Thermochimica Acta, 202 (1992) 113–119
Elsevier Science Publishers B.V., Amsterdam

Determination of the standard enthalpy of formation of Cu_3P by direct-combination drop calorimetry

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(Received 10 September 1991)

Abstract

We determined $\Delta_f H_m^{\ominus}(Cu_3P, cr, 298\ K)$ using direct-synthesis drop calorimetry. We measured $\Delta_r H_m$ which is the enthalpy of the reaction

$3Cu(cr) + P(red, am) \rightarrow Cu_3P(cr)$

at $T = (298 \pm 1)$ K. Our result for $\Delta_r H_m$ is (-39.7 ± 2.1) kJ mol^{-1}. Correcting for $\Delta_f H_m^{\ominus}(P, red, am, 298\ K)$ yields a value for $\Delta_f H_m^{\ominus}(Cu_3P, cr, 298\ K)$ of (-34.8 ± 3.4) kJ mol^{-1}, where the reference state of phosphorus is P(black, orthorhombic).

INTRODUCTION

This paper represents the last report of our investigation of the enthalpies of formation of metal phosphides which we introduced in previous papers [1,2]. Because of experimental difficulties arising from the high vapor pressure of phosporus at high temperature, the phase diagram of the Cu–P system is well established only in the Cu-rich region ($0 \leqslant x \leqslant 0.25$, where x is the mole fraction of P) [3]. Ugai et al. [4] have presented reliable phase data for the range $0.25 \leqslant x \leqslant 0.67$ based on the melting behavior of the system under a high pressure of phosphorus gas. Although there is general agreement in the literature that the compound denoted as Cu_3P is nonstoichiometric, that is, slightly P-rich, its exact homogeneity range is somewhat controversial. Table 1 shows some of the reported homogeneity ranges for this compound. Cu_3P melts at 1295 K, apparently at the stoichiometric composition [4,8]. Other known copper phosphides are CuP_2 [4,5] and Cu_2P_7 [9]. Olofsson [7] presented the crystal structure of Cu_3P and reported that the lattice parameters showed appreciable depen-

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TABLE 1

Reported homogeneity ranges for Cu_3P

Homogeneity range	Temperature (K)	Reference
$0.256 < x$	1273	5
$0.256 < x < 0.267$	833	6
$0.262 < x < 0.268$	973	7
$x < 0.275$	973	4
$x < 0.31$	1106	4
$x < 0.275$	1258	4

dence on the composition. Two previous studies addressed the enthalpy of formation for Cu_3P with very different results [10,11].

EXPERIMENTAL

We prepared our samples from turnings milled from Cu rod (9.5 mm in diameter; > 99.999%; Johnson Matthey/Aesar Group, catalog no. 10156) and crushed lump red amorphous phosphorus (> 99.999% with respect to metallic contamination, Morton Thiokol/Alfa Products, catalog no. 00248). The Cu turnings were milled with a dedicated carbide burr no more than 5 h before use and then sized to −100 mesh (< 150 μm in cross-section; up to about 2 mm in length). The phosphorus was crushed, sized to −100 mesh (< 150 μm), washed with water and then ethanol, and vacuum dried. The two components were ground together in a dry agate mortar, pressed into pellets, and the pellets were sealed into fused silica capsules under vacuum. We formulated the components to a composition of $x = 0.262$.

Sample 1 was placed in a test furnace in order to determine whether the capsule would withstand the phosphorus vapor pressure at the working temperature of the calorimeter. The remaining capsules were dropped into a Calvét-type twin calorimeter, which has been described in detail in a previous publication [12]. The calorimeter was calibrated by dropping slugs of gold (> 99.99%) into the calorimeter and relating the resulting heat effects to the known heat content of that metal [13]. For the present experiments, the receiving vessel inside the calorimeter was a gold crucible. We dropped sample 2 only once, and then had the product material examined by powder X-ray diffraction and by scanning electron microscopy (SEM) with X-ray microprobe analysis in order to determine whether we had formed a homogeneous product. The first drop for each of the remaining samples was used to measure $\Delta_{r_1}H$, the enthalpy of the reaction

$$\begin{aligned}&2.82\,\mathrm{Cu(cr)} + \mathrm{P(red,\ am)} + r\mathrm{SiO_2(am)},\ T = (298 \pm 1)K \rightarrow \\ &\quad \mathrm{Cu_3P}(\mathrm{cr},\ x = 0.262) + r\mathrm{SiO_2(am)},\ T = (1052 \pm 2)\mathrm{K} \qquad (1)\end{aligned}$$

where $r = n(\mathrm{SiO_2})/n(\mathrm{Cu_3P})$. Since the silica in the capsule does not undergo chemical reaction, the value of r is arbitrary. Subsequent drops measured $\Delta_{r_2}H$, the enthalpy of the process

$$\mathrm{Cu_3P}(\mathrm{cr}, x = 0.262) + r\mathrm{SiO_2}(\mathrm{am}),\ T = (298 \pm 1)\mathrm{K} \rightarrow$$
$$\mathrm{Cu_3P}(\mathrm{cr}, x = 0.262) + r\mathrm{SiO_2}(\mathrm{am}),\ T = (1052 \pm 2)\mathrm{K} \qquad (2)$$

Because our calorimetric results were in poor agreement with previous work, we had an unreacted pellet of Cu + P examined using SEM in order to confirm that no reaction occurred before the samples were dropped.

RESULTS

A thorough SEM analysis showed that sample 2 contained only a single phase. The SEM analysis of the unreacted pellet showed only two phases which corresponded to the reactant materials. The powder X-ray diffraction pattern collected on the product showed excellent agreement with that collected by Haraldsen [5]. There were no features corresponding to the starting materials or to their oxides. The product was metallic grey, hard and brittle.

Table 2 shows our calorimetric results for $\Delta_{r_3}H_\mathrm{m}$, the enthalpy of the reaction

$$2.82\ \mathrm{Cu}(\mathrm{cr}) + \mathrm{P}(\mathrm{red, am}) \rightarrow \mathrm{Cu_3P}(\mathrm{cr}, x = 0.262),\ T = 298\ \mathrm{K} \qquad (3)$$

where $\Delta_{r_3}H_\mathrm{m} = (\Delta_{r_1}H - \langle\Delta_{r_2}H\rangle)/n(\mathrm{Cu_3P})$. For our calculations we used a formula weight of 209.95 g mol^{-1}.

We calculated $\Delta_\mathrm{f}H^\ominus_\mathrm{m}(\mathrm{Cu_3P}$, cr, 298 K) by correcting $\Delta_{r_3}H_\mathrm{m}$ for $\Delta_\mathrm{f}H^\ominus_\mathrm{m}$(P, red, am, 298 K). Because the results of O'Hare and Lewis [14] and of O'Hare and Hubbard [15] indicate that black phosphorus is more stable than white phosphorus or any form of red phosphorus, we have taken P(black, orthorhombic) as the standard state for that element. The value of $\Delta_\mathrm{f}H^\ominus_\mathrm{m}$(P, red, am, 298 K) was calculated from the results of O'Hare and co-workers [14,15] to be (4.9 ± 2.7) kJ mol^{-1}. Adding this value to our experimental result for $\Delta_{r_3}H_\mathrm{m} = (-39.7 \pm 2.1)$ kJ mol^{-1}, gives $\Delta_\mathrm{f}H^\ominus_\mathrm{m}(\mathrm{Cu_3P}$, cr, 298 K) = (-34.8 ± 3.4) kJ mol^{-1}. The uncertainties in $\Delta_\mathrm{f}H^\ominus_\mathrm{m}$(P, red, am, 298 K) and in $\Delta_\mathrm{f}H^\ominus_\mathrm{m}(\mathrm{Cu_3P}$, cr, 298 K) were calculated as the square root of the sum of the squares of the contributing uncertainties.

DISCUSSION

Table 3 shows our results for $\Delta_\mathrm{f}H^\ominus_\mathrm{m}(\mathrm{Cu_3P}$, cr, 298 K) and $\Delta_\mathrm{f}H^\ominus_\mathrm{m}(\mathrm{Ni_{2.55}P}$, cr, 298 K), together with various results for these compounds from

TABLE 2

Results for the enthalpy of Cu_3P at 298 K

Sample no.	$n(Cu_3P)$ (mmol)	$n(SiO_2)$ (mmol)	$\Delta_{r_1}H$ (J)	$\Delta_{r_2}H$ (J)	$\Delta_{r_3}H_m$ (kJ mol^{-1})
3	5.477	23.04	1351.7	1565.4	−40.7
				1570.6	
				1583.2	
				1579.8	
				1574.8 [a]	
				8.2 [b]	
4	4.762	20.31	1207.6	1389.1	−38.4
				1386.5	
				1399.8	
				1386.7	
				1390.5 [a]	
				6.3 [b]	
5	4.998	22.40	1301.0	1488.7	−37.5
6	4.486	20.83	1200.3	1386.3	−42.2
				1393.6	
				1379.8	
				1398.3	
				1389.5 [a]	
				8.1 [b]	
					−39.7 [c]
					2.1 [b]

[a] $\langle \Delta_{r_2}H \rangle$.

[b] The standard deviation of a population *s*.

[c] $\langle \Delta_f H_m^\ominus \rangle$.

the literature. As the results in this table show, our value for $\Delta_f H_m^\ominus(Cu_3P, cr, 298\ K)$ is in poor agreement with the results of previous investigators. As Gordienko and Viksman [11] have pointed out, the results of Weibke and Schrag [10] for $\Delta_f H_m^\ominus(Cu_3P, cr, 298\ K)$ can be dismissed as being far too negative. The phosphorus vapor pressures predicted by this value would have made the detection of phosphorus impossible under the experimental conditions of Gordienko and Viksman. Although the basic method and experimental conditions of Weibke and Schrag [10] are fairly similar to ours, there are significant differences. Weibke and Schrag used an “adiabatic” calorimeter. This type of calorimeter requires very effective thermal isolation in order to yield meaningful results. Because of the high operation temperature, loss of thermal isolation through radiation might have introduced significant error. Weibke and Schrag did not perform the drop corresponding to reaction (2). They used instead rather dubious heat

TABLE 3

Comparison of present result for enthalpy of formation of Cu_3P with literature values

$\Delta_f H_m^{\ominus}(298\ K)$ kJ (mole of atoms)$^{-1}$	Method	Reference
Cu_3P		
-32 [a]	Direct-combination calorimetry	10
-11.0 [b]	Knudsen effusion	11
-27	Semiempirical model	16
-8.7	Direct-combination calorimetry	This work
Ni_5P_2		
-56 [a]	Direct-combination calorimetry	10
-50	Semiempirical model	11
$Ni_{2.55}P$		
-52	Direct-combination calorimetry	1

[a] Recalculated by the authors to reflect P(black, orthorhombic) as the standard state.

[b] Recalculated by the authors to reflect P(black, orthorhombic) as the standard state, (we have assumed that the original authors used P(α, white) as their standard state).

capacity data to correct their value for the enthalpy of the process roughly corresponding to reaction (1), yielding the enthalpy of the reaction at high temperature, which they report as the enthalpy of formation. Another problem with the results of Weibke and Schrag is the possibility of incomplete reaction. In addition to $Ni_{2.55}P$, Pd_3P and Cu_3P, we investigated Fe_2P and Co_2P. $Ni_{2.55}P$, Fe_2P, and Co_2P all showed indications of incomplete reaction under conditions similar to those used by Weibke and Schrag.

The discrepancy between the result of Weibke and Schrag for $\Delta_f H_m^{\ominus}$ (Cu_3P, cr, 298 K) and ours is surprising because it was so much larger than the discrepancy between our results for $\Delta_f H_m^{\ominus}(Ni_{2.55}P$, cr, 298 K) and Weibke and Schrag's result for $\Delta_f H_m^{\ominus}(Ni_5P_2$, cr, 298 K). ($Ni_5P_2$ is an older designation for $Ni_{2.55}P$; we have divided these enthalpies of formation by the number of atoms in the formula for comparison.) Our preliminary work with Fe_2P and Co_2P is also informative. We obtained values for $\Delta_{r_4} H_m(Me_2P)$, the enthalpy of the reaction

$$2\ Me(cr) + P(black,\ ortho.) \rightarrow Me_2P(mix),\ T = 298\ K \qquad (4)$$

where Me is Fe or Co and "mix" indicates a mixture of phases dominated by Me_2P. Because most of the product material in these experiments was Me_2P, our values for $\Delta_{r_4} H_m(Me_2P)$ should reflect the value of $\Delta_f H_m^{\ominus}$ (Me_2P, cr, 298 K) fairly well. Our value for $\Delta_{r_4} H_m(Fe_2P)$ is -118 kJ mol^{-1}, compared to Weibke and Schrag's value for $\Delta_f H_m^{\ominus}(Fe_2P$, cr, 298 K) of -139 kJ mol^{-1}. Our value for $\Delta_{r_4} H_m(Co_2P)$ is -144 kJ mol^{-1}, compared to Weibke and Schrag's value for $\Delta_f H_m^{\ominus}(Co_2P$, cr, 298 K) of -175 kJ mol^{-1}. (Weibke and Schrag's values for $\Delta_f H_m^{\ominus}(Me_2P$, cr, 298 K) have been corrected to reflect P(black, orthorhombic) as the standard state of phosphorus by the authors.) To summarize, Weibke and Schrag's values of the standard enthalpies of formation are 18%, 22% and 8% more negative than ours for Fe_2P, Co_2P and $Ni_{2.55}P$ respectively. In contrast, Weibke and Schrag's value for $\Delta_f H_m^{\ominus}(Cu_3P, cr, 298\ K)$ is 270% more negative than ours.

Weibke and Schrag used a different procedure for investigating the phosphides of Fe, Co and Ni from that used for the phosphides of Cu. For the Fe, Co and Ni phosphides, they preheated the reactive mixture to between 515 and 621 K before dropping the sample into the calorimeter where it reacted. For the Cu phosphides, the preheating step was skipped. These facts suggest that the error in Weibke and Schrag's results arises from the heat capacity data that they used to calculate them. Any error in the heat capacity data for phosphorus would be magnified in the case of Cu because the difference between the initial and final temperatures was so much larger.

Our result for $\Delta_f H_m^{\ominus}(Cu_3P, cr, 298\ K)$ shows a much smaller discrepancy with the result of Gordienko and Viksman [11]. We feel that their result is somewhat suspect because they detected a mixture of phosphorus species above the solid but used their effusion data to determine the enthalpy of the reaction

$$4Cu_3P(cr) \rightarrow 12Cu(cr) + P_4(gas) \tag{5}$$

Although it was not clear which form of phosphorus Gordienko and Viksman used for their standard state, it is most likely that they used P(α, white) because that form is widely adopted as the standard state and because it is the form that P_4(gas) condenses into. Because our value for $\Delta_f H_m^{\ominus}(Cu_3P, cr, 298\ K)$ was obtained by a much more direct technique, we consider it more reliable.

Table 3 also shows the results from a semiempirical model developed by Miedema and co-workers [16]. This value for $\Delta_f H_m^{\ominus}(Cu_3P, cr, 298\ K)$ can also be dismissed as far too negative; Gordienko and Viksman [11] could not have obtained any results if it were accurate. Again the discrepancy between the semiempirical result and our experimental value is rather large for Cu_3P but much smaller for $Ni_{2.55}P$. It is worth noting that the thermodynamic properties of compounds of the noble metals were included in an early monograph [16] dealing with this model but not in later publications [17,18]. This might suggest that the model was of little value in predicting enthalpies of formation for the binary systems of the noble metals.

ACKNOWLEDGMENTS

This work was supported by grants NSF-CHE8700937 and NSF-CHE9014789, and also benefited from the NSF-MRL grant. We are indebted to Dr. A.M. Davis who performed the SEM examination of our samples.

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