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CHEMISTRY AND STRUCTURAL CHEMISTRY OF PHOSPHIDES AND POLYPHOSPHIDES, PART 32. HEAT CAPACITY MEASUREMENTS OF LiP_{15} AND KP_{15} *

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ABSTRACT

The heat capacities of LiP_{15} and KP_{15} were measured in the temperature range 2–470 K using adiabatic and differential scanning calorimetry. The thermodynamic functions for these compounds were calculated from the heat capacity data. The absolute entropies of LiP_{15} and KP_{15} at 298 K were found to be 386.0 J K^{-1} $mole^{-1}$ and 411.4 J K^{-1} $mole^{-1}$, respectively.

INTRODUCTION

While various phosphides of the alkali metals have been prepared and structurally characterized by von Schnering and co-workers [1], knowledge of the thermochemical properties of these substances remains sparse. In particular, evaluation of vaporization studies performed at high temperatures requires information concerning the heat capacities and absolute entropies of such compounds. The decompositions of alkali metal phosphides having the general formula MP_{15} (M = Li, Na, K) are currently being investigated [2]. To date, no thermodynamic data for these compounds is available.

The work reported here is concerned with measurement of the heat capacities of two such phosphides, namely, LiP_{15} and KP_{15}, in the temperature range 2–470 K. These compounds are isostructural, having a triclinic crystal structure of space group $P\bar{1}$ [3,4]. The experimentally measured heat capacities were used to calculate the various thermodynamic functions such as the standard enthalpy, entropy and Gibbs energy of LiP_{15} and KP_{15}. These thermodynamic functions will be used later in conjunction with vapor pressure measurements to determine the stabilities of these compounds.

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EXPERIMENTAL PROCEDURES

The compounds LiP_{15} and KP_{15} were synthesized by heating lithium, potassium and red phosphorus in quartz ampoules according to the methods described by Wichelhaus [3] and von Schnering and Schmidt [4]. X-Ray powder diffraction patterns obtained for the reaction products were found to be identical to the triclinic diffraction patterns of LiP_{15} and KP_{15} reported by Wichelhaus [3] and Schmidt [5], respectively.

The specific heats of these compounds were measured in the temperature range 2–100 K using an adiabatic calorimeter [6]. A Perkin-Elmer DSC-2 differential scanning calorimeter [7] was used to measure the heat capacities in the range 100–470 K. Adiabatic calorimetry measurements were performed using pressed pellets of LiP_{15} and KP_{15} weighing approximately 2.1 and 2.8 g (± 0.1 mg), respectively. The pellets were 10 mm in diameter and had a thickness of 5 mm. The adiabatic calorimeter data acquisition system [6] and sample holder which were employed [8] have already been described. The error in the smoothed C_p data is estimated to be less than 0.8% ($\Delta T/T < 2 \times 10^{-3}$). For the differential scanning calorimetry measurements, finely powdered samples weighing from 5 to 13 mg were loaded into aluminum pans. Experimental data were fed on-line into a HP 9825 computer via a $4\frac{1}{2}$ digit voltmeter which increases the resolution of the DSC-2 by a factor of 5 with respect to the signal observed on an ordinary strip chart recorder. The temperature scale of the calorimeter was calibrated by observing melting and transition points of indium and various organic material standards. A sapphire sample was used as a calorimetric standard. The temperature error in these measurements did not exceed ± 0.25 K while the absolute calorimetric error of the computed molar specific heat is less than 1.5%. The molecular weight of LiP_{15} and KP_{15} were taken as 471.9 and 504.1, respectively.

RESULTS AND DISCUSSION

The temperature dependence of the experimentally measured heat capacities $C_p(T)$ of LiP_{15} and KP_{15} are represented graphically in Fig. 1. For the sake of clarity, a continuous line is used to represent the large number of experimental points. As shown in the figure, neither phosphide underwent any type of phase transition in the temperature range studied and the heat capacities of these compounds conform to Neumann–Kopp's rule near 300 K. At higher temperatures, $C_p(T)$ of both compounds have identical values, increasing nearly linearly due to anharmonic lattice vibrations. The inset in Fig. 1 depicts the low temperature behavior of the heat capacities. expressed in terms of C_p/T vs. T^2 plotted in the temperature range 0–20 K. The low-temperature limiting values of the Debye temperature are $\theta_0(LiP_{15}) =$

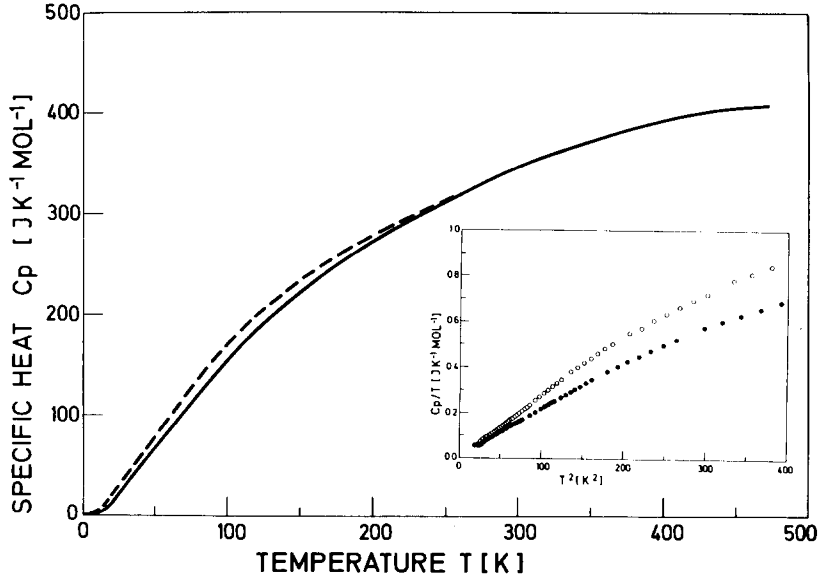

Fig. 1. Specific heat of LiP_{15} (————) and KP_{15}(- - - - - -) as a function of temperature. The insert gives the low-temperature molar heat capacity C_p/T vs. T^2.

238.3 K and $\theta_0(KP_{15}) = 220.0$ K, which were calculated from the formula

$$C_p = \frac{12\pi^4}{5} Nkn \left(\frac{T}{\theta}\right)^3 \tag{1}$$

for $T \leqslant 6$ K, where N is Avogadro's number, k is Boltzmann's constant and n is the number of atoms per molecular unit. As expected, there is no indication of any additional contribution to the lattice specific heat, such as an electronic term, as shown by the adherence of these compounds to the Debye T^3 law.

The more than 1000 experimental data points, including 280 points at $T \leqslant 100$ K were fitted to the $C_p(T)$ curve in three different segments. Five to eight parameters were used in conjunction with the general equation

$$C_p = \sum_{i=1}^{n} p_i T^{i-1}$$

to fit the specific heat to the curve. The standard deviation of the polynomial fit is less than 0.5%. Tables 1 and 2 list the absolute temperatures and molar heat capacity values taken from the smooth curves depicted in Fig. 1. Integration of the heat capacity curves yields the standard enthalpy increment, $H_T^0 - H_0^0$, the standard entropy, S_T^0, and the function $G_T^0 - \mathrm{H}_0^0$, respectively. The values of these functions for LiP_{15} and KP_{15} are also listed in Tables 1 and 2. The standard entropy values of LiP_{15} and KP_{15} at 298.15 K, obtained from the integration of $C_p(T)$ data, are 386.0 ± 2.0 J K^{-1}

TABLE 1

Calculated thermodynamic parameters for $LiP_{15}(s)$ [a]

T (K)	C_p ($J\,K^{-1}\,mole^{-1}$)	$(H_T - H_0^0)$ ($J\,mole^{-1}$)	S_T^0 ($J\,K^{-1}\,mole^{-1}$)	$-(G_T^0 - H_0^0)$ ($J\,mole^{-1}$)
7	0.79	1.40	0.266	0.46
8	1.15	2.36	0.394	0.79
9	1.62	3.74	0.555	1.26
10	2.21	5.64	0.755	1.91
11	2.92	8.19	0.998	2.78
12	3.76	11.5	1.287	3.92
13	4.72	15.8	1.625	5.38
14	5.79	21.0	2.014	7.19
15	6.97	27.4	2.453	9.42
16	8.24	35.0	2.942	12.1
17	9.59	43.9	3.482	15.3
18	11.02	54.2	4.070	19.1
19	12.51	65.9	4.706	23.5
20	14.05	79.2	5.386	28.5
25	22.88	170.5	9.422	65.1
30	30.92	303.5	14.25	124.0
35	40.42	481.7	19.72	208.7
40	49.86	707.5	25.75	322.2
45	58.72	979.3	32.13	466.7
50	67.08	1294	38.76	643.9
60	83.93	2048	52.45	1099
70	103.6	2982	66.82	1695
80	123.4	4188	82.91	2445
90	140.3	5498	98.32	3351
100	160.0	7002	114.1	4413
120	185.9	10485	145.8	7014
140	208.5	14411	176.0	10235
160	234.3	18848	205.6	14053
180	255.5	23753	234.5	18456
200	273.6	29049	262.4	23426
225	293.8	36145	295.8	30461
250	313.6	43736	327.8	38203
275	335.1	51839	358.6	46785
298	344.7	59672	386.0	55351
300	345.4	60363	388.3	56125
325	354.6	69108	416.3	66185
350	367.0	78121	443.0	76929
375	381.6	87477	468.8	88328
400	395.1	97192	493.9	100363
425	403.2	107186	518.1	113015
450	403.0	117283	541.2	126260
470	396.9	125290	558.6	137260

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[a] The absolute error in heat capacity is less than 1.5% for $T \geqslant 100$ K and 0.8% for $T < 100$ K

TABLE 2

Calculated thermodynamic parameters for $KP_{15}(s)$ [a]

T (K)	C_p ($J\ K^{-1}\ mole^{-1}$)	$(H_T^0 - H_0^0)$ ($J\ mole^{-1}$)	S_T^0 ($J\ K^{-1}\ mole^{-1}$)	$-(G_T^0 - H_0^0)$ ($J\ mole^{-1}$)
7	0.96	1.72	0.329	0.58
8	1.43	2.90	0.486	0.99
9	2.05	4.63	0.689	1.57
10	2.84	7.06	0.945	2.38
11	3.78	10.4	1.258	3.47
12	4.87	14.7	1.633	4.92
13	6.09	20.2	2.070	6.77
14	7.43	26.9	2.570	9.08
15	8.88	35.1	3.131	11.9
16	10.42	44.7	3.754	15.4
17	12.07	55.9	4.435	19.5
18	13.83	68.9	5.174	24.3
19	15.71	83.6	5.971	29.8
20	17.74	100.4	6.828	36.2
25	27.59	214.1	11.87	82.5
30	37.47	376.5	17.76	156.3
35	48.01	590.0	24.32	261.2
40	58.90	857.2	31.44	400.4
45	69.21	1178	38.99	576.3
50	79.24	1550	46.81	790.7
60	95.71	2426	62.74	1338
70	115.9	3479	78.93	2046
80	137.2	4749	95.85	2920
90	163.7	6225	113.2	3964
100	173.6	7871	130.5	5183
120	200.0	11623	164.7	8137
140	222.0	15844	197.2	11759
160	243.5	20512	228.2	16015
180	263.0	25573	258.1	20880
200	278.9	30997	286.6	26329
225	296.3	38187	320.5	33922
250	314.0	45824	352.7	42339
275	337.1	53966	383.7	51544
298	352.1	61902	411.4	60689
300	353.2	62607	413.7	61514
325	365.0	71589	442.5	72220
350	375.3	80843	469.9	83268
375	385.5	90353	496.2	95706
400	395.7	100118	521.4	108427
425	404.4	110125	545.6	121766
450	408.9	120304	568.9	135700
460	408.7	124393	577.9	141434

[a] The absolute error in heat capacity is less than 1.5% for $T \geqslant 100$ K and 0.8% for $T < 100$ K.

mole^{-1} and 411.4 ± 2.0 J K^{-1} mole^{-1}, respectively.

At low temperatures the ratio of the Debye temperature, θ_0, of LiP_{15} to that of KP_{15} was found to have a value of 1.08. In the case of cubic mono or diatomic compounds, the relationship

$$\frac{\theta_0(1)}{\theta_0(2)} = \frac{a_2}{a_1}\left[\frac{M_1}{M_2}\right]^{1/2}$$

where M_1 and M_2 are the molecular weights of compounds 1 and 2, and a_1 and a_2 are their respective lattice parameters, is valid at low temperatures ($T \leqslant \theta_0/50$). Empirically, more complex substances, such as KNO_3 and $NaNO_3$, generally obey the equation

$$\frac{\theta_0(1)}{\theta_0(2)} = \left[\frac{M_2}{M_1}\right]^{1/2}$$

In such instances all atoms contribute to the low-temperature lattice vibrations. This contribution may be in the form of the vibration of an individual atom, or as part of a strongly bonded cluster of atoms which acts as a single, heavy unit. In the case of the phosphides LiP_{15} and KP_{15}, the individual, light-weight, covalently bonded phosphorus atoms are not expected to noticeably contribute to the specific heats of these compounds at low temperatures ($T \leqslant \theta/10$). The ratio $[M(KP_{15})/M(LiP_{15})]^{1/2}$ has a value of 1.02, and the foregoing equality is not fulfilled, indicating that not all atoms participate in the soft vibrational modes at low temperature. von Schnering and Schmidt [4] reported that each alkali metal cation has six nearest phosphorus neighbors, which are distributed among four separate P_{15}^- units. Taking the lattice vibrations of these six nearest neighbors and the metal cation into account, the ratio $[\theta_0(LiP_{15})/\theta_0(KP_{15})]$ takes on a value of 1.08, which is in excellent agreement with the experimentally obtained value given earlier. This result indicates that the covalent bonding within the P_{15}^- units and the ionic interaction between the metal cation and the polyanion produce two distinctly separate sets of vibrational excitations within the lattice. At low temperatures, inter-chain vibrations, which are partially transmitted through the alkali metal cation, occur, as evidenced by the behavior described. At higher temperatures ($T \geqslant \theta/10$), intra-chain vibrations, that is vibrations propagated through the covalently bonded phosphorus chains, are the dominant vibrational modes. The unusual temperature dependence of the Debye temperatures, $\theta(T)$, of LiP_{15} and KP_{15} are caused by these high-frequency vibrations. The Debye temperatures of these compounds increase almost threefold from low temperature to room temperature [at 50 K, $\theta(LiP_{15}) = 370$ K, $\theta(KP_{15}) = 345$ K; at 200 K, $\theta(LiP_{15}) = 580$ K, $\theta(KP_{15}) = 565$ K] as a result of intra-chain lattice vibrations.

Dilatometery experiments of KP_{15} were also performed near room temperature in an effort to calculate the difference between C_p and C_v. The increase in volume of KP_{15} was found to be directly proportional to the absolute temperature in the range 291–373 K. The coefficient for the thermal expansion of KP_{15} is $(4.9 \pm 0.2) \times 10^{-6}$.

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REFERENCES

1 H.G. von Schnering, in A.L. Rheingold (Ed.), Homoatomic Rings, Chains and Macromolecules, Elsevier, Amsterdam, 1977.
2 R.P. Santandrea and H.G. von Schnering, to be published.
3 W. Wichelhaus, Dissertation, University of Münster, 1973.
4 H.G. von Schnering and H. Schmidt, Angew. Chem., 79 (1967) 323.
5 H. Schmidt, Dissertation, University of Münster, 1970.
6 E. Gmelin, Thermochim. Acta, 29 (1979) 1.
7 M.J. O'Neill, Anal. Chem., 38 (1966) 1331.
8 E. Gmelin and K. Ripka, Cryogenics, 21 (1981) 117.
9 T.K. Chattopadhyay and H.G. von Schnering, Z. Kristallogr., in press.