## CHEMISTRY

Stability and Vaporization Behaviour of Group IV–VI Transition Metal Monophosphides

THE vaporization properties of Group IV–VI transition metal monophosphides were investigated in order to obtain knowledge of their thermodynamic stability and of the possible existence of binary gaseous molecules between phosphorus and the respective transition metal. For this purpose, a Knudsen effusion–mass spectrometer assembly similar to that described by Chupka and Inghram[1] was used. Included in the investigation were the monophosphides of titanium, zirconium, hafnium, niobium, tantalum, molybdenum and tungsten.

The primary phosphorus species observed in the vapour above the condensed phase were P, P_2 and P_4. In the temperature range $1,000° - c.\ 1,800°$ K, diatomic phosphorus was the major species. At higher temperatures monatomic phosphorus also became an important vapour component. Tetratomic phosphorus was, under all conditions, either a minor species or was not detectable. In no case has a gaseous species containing both metal and phosphorus been observed. This has been checked especially for the monomeric monophosphides. The concentration of such species in the vapour phase at the temperatures and pressures investigated is at least 100–1,000 times less than that of the major vapour species. With respect to the formation of binary gaseous molecules, the transition metal phosphides appear to behave similar to the corresponding nitrides for which no binary gaseous molecules have been observed.

All phosphides investigated vaporize according to equation (1) by decomposition into phosphorus vapour and a solid phase of lower phosphorus content.

$$\frac{z}{x} MP_{1-\delta} = \frac{z}{x} MP_{1-\delta-x} + P_z \tag{1}$$
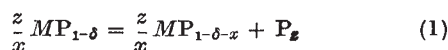
where $0 < x < 1-\delta$ and z is either 1, 2 or 4; δ is approximately 0·04 for TiP and NbP, and 0·08 for α-ZrP. For the other phosphides it is apparently close to zero.

From X-ray diffraction analysis of the residue, it was found that the condensed phase of lower phosphorus content, which is in equilibrium with the monophosphide, is phosphorus-saturated tungsten metal and sub-phosphides of the composition $MoP_{0·7}$ and $TiP_{0·6}$ in the respective systems.

Analysis of the phosphorus ion-intensity as a function of phosphorus content in the condensed phase at constant temperature indicates the presence of a homogeneity range for the TiP phase that extends between $TiP_{0·96-0·945}$ at 1,700° K. No indication for a homogeneity range was found for MoP, WP, and α-ZrP.

The ion-intensities of P_2^+ were correlated to vapour pressures through silver calibration[2]. The ratio in electron multiplier efficiencies for P_2^+/Ag^+ was 3·0. The ionization cross-sections for silver and monatomic phosphorus were obtained from Otvos and Stevenson[3]. For the phosphorus dimer the value of 21·8 was estimated. The possibility of a very low vaporization coefficient was not taken into account. The P_2-dissociation pressures obtained for the phosphorus-deficient boundary composition of the respective phosphide as a function of temperature were used for the calculation of the partial molal free enthalpies of phosphorus dissociation, $\Delta \bar{G}_T°[P_2]$. The results are listed in Table 1 for 1,000° K, 1,500° K and 2,000° K. Also included is the temperature-range over which the experimental pressure measurements were made. For hafnium and tantalum monophosphides the determination of the temperature-pressure relationship was complicated by the apparent presence of a diffusion barrier, and, in the case of tantalum monophosphide, by reaction of phosphorus vapour with the tantalum effusion cell. From the possible observations it can be estimated that, at 2,000° K, the stability of tantalum monophosphide is comparable with

that of α-ZrP and the stability of hafnium monophosphide is considerably higher than that of α-ZrP and similar to that of thorium subphosphide ($ThP_{0·7}$) (ref. 4) and uranium monophosphide[5]. The results presented in Table 1 show that the stability of the monophosphides of group IV increases markedly with atomic number. The same appears to be the case for the group V monophosphides of niobium and tantalum, while for molybdenum and tungsten monophosphides the stability trend is reversed. Within a period the stability decreases with atomic number. This decrease is most pronounced in third transition period.

Table 1. PARTIAL MOLAL FREE ENTHALPIES OF P_2-DISSOCIATION FOR SELECTED TRANSITION METAL MONOPHOSPHIDES

Compound	Temperature range of pressure measurement (° K)	$\Delta \bar{G}_T°$ [P_2] in kcal/mole P_2		
		1,000° K	1,500° K	2,000° K
$TiP_{0·94}$	1,295–1,705	55·8	40·8	25·9
$ZrP_{0·82}$	1,770–2,120		66·8	51·1
$NbP_{0·95}$	1,200–1,450	55·4	34·0	12·7
MoP	1,190–1,450	54·3	28·3	
WP	950–1,250	36·7	17·3	

A comparison of the stability of the groups IV–VI transition metal monophosphides with the corresponding nitrides is attempted on the basis of information reviewed by Storms[6]. Such a comparison is only of relative significance for the groups IV and V compounds because of the strong dependence of the non-metal activity on the composition in a given binary system, and the difficulty of comparing compounds of exactly the same stoichiometry. For the groups IV and VI nitrides the family trends appear to be similar to those found for the corresponding phosphides, but are less pronounced. The trends within a period are also in the same direction as indicated for the phosphides, but are considerably more pronounced. As a result, the group IV nitrides, especially titanium nitride, are of higher stability than the corresponding phosphides; whereas the group V mononitrides appear to be somewhat less stable and the group VI mononitrides significantly less stable than the corresponding monophosphides. The high thermodynamic stability of hafnium monophosphide, α-zirconium monophosphide and tantalum monophosphide, together with their reported resistance to chemical attack, makes these compounds attractive for special high-temperature applications. The rather low stability of WP and the non-existence of a lower tungsten phosphide above 1,000° C make tungsten metal a promising oxygen-free container material for the more stable phosphides.

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[1] Chupka, W. A., and Inghram, M. G., J. Phys. Chem., 59, 100 (1955).
[2] Inghram, M. G., Chupka, W. A., and Porter, R. F., J. Chem. Phys., 23, 2159 (1955).
[3] Otvos, J. W., and Stevenson, D. P., J. Amer. Chem. Soc., 78, 546 (1956).
[4] Gingerich, K. A., and Efimenko, J., Thermodynamics of Nuclear Materials, 477 (Intern. Atomic Energy Agency, Vienna, 1962).
[5] Gingerich, K. A., Lee, P. K., and Efimenko, J., Nature, 200, 774 (1963).
[6] Storms, E. K., LAMS-2674 (Part II), Chem. TID-4500, seventeenth ed. (Las Alamos Scientific Laboratory, Los Alamos, New Mexico, October 1962).

Molecular Orbital Theory and Experimentally Determined Energy-levels

ONE of the more successful descriptions of the electronic structure of aromatic hydrocarbons has been given by molecular orbital theory. Originally formulated by Huckel[1], it has been developed and modified by many different authors. An account of the molecular orbital theory in its various forms has been given by Daudel,