our observations strongly suggest that the samarium phase described in earlier reports resulted from oxygen and/or hydrogen contamination. Spedding et al. were unable to explain why the trimetal monocarbide existed in some lanthanide systems but not in others. We believe that the presence or absence of anionic contaminants could account for such behavior.

However, the existence of ordered (rhombohedral) and disordered (cubic) dimetal monocarbides of the heavier rare earths has been confirmed[14,19] and it is obvious that the entire list of metal-rich carbides reported by Spedding et al. are not ternary phases. For ytterbium, the following carbon-containing cubic phases have been characterized: $YbO_{0.50}C_{0.47}$ (a_0 = 4.857 Å), $YbCH_{0.5}$ (a_0 = 4.974 Å), and $YbC_{0.5}$ (a_0 = 5.001 Å).[7,12,18] Studies of additional ternary systems of samarium and other lanthanides are needed to resolve the questions raised in this report. As part of our effort with the Sm–O–C system, thermodynamic values for the dicarbide, the Pu_2C_3-type carbide, and the oxide carbide have been obtained from equilibrium measurements and will be described in forthcoming reports.

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Registry No. Sm, 7440-19-9; O, 17778-80-2; C, 7440-44-0.

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Vaporization Behavior of MnP(s) and the Thermodynamics of the Manganese–Phosphorus System[1]

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The vaporization reaction $4MnP(s) = 2Mn_2P(s) + P_2(g)$ has been studied by mass-loss effusion in the temperature range 1071–1192 K. The reaction is kinetically inhibited. From equilibrium measurements the enthalpy of reaction at 298.15 K was found to be 35.1 ± 1.0 kK. The enthalpies of formation and atomization of MnP(s) were evaluated as −12.5 ± 0.6 and 86.2 ± 0.6 kK, respectively; the corresponding values for $Mn_2P(s)$ were −18.1 ± 0.7 and 125.4 ± 0.7 kK. An unexpectedly low value for the atomization enthalpy of MnP was confirmed. The trends in atomization enthalpies of MnP, FeP, CoP, and NiP were made reasonable by adding the respective valence-state preparation energies, thereby giving the atomization enthalpies to valence-state atoms.

Introduction

The atomization enthalpy of a solid compound may be used as a measure of its stability and of the strength of its chemical bonds. The atomization enthalpies of the phosphides of manganese, iron, cobalt, and nickel, as calculated from data in the literature,[2-7] are shown in Figure 1, and it is evident that the manganese phosphides appear to have significantly lower stabilities than the other phosphides. The atomization enthalpies of the manganese phosphides are all dependent on the enthalpy of formation of MnP(s) derived from combustion calorimetry.[2b] Because the manganese phosphides differ so markedly from the phosphides of iron, cobalt, and nickel, it was decided to study the thermodynamics of the Mn–P system in a way such that the enthalpy of formation of MnP could be evaluated independently of the heat of combustion. This was accomplished by a mass-loss effusion study of the reaction

$$4MnP(s) = 2Mn_2P(s) + P_2(g) \tag{1}$$

which, when combined with the results of the solid-state galvanic cell studies by Baratashvili and co-workers[3] of the reaction

$$Mn(s) + MnP(s) = Mn_2P(s) \tag{2}$$

and the enthalpy of formation[8] of $P_2(g)$

$$2P(s, red) = P_2(g) \tag{3}$$

gives the enthalpy of formation of MnP(s)

$$Mn(s) + P(s, red) = MnP(s)$$

$$(4) = -{}^1/_2(1) + (2) + {}^1/_2(3)$$

$$\Delta H_f^\circ(MnP) = -\tfrac{1}{2}\Delta H_1^\circ + \Delta H_2^\circ + \tfrac{1}{2}\Delta H_3^\circ$$

Experimental Section

Samples for the effusion study were prepared in the manner described earlier[6] by direct combination of manganese powder (99.95%) and red phosphorus (99.9%), both obtained from CERAC/Pure, Inc. Weighed quantities of manganese and phosphorus were loaded in a 7-mm o.d. Vycor tube in an inert-atmosphere glovebox. The tube had previously been outgassed by heating under high vacuum and was transferred to the glovebox without exposure of its inner walls to air. After being loaded, the tube was transferred to the vacuum system, again without air exposure, and the sample ampule was sealed off under high vacuum. The ampule typically was heated to about 700 °C for a period of 15–20 h. Precautions described earlier[6] were used to prevent a catastrophic buildup of phosphorus pressure. The presence of both MnP and Mn_2P, before and after effusion runs, was confirmed by comparison of the X-ray powder diffraction pattern with patterns calculated by computer[9] from published structural data.[10,11]

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(1) (a) Supported by Office of Basic Energy Sciences, U.S. Department of Energy. (b) Thermochemical data in this paper are given in "rational" units; values in other units may be obtained by multiplying by the appropriate value of the gas constant, *R*.

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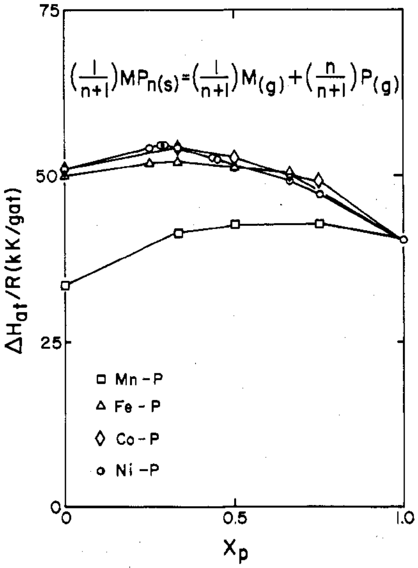

Figure 1. Atomization enthalpies (per gram-atom) for some metal phosphides.

Effusion cells were fabricated from a 1.59-cm graphite rod after the earlier design[6] but were provided with a molybdenum liner to prevent the samples from coming into contact with the graphite. The effective inertness of molybdenum toward phosphorus vapor under the conditions of these experiments was documented by the absense of molybdenum phosphide peaks in the X-ray diffraction pattern of an interior wall of the liner. Cell C-1 had a knife-edged orifice; cells C-2 and C-7 had channel orifices. The effective office areas of the cells were calibrated by using potassium chloride as a standard; data for KCl(g) and K_2Cl_2(g) were taken from ref 12.

The effusion apparatus, with calibration and operation procedures, has been described previously.[6,13] It consists of a vacuum system, induction heater with eddy current concentrator, temperature controller, and recording vacuum balance.

Results

The primary data were the temperature, corrected for thermocouple calibration, and the rate of mass loss determined from the readout of the recording vacuum balance. Individual experiments were of sufficient duration to reduce the uncertainty in the slope of the mass–time plot to less than 5%. Partial pressures of P_2(g) in the cell were calculated from the rate of mass loss, by assuming P_2(g) and P_4(g) to be in equilibrium and using the modification of the Knudsen effusion equation derived earlier[6]

$$P(P_2) = \frac{K}{2\sqrt{2}}\left[\left(1 + \frac{Cm}{aK}\left(\frac{T}{M}\right)^{1/2}\right)^{1/2} - 1\right]$$

where $P(P_2)$ is given in atmospheres, K is the equilibrium constant for $P_4(g) = 2P_2(g)$, m is the rate of mass loss in mg/min, T is the Kelvin temperature, a is the effective orifice area in cm², M is the molecular weight of P_2, and $C = 2.127 \times 10^{-6}$ is a conversion factor.

The results are presented in Figure 2 and Table I. While the results with cell C-1 ($a_{eff} = 1.22 \times 10^{-3}$ cm²) gave an apparently satisfactory plot of log $P(P_2)$ vs. $1/T$, cells C-2 ($a_{eff} = 9.67 \times 10^{-5}$ cm²) and C-7 ($a_{eff} = 5.37 \times 10^{-5}$ cm²) gave higher pressures. Hence it must be concluded that equilibrium was not achieved with cell C-1 and that the vaporization is kinetically inhibited. Data obtained with cell C-1 were not used in subsequent thermochemical calculations. The close agreement in results with cells C-2 and C-7, even though their effective areas differ by almost a factor of 2, is taken as evidence that equilibrium had been achieved with these cells. There was no evidence of departure from molecular flow conditions.

Table I. Data for Reaction $4MnP(s) = 2Mn_2P(s) + P_2(g)$

T, K	$10^3\Delta W/\Delta t$, mg/min	$-\ln P(P_2)$	$\Delta\Phi'/R$	$\Delta H^\circ_{298.15}/R$, kK
	Cell C-1, $a_{eff} = 1.22 \times 10^{-3}$ cm²			
1132	8.75	11.38		
1071	2.19	12.79		
1163	25.0	10.32		
1119	7.06	11.60		
1147	16.1	10.76		
1105	5.25	11.90		
1165	24.4	10.34		
1127	9.89	11.26		
1150	17.5	10.68		
1101	4.44	12.07		
	Cell C-2, $a_{eff} = 9.67 \times 10^{-5}$ cm²			
1096	1.68	10.53	21.42	35.01
1126	3.44	9.80	21.40	35.13
1153	7.50	9.02	21.38	35.05
1168	11.4	8.59	21.37	35.00
1146	6.17	9.21	21.39	35.07
1166	9.60	8.76	21.37	35.14
1156	7.36	9.03	21.38	35.15
1134	3.44	9.79	21.39	35.36
1121	2.94	9.96	21.40	35.15
1173	12.3	10.03	21.37	35.05
1104	2.10	10.30	21.41	35.01
1140	5.21	9.38	21.39	35.08
1134	4.00	9.65	21.39	35.20
1192	18.8	8.09	21.36	35.10
1181	14.0	8.38	21.37	35.13
1100	2.09	10.31	21.41	34.90
1086	1.40	10.72	21.43	34.91
1076	0.773	11.31	21.43	35.23
	Cell C-7, $a_{eff} = 5.37 \times 10^{-5}$ cm²			
1147	2.77	9.42	21.39	35.33
1157	3.88	9.08	21.38	35.24
1125	1.75	9.89	21.40	35.20
1160	4.56	8.92	21.38	35.14
1157	3.95	9.06	21.38	35.22
1147	2.44	9.54	21.39	35.47
1161	4.22	8.99	21.38	35.26
1135	2.00	9.75	21.39	35.34
			av	35.1

Although high-temperature heat capacity data have been reported[4] for MnP(s) and Mn_2P(s), the required data for calculation of the absolute entropies are not available. Hence it was necessary to estimate the entropies. In comparison with the entropies of the manganese silicides,[14] the entropies of the manganese phosphides were estimated as $S^\circ_{298.15}/R(MnP) = 5.2_8$ and $S^\circ_{298.15}/R(Mn_2P) = 8.6_6$. Heat capacity and entropy data for P_2(g) and P_4(g) were taken from the compilation of Stull and Sinke.[8]

From the least-squares slope of log $P(P_2)$ vs. $1/T$, the second-law enthalpy at 1140 K for reaction 1 is calculated to be $\Delta H^{\circ II}/R = 34.2 \pm 2$ kK, and, using $\Delta(H^\circ_{1140} - H^\circ_{298.15})$ evaluated from ΔC_p, $\Delta H^\circ_{298.15}/R = 35.0 \pm 2.0$ kK. The third-law enthalpies of reaction $\Delta H^{\circ III}_{298.15}/R$ given in the last column of Table I were obtained by using free energy functions $\Phi' \equiv -(G^\circ_T - H^\circ_{298.15})/T$ calculated from the entropy and heat capacity data discussed above. The mean value $\Delta H^{\circ III}_{298.15}/R = 35.1 \pm 1.0$ kK is in excellent agreement with the second-law result.

Combination of the third-law enthalpy of reaction 1 with the third-law enthalpy of reaction 2, $\Delta H^\circ_{298.15}/R = -5.6_5$ kK,

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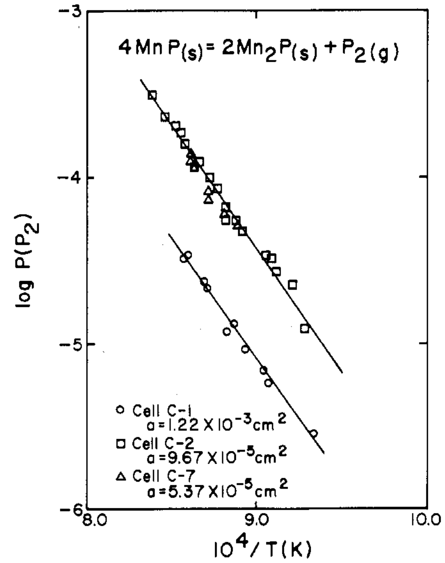

Figure 2. log $P(P_2)$ vs. $1/T$ for the reaction $4MnP(s) = 2Mn_2P(s) + P_2(g)$.

calculated from the data of Baratashvili and co-workers[3] and using the same free energy functions of MnP and Mn_2P, together with the enthalpy of reaction 3, as noted above, yields the enthalpy of formation of MnP(s), $\Delta H_f{}^\circ{}_{298.15}/R = -12.5 \pm 0.6$ kK, which is in satisfactory agreement with the value −11.6 kK obtained by combustion calorimetry.[2b] The derived enthalpy of atomization of MnP(s) is $\Delta H_{at}{}^\circ{}_{298.15}/R = 86.2 \pm 0.6$ kK. The data also yield the enthalpy of formation of $Mn_2P(s)$, $\Delta H_f{}^\circ{}_{298.15}/R = -18.1 \pm 0.7$ kK, and its atomization enthalpy, $\Delta H_{at}{}^\circ{}_{298.15}/R = 125.4 \pm 0.7$ kK.

Uncertainty limits were assigned as follows. The effect of increments of 5% in the pressure applied in opposite senses at the extreme temperatures of the measurements combined with temperature increments of 2 K, also applied in opposite senses at the extreme temperatures, produces a change of 1.7 kK in the second-law enthalpy of reaction 1. An uncertainty of 0.1 in $S^\circ{}_{298.15}/R$ for both MnP and Mn_2P yields an uncertainty of 0.7 kK in the third-law enthalpy of reaction 1 at 298.15 K. Other uncertainties were assumed to be 0.3 kK. The uncertainty in the enthalpy of reaction 2 was assumed to be 0.5 kK, which leads to an uncertainty of 0.6 kK in the enthalpies of formation and atomization of MnP(s) and 0.7 kK in the enthalpies of formation and atomization of $Mn_2P(s)$. Uncertainties in the tabulated values for the elements[8] are not included.

Discussion

The low atomization enthalpy of manganese monophosphide and of the other manganese phosphides has been confirmed in the present study, and it is instructive to seek an explanation for this apparent anomaly. Other properties of MnP exhibit no marked departure from those of the monophosphides of the elements which follow manganese in the periodic table. MnP has the same crystal structure as FeP and CoP[10] and shares many structural features with NiP.[15] Furthermore, X-ray photoelectron spectra of both the valence-conduction band and core-level regions of monophosphides of the first transition-metal series show smooth trends in which MnP is in no way unique.[16] A clue to the problem is found in the low enthalpy of sublimation of manganese compared to that of iron, cobalt, and nickel; see the extreme left points of Figure 1. The enthalpies of sublimation of the first-row transition metals[8] are shown in the lowest set of points in Figure 3, and it is seen that there are two maxima with a minimum at manganese. This behavior was addressed by Griffith,[17] who rationalized the trends by taking into account the valence-state preparation energy (VSPE). This energy consists of the promotion energy from the ground state of the gaseous atom to the center of gravity of the lowest term of the $d^{n-1}s$ configuration plus the energy required to uncouple the spins. When VSPEs are added to the respective enthalpies of sublimation, the set of points is produced (Figure 3) having a maximum at chromium and falling regularly on either side. The pattern in these enthalpies of sublimation (to hypothetical valence-state atoms) is intuitively reasonable in that the number of unpaired (bonding) electrons in the $d^{n-1}s$ configuration reaches a maximum of 6 at chromium. The manner in which the atomization enthalpies of the monophosphides plotted in Figure 3 parallels the enthalpies of sublimation of the metals suggests strongly that the same rationale may be used for the phosphides, and the addition of the respective VSPEs produces the topmost set of points in Figure 3. Since MnP has the greatest atomization enthalpy to valence-state atoms of the four phosphides, we conclude that its bonding is strongest, which is consonant with manganese having the greatest number of bonding electrons in the valence state.

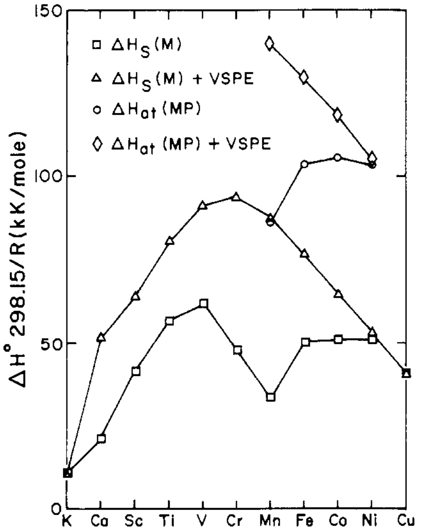

Figure 3. Sublimation enthalpies of metals and atomization enthalpies (per mole) of some monophosphides to ground-state atoms and to valence-state atoms.

The close parallel between the enthalpies of sublimation of the metals and the atomization enthalpies of the monophosphides provides a criterion for estimation of the stability of phosphides not yet studied. On this basis the enthalpies of formation of monophosphides of all first-row transition elements are estimated to be about −13 kK. However, the accuracy of the estimates appears strongly to depend on bond type, since the enthalpy of formation of ScP, which has substantial ionic character,[16] has been measured[18] to be −44.2 kK. Furthermore, transition-metal phosphides generally have greater atomization enthalpies than the corresponding sulfides,[19] but MnS, which has considerable ionicity,[20] has an atomization enthalpy of 87.9 kK which is significantly greater than the value for MnP.

Registry No. MnP(s), 12032-78-9; $Mn_2P(s)$, 12333-54-9.

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