THE SUBLIMATION AND THERMODYNAMIC PROPERTIES OF THE ALKALI METAL PHOSPHIDES $Na_3P_7(s)$, $K_3P_7(s)$, $Rb_3P_7(s)$ AND $Cs_3P_7(s)$ *

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ABSTRACT

The vaporization of solid alkali metal phosphides, Na_3P_7, K_3P_7, Rb_3P_7 and Cs_3P_7, has been characterized using the Knudsen effusion technique in combination with a quadrupole mass spectrometer and a thermobalance. Mass spectra correlated with previous accounts of the sublimation of phosphides and thermodynamic calculations show that the vapor species above these compounds are the monatomic alkali metals, $P_4(g)$ and $P_2(g)$. These compounds were found to sublime congruently according to the general reaction

$$M_3P_7(s) = 3 M(g) + 7/4 P_4(g)$$
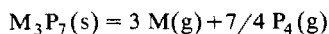
where M = Na, K, Rb, Cs. Total pressures were determined from mass-loss data and second-law entropies and enthalpies of sublimation were also calculated. The standard enthalpies of formation, $\Delta H^0_{298,f}$, for $Na_3P_7(s)$, $K_3P_7(s)$, $Rb_3P_7(s)$ and $Cs_3P_7(s)$ were found to be -119 ± 10, -114 ± 16, -118 ± 8 and -66 ± 6 kJ mol^{-1}, and the standard entropies, S^0_{298}, of these compounds are 509, 612, 689 and 756 J K^{-1} mol^{-1}, respectively. The large entropy contribution to the stability of these compounds makes them unique among alkali metal phosphides.

The values of ΔH^0_T and ΔS^0_T for the crystalline to plastically crystalline phase transition were found to be 35.5 kJ mol^{-1} and 47 J K^{-1} mol^{-1} (Na_3P_7), 10.1 kJ mol^{-1} and 19 J K^{-1} mol^{-1} (K_3P_7), 5.8 kJ mol^{-1} and 12 J K^{-1} mol^{-1} (Rb_3P_7), and 19.6 kJ mol^{-1} and 35 J K^{-1} mol^{-1} (Cs_3P_7), respectively, by DSC measurements.

INTRODUCTION

Since 1965, we have prepared numerous phosphides of the alkali metals and have characterized their crystal structures [2,3]. Information concerning the thermodynamic stability of these compounds, on the other hand, is virtually non-existent. The work reported here represents part of an ongoing

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study in this laboratory of the decomposition and sublimation of various alkali metal phosphides. As a result of these investigations, the standard enthalpies of formation and relative stabilities of these compounds will be determined.

The alkali metals Na, K, Rb and Cs each form a series of phosphides. Compounds having the general formula M_3P_7 provide an interesting and useful starting point for vaporization studies. As we shall report in subsequent papers [9], phosphides having both metal-rich compositions, such as $M_3P(s)$ and $MP(s)$, and phosphorus-rich compositions, such as $MP_{15}(s)$, decompose to yield solid $M_3P_7(s)$. On a molecular scale, the M_3P_7 compounds are isostructural, consisting of P_7^{3-} cages bonded to three alkali metal cations [5]. The phosphide $Na_3P_7(s)$ has an orthorhombic crystal structure and $K_3P_7(s)$ crystallizes in a similar low-symmetry structure, details of which are unknown up to now [6–8]. Na_3P_7, K_3P_7, Rb_3P_7 and Cs_3P_7 undergo crystalline to plastic crystalline transitions to a cubic structure in the range between 760 and 568 K [7]. Because of the use of these phosphides as starting materials in the synthesis of other compounds which contain the P_7^{3-} cage unit [10], some knowledge of the thermodynamic properties of M_3P_7 compounds is desirable.

In order to investigate the sublimation of $Na_3P_7(s)$, $K_3P_7(s)$, $Rb_3P_7(s)$ and $Cs_3P_7(s)$, we have employed the Knudsen effusion technique in conjunction with a quadrupole mass spectrometer and thermobalance. For each substance, we used experimental data to calculate total pressures, enthalpies and entropies of sublimation, standard entropies, and standard heats of formation for the four solid compounds studied.

EXPERIMENTAL PROCEDURES

The compounds Na_3P_7, K_3P_7, Rb_3P_7 and Cs_3P_7 were synthesized directly from stoichiometric amounts of the appropriate alkali metal and electronic grade red phosphorus. Synthesis reactions were carried out in sealed, evacuated ampoules made from Solidex, in the case of Na_3P_7 and K_3P_7, or, as in the case of Rb_3P_7 and Cs_3P_7, quartz tubing. The sodium–phosphorus mixture was heated to about 770 K and the resulting reaction product was then vacuum sublimed. This product was then used in vaporization studies. The syntheses of K_3P_7, Rb_3P_7 and Cs_3P_7 were performed at approximately 730 K. The reaction product was ground and then annealed at 730 K. The annealed substance was used in later experiments. The purity of the alkali metals used in the synthesis of the above compounds was 99% (alkali metals supplied by Riedel-deHaen AG; red phosphorus from Hoechst-AG-Knapsack).

Crystallographic identities of all starting compounds were established by Guinier–Simon X-ray powder diffraction data [11]. We found the diffraction

patterns obtained for all starting materials to be identical to diffraction patterns reported previously for Na_3P_7, K_3P_7, Rb_3P_7 and Cs_3P_7 [12,13].

An Extranuclear quadrupole mass spectrometer was used to identify the vapor species in the sublimation of Na_3P_7, K_3P_7, Rb_3P_7 and Cs_3P_7. The Knudsen cell used in mass spectrometry experiments was made from tantalum and had an orifice area of approximately 2×10^{-3} cm^2. About 200 mg of sample were loaded into the Knudsen cell for each experimental run. The crucible and sample were heated by a tungsten furnace which extended well above and below the Knudsen cell. Separation of ion intensity originating from the sample and the background species was achieved by the placement of a pneumatically operated shutter between the Knudsen cell and ionization chamber. Sample temperatures were measured with a Pt/Pt–Rh thermocouple inserted into a well in the floor of the crucible.

A Netzsch thermobalance was used to measure absolute pressures of the compounds studied. Mass-loss measurements were made using graphite Knudsen cells. The vapor pressure above each phosphide was determined using two different Knudsen cell orifices. Effective orifice areas were measured by vaporizing elemental silver and were found to be 2.29×10^{-4} and 3.66×10^{-3} cm^2, respectively. Approximately 200 mg of starting material were used in each thermal balance run. Sample temperatures were measured with an Ni–Cr/constantan thermocouple which was inserted into a well in the floor of the Knudsen cell.

Guinier–Simon X-ray powder diffraction techniques were used to identify solid vaporization residues [11]. The heats of transition for the four compounds were measured with a Perkin-Elmer DSC-2 differential scanning calorimeter. Approximately 20–35 mg of sample were sealed into aluminum vapor pressure sample pans for use in calorimetry experiments. Measurements and calibration techniques which were used in the differential scanning calorimetry measurements are described elsewhere [14].

RESULTS AND DISCUSSION

The vapor phases which were present above different samples of solid Na_3P_7, K_3P_7, Rb_3P_7 and Cs_3P_7 were characterized by performing systematic mass scans in the 0–400 mass range. Peaks corresponding to the masses of the appropriate monatomic metal ion ($M^+ = Na^+$, K^+, Rb^+, Cs^+) and the phosphorus species P^+, P_2^+, P_3^+ and P_4^+ were observed for each solid sample. No diatomic metal or metal–phosphorus molecules were detected in any of the mass spectra. Ionization efficiency measurements, carried out on various samples, revealed that the ions P^+ and P_3^+, having high appearance potential values, were products of fragmentation reactions within the ionization chamber of the mass spectrometer. The low appearance potentials, in the 5–6 eV range, which were observed for the respective alkali metal ions Na^+, K^+,

TABLE 1

Thermochemical values used in the evaluation of vapor pressure measurements on the alkali metal phosphides Na_3P_7, K_3P_7, Rb_3P_7, and Cs_3P_7

(a) Standard enthalpies of formation and absolute entropies taken from ref. 18.

Species	ΔH^0_{298} (kJ mol^{-1})	S^0_{298} (J K^{-1} mol^{-1})
$P_2(g)$	178.6	218.9
$P_4(g)$	128.7	279.9
Na(g)	107.8	153.6
K(g)	89.1	160.3
Rb(g)	82.0	170.0
Cs(g)	77.5	175.6
P(red, s)	0	22.8
Na(s)	0	51.2
K(s)	0	64.8
Rb(s)	0	75.7
Cs(s)	0	85.2

(b) Heat capacity data: $C_p = A + B10^{-3}T + C10^5T^{-2}$ *(J K^{-1} mol^{-1})*

Species	A	B	C	Ref.
$P_2(g)$	36.30	0.799		18
$P_4(g)$	81.85	0.678		18
Na(g)	20.79			18
K(g)	20.73	0.075		18
Rb(g)	20.79			18
Cs(g)	20.80			18
Na(s)	14.79	44.23		18
K(s)	7.84	71.91		18
Rb(s)	13.68	57.40		18
Cs(s)	44.48	−7.26	−8.94	18
P(red, s)	16.95	14.89		18
$Na_3P_7(s)$	272.2	64.56	−41.86	a
$K_3P_7(s)$	280.8	20.71	−41.86	a
$Rb_3P_7(s)$	284.7	17.33	−41.86	a
$Cs_3P_7(s)$	286.8	15.99	−41.86	a

(c) Heats of transition for crystalline → plastic phase transitions

Species	T (K)	$\Delta H^0_t(T)$ (kJ mol^{-1})	$\Delta S^0_t(T)$ (J K^{-1} mol^{-1})	Ref.
$Na_3P_7(s)$	795	35.5±0.5	47.0±0.5	7
$K_3P_7(s)$	538	10.1±0.5	19.0±0.5	7
$Rb_3P_7(s)$	480	5.8±0.5	12.0±0.5	7
$Cs_3P_7(s)$	568	19.6±0.5	35.0±0.5	7

[a] Estimated from C_p increments and Kelley's formula.

Rb^+ and Cs^+, indicated that they were products of direct ionization of neutral species effusing from the Knudsen cell. The species P_4^+ and P_2^+ were also assumed to be parent ions. The vapor species present within the Knudsen cell, based upon mass spectra, are thus the gaseous monatomic alkali metal (Na, Rb, K or Cs), $P_2(g)$ and $P_4(g)$.

Several factors prevented direct identification of the dominant phosphorus species present in the Knudsen cell from the mass spectrometry results. The first problem is that the experimentally observed P_2^+ intensity is actually a combination of the intensities of P_2^+ parent ions and P_2^+ fragment ions. The proportion of P_2^+ parent to P_2^+ fragment could not be experimentally ascertained. The second problem encountered in determining the true P_2–P_4 gas-phase relationship within the Knudsen cell is that the observed P_2^+ and P_4^+ ion intensities may be affected by reactions occurring within the mass spectrometer, yet outside of the sample container. This phenomenon has been reported in the study of different phosphides [15–17], using modulated beam techniques, under temperature and pressure conditions which approximate those employed in the present study. In light of the information available, mass spectra alone provided insufficient information concerning the relative concentrations of $P_2(g)$ and $P_4(g)$.

In order to ascertain the relative abundances of $P_2(g)$ and $P_4(g)$, available thermochemical data, listed in Table 1, were used to determine the equilibrium constant for the dissociation reaction

$$P_4(g) = 2 P_2(g) \tag{1}$$

at temperatures and pressures in operation during the thermobalance experiments. These calculations demonstrated that, under all experimental conditions encountered, the dominant phosphorus species present within the Knudsen cell is $P_4(g)$.

Solid vaporization residues from mass spectrometer and thermobalance experiments produced X-ray powder diffraction patterns which were identical to patterns obtained for the original solid starting materials. Since the composition of these phosphides remains unchanged after extensive vaporization and both metal and phosphorus constituents are present in the gas phase within the Knudsen cell, a dissociatively congruent sublimation scheme may be postulated to describe the behavior of M_3P_7 compounds. Based upon mass spectra, thermodynamic calculations and analyses of solid reaction products, $Na_3P_7(s)$, $K_3P_7(s)$, $Rb_3P_7(s)$ and $Cs_3P_7(s)$ therefore sublime according to the general reaction

$$M_3P_7(s) = 3 M(g) + x7/4 P_4(g) + (1 - x)7/2 P_2(g) \tag{2}$$
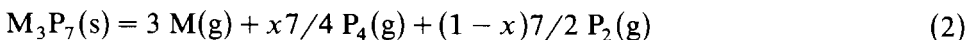
where M represents Na, K, Rb and Cs and x is the amount of P_4 of the total phosphorus gas calculated for each individual point from the thermochemical data listed in Table 1.

The results of all vapor pressure measurements, carried out using two different Knudsen effusion orifices, are graphically represented for Na_3P_7,
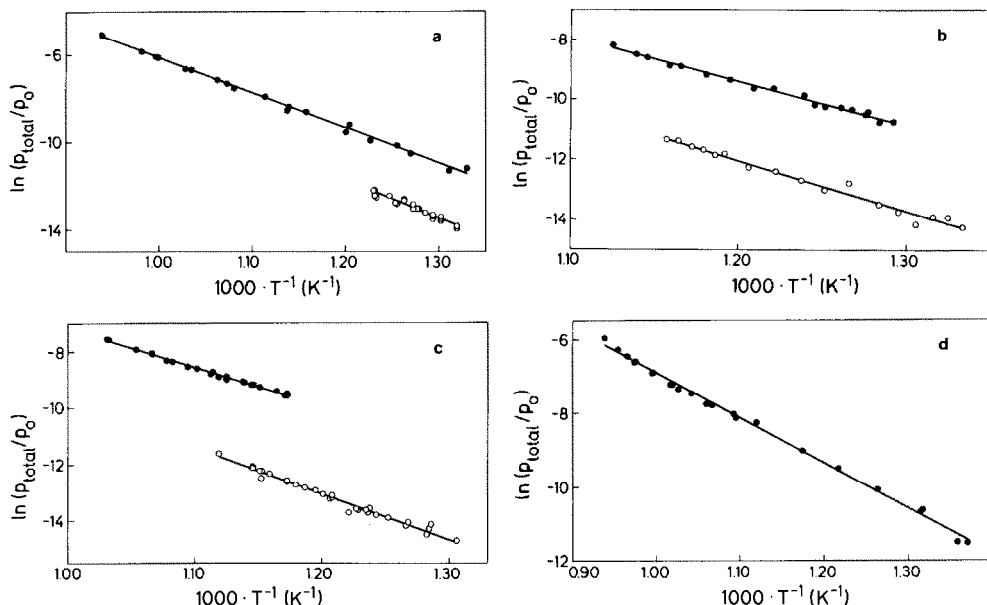
Fig. 1. The values of $\ln(P_{\text{total}}/P_0)$ for ($P_0 = 1.013 \times 10^5$ Pa) plotted as a function of $1/T$ for (a) $Na_3P_7(s)$; (b) $K_3P_7(s)$; (c) $Rb_3P_7(s)$; and (d) $Cs_3P_7(s)$. (●) Orifice area 2.29×10^{-4} cm^2 (used in calculations); (○) orifice area 3.66×10^{-3} cm^2, in (d) 9.38×10^{-5} cm^2.

K_3P_7, Rb_3P_7 and Cs_3P_7 in Figs. 1a, b, c and d, respectively. The logarithm of total pressure is plotted as a function of $1/T$ for each group of measurements. The $P_2(g)$ partial pressure arising from the dissociation of P_4 according to reaction (1) is also included in the total pressure. The lines drawn through the individual sets of data represent linear least-squares treatments of experimental results from which vapor pressure equations listed in Table 2 were calculated. As shown in Figs. 1a–c, the total pressures measured above these phosphides with the 2.29×10^{-4} cm^2 Knudsen cell orifice are at least seven times greater than the pressures observed when a larger (3.66×10^{-3} cm^2) orifice was employed. These observed pressure differences for each phosphide indicate that an undersaturation of the vapor phase and thus significant deviations from solid–gas equilibrium occurred when the larger orifice was used. The sensitivity of the total pressure to the increase in orifice area suggests that the sublimation of this class of phosphides, like that of elemental red phosphorus [19], may be kinetically hindered. As in the case of red phosphorus, the dissociation of complex M_3P_7 units to produce $P_4(g)$ and monatomic alkali metal vapor may require some rearrangement or reordering of the solid.

The equilibrium constant K_p for reaction (2) is given by the expression

$$K_p = [p(M)]^3 [p(P_4)]^{x7/4} [p(P_2)]^{(1-x)7/2}$$ (3)

TABLE 2

Vapor pressure equations, second-law enthalpies and entropies obtained for sublimation, and calculated enthalpies of formation and entropies of $Na_3P_7(s)$, $K_3P_7(s)$, $Rb_3P_7(s)$ and $Cs_3P_7(s)$. The vapor pressures are given by $\ln(p/p_0) = -AT^{-1} + B$ with $p_0 = 1$ Pa

	Na_3P_7	K_3P_7	Rb_3P_7	Cs_3P_7
Temperature range (K)	752–1066	744–889	853–970	730–1066
Orifice area (cm^2)	2.29×10^{-4}	2.29×10^{-4}	2.29×10^{-4}	9.38×10^{-5}
A (K)	16.1 ± 0.2	14.7 ± 0.2	13.8 ± 0.2	12.2 ± 0.2
B	21.5 ± 0.2	19.8 ± 0.2	18.2 ± 0.2	16.8 ± 0.2
$\Delta H_{(react.\ 2)}(T)$ (kJ mol^{-1})	639 ± 10	583 ± 14	549 ± 8	484 ± 6
$\Delta S_{(react.\ 2)}(T)$ (J K^{-1} mol^{-1})	360 ± 12	290 ± 18	231 ± 9	176 ± 7
$\Delta H_f^0(T)$ (kJ mol^{-1})	50.9 ± 10	33 ± 14	53 ± 8	103 ± 6
$S^0(T)$ (J K^{-1} mol^{-1})	819 ± 12	895 ± 18	1002 ± 9	1066 ± 7

where $p(M)$, $p(P_4)$ and $p(P_2)$ are the partial pressures of the gaseous alkali metal, $P_4(g)$ and $P_2(g)$, respectively. Pressures and K_p values were calculated from mass-loss data. Figures 2a, b, c and d show values of $\ln K_p$ plotted versus $1/T$ for Na_3P_7, K_3P_7, Rb_3P_7 and Cs_3P_7, respectively. The lines drawn through the data represent linear least-squares treatments of the experimental results. Second-law enthalpies and entropies of reaction (2)
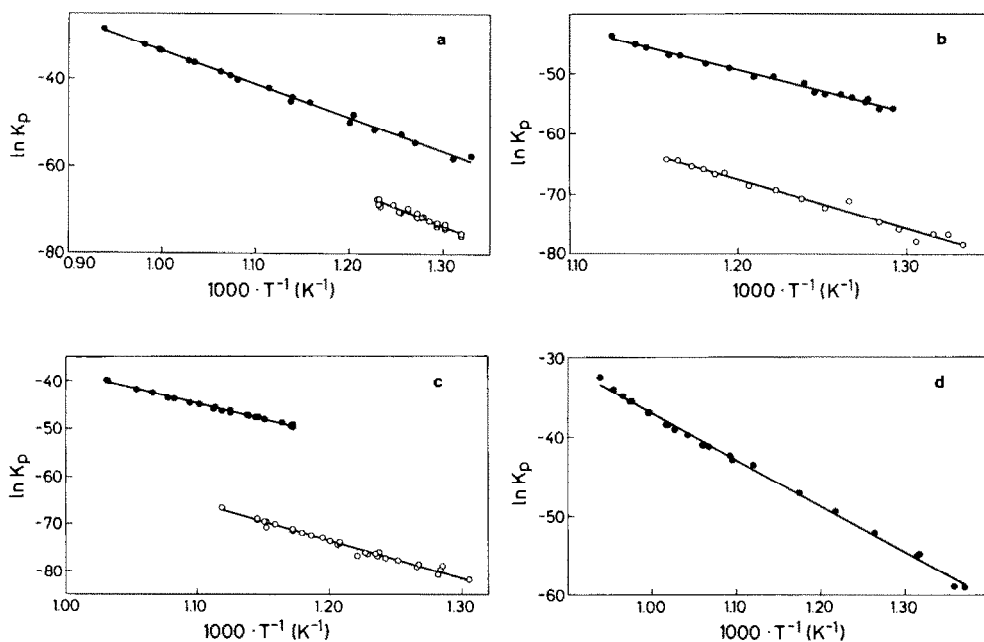

Fig. 2. The values of $\ln K_p$ obtained for the sublimation of (a) $Na_3P_7(s)$; (b) $K_3P_7(s)$; (c) $Rb_3P_7(s)$ and (d) Cs_3P_7 according to reaction (2) plotted versus $1/T$.

were calculated from the slopes and intercepts of the lines. The heat capacities of products and reactants represented in reaction (2) which were used to calculate ΔH^0_{298} and ΔS^0_{298} are listed in Table 1. The heat capacities given in Table 1 for the M_3P_7 compounds were estimated from specific heat increments of the alkali metals and phosphorus, combined with the formula of Kelley [21]. The absence of necessary thermodynamic data for these compounds precluded the calculation of third-law enthalpies. Differential scanning calorimetry experiments were used to measure the respective heats of transition. Na_3P_7 transition to the plastic crystalline phase occurred at 795 K during sample heating. A slight hysteresis was observed upon cooling of the sample, and the reverse transition took place between 730 and 720 K. Heats of transition for the heating and cooling cycles were determined to be 35.5 ± 0.5 and -34.9 ± 0.5 kJ mol^{-1}, respectively. The K_3P_7 transition to the plastic crystalline state was observed at 538 K and the enthalpy associated with the phase change is 10.1 ± 0.5 kJ mol^{-1} [7]. The values for Rb_3P_7 are 5.8 kJ mol^{-1} at 480 K and for Cs_3P_7 19.6 kJ mol^{-1} at 568 K [7]. The results of the calorimetry experiments are listed in Table 1.

The values of second-law enthalpies and entropies of reaction (2) at 298 K are listed in Table 2. As seen, the enthalpies of sublimation, which were obtained with the Knudsen cell orifice having an area of 3.66×10^{-3} cm^2, are significantly greater than the heats of reaction obtained when the cell having an orifice area of 2.29×10^{-4} cm^2 was employed. The enthalpies and total pressures which were measured with the larger Knudsen cell orifice apparently do not represent a situation which approximates solid–gas equilibrium. Only the data obtained with the smaller orifice can thus be assumed to represent equilibrium conditions within the crucible. The general equation

$$\Delta H^0_{298}[M_3P_7(s)] = 3 \, \Delta H^0_{298}[M(g)] + 7/4 \Delta H^0_{298}[P_4(g)] - \Delta H^0_{298(react. 2)} \qquad (4)$$

allows the standard heats of formation of $Na_3P_7(s)$, $K_3P_7(s)$, $Rb_3P_7(s)$ and Cs_3P_7 to be calculated from second-law heats of reaction (2) and the enthalpies of formation of the appropriate alkali metal gas and $P_4(g)$ which are listed in Table 1. The values of ΔH^0_{298} obtained for these phosphides are listed in Table 3.

Similarly, the expression

$$S^0_{298}[M_3P_7(s)] = 3 \, S^0_{298}[M(g)] + 7/4 \cdot S^0_{298}[P_4(g)] - \Delta S^0_{298(react. 2)} \qquad (5)$$

permits the standard entropies of $Na_3P_7(s)$, $K_3P_7(s)$, $Rb_3P_7(s)$ and $Cs_3P_7(s)$ to be determined from second-law entropies of reaction (2) and the standard entropies of the gaseous elements given in Table 1. In addition, values of $\Delta G^0_{298,f}$ for these alkali metal phosphides were calculated. The obtained entropies and free energies are listed in Table 3.

Three observations can be made concerning the information given in Table 3 for these three phosphides. First, the solid compounds Na_3P_7, K_3P_7, Rb_3P_7 and Cs_3P_7 are approximately equal in terms of thermodynamic

TABLE 3

Standard enthalpies of formation, absolute entropies and free energies of formation obtained for plastically crystalline $Na_3P_7(s)$, $K_3P_7(s)$, $Rb_3P_7(s)$ and $Cs_3P_7(s)$, using experimental second-law data from Knudsen effusion measurements made with an effective orifice area of 2.29×10^{-4} cm^2

Compound	ΔH_{298}^0 (kJ mol^{-1})	S_{298}^0 (J K^{-1} mol^{-1})	ΔG_{298}^0 (kJ mol^{-1})
$Na_3P_7(s)$	-119 ± 10	510 ± 12	-271 ± 10
$K_3P_7(s)$	-66 ± 6	756 ± 7	-291 ± 6
$Rb_3P_7(s)$	-114 ± 14	612 ± 18	-296 ± 14
$Cs_3P_7(s)$	-118 ± 8	689 ± 12	-324 ± 8

stability. Second, their standard enthalpies of formation lie within experimental error limits of each other. This, plus the fact that structural differences exist among these compounds at 298 K (Na_3P_7 crystallizes orthorhombic, the low-temperature crystal structures of K_3P_7 and Rb_3P_7 are unknown up to now, the high-temperature forms of Na_3P_7, K_3P_7, Rb_3P_7 and Cs_3P_7 are cubic and plastically crystalline), does not allow a trend in formational enthalpies with respect to alkali cation size to be made. Third, based upon results listed in Table 3 is that the entropy contribution to the thermodynamic stabilities, $\Delta G_{298,f}^0$, of such compounds is significant, as the values of $\Delta H_{298,f}^0$ of Na_3P_7, K_3P_7, Rb_3P_7 and Cs_3P_7 are -119, -114, -118 and -66 kJ mol^{-1} and $\Delta G_{298,f}^0$ are -271, -296, -323 and -291 kJ mol^{-1}, respectively. This means that the thermodynamic stability of these compounds will increase with increasing temperature, relative to the stabilities of other alkali metal phosphides. The result of this is that both metal-rich and phosphorus-rich compounds will decompose to the M_3P_7 composition. The relative stabilities of different compounds in the potassium–phosphorus and sodium–phosphorus systems will be discussed in depth in a forthcoming paper [9].

The absolute entropies of the M_3P_7 compounds are large with respect to the entropies normally observed for solid compounds. On a g-atom basis,

TABLE 4

Standard enthalpies of formation, absolute entropies and free energies of formation obtained for the low-temperature phases of $Na_3P_7(s)$, $K_3P_7(s)$, $Rb_3P_7(s)$ and $Cs_3P_7(s)$ using experimental second-law data from Knudsen effusion measurements and the transition energies

Compound	$\Delta H_{298,f}^0$ (kJ mol^{-1})	$S_{298,f}^0$ (J K^{-1} mol^{-1})	$\Delta G_{298,f}^0$ (kJ mol^{-1})
$Na_3P_7(s)$	-165	445	-298
$K_3P_7(s)$	-124	596	-302
$Rb_3P_7(s)$	-124	681	-327
$Cs_3P_7(s)$	-85	724	-301

S_{298}^0 for Na_3P_7 is 45 J K^{-1}; for K_3P_7, 60 J K^{-1}; for Rb_3P_7, 69 J K^{-1}; and for Cs_3P_7, 72 J K^{-1}. These values are significantly greater than values calculated for other molecular compounds, namely P_4S_3 ($S_{298}^0 = 29$ J K^{-1} g-atom^{-1}); P_4Se_3 ($S_{298}^0 = 34$ J K^{-1} g-atom^{-1}), P_4S_{10} ($S_{298}^0 = 38$ J K^{-1} g-atom^{-1}) [20] and white phosphorus ($S_{298}^0 = 41$ J K^{-1} g-atom^{-1}) [18]. The large entropies of the M_3P_7 compounds may be attributed to strong vibrational modes present at high temperatures. Such modes have been detected by Raman spectroscopy for Na_3P_7 [4]. Large differences exist between the transitional enthalpies and entropies which were obtained for K_3P_7 and Na_3P_7. Since the plastically crystalline phases of both these compounds have been well characterized by X-ray diffraction [8], the difference between the two phosphides must stem from their crystalline states. The much smaller enthalpy of transition observed for Rb_3P_7 suggests that some mobility of Rb_3P_7 units must exist within the solid phase of this compound and should be investigated further.

SUMMARY

The vaporization properties of the alkali metal phosphides $Na_3P_7(s)$, $K_3P_7(s)$, $Rb_3P_7(s)$ and Cs_3P_7 have been characterized. Mass spectrometry and X-ray powder diffraction techniques were used to identify vapor-phase products and solid residues. Experimental results plus thermodynamic calculations show that the solid remained unchanged during vaporization and these compounds sublime congruently, producing gaseous monatomic alkali metal and $P_4(g)$.

Absolute pressures were measured using the Knudsen effusion technique and a thermobalance. Large deviations from equilibrium were observed when the effective orifice area of the effusion cell was increased, as evidenced by a decrease in the total pressure within the crucible and an increase in reaction enthalpy when the larger orifice was employed. Pressure data were used to determine second-law enthalpies and entropies of sublimation for these compounds. The heats of transition of $Na_3P_7(s)$ and $K_3P_7(s)$ from room-temperature orthorhombic to high-temperature cubic plastically crystalline phases were measured. The large differences in the ΔH^0 and ΔS^0 values ($\Delta H^0 = 35.5$ and 5.8 kJ mol^{-1}; $\Delta S^0 = 47.0$ and 12.0 J K^{-1} mol^{-1}, respectively) for these transitions indicate that within the crystalline phase Rb_3P_7 the structural units possess some additional mobility, accounting for the smaller transitional entropy of this phosphide. Calorimetric results were combined with Knudsen effusion data to yield standard entropies, enthalpies of formation and free energies of formation of $Na_3P_7(s)$, $K_3P_7(s)$, $Rb_3P_7(s)$ and $Cs_3P_7(s)$, respectively. The stabilities of $Na_3P_7(s)$ and $K_3P_7(s)$ with respect to the other compounds in the sodium–phosphorus and potassium–phosphorus systems will be discussed in a forthcoming paper [9].

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