from lithium fluoride and phosphoric pentafluoride takes place at cooling of sample in the sealed crucible (Fig. 3). It is necessary to note that values of endothermic effect presented in Table 1 can not be attributed to heat of decomposition of the whole of the specimen.

Study of $LiPF_6$ decomposition in crucible with the remove of gaseous products of decomposition

DSC curves of two samples of $LiPF_6$ were recorded by discrete «heating-cooling» cycles. Measurements for each sample were carried out by series consisting of three cycles. Results of study of $LiPF_6$ decomposition heat are given in Tables 2, 3 and Figs 4, 5. Values of thermal effects in Tables are presented as well in mJ as in J per gram of initial sample mass. The last value is more convenient for comparison of the results obtained in consecutive cycles.

Sample $LiPF_6$ (1)

The initial study of sample 1(cycle 1) was performed following the program used earlier for study of $LiPF_6$ decomposition in hermetically sealed stainless steel calorimetric crucible (mass 0.1602(5) g, series 1).

Cycle 1 (Fig. 4a): heating in the range 297–548 K (rate 2 K min^{-1}) – isothermal stage (10 min) - cooling from 548 to 323 K (rate 2 K min^{-1}).

Weighing the sample 1 after the cycle 1 showed that it is heavier (0.04741 g) than theoretical value of LiF mass (0.0274 g) for the full decomposition of $LiPF_6$-1. It can be considered as the incomplete decomposition of $LiPF_6$ sample. From other side,

Table 2 Parameters of endothermic effects in the heating curves of lithium hexafluorophosphate (crucible with gas remove)

Cycle, Scanning rate	Peak I		Peak II	Peak III		Peak IV	Δ_rH		
	T_e/ K	T_p/ K	T_p/ K	T_e/ K	T_p/ K	T_p/ K	Integrating range/ K	mJ	J g^{-1}
Sample LiPF$_6$-1; mass 0.1602 g (series 1)									
Cycle 1 2 K min^{-1}	467.3	470.5	489.3	491.3	499.6	520.5	457–544	73492±97	458.61±0.60
Cycle 2 5 K min^{-1}	465.9	473.8		486.2	503.0		431–543	11032±105	68.84±0.65
Cycle 3 5 K min^{-1}	467.4	472.9		486.5	499.3		430–538	1624±11	10.13±0.07
						Total effect of three heatings		86148±213	537.58±1.32
Sample LiPF$_6$-2; mass 0.1221 g (series 2)									
Cycle 1 5 K min^{-1}	466.2	472.8				522.0, 532.7	433–576	59331±30	485.92±0.24
Cycle 2 5 K min^{-1}			477.4	490.9			405–532	5251.2±105.5	43.01±0.86
Cycle 3 5 K min^{-1}			477.1	491.2			408–518	1587.4±24.7	13.00±0.20
						Total effect of three heatings		66170±160	541.93±1.30

Table 3 Parameters of exothermal effects in cooling curves of lithium hexafluorophosphate (crucibles with gas remove)

Cycle, scanning rate	T_e/ K	T_p/ K	$-\Delta_r H$		
			Integrating range/ K	mJ	J g^{-1}
		LiPF$_6$-1; mass 0.1602 g (series 1)			
Cycle 1, 2 K min^{-1}	425.4	420.5	442–393	3657±17	22.82±0.11
Cycle 2, 5 K min^{-1}	425.9	413.0	454–386	882.9±17.1	5.509±0.107
Cycle 3, 5 K min^{-1}	417.3	406.8	421–397	48.04±0.34	0.300±0.002
		Total effect of three coolings		4587.9±34.4	28.63±0.22
		LiPF$_6$-2; mass 0.1221 g (series 2)			
Cycle 1, 5 K min^{-1}	411.5	403.9	435–367	3014.9±8.5	24.69±0.07
Cycle 2, 5 K min^{-1}	413.1	399.1	437–360	1189.3±28.0	9.74±0.23
Cycle 3, 5 K min^{-1}	424.0	397.8	432–367	369.5±13.0	3.03±0.11
		Total effect of three coolings		4573.7±49.5	37.46±0.41

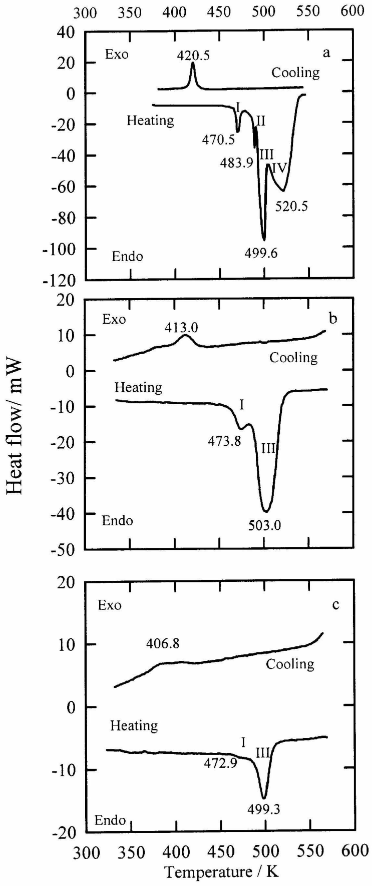

Fig. 4 DSC curves of heating and cooling of sample $LiPF_6$-1: a – cycle 1, b – cycle 2, c – cycle 3

at sample cooling the exothermic effect in DSC curve was observed (Fig. 4a), which can be assumed as the reverse reaction of formed LiF with gaseous PF_5 remained in crucible volume. Lithium fluoride has no phase transition in this temperature region.

In four days the cycle 2 for sample 1 (Fig. 4b) was conducted (sample mass is 0.04741 g): heating from 293 to 573 K (rate 5 K min^{-1}) – isothermal stage (5 min) – cooling from 573 to 323 K (rate 5 K min^{-1}).

Just after this study the cycle 3 (Fig. 4c) was carried out following the program described for the cycle 2. Mass of sample after decomposition in the cycles 2 and 3 (0.0285 g) was 4% more than theoretical value of LiF mass (0.0274 g).

As one can see from Table 2 and Fig. 4a, at the first heating (cycle 1) with rate 2 K min^{-1} the decomposition in the temperature range 460–542 K takes place. The total endothermic effect consists of four non–resolved peaks I–IV. Peaks I–III relate to the ascending peak slope. Peak I temperature T_e = 467.3 K can be considered as the de-

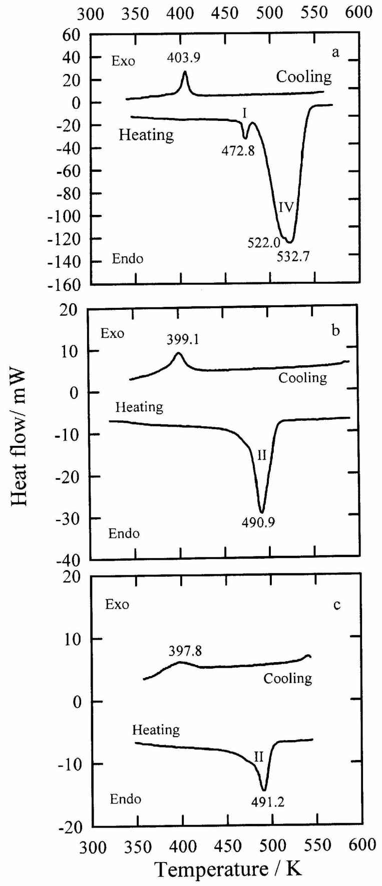

Fig. 5 DSC curves of heating and cooling of sample $LiPF_6$-2: a – cycle 1, b – cycle 2; c – cycle 3

composition onset. The highest peak III was observed at $T_p = 499.6$ K, and the main peak IV at $T_p = 520.5$ K.

In the cycles 2 and 3 peak III is the main (Table 2 and Figs 4b, 4c) and peak I corresponds to the onset of substance decomposition.

The heat of endothermic effect of cycle 1 is 458.6 J g^{-1}, while the total heat of three cycles is 537.6 J g^{-1} (Table 2). In the first cycle 85% of total decomposition heat was released. Calculation of mass balance of $LiPF_6$ decomposition by equation $(1-x)$ $LiPF_6$ $(c) \rightarrow x$ LiF (c) + PF_5 (g) gives the sample mass 0.04729 g after the decomposition of 85% of sample mass which is near to experimental value 0.04741 g.

Sample $LiPF_6$ (2)

Study of the second sample (mass 0.1221 g, series 2) was carried out in three identical cycles one after another without the intermediate sample weighing: heating from 293 to 573 K (rate 5 K min^{-1}) – isothermal stage (5 min) – cooling from 573 to 323 K (rate 5 K min^{-1}).

At the first heating with scanning rate 5 K min^{-1} (Table 2 and Fig. 5a) decomposition proceeds in the range 440–570 K. Two peaks were observed in the DSC curve of first heating (cycle 1: peak I ($T_e = 466.2$ K) and non-resolved peak IV ($T_p = 522.0$ and 532.7 K). Peaks II (Table 2 and Figs 5b, 5c) which relate to peak II of endothermic effect in heating curve of sample $LiPF_6$-1 (cycle 1) were observed at the second (cycle 2) and third (cycle 3) heatings. Mass of sample 2 after cycles 1–3 was 0.0240 g. This value is 15% more than theoretical one (0.02085 g) for LiF.

Values of endo- and exothermic effects in DSC curves at consecutive heating/cooling cycles decrease sequentially (Tables 2, 3).

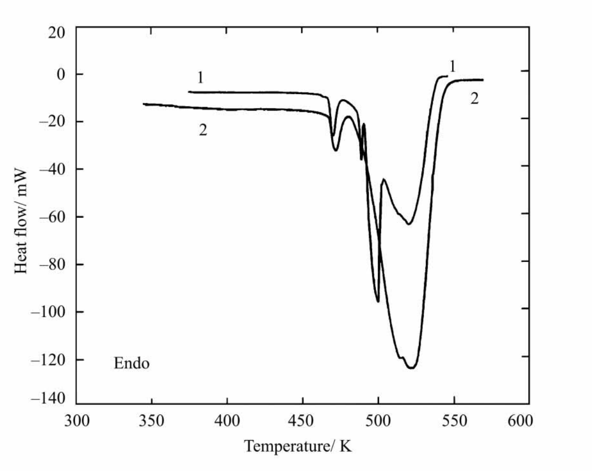

Fig. 6 Comparison of endothermic effects in DSC curves at heating with different scanning rates: 2 (1) and 5 (2) K min^{-1}

DSC curves for initial heating of samples 1 and 2 at different rates (2 and 5 K min^{-1}) are presented in Fig. 6. One can see that position of peaks I (which relate to decomposition onset) is unchanged.

It is interesting to compare DSC curves of $LiPF_6$ decomposition in hermetically sealed crucible and crucible with removing of gaseous products of reaction. Both curves were recorded at the same scanning rate – 2 K min^{-1}. Heating–cooling curves of $LiPF_6$ decomposition in different crucibles are presented in Fig. 7. One can see that the sole peak in DSC heating curve for sample studied in sealed crucible ($LiPF_6$ sample 3 from Table 1) coincides with peak I of sample $LiPF_6$-1 as for temperature as for heat effect taking into account the sample masses.

So, based on the results of cooling in cycle 1 of $LiPF_6$-1, the endothermic peak in the heating curve of lithium hexafluorophosphate studied in sealed crucible (Fig. 3) may be identified only with the decomposition of $LiPF_6$ and not with the structural phase transition in this substance as no thermal effect at temperature 459.5 K (tem-

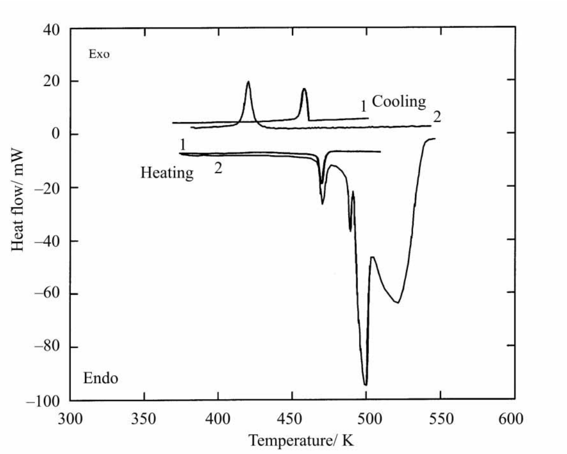

Fig. 7 Comparison of DSC curves of heating and cooling of $LiPF_6$ decomposition in sealed crucible (1) and crucible with gas remove (2) for the same heating rate (2 K min^{-1})

perature of reverse peak for $LiPF_6$ sample 3 from Table 1) was found although few percents of $LiPF_6$ mass was not decomposed in this run (sample $LiPF_6$-1; series 1).

Heat capacity of $LiPF_6$ in the temperature range 298–470 K

To derive the reaction enthalpy to the standard temperature 298.15 K it is necessary to know the heat capacity of initial substances and final products of reaction.

Heat capacity measurements of $LiPF_6$ were carried out at continuous heating in the temperature range 298–450 K with the rate 2 K min^{-1}. The sample mass was

Table 4 Smoothed heat capacity and enthalpy change of $LiPF_6$

T/ K	$C_p^0(T)$/ J K^{-1} mol^{-1}	$H^0(T)-H^0(298.15\ K)$/ J mol^{-1}	T/ K	$C_p^0(T)$/ J K^{-1} mol^{-1}	$H^0(T)-H^0(298.15\ K)$/ J mol^{-1}
298.15	151.1	0	390	182.2	15420
300	151.9	303.0	400	184.8	17260
310	155.8	1841	410	187.3	19120
320	159.6	3418	420	189.6	21000
330	163.2	5033	430	191.7	22910
340	166.7	6682	440	193.6	24830
350	170.1	8367	450	195.2	26780
360	173.3	10080	460	196.6	28740
370	176.4	11830	470	197.7	30710
380	179.4	13610			

0.2204 g (almost full fill of crucible by powder sample). It was found that heat capacity anomaly of lithium hexafluorophosphate decomposition appears at 410 K. Thus, the regular heat capacity at decomposition temperature ($T_e = 467$ K) can be evaluated by extrapolation of regular heat capacity determined for the region 298–410 K.

Heat capacity data in the temperature region 307–410 K were approximated by the Meier-Kelly type equation $C_p(T) = a+bT - cT^{-2}+dT^2+eT^3+fT^4$, where the equation coefficients are $a = 113.9758$; $b = 0.2213438$; $c = 2122892$; $d = -5.352194\cdot10^{-4}$; $e = 2.600709\cdot10^{-6}$; $f = -3.328746\cdot10^{-9}$.

Scatter of experimental data was less than 0.5%. Smoothed heat capacity values $C^0_p(T)$ and the enthalpy change $H^0(T) - H^0(298.15 \text{ K})$ are given in Table 4.

One must be constantly bear in mind that heat capacity data studied by DSC may differ from studied in equilibrium state. But in this study we are interested not in real heat capacity values but in the values of enthalpy increment from reaction temperature to standard one.

Calculation of enthalpy of decomposition and enthalpy of formation

Decomposition enthalpy of lithium hexafluorophosphate was estimated based on the experimental DSC data (Tables 2, 3). In calculating scheme the enthalpy of decomposition will be equal to the sum of endothermic effects in all three cycles minus the sum of all exothermic effects. As it was written above, the thermal events in the cooling curves were attributed to the reverse reaction of $LiPF_6$ formation from LiF and PF_5.

The preliminary calculation of decomposition enthalpy using the initial sample masses gives the following results (results of intermediate calculations and errors are given with the excess of significant figures):

Sample 1: $\Delta_d H = 77.301\pm0.234$ kJ mole^{-1}
Sample 2: $\Delta_d H = 76.632\pm0.260$ kJ mole^{-1}.

As well as the sample mass after decomposition differs from theoretical LiF mass value, the correction of decomposition enthalpy was made:

Sample 1: $\Delta_d H = 77.855\pm0.234$ kJ mole^{-1}
Sample 2: $\Delta_d H = 78.661\pm0.260$ kJ mole^{-1}.

The average value of decomposition enthalpy at temperature 467 K (taken as the decomposition temperature) is

$\Delta_d H$ ($LiPF_6$, c, 467 K) = 78.258±0.494 kJ mole^{-1}.

Table 5 Enthalpy change of reaction products and initial substance/ kJ mol^{-1}

ΔH (LiF, c) [2]	ΔH (PF_5, g) [3]	ΔH ($LiPF_6$, c)	ΔH
7.723	16.386	30.117	- 6.008

Kirchhoff equation was used to derive the enthalpy value to standard conditions $\Delta_dH(298.15\text{ K}) = \Delta_dH(467\text{ K}) - \Delta H$, where ΔH is the sum of enthalpy change of reaction products minus enthalpy change of initial substance in the temperature range 298.15–467 K (Table 5).

Decomposition enthalpy at 298.15 K is $\Delta_dH(\text{LiPF}_6, c, 298.15\text{ K}) = 84.266$ kJ mole^{-1}. And, so, enthalpy of LiPF_6 formation from fluorides is: $\Delta_fH^{\text{fluor}}(\text{LiPF}_6, c, 298.15\text{ K}) = -84.27\pm1.34$ kJ mole^{-1} (the error of this value includes the errors of integrating and determination of thermal effects).

Now we are able to calculate the enthalpy of lithium hexafluorophosphate formation from elements in standard state using the known values of formation enthalpy for substances in the reaction: LiF (c) + PF_5 (g) = LiPF_6 (c):

$\Delta_fH(\text{LiPF}_6, c, 298.15) = \Delta_fH(\text{LiF}, c, 298.15\text{ K}) + \Delta_fH(\text{PF}_5, g, 298.15\text{ K}) + \Delta_fH^{\text{fluor}}(\text{LiPF}_6, c, 298.15\text{ K})$.

Enthalpy values for PF_5 and LiF were quoted from [3, 4]: $\Delta_fH(\text{LiF}, c, 298.15\text{ K}) = -618.3\pm0.7$ kJ mole^{-1}, $\Delta_fH(\text{PF}_5, g, 298.15\text{ K}) = -1593.3\pm1.3$ kJ mole^{-1}. And, finally, the standard enthalpy of LiPF_6 formation from elements in standard state is $\Delta_fH^0(\text{LiPF}_6, c, 298.15\text{ K}) = -2296\pm3$ kJ mol^{-1}. This value adequately correlates with the results reported in [1] for other alkali metal hexafluorophosphates.

Conclusions

DSC study of LiPF_6 decomposition showed that it proceeds in the temperature range 450–550 K at normal pressure. It was shown that decomposition of lithium hexafluorophosphate was sufficiently suppressed by pressure increase of gaseous PF_5. Enthalpy of formation of lithium hexafluorophosphate was calculated based on the DSC study of heat capacity and enthalpy of thermal decomposition.

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