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CHEMISTRY AND STRUCTURAL CHEMISTRY OF PHOSPHIDES AND POLYPHOSPHIDES. 45. THE THERMAL DECOMPOSITION AND THERMODYNAMIC PROPERTIES OF THE ALKALI METAL PHOSPHIDES $LiP_{15}(s)$, $NaP_{15}(s)$, $KP_{15}(s)$, $RbP_{15}(s)$ AND $CsP_{15}(s)$

ROBERT P. SANTANDREA, CHRISTIAN MENSING
and HANS GEORG VON SCHNERING *

Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-7000 Stuttgart 80 (F.R.G.)

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ABSTRACT

The thermal decomposition of the alkali metal phosphides $LiP_{15}(s)$, $NaP_{15}(s)$, $KP_{15}(s)$, $RbP_{15}(s)$ and $CsP_{15}(s)$ has been studied using mass spectrometry, thermogravimetry and the Knudsen effusion technique. All five compounds were found to decompose under vacuum conditions directly to the corresponding $M_3P_7(s)$ phases by the loss of phosphorus in the form of $P_4(g)$ according to the general equation

$$MP_{15}(s) = 1/3M_3P_7(s) + 19/6P_4(g)$$

($M = Li$, Na, K, Rb, Cs). Pressures were determined from Knudsen effusion data. The standard enthalpies of formation of $NaP_{15}(s)$, $KP_{15}(s)$, $RbP_{15}(s)$ and $CsP_{15}(s)$ were found to be −139, −118, −110 and −109 kJ mol^{-1}. The second-law standard values of decomposition of $LiP_{15}(s)$, $NaP_{15}(s)$, $KP_{15}(s)$, $RbP_{15}(s)$ and $CsP_{15}(s)$ were determined to be 556, 486, 494, 489 and 493 kJ mol^{-1} for the enthalpy and 798, 685, 686, 696 and 689 J K^{-1} mol^{-1} for the entropy, respectively.

INTRODUCTION

The alkali metal phosphides $MP_{15}(s)$ ($M = Li$, Na, K, Rb and Cs) have been previously synthesized and structurally characterized by Von Schnering and Schmidt [1] and Wichelhaus [2]. They are isotypic and exhibit a triclinic crystal structure with $P\bar{1}$ symmetry, containing tubular P_{15}^{1-} units [4]. Recent studies of these phases have been concerned with their thermodynamic stabilities relative to other alkali metal phosphides. Along these lines, the heat capacities of LiP_{15} and KP_{15} have been measured [5] and standard thermodynamic functions have been calculated from the C_p data. Recently vapor pressure data of the KP_{15} decomposition were reported by Marek et al. [3]. In this paper we describe the thermal decomposition of the polyphos-

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* To whom all correspondence should be addressed.

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phides $LiP_{15}(s)$, $NaP_{15}(s)$, $KP_{15}(s)$, $RbP_{15}(s)$ and $CsP_{15}(s)$. The decomposition reactions were studied by means of the Knudsen effusion technique coupled with high temperature mass spectrometry and thermogravimetry. Vapor pressures, enthalpies and entropies of reaction were determined from the experimentally obtained data. The standard heats of formation of $LiP_{15}(s)$, $NaP_{15}(s)$, $KP_{15}(s)$, $RbP_{15}(s)$ and $CsP_{15}(s)$ were calculated using previously obtained values of the formation of $M_3P_7(s)$ phases [6,7].

EXPERIMENTAL PROCEDURES

The compounds MP_{15} were synthesized from high purity elements (alkali metals, 99%, Riedel-de Haën; red phosphorus, 99% electronic grade, Hoechst AG-Knapsack) according to the procedures described by Wichelhaus [2] but using niobium tubes instead of quartz ampoules as reaction vessels. This prevents additional metal consumption. Stoichiometric amounts of red phosphorus and alkali metals were loaded into the niobium tube together with catalytic amounts of iodine, or in the case of KP_{15}, of sulfur. The reaction vessels were heated in a protective argon atmosphere to about 820 K for 48 h. The Simon–Guinier X-ray powder diffraction technique [8] was used to characterize the reaction products crystallographically and ascertain their purity. The diffraction patterns obtained for the solid products were in all cases identical to those reported for the MP_{15} phases in question [2,9].

A quadrupole mass spectrometer (Extranuclear Laboratories, Pittsburgh) was used to identify the vapor species evolved during the decomposition of the various alkali metal phosphides. The Knudsen cell employed in high temperature mass spectrometry experiments was fabricated from high purity tantalum rod and had an orifice area of approximately 2×10^{-3} cm^2. Samples ranging in weight from 80 to 300 mg were loaded into the Knudsen cell for each experimental run. The crucible and sample were heated by a furnace which consisted of a tungsten wire wrapped around a cylindrical alumina core. The furnace extended well above and below the Knudsen cell. Sample temperatures were measured with a Pt/Pt–Rh thermocouple inserted into a well in the floor of the crucible. Separation of ion intensities originating from the sample and from the background intensities was achieved by placement of a pneumatically operated shutter between the Knudsen cell and ionization chamber.

Thermogravimetric and absolute pressure measurements were performed on a Netzsch thermal balance. Knudsen cells employed in these experiments were machined from high purity graphite or molybdenum rod. The effective orifice areas of the cells were calibrated by vaporizing elemental silver or CsCl at different temperatures. The resulting effective areas ranged between 3.66×10^{-3} and 9.38×10^{-5} cm^2 with an error of less than 5%. The cells had a volume of approximately 0.42 cm^3 and were filled with more than 300 mg of sample per run. The decomposition pressures of each compound were measured with various Knudsen cells to discover deviations from the expected equilibrium. No difference was observed in the initial measured phosphorus pressure when the amount of phosphide varied from 85 to 190 mg, indicating a saturated vapor phase within the Knudsen cell. Mass loss rates were continuously recorded during the thermal balance experiments. Higher initial amounts of sample permitted the collection of more isothermal measurement points, especially at higher temperatures. The temperature range used was restricted by the sensitivity of the balance on the one hand and the need to economize sample and the prevention of diffusion problems inside the sample on the other. The Simon–Guinier X-ray powder diffraction method [8] was used to identify the solid residues of the vaporization experiments.

RESULTS AND DISCUSSION

Under the experimental conditions 350–650 K, mass spectra taken with a normal ionizing electron energy of 70 eV revealed the vapor phase above each of the MP_{15} alkali metal phosphides to consist almost entirely of $P_4(g)$. No alkali metal could be found and similar spectra to those obtained evaporating elemental red phosphorus are observed. In all experimental runs, the phosphorus species P^+ $(m/e = 31)$, P_2^+ $(m/e = 62)$, P_3^+ $(m/e = 93)$ and P_4^+ $(m/e = 124)$ were the only ions which originated from the solid sample. The presence of P^+ and P_3^+ was attributed to the fragmentation of larger species, namely $P_4(g)$, which was the most abundant ion. Similarly, the high ionization energies employed in the mass spectrometry measurements as well as the present information concerning the $P_4(g)$–$P_2(g)$ equilibrium [10] indicate that the majority of the observed P_2^+ ion intensity is a result of $P_4(g)$ fragmentation.

The vacuum thermogravimetric analysis of all samples revealed that the respective decompositions of MP_{15} to the corresponding solid products takes place in a single step. This is surprising since there are many phases known between $MP_{15}(s)$ and $M_3P_7(s)$ such as $LiP_7(s)$, LiP_5, NaP_7, Na_3P_{11} and MP_{11}, $MP_{10.3}$, MP_7, M_3P_{11} for M = K, Rb and Cs. Experiments carried out under Ar atmosphere show an increased decomposition temperature and a discontinuous TG curve which can be attributed to the intermediate formation of the phases mentioned above.

Based upon the exclusive loss of phosphorus under vacuum through the evolution of $P_4(g)$, as shown by the mass spectrometric results, the composition of the solids changes from MP_{15} to M_3P_7 (M = Li, Na, K, Rb and Cs) [6,11]. X-ray powder diffraction patterns are identical to those reported by Wichelhaus [2] and Hönle [12] for Li_3P_7, Na_3P_7, K_3P_7, Rb_3P_7 and Cs_3P_7, respectively. The combined mass spectrometry, thermogravimetry and X-ray

TABLE 1

Vapor pressure equations obtained for LiP_{15}, NaP_{15}, KP_{15}, RbP_{15} and CsP_{15} (preference is given to every first line)
$\ln p_{total}(Pa) = B - A \times 10^3\ T^{-1}$

Compound	Orifice area (cm^2)	Temperature range (K)	A	B
LiP_{15}	1.56×10^{-4}	523–572	20.4(8)	40.0(14)
	2.29×10^{-4}	518–593	20.5(2)	40.2(3)
NaP_{15}	5.58×10^{-4}	473–529	17.9(6)	36.1(11)
	6.82×10^{-4}	454–531	18.5(2)	37.2(4)
	2.70×10^{-4}	501–566	19.0(2)	38.2(4)
KP_{15}	9.38×10^{-5}	502–600	18.0(3)	35.8(5)
	2.29×10^{-4}	541–620	19.3(8)	36.9(13)
	3.66×10^{-3}	483–562	21.0(6)	38.5(11)
RbP_{15}	2.70×10^{-4}	472–555	18.0(2)	36.3(5)
	5.58×10^{-4}	475–566	17.6(2)	34.9(4)
	1.93×10^{-3}	443–521	17.0(2)	33.4(5)
CsP_{15}	1.56×10^{-4}	488–577	18.0(2)	35.9(4)

diffraction studies thus show that the decomposition follows the general equation (1)

$$MP_{15}(s) = 1/3M_3P_7(s) + 19/6P_4(g) \qquad (1)$$

(M = Li, Na, K, Rb and Cs)

Phosphorus pressures of each compound and the resulting thermodynamic data were calculated from mass loss measurements based upon the occurrence of reaction (1). Different Knudsen effusion orifices were used to measure the P_4-pressure of each phosphide. The results of the vapor pressure measurements for all $MP_{15}(s)$ phases are listed in Table 1, which gives the vapor pressure equations valid for the indicated temperature range. The reaction enthalpy and entropy for the reaction conditions are listed in Table 2. They are obtained by the temperature dependence of the equilibrium constant K_p, which, for reaction (1) is given by the expression

$$K_p = p_{(P_4)}^{19/6} \qquad (2)$$

Second law enthalpies and entropies of reaction (1) at 298 K were determined from the measured P_4 pressure and the appropriate heat capacity data in Table 3. The heat capacities and ΔC_p values for reaction (1) were estimated from the heat capacities of the elements using Neumann–Kopp's rule. Independent values of ΔS^0_{298} for the decomposition of MP_{15} were calculated from the entropies of $M_3P_7(s)$ obtained previously [6,7] and the entropy of $MP_{15}(s)$. For the latter only LiP_{15} and KP_{15} were known [5]; the

TABLE 2

Enthalpies and entropies of reaction obtained for LiP_{15}, NaP_{15}, KP_{15}, RbP_{15} and CsP_{15} (preference is given to every first line)

Compound	Orifice area (cm^2)	Temperature range (K)	ΔH^0_T(rxn) (kJ mol^{-1})	ΔS^0_T(rxn) (J K^{-1} mol^{-1})
LiP_{15}	1.56×10^{-4}	523-572	537(20)	751(36)
	2.29×10^{-4}	518-593	540(4)	754(8)
NaP_{15}	5.58×10^{-4}	473-529	471(15)	647(30)
	6.82×10^{-4}	454-531	488(5)	676(11)
	2.70×10^{-4}	501-566	501(6)	700(12)
KP_{15}	9.38×10^{-5}	502-600	475(8)	639(14)
	2.29×10^{-4}	541-620	507(20)	668(35)
	3.66×10^{-3}	483-562	554(15)	711(29)
RbP_{15}	2.70×10^{-4}	472-555	473(6)	653(12)
	5.58×10^{-4}	475-566	464(5)	615(10)
	1.93×10^{-3}	443-521	447(6)	577(13)
CsP_{15}	1.56×10^{-4}	488-577	474(6)	641(12)

other MP_{15} entropy values were estimated from the elemental contribution and are presented in Table 4. The results for standard conditions of the reaction are summarized in Table 5.

The heats of reaction (1) were used to calculate standard enthalpies of formation of the MP_{15} phases (M = Na, K, Rb and Cs). The enthalpies of

TABLE 3

Thermochemical values used in the evaluation of vapor pressure measurements of the alkali metal phosphides LiP_{15}, NaP_{15}, KP_{15}, RbP_{15} and CsP_{15}
$C_p = A + B\times10^{-3}T + C\times10^{5}T^{-2}$ (J K^{-1} mol^{-1})

Species	A	B	C	ref.
P_4(g)	81.887	0.678	−13.45	13
Li_3P_7(s)	278.8	25.3	−41.9	[a]
Na_3P_7(s)	272.2	64.6	−41.9	[a]
K_3P_7(s)	280.8	20.7	−41.9	[a]
Rb_3P_7(s)	284.7	17.3	−41.9	[a]
Cs_3P_7(s)	286.8	16.0	−41.9	[a]
LiP_{15}(s)	382.2	109.6	−60.9	5
NaP_{15}(s)	385.1	140.2	−67.0	[b]
KP_{15}(s)	399.4	93.9	−67.5	5
RbP_{15}(s)	382.6	152.0	−67.0	[b]
CsP_{15}(s)	380.5	159.2	−67.0	[b]

[a] Estimated from heat capacities of solid alkali metals and red phosphorus given in ref. 13.
[b] Estimated from heat capacities of the elements and LiP_{15} and KP_{15} given in ref. 5.

TABLE 4

Standard enthalpies of formation and absolute entropies

Species	$\Delta H^0_{298,f}$ (kJ mol^{-1})	Ref.	ΔS^0_{298} (J K^{-1} mol^{-1})	Ref.
$P_4(g)$	128.7	13	280.0	13
$Li_3P_7(s)$			375	[a]
$Na_3P_7(s)$	−225.5	7	485	7
$K_3P_7(s)$	−118.8	6	592	6
$Rb_3P_7(s)$	−94.4	6	683	6
$Cs_3P_7(s)$	−68.6	6	708	6
$LiP_{15}(s)$			386	5
$NaP_{15}(s)$			403	[a]
$KP_{15}(s)$			411.4	5
$RbP_{15}(s)$			424	[a]
$CsP_{15}(s)$			432	[a]
P(red, s)	0		22.8	13

[a] Estimated from S^0_{298} of $LiP_{15}(s)$ and $KP_{15}(s)$ listed in ref. 5.

formation can be expressed in terms of the enthalpy of reaction (1) and the heats of formation of products and reactants according to the general equation

$$\Delta H^0_{298,f}(MP_{15}(s)) = 1/3\Delta H^0_{298,f}(M_3P_7(s)) + 19/6\Delta H^0_{298,f}(P_4(g)) - \Delta H^0_{298,rxn} \tag{3}$$

Table 6 gives the second and third law values of $\Delta H^0_{298,f}$ and $\Delta G^0_{298,f}$ for

TABLE 5

Second law enthalpies and entropies, and third law enthalpies of reaction (1) obtained for LiP_{15}, NaP_{15}, KP_{15}, RbP_{15} and CsP_{15} (preference is given to every first line)

	Orifice area (cm^2)	ΔH^0_{298}(rxn) (kJ mol^{-1})		ΔS^0_{298}(rxn) (J K^{-1} mol^{-1})
		Second law	Third law	
LiP_{15}	1.56×10^{-4}	556(20)	505(40)	798(36)
	2.29×10^{-4}	561(4)	508(9)	804(8)
NaP_{15}	5.58×10^{-4}	486(15)	477(30)	685(30)
	6.82×10^{-4}	502(5)	485(11)	713(11)
	2.70×10^{-4}	518(6)	492(12)	743(12)
KP_{15}	9.38×10^{-5}	494(8)	490(15)	686(14)
	2.29×10^{-4}	530(20)	516(40)	720(35)
	3.66×10^{-3}	571(15)	547(30)	754(29)
RbP_{15}	2.70×10^{-4}	489(6)	488(12)	696(12)
	5.58×10^{-4}	482(5)	492(11)	660(10)
	1.93×10^{-3}	462(6)	484(13)	616(13)
CsP_{15}	1.56×10^{-4}	493(6)	494(12)	689(12)

TABLE 6

Standard heat of formation obtained for NaP_{15}, KP_{15}, RbP_{15} and CsP_{15} from experimental Knudsen effusion data (preference is given to every first line)

Compound	Orifice area (cm^2)	$\Delta H^0_{298,f}$ (kJ mol^{-1})		$\Delta G^0_{298,f}$ (kJ mol^{-1})	
		Second law	Third law	Second law	Third law
NaP_{15}	5.58×10^{-4}	−153(15)	−139(15)	−261(30)	−256(15)
	6.82×10^{-4}	−170(5)	−141(5)	−269(11)	−258(5)
	2.70×10^{-4}	−186(6)	−139(6)	−276(12)	−256(6)
KP_{15}	9.38×10^{-5}	−126(8)	−118(8)	−245(15)	−241(8)
	2.29×10^{-4}	−161(20)	−134(20)	−270(40)	−256(20)
	3.66×10^{-3}	−203(15)	−159(30)	−301(30)	−282(15)
RbP_{15}	2.70×10^{-4}	−113(6)	−110(6)	−238(12)	−237(6)
	5.58×10^{-4}	−106(5)	−121(5)	−241(11)	−248(5)
	1.93×10^{-3}	−85(6)	−122(6)	−234(13)	−248(6)
CsP_{15}	1.56×10^{-4}	−108(6)	−109(6)	−238(12)	−238(6)

$NaP_{15}(s)$, $KP_{15}(s)$, $RbP_{15}(s)$ and $CsP_{15}(s)$ using the different cell orifices. The lack of thermodynamic data on $Li_3P_7(s)$ prevented calculation of an independent entropy value and third law enthalpy for the decomposition of $LiP_{15}(s)$.

The Knudsen effusion data for all MP_{15} phases are represented graphically in terms of $\ln(p(P_4)/Pa)$ versus $1/T$ in Fig. 1. The lines drawn through the data represent linear least-squares treatments of the experimental results.

Shorter time was needed to reach constant pressure inside the cell when compounds of the larger cations were measured. In the case of LiP_{15} about 5% of the sample had to be decomposed until an explosion-like increase in pressure gave the values indicated in Tables 1 and 2. Similar but somewhat less dramatic was the case for NaP_{15}. For the rest of the compounds studied, only a short "cleaning" period at measuring conditions was necessary. The species observed during this time were mainly water, phosphorus oxides and phosphanes. They remained even at the beginning of the decomposition reaction, and care should be taken when measuring samples that are not absolutely clean in closed systems. Storage of the samples under dry conditions is therefore recommended.

With respect to red phosphorus, the evaporation of P_4 from MP_{15} is strongly activated. Under vacuum conditions, it is possible to decompose the $MP_{15}(s)$ without evaporating an excess of elemental red phosphorus. It is not possible to reach vapor pressure equilibrium over Hittorf's phosphorus even in our smallest Knudsen cell.

As can be seen in the graphic representation of the vapor pressures, the results with larger cell holes are obtained under non-equilibrium conditions

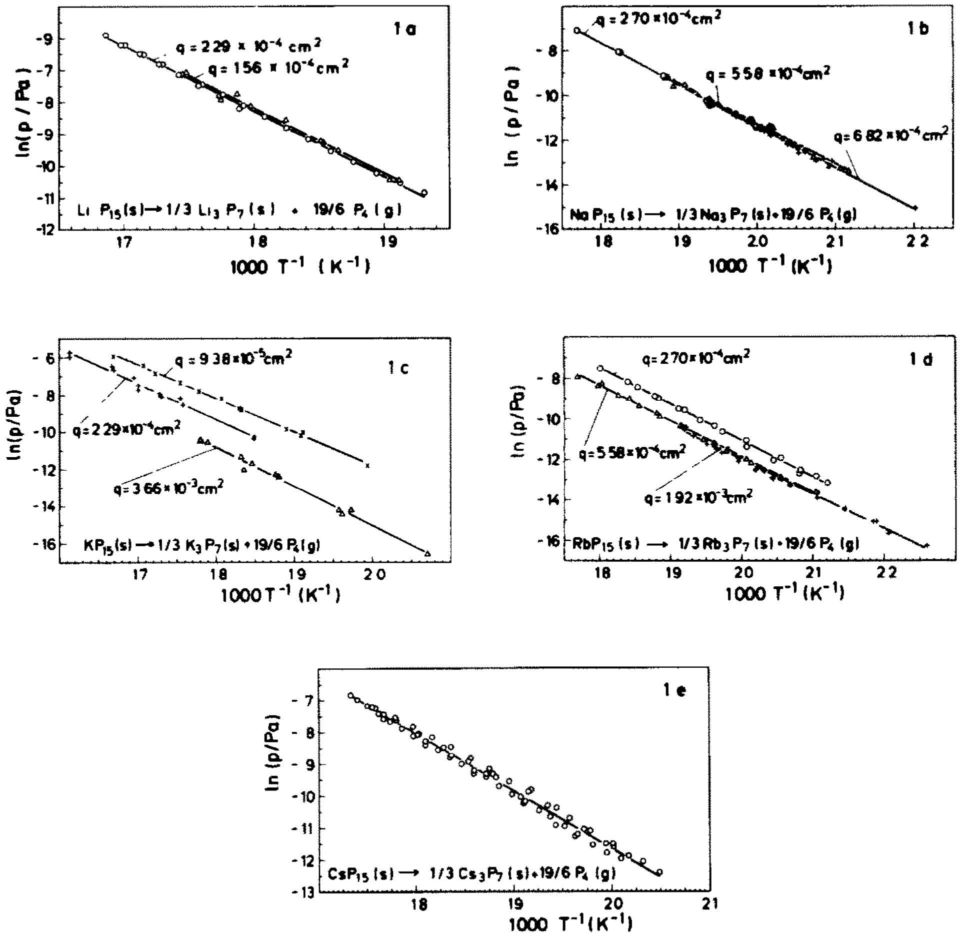

Fig. 1. Values of $\ln(p(P_4)/Pa)$ obtained for LiP_{15}, NaP_{15}, KP_{15}, RbP_{15} and CsP_{15} plotted as functions of $1/T$.

since there is a drop with respect to the results obtained with smaller orifices. The measurements with the best agreement between second and third law are considered to be closest to equilibrium. From these, the third law values are given preference since the temperature range is not excessively wide. In general the enthalpies of reaction calculated from the highest vapor pressure line coincides best with the third law values. When measuring phosphides under decomposition, the smallest cell orifice should be used.

Differences were noted between second and third law quantities which were obtained for the decomposition of LiP_{15}. The second law entropy of reaction (1) is significantly larger than the value calculated for the decomposition from independent entropies. The calculated second law entropy for $LiP_{15}(s)$ of about 214 J K^{-1} mol^{-1} is far too low compared with the known value of 386 J K^{-1} mol^{-1} [5], even considering the use of an estimated value for Li_3P_7(s). This discrepancy may arise from the inadvertent "skewing" of the linear least squares calculation by erroneous data at either extreme of the temperature range over which mass loss measurements were carried out. A greater kinetic hindrance in evaporation at lower temperatures may contribute to this effect. For NaP_{15}(s) the difference is smaller and the results agree within the wide error limits. The second and third law enthalpies of the decomposition for the rest of the MP_{15} phases are within the experimental error limits.

The vapor pressure function for KP_{15}(s) given in Table 1, is compared with the vapor pressure studies made by Marek et al. [3] about 200 K higher with the independent quartz Bourdon gauge method. The temperature range is more than twice that of ours. Because of the closed system, best approximation to equilibrium is possible. The extrapolated Knudsen pressure line touches the high temperature region of Marek's data set which is the zone where the highest point abundancy is found. This confirms the absolute pressure in this temperature range. On the other hand, our enthalpy and entropy values for the decomposition reaction of KP_{15}(s) are higher by a factor of 1.36 and outside error limits. With the Knudsen method a tendency to find lower reaction enthalpies for KP_{15}(s) with smaller cell orifices is noted. This results from the difficulty to achieve equilibrium at lower temperatures; but with the smallest cell orifice, the known entropy for KP_{15}(s) [5] is found within error limits according to the second law Knudsen method. It indicates that the 9.38×10^{-5} cm^2 orifice is sufficiently small to reach equilibrium and the possible inconvenience mentioned is not encountered. Preference is therefore given to the enthalpy calculated from the Knudsen data. The decreased enthalpy found by Marek et al. may be attributed to some remaining impurities which are difficult to remove and will increase the total pressure inside the closed system, especially at lower temperatures. Additional phases like $KP_{10.3}$ or K_3P_{11} may occur at higher temperatures as applied for the Bourdon gauge method and which could be observed with the argon experiments.

SUMMARY

The thermal decomposition of the alkali metal phosphides LiP_{15}(s), NaP_{15}(s), KP_{15}(s), RbP_{15}(s) and CsP_{15}(s) have been characterized. The vapor phase above each of these compounds has been identified by mass spectrometry to predominantly consist of P_4. Thermogravimetry and X-ray diffraction studies have demonstrated that under vacuum conditions these phosphides decompose in one step to M_3P_7(s). Other known phases are not obtained by vacuum decomposition. The Knudsen technique was employed in the measurement of decomposition pressures above these compounds. A change in effusion orifice area had some effect upon the P_4 pressures

observed above the MP_{15} compounds. Sufficiently small cell orifices could be used to achieve equilibrium. The pressure data was used to calculate the second-law standard values of decomposition of $LiP_{15}(s)$, $NaP_{15}(s)$, $KP_{15}(s)$, $RbP_{15}(s)$ and $CsP_{15}(s)$ which were determined to be 556(20), 486(15), 494(8) and 493(6) kJ mol^{-1} for the enthalpy and 798(36), 685(30), 689(14), 696(12) and 689(12) J K^{-1} mol^{-1} for the entropy, respectively. The standard enthalpies of formation of $NaP_{15}(s)$, $KP_{15}(s)$, $RbP_{15}(s)$ and $CsP_{15}(s)$ were determined from third law results to be – 139(15), – 118(8), – 110(6) and – 109(6) kJ mol^{-1}, respectively. Comparison of these results with those obtained for $Na_3P_7(s)$, $K_3P_7(s)$, $Rb_3P_7(s)$ and $Cs_3P_7(s)$ show that the latter compounds are stable with respect to both phosphorus-rich and metal-rich compounds in these systems.

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