

HIGH-TEMPERATURE BEHAVIOR AND THERMODYNAMIC PROPERTIES
OF THE COMPOUNDS Cu_3P AND CuP_2

S. P. Gordienko and G. Sh. Viksman

UDC 536.7:546.18:546.56

Alloys and individual compounds of the Cu-P system are included in the composition of various silver-free solders [1, 2]. Copper and phosphorous in the vapor state are toxic and therefore from an ecological point of view it is important to have available data on the composition and partial pressure of the constituents of copper phosphide vapor at increased temperature, particularly soldering temperatures. It is known that in the 900-1200°K range copper phosphide disproportionates to Cu_3P with the liberation into vapor of P_4 molecules [3, 4], the pressure of which is $10\text{-}10^5$ Pa. According to indirect data [3] it may be concluded that Cu_3P dissociates into copper and phosphorous vapor. The vapor pressure of the Cu_3P vapor may be calculated using the Gibbs-Helmholtz equation with the use of the standard enthalpies of formation and the thermodynamic functions of the participants in the dissociation reactions. However, the thermodynamic functions of copper phosphides are not known and information on the enthalpies of formation is contradictory [2-8].

The purpose of this work was an investigation of the dissociation of Cu_3P , determination of the thermodynamic functions of CuP_2 and Cu_3P in the $298^\circ\text{K} - T_{\text{melt}}$ range using the method of [9], and calculation of the standard enthalpies of formation.

The basis of determination of the thermodynamic functions was the melting points of the compounds [2], the elements, and their constituents (the phosphorous was assumed to be red phosphorous*) and the standard entropies of the elements [10, 11]. The calculation results are shown in Table 1. The characteristics of the elements were taken from [10].

The differences between the determined and the standard [8] entropies of Cu_3P and CuP_2 phosphides do not exceed -0.4 and -3.0 J/mole·deg, respectively. The entropy of the reaction of disproportionation of copper phosphide at 1006°K is 205.98 [3] and judging from the reference [11] and calculated (Table 1) data 180.14 J/mole·deg, that is, the difference is 12%. The comparisons made make it possible to assume that the error in determination of the functions does not exceed 12%.

To investigate the behavior of Cu_3P at increased temperatures the method of mass-spectrometric analysis of the vapor with the Knudsen method of evaporation was used. This method makes it possible to establish the composition of the vapor and in combination with the results of x-ray diffraction analysis the type of evaporation reactions and in isothermal evaporation to determine the partial pressures of the constituents of the vapor and to calculate the standard enthalpy of the reaction of formation of the analyzed compound. It should be noted that the accuracy in determination of the pressure by this method does not exceed 50%. In connection with this repeated measurements are undesirable. In addition such an error in determination of the pressure leads to an error in calculation of the enthalpy of the reaction at 1000°K of not more than 4 kJ. The method of investigation is similar to that described in [12].

The Cu_3P phosphide was obtained by ampul synthesis from especially pure components, V3 copper (Interrepublic TU 14-15-1-65) and 9-5 red phosphorous (TU 6-09-3507-74). The structure of the Cu_3P compound was hexagonal with parameters of $a = 0.707$ and $c = 0.714$ nm.†

The composition of the vapor was analyzed in the 28-200 atomic mass unit range at temperatures of $1150\text{-}1400^\circ\text{K}$ and an energy of ionizing electrons of 25-30 eV. At low temperatures

*Red phosphorous sublimes without melting. In the calculations the temperature of transformation to the vapor phase, 704°K [10], was used.

†The synthesis and identification of the compound Cu_3P were done by V. B. Chernogorenko.

Institute of Problems of Material Science, Academy of Sciences of the Ukrainian SSR.
Translated from Poroshkovaya Metallurgiya, No. 7(271), pp. 82-85, July, 1985. Original article submitted January 9, 1984.

TABLE 1. Thermodynamic Characteristics of Copper Phosphides, J/mole·deg

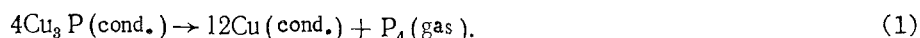
T, K	$C_p^\circ(T)$	$H^\circ(T) - H^\circ(298,15 K) 10^3$	$S^\circ(T)$	$\Phi^\circ(T)$
Cu ₃ P composition (solid)				
298,15	84,60	0	118,82	118,82
300	84,83	0,157	119,35	118,83
400	94,05	9,148	145,15	122,28
500	99,71	18,853	166,78	129,07
600	103,97	29,045	185,35	136,94
700	107,58	39,626	201,66	145,05
800	110,83	50,549	216,24	153,05
900	113,87	61,785	229,47	160,82
1000	116,79	73,319	241,62	168,30
1100	119,63	85,141	252,89	175,49
1200	122,41	97,244	263,41	182,37
1295	125,02	108,992	272,85	188,67
Cu ₂ P composition (solid)				
298,15	58,76	0	71,30	71,30
300	58,98	0,109	71,66	71,31
400	67,39	6,473	89,91	73,73
500	72,38	13,478	105,52	78,56
600	76,01	20,905	119,05	84,21
700	79,00	28,660	131,00	90,06
800	81,66	36,695	141,73	95,86
900	84,11	44,985	151,49	101,51
1000	86,45	53,514	160,47	106,96
1100	88,70	62,272	168,82	112,21
1164	90,11	67,995	173,87	115,45

TABLE 2. Results of Isothermal Evaporation of Cu₃P

T, K	Weight of the specimen, 10 ³ g	Diam. of effusion aperture, 10 ⁻³ m	Diaphragm thickness, 10 ⁻⁴ m	Time of total evaporation, 10 ³ sec	Pressure of P ₄ molecules, Pa	Enthalpy of atomization $\Delta H_{at}^\circ(298)$, kJ/mole
1178	0,98	0,20	0,15	3,18	1,02	315,9
1238	0,97	0,19	0,15	1,14	3,21	320,1
1292	0,73	0,16	0,15	0,78	8,22	324,3

P₄⁺, P₂⁺, P₃⁺, and P⁺ were present in the mass spectra (in the order of descending intensity of the ion flow) and at high temperatures Cu⁺ ions. The detection of atomic copper in the vapor only at high temperature is the result of the 5·10⁻² Pa sensitivity of the instrument, which is higher than the vapor pressure of pure copper at temperatures below T_{melt} of Cu [10]. In isothermal evaporation the intensities of the ion flows of the constituents of the vapor remained practically unchanged until complete evaporation.

These results in combination with the data of calculation of the composition of the phosphorous vapor [13] make it possible to conclude that at temperatures less than the T_{melt} of Cu₃P the main constituent of the vapor is P₄ molecules:

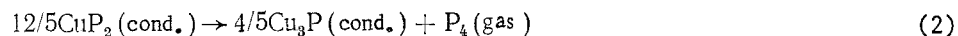


In connection with the fact that the interaction of liquid Cu₃P with the copper liberated as the result of the occurrence of this reaction leads to the formation of alloys the composition of which changes continuously, further investigations were made at temperatures below the T_{melt} of Cu₃P. The dissociation pressure of Cu₃P was determined on the basis of the results of isothermal evaporation at the temperatures shown in Table 2.

The average value of the standard enthalpy of the reaction of dissociation (1) was 320.1 ± 4.2 kJ/mole. The standard enthalpy of formation of Cu₃P (cond.) calculated from this value and reference data [11] was -65.3 kJ/mole, which differs significantly from the literature data of -36.0 ± 2.0 [5-7], -32.0 [2], and -30.82 ± 4.0 kcal/mole [8]. It should be noted that in the first and only experimental work [5] on determination of the enthalpy of formation of Cu₃P from red phosphorous and copper by synthesis in an adiabatic calorimeter a value of -36.0 kcal/mole at ~900°K was obtained. In subsequent reference publications [6-8] it was changed without an indication of the new sources of information or the method of determination and was given at 298°K. In the domestic reference literature all of these figures have been copied

without a critical consideration and frequently they have been arbitrarily ascribed accuracies of ± 1 , ± 2 , or ± 2.5 kcal. If it is assumed that the values of the enthalpy of formation of Cu_3P given in the reference literature are reliable and the data of Table 1 of this work differs insignificantly from the true values, then according to the Gibbs-Helmholtz equation (Third Law of Thermodynamics) for reaction (1) at 1290°K we obtain a pressure of the P_4 molecules of $6 \cdot 10^{-10}$ (-30.82) or $7 \cdot 10^{-14}$ Pa (-36.0 kcal/mole). The values of the pressure lie far beyond the limits of sensitivity of the instrument used in this work and the P_4 molecules may not be detected in mass-spectra.

A similar situation is observed for the enthalpy of formation of copper diphosphide, the value of which has been given as -28.6 [2], -23.5 ± 2 [7], and -21.52 ± 2.5 kcal/mole [8]. In addition in [2] its value is given with a reference to a nonexistent work and in [8] reference is made to [4], which gives only the value of the enthalpy of the reaction of disproportionation of copper diphosphide



at an average test temperature of 970°K : $\Delta H^\circ = 52.0 \pm 0.08$ kcal. In another work [3] this reaction was also experimentally investigated and $\Delta H^\circ(1068) = 51.16$ kcal was obtained.

The fact that the experimental results of [3, 4] in the general temperature area of investigation practically coincide makes it possible, using the data of Table 1 and [10, 11], to assume $\Delta H^\circ(298) = 167.4 \pm 4.0$ kJ/mole and to find $\Delta H_f^\circ(298)$, $\text{CuP}_2(\text{sol.}) = -66.9$ kJ/mole. The latter value does not differ so significantly from the literature data but, if the values presented in [7] or [8] are taken into consideration, then the calculated partial pressure in reaction (2) is more than twice the experimental results.

Therefore, copper diphosphide disproportionates at temperatures of 960 – 1158°K , and at 1150 – 1295°K Cu_3P phosphide dissociates. In both cases the main constituent of the vapor is P_4 molecules, the partial pressure of which at soldering temperatures is 10^5 and 10 Pa, respectively. The standard enthalpies of formation of CuP_2 and Cu_3P are -66.9 and -65.3 kJ/mole.

LITERATURE CITED

1. P. E. Petrunin, Handbook on Soldering [in Russian], Mashinostroenie, Moscow (1984).
2. G. V. Samsonov and L. L. Vereikina, Phosphides [in Russian], Izd. Akad. Nauk UkrSSR (1961).
3. Ya. A. Ugai, V. R. Pshestanchik, V. Z. Anokhin, and O. Ya. Gukov, "The temperature relationship of dissociation and the thermodynamic parameters of CuP_2 ," *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **8**, No. 1, 40–43 (1972).
4. H. Haraldsen, "Beiträge zur systematischen verwandtschaftserd über die phosphide deskupfers," *Z. Anorg. Allgem. Chem.*, **240**, 337–348 (1939).
5. F. Weibke and G. Schrag, "Die Biedungswärmch der Niederen Phosphide eienger schwermetalle," *Z. Electrochem.*, **47**, No. 3, 228–238 (1941).
6. O. Kubaschewski and I. Catteral, Thermodynamic Data of Alloys, Pergamon Press, London (1956).
7. O. Kubaschewski and E. Evans, Metallurgical Thermochemistry, Pergamon Press, London (1958).
8. O. Kubashevskii and G. B. Olkok, Metallurgical Thermochemistry [in Russian], Metallurgiya, Moscow (1982).
9. T. A. Chubanidze, A. P. Oklei, and M. A. Zhuruli, "The energy of interaction in the Si–B system," *Izv. Akad. Nauk SSSR, Met.*, No. 3, 199–201 (1982).
10. R. Hultgren, P. Desai, D. Hawkins, et al., Selected Values of the Thermodynamic Properties of the Elements, Amer. Soc. Met., Ohio (1973).
11. V. P. Glushko, The Thermodynamic Properties of Individual Substances [in Russian], Vol. 1, Nauka, Moscow (1978).
12. M. N. Abdusalyamova, G. Sh. Viksman, S. P. Gordienko, et al., "The area of homogeneity of monoantimonides of lanthanum, praseodymium, and samarium," *Poroshk. Metall.*, No. 12, 51–55 (1980).
13. I. S. Kulikov, The Thermal Dissociation of Compounds [in Russian], 2nd ed., Metallurgiya, Moscow (1969).