NOV 12 1964

Report No. NYO-2541-1

STUDY OF HIGH TEMPERATURE PROPERTIES OF TRANSITION METAL PHOSPHIDES
AND RELATED REFRACTORY MATERIALS

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Contract No. At(30-1)-2541

United States Atomic Energy Commission

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FINAL REPORT

April 1, 1960, through October 31, 1964

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STUDY OF HIGH TEMPERATURE PROPERTIES OF TRANSITION METAL PHOSPHIDES AND RELATED REFRACTORY MATERIALS

I. OBJECTIVES

This investigation was undertaken in order to obtain knowledge of the preparation, constitution, crystal chemistry, thermal stability and selected properties of transition metal phosphides that were expected to be of high thermodynamic stability. This knowledge was desirable in order to obtain a better understanding of the nature of these compounds. It was also expected that this basic knowledge of selected properties would permit an evaluation of their potential usefulness as oxygen-free refractory materials for special high-temperature applications.

At first, emphasis was placed on the study of the titanium and zirconium phosphides, since these compounds were expected to combine best high temperature stability and resistance to chemical attack. In view of their potential nuclear applications, uranium and thorium phosphides were studied in detail after recognition of their high chemical and thermodynamic stability. Other phosphides expected to be of high thermodynamic stability were those of hafnium, the lanthanides and the group V transition metals. In search of suitable oxygen-free container materials for the phosphides to be investigated at higher temperatures, the phosphides of tungsten, molybdenum and rhenium have been studied because they were expected to have a rather low stability.

II. EXPERIMENTAL RESULTS

Some of the details of the research have already been given in the annual progress reports and in the publications listed in section IV. The papers which are projected or being prepared will conclude the presentation of all the results, their interpretation and correlation. In the following, a summary of the results and the methods used will be given for the different areas of investigation. For more detailed description of the results, reference is made to the papers listed in section IV.

A. Preparation of Phosphides.

The principle method used for the preparation of transition metal phosphides was the direct combination of the elements. Various modifications were applied. An important development was the extension of the conventional "Faraday method" (reaction in a sealed evacuated fused silica tube) to temperatures up to 1850°C.,¹⁶ which was applied to thorium and zirconium phosphides. This method was successfully applied to thorium phosphides; however, in the case of zirconium phosphides, alloy formation with the tungsten container at high temperatures was observed. Another new approach applied to titanium phosphides was a dynamic variation in which phosphorus vapor was passed over the hot metal, argon being used as the carrier gas.¹⁷

For the preparation of phosphide samples with very small particle size, a reaction between metal hydride and phosphine with hydrogen as a carrier gas was used.^{17,26}

All these reactions ultimately yield the highest phosphide that is

thermodynamically stable at the temperature and phosphorus partial pressure conditions of preparation.

In order to obtain the more stable lower phosphides, the phosphides prepared as described above were thermally degraded in high vacuum at temperatures between 1200 and 2400°C.¹⁶ In this way, pure samples of ThP_{1-x} , UP and α -ZrP were prepared.

For the study of the phase relationships in the metal-rich portion of binary systems, samples were prepared by mixing stoichiometric amounts of metal powder and phosphide, pressing the mixtures to pellets and annealing the pellets under inert conditions.^{16,17} In the case of titanium phosphides, some of these pellets were subsequently arc-melted for better equilibration.

B. Chemical Analysis.

Chemical composition of the phosphide products was commonly obtained after synthesis from the weight gain of the metal or from the weight loss after thermal degradation assuming it to be solely due to phosphorus.

New wet chemical analytical methods for the major components have been developed for the titanium¹⁷ and thorium¹⁹ phosphides. Standard wet techniques were applied to phosphides of zirconium and hafnium. Chemical analysis for nitrogen and oxygen was performed in selected cases by the micro-Kjedahl method and the LECO fusion technique, respectively.

X-ray fluorescence analysis was applied to the zirconium phosphides by Dr. Eulenberger. Preliminary results show a linear dependence of the fluorescent intensities with the composition for zirconium and phosphorus.

C. Constitution of Binary Phosphide Systems.

The constitution of some binary phosphide systems has been investigated

by X-ray powder diffraction and mass spectrometric techniques. In some cases, microscopic and electron microprobe analysis were additionally applied. Crystal chemical studies of new phases and refinements of lattice parameters of previously known phases were also carried out. To facilitate the evaluation of X-ray data, a set of Fortran programs for the IBM 7074 computer have been prepared.

In the thorium-phosphorus system,^{15,16} the existence of two phases, the monophosphide, ThP_{1-x} , and Th_3P_4 , was confirmed. It could be shown that no stable higher phosphide exists. Th_3P_4 was found to be stoichiometric. Thorium monophosphide, which crystallizes in the NaCl-type structure was found to have an existence range of $\text{ThP}_{0.96}$ to $\text{ThP}_{0.55}$ at 1000°C . with lattice parameters of 5.8400 and 5.8300 Å., respectively, for the boundary compositions. Within the existence range, the lattice parameter is a linear function of composition. It was found that at higher temperatures the phosphorus-rich phase boundary in co-existence with Th_3P_4 shifts to a lower P/Th atomic ratio, and the thorium-rich boundary in co-existence with phosphorus-saturated thorium metal shifts to a higher P/Th ratio. No other intermediate phases could be detected in the temperature range from 1000 to 2000°C .

In the titanium-phosphorus system,¹⁷ a previously unknown phase Ti_5P_3 was found, and its crystal structure was determined by single crystal analysis. It crystallizes in the hexagonal D_{8h} type (Mn_5Si_3) with the space group $\text{P6}_3/\text{mcm}$.⁶ The lattice parameters were found as follows: $a = 7.234$ Å.; $c = 5.090$ Å.; $c/a = 0.704$. The previously known phases Ti_3P and TiP were confirmed. It could be shown that at high temperatures phosphorus is slightly soluble in alpha titanium. It was also shown

that the phases Ti_5P_3 and TiP exhibit ranges of existence. There is evidence that at least one additional phase exists in each of the composition regions $TiP_{0.33 - 0.60}$ and $TiP_{0.7 - 0.9}$.

In the zirconium-phosphorus system, the structural transformation of the hexagonal β -ZrP to the cubic α -ZrP at elevated temperatures has been investigated and explained by a model.³ In the study of the phase relationships of the composition range $ZrP_{0.5 - 1.0}$, it was found that temperatures above $1400^\circ C$. will be needed to obtain equilibrium within a reasonable length of time. At this temperature, however, unresolved container problems were encountered. Preliminary results, as obtained by Dr. Eulenberger, indicate the existence of two phases with approximate compositions $ZrP_{0.7}$ and $ZrP_{0.5}$ in addition to α -ZrP and β -ZrP. No evaluation of these phases as to elementary cell and exact stoichiometry was possible because of poor crystallization. There is also indication of a third previously unknown zirconium phosphide in this range. In the composition region $Zr - ZrP_{0.5}$ a low-melting eutectic was observed.

In the praseodymium-phosphorus system, the monophosphide was found to be the only stable phosphide phase. The monophosphide phase which crystallizes in the NaCl-structure has an existence range with a considerable range in lattice parameter from $a = 5.912 \text{ \AA}$. at a composition that corresponds closely to stoichiometry, to $5.870 \text{ \AA}$. at a composition of approximately $PrP_{0.9}$. Praseodymium monoarsenide also exhibits a range of homogeneity with variable lattice parameter. In addition, a previously unknown phase was found in the praseodymium-arsenic system at a composition close to $PrAs_{0.5}$ as obtained from the weight gain. This phase crystallizes in the anti- Th_3P_4 structure.²⁰ There is indication that this phase disproportionates at high temperatures.

In the system tungsten-phosphorus, the phase relationships and crystal chemistry were studied by mass spectrometry⁷ and X-ray diffraction analysis. At temperatures above 1000°C., tungsten monophosphide was found to co-exist with phosphorus-saturated metal. The W_3P phase which had been occasionally found by other workers in preparations performed at temperatures below 1000°C. was studied by single crystal analysis by Dr. Eulenberger. The preliminary results are compatible with the space group $I\bar{4}$ which, together with the lattice parameters, provides evidence that W_3P is isostructural with Ni_3P .

In the system molybdenum-phosphorus, a new phase $MoP_{0.7}$ was found by thermal degradation of MoP at 1200°C. From thermodynamic evidence as obtained from mass spectrometry, this phase is predicted to disproportionate at lower temperatures.¹²

Preliminary mass spectrometric results also indicate a solubility of phosphorus in molybdenum, tungsten, and tantalum.

In order to facilitate structural analysis of new phosphide phases, a survey of the crystal chemistry of selected transition metal arsenides was performed by Dr. Eulenberger in the expectation that some of them were isostructural with the corresponding phosphides. In this connection, sub-arsenides of titanium, zirconium, niobium, tantalum and probably molybdenum and the monoarsenide of molybdenum were identified as new phases which have not been reported elsewhere.

During an initial period of this program, while equipment for doing work under inert conditions was being set up, the crystal chemistry of the system $ThO_2 - Eu_2O_3$ was studied.¹

D. Measurement of Vapor Pressures.

A large part of the research program was devoted to the study of the

vaporization behavior and measurement of vapor pressures of transition metal phosphides. The development of suitable static methods for the determination of phosphorus decomposition pressures was begun by using Bourdon gauge and radio tracer techniques.

1. High Temperature Mass Spectrometry: Availability of a Knudsen cell mass spectrometry assembly at the National Bureau of Standards in Washington D.C. and at the Nuclide Corporation, State College, Pennsylvania, made it possible to study not only the phosphorus decomposition pressures but also the composition of the vapor. Therefore, a survey of the vaporization of all phosphides of interest was undertaken in order to obtain knowledge of the composition of the saturated vapor and stability trends for the phosphides.

Phosphides of titanium, zirconium, hafnium, niobium, tantalum, molybdenum, tungsten, praseodymium, thorium, and uranium were included in the mass spectrometric survey study. No molecular vapor species containing both metal and phosphorus atoms have been observed, with the possible exception of Pr_2P . Only UP was found to vaporize congruently or almost congruently by decomposition into the gaseous elementary species. All other phosphides were found to vaporize incongruently by decomposition into phosphorus and a condensed phase of lower phosphorus content. The decomposition reaction can be expressed by the following equations:

where M represents a transition metal and y represents the P/M atomic ratio of the phosphide investigated. The variable parameter x indicates the decrease in the P/M ratio of the phase that decomposes. The resulting phase MP_{y-x} may be phosphorus-saturated metal or a new, condensed phase of lower

phosphorus content, or it may be a composition within the existence range of the same phase; z is either 1, 2, or 4.

At 2000°K., the order of decreasing stability with reference to the composition in equilibrium with the next lower phosphide or the phosphorus-saturated, condensed metal, respectively, was found to be: $\text{ThP}_{0.65} > \text{HfP}_{1-x} \approx \text{UP} > \text{PrP}_{1-x} \approx \alpha\text{-ZrP} \approx \text{PaP} \gg \text{TiP} > \text{NbP} > \text{MoP} \approx \text{Th}_3\text{P}_4 > \text{WP}$. The selected corresponding thermodynamic data are presented in Table I.^{2,4,5,9,10,13}

The mass spectrometric method has also been applied to obtain information on the width of the homogeneity range of the phases studied.^{2,5,11,12,16,17} As has been mentioned above, thorium monophosphide and praseodymium monophosphide were found to have large homogeneity ranges. Existence ranges could also be detected for the phases TiP , $\beta\text{-ZrP}$, and NbP . An extremely narrow homogeneity range was found for MoP .

In the case of praseodymium monophosphide, the partial thermodynamic properties have been studied as a function of composition. An increase in the partial molar heat of P_2 decomposition from 78 kcal. at the phosphorus-rich boundary composition to approximately 130 kcal. at the praseodymium-rich boundary composition was observed.^{14,18} The partial free energy of formation in all cases where homogeneity ranges were involved was observed to decrease significantly with decreasing phosphorus content within the homogeneity range.

Detailed thermodynamic studies were performed for tungsten monophosphide,⁷ molybdenum monophosphide,¹² and uranium monophosphide.⁸ The temperature dependence of the P_2 decomposition pressures of WP and MoP can be expressed by the equations $\log p \text{ (atm.) } [\text{P}_2] = (-16534/T) + 8.501 \pm 0.111$ and $\log p \text{ (atm.) } [\text{P}_2] = (-23566/T) + 11.6594 \pm 0.0335$, respectively. The total pressure over uranium monophosphide can be expressed by the equation

Table I: SELECTED PARTIAL THERMODYNAMIC PROPERTIES PER MOLE P_2 FOR SOME TRANSITION METAL PHOSPHIDES

Phase Studied	Composition Range (MP_{y-x}) Investigated	Temperature Range ($^{\circ}K$) of P_2 -Partial Pressure Measurement	$\Delta H_T^{\circ} \pm$ S. D. [kcal/mole P_2]	ΔG_{2000}° [kcal/mole P_2] ^{a)}
WP	WP _{0.95 - 0.65}	950 - 1250	75.66 $\pm$ 1.06	• 2.1
MoP	MoP _{1.0 - 080}	1190 - 1450	106.46 $\pm$ 0.65	- 2.2
NbP	NbP _{0.96 - 94}	1200 - 1450	98.17 $\pm$ 3.35	-13.8
TiP	TiP _{0.94 - 85}	1295 - 1705	86.05 $\pm$ 2.72	-25.8
α -ZrP	ZrP _{0.94 - 85}	1770 - 2120	113.79 $\pm$ 1.37	-51.8
Th ₃ P ₄	ThP _{1.33 - 0.96}	1040 - 1340	82.95 $\pm$ 0.75	- 2.1
"ThP"	ThP _{0.68 - 0.63}	2030 - 2250	155.11 $\pm$ 3.75	-68.0
UP	UP	1850-2150	105.46 $\pm$ 1.66	-64.7

a) Estimated values for HfP_{1-x}, PrP_{1-x} and TaP_{1-x} are -65, -55, and -50 [kcal/mole P_2], respectively.

$\log p \text{ (atm.) } \overline{[total]} = (-26917/T) \pm 7.4033$. The equilibrium constant K_p for the reaction $UP_{(s)} = U_{(g)} + P_{(g)}$ can be expressed by the equation:

$\log K_p = (-54888/T) + 14.6056 \pm 0.1392$. The corresponding free energy change in cal. is: $\Delta G_T^\circ = 251200 - 66.8 T$ and the heat of vaporization in kcal. is:

$\Delta H_{2000}^\circ = 251.17 \pm 4.88$. The temperature ranges over which measurements have been made are given in Table I.

A mixture of uranium monophosphide and uranium dioxide was included into the vaporization study^{4,8,24} to investigate the function of oxygen contaminant in UP on vaporization and to study the possible function of a UP additive to uranium dioxide base nuclear fuel elements at high temperatures. The vaporization occurs according to the following equations:

Equation 3 appears to be the predominant one. The $UO:UO_2$ ratio above a solid $UP - UO_2$ mixture appears to be similar to the one in equilibrium with a condensed $U - UO_2$ mixture. The excellent chemical stability, the high melting point, and the similarity in vaporization characteristics may make UP a promising additive in UO_2 fuel elements that would, at temperatures above approximately 1200°C ., possibly protect the latter against mechanical disintegration caused by the formation of higher uranium oxides.

2. Development of Static Methods for Phosphorus Decomposition Measurements:

An apparatus for the determination of phosphorus decomposition pressures at temperature below 1000°C . has been set up by Mr. R. Newman.²⁶ It was similar to that used by Biltz and co-workers but utilized a spoon gauge rather than a quartz spiral manometer. The apparatus was used for the redetermination of the phosphorus dissociation pressures of ZrP_2 . The results obtained by

Strotzer, et al.* were essentially confirmed.²⁷

The development of the static method for use at high temperatures utilizing induction heating and a quartz spiral manometer was begun.^{27,28} At these high temperatures, however, serious container problems are encountered by the high reactivity of phosphorus vapors. Preliminary work indicates the use of tungsten, rhenium, and graphite as susceptors for heating with radio frequency. As shielding material, zirconia appears to be most suitable. Before a further development of this method can be undertaken, more basic information on the interactions at such high temperatures between phosphorus vapor and container materials needs to be obtained.

An apparatus for the determination of phosphorus decomposition pressures using radio active P^{32} as a tracer has been constructed for application up to 1000°C . This experimental work was done by Miss Carolyn Barten under the direction of Professor W. W. Miller. The method applied was to first determine phosphorus activity of a fixed volume of vapor vs. temperature curve for a sample of white phosphorus for calibration of the apparatus. Then a suitable modification of the same procedure was applied to determine the P^{32} activity of the vapor in equilibrium with WP at various temperatures. The radioactive phosphorus was prepared by irradiating quartz ampoules containing phosphorus near the core of the Pennsylvania State University swimming reactor for six weeks. The same active phosphorus sample was used for preparation of WP and for the calibration of the apparatus. Preliminary vapor pressure measurements for the tungsten monophosphide were obtained. They indicate the applicability of the method for phosphorus decomposition pressure measurements at temperatures up to 1000°C . and pressures in the range between 10^{-8} to 10^{-4} atm.

*E. F. Strotzer, W. Biltz, and K. Meisel, Z. anorg. allgem. Chem. 239, 216 (1938).

under static conditions. The method is expected to complement mass spectrometric measurements of less stable phosphides. It would eliminate the influence of a low vaporization coefficient.

E. Measurements of Physical and Chemical Properties.

1. Thermal Expansion of TiP, ZrP and HfP: The thermal expansion of the isostructural hexagonal monophosphides of titanium, zirconium and hafnium has been studied by means of X-ray powder diffraction.²⁷ Besides the thermal expansion coefficient being an important material property needed in potential high temperature application, such a study was expected to yield knowledge of the bonding within the individual phosphides as well as any variations within the series. The fact that the unit cell is hexagonal permits the study of directional expansion and thus directional evaluation is possible. High precision measurements of temperature and lattice parameters were performed by using a Seemann-type of film camera over the temperature range from room temperature to 1300°C. The coefficient of thermal expansion above 400°C. in $(^{\circ}\text{C})^{-1} \times 10^{-6}$ were found as follows: TiP, $\alpha_a = 13.0$, $\alpha_c = 0.35$; ZrP, $\alpha_a = 7.6$, $\alpha_c = 6.8$; HfP, $\alpha_a = 7.9$, $\alpha_c = 7.4$. Below 400°C., the thermal expansion coefficient was found to be more complex. A complete evaluation of all data will be presented at a future date.²³

2. Magnetic Properties of Thorium Phosphides: The magnetic susceptibilities of the thorium phosphides have been measured by the Guoy method over the temperature range from -196°C. to 25°C. Th_3P_4 was found to be diamagnetic with a mass susceptibility $\times 10^{-6}$ of -0.03^{15} at 25°C. The ThP_{1-x} phase was found to be weakly paramagnetic and the composition dependence of the magnetic susceptibility was established. At 25°C the mass susceptibility of $\times 10^{-6}$ was 1.6, 2.0, 0.5, and 0.5 for $\text{ThP}_{0.92}$, $\text{ThP}_{0.75}$, $\text{ThP}_{0.61}$, and $\text{ThP}_{0.52}$ respectively.²¹

3. Bonding in Phosphides: The results of the study of thorium monophosphide have been used to make a comparison between the sulfides and phosphides of cerium, thorium and uranium. This was developed into a discussion of chemical bonding in the general class of MX compounds of rock salt structures that are not predominately ionic. The bonding in thorium monophosphide can be described in terms of electron deficient covalent bonds. Some metallic bonding is present, due to a "free" d electron in thorium which enters a metallic bond.²¹

4. Phosphidation of Zirconium: The reaction between phosphorus vapor of one atmosphere and zirconium metal has been studied over the temperature range from 500 to 1100°C.²² From the temperature dependence of the reaction rate, it could be shown that below 700°C. a reaction with a very low activation energy is rate determining. At higher temperatures a second process with a higher activation energy is superimposed. The first process is believed to be associated with the formation of a subphosphide layer of about 1 to 2 micron thickness. Further phosphidation leads to the hexagonal β -ZrP phase. From the study of the reaction rate at 1000°C. as a function of product layer thickness, it was found that at approximately 50 microns the phosphide layer becomes protective. The intermediate subphosphide layer has been studied by microscopic, X-ray diffraction, and electron microprobe techniques. Preliminary results indicate that it is a non-cubic phase with a P/Zr atomic ratio of approximately 0.6.

5. Rate of Oxidation of Zirconium Phosphide: The rate of oxidation of bars of zirconium metal and zirconium metal coated with zirconium phosphide has been studied by high temperature X-ray diffractometer techniques. The phosphide layer impedes the rate of oxidation of zirconium metal. However, the protection does not appear to be significant. The

analysis of the data appears to be complex, in part due to the formation of reaction products of unknown structure. Powdered zirconium phosphide, ZrP, has been oxidized in air and the weight change has been followed on a thermobalance. The oxidation starts well below 1000°C. and occurs in distinct steps.²⁶

III. IMPLICATIONS OF THIS RESEARCH PROGRAM

From a technological viewpoint, this research program has lead to the recognition of some transition metal phosphides as a new group of oxygen-free refractory materials. The monophosphides of uranium and thorium are of particular interest in high temperature nuclear fuel technology. These phosphides combine high melting points and low vapor pressures with a chemical resistance that is superior to that of other oxygen-free refractory materials. Noteworthy is the apparent compatibility of uranium monophosphide with uranium dioxide. The monophosphides of group IV-VI transition metals are of interest as potential coatings at elevated temperatures because of their known high corrosion resistance. They were found to be somewhat less stable at high temperatures than the uranium and thorium compounds. The zirconium monophosphide appears to be the most promising compound for nuclear technology applications because of its high stability, low neutron absorption capability, and a higher oxidation resistance than zirconium.

Besides the applied implications of this research program, a better understanding of the nature of these compounds has been obtained from the thermodynamic, structural, magnetic, and thermal expansion properties studied. The transition metal phosphides appear to be an intermediate group between the more common types of compounds. There are indications of alloy-type behavior especially for the lower phosphides of zirconium and titanium.

The unexpected large number of phases, the observation that some of these phases are nonstoichiometric and exhibit ranges of homogeneity, as well as the observation of metallic luster and considerable mechanical hardness are indicative of this. Of particular interest is the occurrence of the monophosphide phases of thorium, uranium, rare earth metals (praseodymium), zirconium, and hafnium with NaCl-type structure. All these phases are apparently phosphorus deficient and some of them form wide homogeneity ranges. They appear to be related in this and their properties to corresponding typical interstitial compounds such as carbides and nitrides but exhibit a separation of the metal lattice due to the larger size of the phosphorus atom as compared with carbon or nitrogen atoms. As has been shown for thorium monophosphide, this separation leads to a more covalent character of these compounds with some metallic character still present. Because of the rather high electronegativity of phosphorus, an ionic component of bonding, the size of which is related to the electronegativity difference of the components, must be superimposed in all phosphides studied.

Another important contribution of this research program is the refinement and the development of high temperature research techniques. In the preparative area, the high temperature Faraday method is expected to become a valuable tool for the preparation and phase studies involving high melting compounds with reactive non-metals of relatively high volatility. A further development of this preparative method would be the anticipated method for phosphorus decomposition pressure measurements above 1000°C . under static conditions.

In the area of vaporization reactions, high temperature mass spectrometry has been systematically applied for the first time to the study of incongruent vaporization processes. As a consequence, the width of homogeneity

ranges of nonstoichiometric compounds has been determined. Improvements in the precision of vapor pressure measurements by measuring relative multiplier efficiencies, relative ionization cross sections (P_2) and the degree of vapor reaction of the cell have also been achieved. Another new development utilizing this method is the investigation of the composition function of thermodynamic properties of binary compounds with an homogeneity range.

Combined with the application of the parametric X-ray method, which has been refined to high precision in the course of this program, and with chemical analysis, these new methodical approaches are expected to be valuable tools for the study of the phase relationships and thermodynamic properties of oxygen-free refractory compounds.

IV. PUBLICATIONS

A. Papers Published or in Press.

- (1) K. A. Gingerich. The Effect of Temperature on Some Rare-Earth Sesquioxide-Thoriumdioxide Systems. J. F. Nachmann and C. E. Lundin, eds., "Rare Earth Research," Gordon and Breach Science Publishers, New York, 1962, pp. 321-327.
- (2) K. A. Gingerich and J. Efimenko. Thermodynamic Study of the Thorium Phosphides with a Mass Spectrometer. "Thermodynamics of Nuclear Materials," International Atomic Energy Agency, Vienna, 1962, pp. 477-486.
- (3) K. S. Irani and K. A. Gingerich. Structural Transformation of Zirconium Phosphide. J. Phys. Chem. Solids 24, 1153-1158, 1963.
- (4) K. A. Gingerich, P. K. Lee and J. Efimenko. Vaporization of Uranium Monophosphide. Nature 200, 774-776, 1963.
- (5) K. A. Gingerich, Stability and Vaporization Behaviour of Group IV-VI Transition Metal Monophosphides. Nature 200, 877, 1963.
- (6) G. Brauer, K. Gingerich and M. Knausenberger. Kristallstruktur des Titanphosphids Ti_5P_3 . Angew. Chem. 76, 187, 1964. Crystal Structure of Titanium Phosphide Ti_5P_3 . ibid. Intern. Ed. 3, 231, 1964.
- (7) K. A. Gingerich, Vaporization Behavior and Phosphorus Decomposition Pressures of Tungsten Monophosphide. J. Phys. Chem. 68, 768-772, 1964.
- (8) K. A. Gingerich and P. K. Lee, Mass Spectrometric Study of the Vaporization of Uranium Monophosphide, J. Chem. Phys. 40, 3520-3526, 1964.
- (9) K. A. Gingerich. Vaporization and Stability of Some Transition Metal Monophosphides. Angew. Chem. 76, 582, 1964.
- (10) K. A. Gingerich. Thermodynamic Properties of Selected Transition Metal Phosphides. Argonne Nat'l Lab. Report. ANL-6856, 8-10, (1964).
- (11) K. A. Gingerich. Praseodymium-Group V Compounds I: Vaporization Behavior and Nonstoichiometry of PrP , $PrAs$, $PrSb$ and $PrBi$. K. S. Vorres, ed., "Rare Earth Research," Gordon and Breach Science Publishers, New York, 1964, pp. 245-255.

- (12) K. A. Gingerich. Tensimetric Analysis of the MoP-MoP_{0.7} Partial System with a Mass Spectrometer and Phosphorus Decomposition Pressures and Homogeneity Range of Molybdenum Monophosphide, J. Phys. Chem. 68, 2514-2522 (1964).
- (13) K. A. Gingerich. Vaporization of Transition Metal Phosphides, Proceedings, International Symposium of High Temperature Technology, September 8-11, 1963, Asilomar, California (In press).
- (14) K. A. Gingerich. The Application of High Temperature Mass Spectrometry to the Study of the Composition Function of Thermodynamic Properties in Non-Stoichiometric Compounds, "Advances in Mass Spectrometry," Vol. III, Institute of Petroleum, London, (In press).

B. Papers Submitted.

- (15) K. A. Gingerich and D. W. Wilson. Preparation and Properties of Th₃P₄ and the Phase Studies of the Partial System ThP-P.
- (16) K. A. Gingerich and D. W. Wilson. Preparation and Properties of ThP_{1-x} and Phase Studies of the Partial System Th-ThP.
- (17) M. Knausenberger, G. Brauer and K. A. Gingerich. Preparation and Phase Studies of the Titanium Phosphides.
- (18) K. A. Gingerich. Application of High Temperature Mass Spectrometry to the Determination of the Enthalpy - Composition Function of Non-Stoichiometric Binary Compounds.
- (19) D. W. Wilson and K. A. Gingerich. Chemical Analysis of the Thorium Phosphides.

C. Future Publications (Manuscripts in Preparation or Projected).

- (20) G. R. Eulenberger and K. A. Gingerich. Praseodymium - Group V Compounds II: The Structure of Praseodymium Arsenide, Pr₄As₃.
- (21) D. W. Wilson and K. A. Gingerich. Magnetic Susceptibilities and Experimental Evidence of Bonding in Rock Salt Structure of Thorium Phosphide.
- (22) F. F. H. Freund and K. A. Gingerich. Phosphidation of Zirconium.
- (23) K. A. Gingerich and P. Ficalora. Thermal Expansion of TiP, ZrP, and HfP.
- (24) K. A. Gingerich. Mass Spectrometric Study of the UP-UO₂ System.
- (24a) B. A. Scott, R. A. Bernheim and K. A. Gingerich. Temperature Dependence of the P³¹ Knight Shift in Uranium Monophosphide.

D. Technical Reports Submitted.

- (25) Karl A. Gingerich, Martin Knausenberger, Carolyn O. Barten and Walter Riegel. Progress Report for the Period April 1, 1960 to December 31, 1963.
- (26) Karl A. Gingerich. Progress Report for the Period January 1, 1961 to December 1, 1961.
- (27) Karl A. Gingerich. Progress Report for the Period January 1, 1962 to December 1, 1962.
- (28) Karl A. Gingerich. Progress Report for the Period January 1, 1963 to November 30, 1963.