ENERGIES AND BONDING IN MANGANESE PHOSPHIDES

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MASTER

Clifford E. Myers, Elyse D. Jung, Diana J. Simpson,
Elizabeth L. Patterson, and Jeffrey I. Melzer

Department of Chemistry
State University of New York at Binghamton
Binghamton, New York 13901

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ABSTRACT

Manganese monophosphide and other first row transition metal phosphides have been studied by X-ray photoelectron spectroscopy in collaboration with colleagues at Ames Laboratory (U.S.D.O.E.). Electron binding energies of both valence-conduction band and core level electrons show an evolution of metallic behavior in the series ScP, TiP, VP, MnP, FeP, and in the series FeP, Fe₂P, Fe₃P.

Phosphorus dissociation pressure measurements on MnP lead to:

when the data are treated by the third law method using estimated entropies.

Combination of this result with published data yields:

$$\Delta H_{\text{f}, 298.15}^{\circ}(\text{MnP}) = -12.5 \pm 0.6 \text{ kK}$$

which is in satisfactory agreement with the published value:

$$\Delta H_{\text{f}, 298.15}^{\circ} = -11.6 \text{ kK}.$$

The apparently low value of the atomization enthalpy of MnP is confirmed and is attributed to a high valence state preparation energy.

A study of the congruent vaporization of Mn₂P has been initiated. Apparatus for solid state galvanic cell measurements on metal phosphide systems has been fabricated and assembled. Studies are proceeding on a high pressure synthesis of MnP₃.

X-RAY PHOTOELECTRON SPECTROSCOPY

The details of XPS studies were summarized in the last annual report. In our work of the past year we found that an instrumental difficulty, discovered after completion of our first measurements, required a reinvestigation of the compounds studied earlier. This work is now virtually complete. The results on the valence-conduction band regions of the spectra of the monophosphides of Ti, V, Mn, and Fe have been confirmed and show increasing metal-metal d-d and metal-phosphorus d-p interactions through the series. In addition there is a regular shift in the position of the conduction band maximum, relative to the Fermi energy, in the series FeP (3.5 eV), Fe_2P (3.4 eV), Fe_3P (3.2₅ eV), and Fe (1.3 eV) which is indicative of increasing metallic character in the series. Furthermore, the shifts in the core level peaks, compared with those of the respective elements now indicate a more gradual transition from ionic to metallic bonding. See Tables 1 and 2.

[Note: The XPS measurements were made at Ames Laboratory (U.S.D.O.E.), Iowa State University, in collaboration with Professor H. F. Franzen and Mr. J. W. Anderegg. Preparation and characterization of samples was done at SUNY-Binghamton.]

MASS-LOSS EFFUSION

The study of the vaporization behavior of MnP has been completed and published (1). A reprint is appended. The results of the initial study were confirmed, and the low enthalpy of atomization of $\text{MnP}_{(s)}$ is understood to result from a large valence state preparation energy. The enthalpies of formation and atomization of $\text{MnP}_{(s)}$ at 298.15 K are respectively -12.5 ± 0.6 kK and 86.2 ± 0.6 kK; the corresponding values for $\text{Mn}_2\text{P}_{(s)}$ are -18.1 ± 0.7 kK and 125.4 ± 0.7 kK. In "rational" units; values in other units obtained by multiplying by appropriate value at R. These values are in "rational" units; values in other units may be obtained upon multiplying by the appropriate value of the gas constant R.

During the vaporization of MnP, the X-ray powder diffraction lines of that compound diminish in intensity while those of Mn₂P increase. Furthermore, when Mn₃P-Mn₂P mixtures are heated in vacuum, the diffraction lines of Mn₃P eventually disappear, leaving only those of Mn₂P. Therefore, within the homogeneity range of Mn₂P there is a congruently vaporizing composition, and we have initiated a study of the vaporization of Mn₂P. Preliminary results indicate that the required temperatures for the study are in the range 1200-1400 K.

SOLID STATE GALVANIC CELLS

The apparatus is almost completely assembled for studying the cells:

with cell reaction

and

with cell reaction

These studies will be made in the temperature range 800-1100 K. The cell itself consists of a metal-metal fluoride pellet and a phosphide-metal fluoride pellet on either side of a single crystal disk of CaF₂. The pellets are mounted in molybdenum holders, and the electrical leads are molybdenum wire. Temperatures will be measured with a calibrated thermocouple. The cells will be studied under flowing argon which will pass over activated alumina and hot titanium before reaching the cell. In addition, tantalum strips will be placed near the cell in the hot zone to act as a getter for oxygen. The ceramic

envelope containing the cell and protecting it from air can be evacuated to about 10^{-5} torr before beginning flow of argon. The cell assembly is arranged so that argon which comes in contact with one side of the cell does not subsequently come in contact with the other, thereby preventing transfer of fluorine from one electrode to the other through the gas phase. EMFs will be measured with a guarded DC differential voltmeter capable of reading to the nearest 0.01 mV and having an input impedance said to be infinite at null.

HIGH PRESSURE SYNTHESIS

We have completed and published a high pressure study of melting temperatures in the gold-phosphorus system (2) which was not specifically subsumed under this contract. A reprint is appended.

We have begun to apply the high pressure techniques to a synthesis of MnP_3 with a goal of obtaining single crystals for X-ray crystallography.

REFERENCES

1. C. E. Myers, E. D. Jung, and E. L. Patterson, INORG. CHEM., 19, 532 (1980).
2. C. E. Myers, J. I. Melzer, and N. F. Marley, INORG. NUCL. CHEM. LETT., 16, 19 (1980).

Reprints Removed

Table 1

Metal $2P_{3/2}$ Binding Energies (eV)

	<u>M</u>	<u>MP</u>	<u>MS</u>
Sc	398.3	399.4	
Ti	454.3	454.8	454.0
V	512.6	512.6	
Mn	638.9	639.0	640.8
Fe	706.9	707.1	

Table 2

Phosphorus $2P_{3/2}$ Binding Energies (eV)

P	129.9
ScP	127.7
TiP	128.4 ⁵
VP	129.1
MnP	129.4
FeP	129.5