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COLLEGE OF
CHEMISTRY
AND PHYSICS

THE PENNSYLVANIA STATE UNIVERSITY

UNIVERSITY PARK, PENNSYLVANIA

TID-19990

A STUDY OF HIGH TEMPERATURE PROPERTIES OF TITANIUM AND ZIRCONIUM PHOSPHIDES AND RELATED REFRACTORY MATERIALS

Progress Report for the Period

January 1, 1963 to November 30, 1963

MASTER

Submitted by

Karl A. Gingerich

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The concern of this project is to study the phase relationships and the physical, thermodynamic and high temperature properties of transition metal phosphides, particularly those of zirconium and titanium. This study will provide information on the basic properties of these materials, thus aiding their evaluation for potential applications.

Equipment Design

The construction of the apparatus for static determination of phosphorus dissociation pressures using a spoon gauge or a quartz spiral manometer and induction heating has been almost completed. Difficulties with the heating chamber, in particular with the container and heat shield materials have been mounting. Tungsten shields appear to be too brittle after heat treatment to be useful. This might be because of solid solution formation of phosphorus with tungsten or because of the heat treatment itself. Rhenium sheet and zirconia tubing are now being considered and testing is in progress.

The apparatus for using radioactive phosphorus has been completed in a preliminary form as was indicated in an earlier report, and tested with radioactive white phosphorus. Preliminary experiments with tungsten monophosphide have shown the method to be feasable for the study of phosphides.

Preparation and Chemical Analysis of Phosphides

The Faraday method has been extended to higher temperatures, where radio frequency was used for heating the end containing the metal. This variation has been found particularly useful for the preparation of thorium subphosphide and samples in the Zr-ZrP system. Details will be given in the thesis by Mr. D. W. Wilson and the projected correlated paper. A suitable variation of the Faraday method for safe preparation of radioactive samples has also been developed in which the quartz tube containing the sample is situated inside a gradient steel tube to protect against potential explosions. Wet techniques, x-ray fluorescence, optical spectroscopy, and electron microprobe analysis are being used for the chemical analysis of phosphides.

X-Ray Diffraction Studies

The constitution of the systems Ti-P, Zr-P, and Th-P has been studied further. The investigation of the Ti-P system at the Chemisches Laboratorium in Freiburg is being brought to a preliminary conclusion at the end of this contract year. The results will be summarized in a doctoral thesis by Mr. Knausenberger. The phase Ti_5P_3 could be established. A single crystal structural analysis showed that it has the Mn_5Si_3-type structure. A second, cubic phase with high titunium content has been characterized by its x-ray diffraction pattern. A third previously unknown phase with a composition near Ti_2P has not been resolved yet.

The partial system ZrP-$ZrP_{0.5}$ has been studied by annealing stoichiometric mixtures of ZrP and $ZrP_{0.5}$ in a tungsten cell in high vacuum to 1400°C for one hour, and analysing x-ray diffractometer patterns of the products. The preliminary results indicate that the region $ZrP_{1.0}$-$ZrP_{0.5}$ contains four phases: The hexagonal β-ZrP, the cubic α-ZrP with a composition near $ZrP_{0.9}$ and two additional rather complicated phases with compositions near $ZrP_{0.7}$ and $ZrP_{0.5}$.

In the system Th-P, no new phases were found in the range Th-Th_3P_4. The extent of the homogeneity range of the ThP phase was determined by tensiometric, chemical, and X-ray analyses. High precision lattice paratmeter determinations were made to establish the lattice parameter-composition relationship within the ThP phase. At 900°C the homogeneity range was found to extend between the compositions $ThP_{0.96}$ and $ThP_{0.55}$. The lattice parameters are 5.8365 Å and 5.8291 Å, respectively. It has also been established that the thorium rich boundary shifts considerably to lower phosphorus content at high temperature. At 1850°C the lower phase boundary has a lattice parameter of 5.8249 Å.

A single crystal structural analysis of W_3P is in progress. Weissenberg photographs around the c-axis were taken with CuK_α and MoK_α radiation respectively. The equator and the first and the second layer lines were registered by CuK_α radiation for determining the elementary cell and the space group. Two sets of MoK_α equator photographs were prepared applying the multiple film technique in order to obtain a sufficient number of intensities for structure determination.

A set of precession photographs of the (Okl) reflections with different exposure times has been made. A precision determination of the lattice parameters by means of powder diagrams is intended as well as determination of the atomic parameters by means of two dimensional Fourier synthesis.

Vaporization and Thermodynamic Properties of Phosphides

Mass Spectrometric Study of Vaporization: The mass spectrometric study of tungsten, molybdenum, tantalum and praseodymium phosphides has been continued. Preliminary results indicate that tungsten, molybdenum and tantalum form rather stable solid solutions with phosphorus. Aluminum phosphide was included to obtain information of its stability and suitability for the determination of the relative ionization cross sections of P and P_2.

The analysis of mass spectrometric data obtained previously has been continued in order to obtain knowledge of the vapor composition, mode of vaporization and thermodynamic stability of the respective phosphides. The mass spectrometric results have also been used jointly with parallel x-ray studies to obtain information on the constitution of the respective binary systems, in particular information on the occurance and extent of homogeneity ranges present. Part of the results have been presented at national and international scientific meetings and have been submitted for publication. Details can be obtained from the corresponding attached reports.

Static Determination of Phosphorus Dissociation Pressures: The phosphorus dissociation pressures of tungsten have been measured using radioactive phosphorus. The method appears to be useful but requires further development. The experimental results are being evaluated.

Selected Chemical and Physical Properties of Phosphides

Phosphidation of Zirconium: The intermediate subphosphide reaction layer formed in the direct reaction between phosphorus and zirconium has been further studied by electron microprobe techniques. Preliminary results indicate its composition to be $ZrP_{0.6}$.

Magnetic Susceptibilities of Thorium Phosphides: The magnetic susceptibilities of thorium phosphides have been measured and are being evaluated. The results will be included in the thesis of Mr. Wilson.

Thermal Expansion of TiP, ZrP and HfP: The measurement of the thermal expansion of TiP, ZrP, and HfP has been completed and the results have been summarized in a thesis by Mr. P. Ficalora. A technical paper including this work is in preparation.

Paper 1

VAPORIZATION OF URANIUM MONOPHOSPHIDE*

In the search for new oxygen-free refractory materials, we have found that the subphosphide of thorium, $ThP_{0.7}$, has a high thermodynamic stability (1) which is comparable to that of uranium monosulphide (2). We have included the uranium monophosphide, UP, and its mixtures with uranium dioxide in our studies(3). Since recent reports (4)(5) indicate the potential usefulness of uranium monophosphide for high temperature reactor application, we would like to present our preliminary results concerning the thermodynamics of vaporization of uranium monophosphide.

The uranium monophosphide was prepared by reaction of the elements using the Faraday method and thermally degrading the resulting triuranium tetraphosphide, U_3P_4 to uranium monophosphide at 1400° C. Analysis showed that it contained 0.38% of oxygen. An x-ray diffraction pattern showed the presence of uranium monophosphide and traces of uranium dioxide. The mass spectrometric investigation was done with an instrument at the National Bureau of Standards similar to that described by Chupka and Inghram(6). A tantalum Knudsen effusion cell with a tungsten liner was used. Temperatures were measured with a calibrated optical pyrometer under black body conditions.

The vaporization of uranium monophosphide was investigated over the temperature range from 1750 - 2250° K. During its vaporization, the major primary ion species observed and measured were U^+, P^+, P_2^+, and UO^+. In a uranium monophosphide-uranium dioxide mixture, the UO_2^+ ion was also a major species. In no case was gaseous uranium monophosphide observed. X-ray analysis of the residue left in the effusion cell from the uranium monophosphide samples showed only lines of uranium monophosphide. Lines of uranium dioxide could no

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* To be published in *Nature*, London.

longer be detected. On the basis of these observations, we suppose that uranium monophosphide vaporizes congruently over the temperature range measured according to the following reaction:

$$(1)\quad UP_{(s)} = U_{(g)} + \frac{1}{x} P_{x(g)} \qquad (x = 1 \text{ or } 2)$$

Oxygen impurities in the uranium monophosphide sample are believed to react according to:

$$(2)\quad UP_{(s)} + UO_{2(s)} = 2\ UO_{(g)} + \frac{1}{x} P_x \qquad (x = 1 \text{ or } 2)$$

The observations that no uranium dioxide could be detected in the residue and that the UO^+ ion intensity decreased in relation to the U^+ ion intensity as the vaporization progressed indicate that reaction (2) is preferred to reaction (1). If the uranium dioxide content becomes large, reaction (2) becomes the predominant reaction. The appearance of the UO_2^+ ion resulting from the vaporization of uranium dioxide according to

$$(3)\quad UO_{2(s)} = UO_{2(g)}$$

is also observed.

The ion intensities are correlated to vapor pressures through silver calibration(6)(7). The difference in electron multiplier efficiencies of Ag^+ and the ionic species observed above uranium monophosphide was determined experimentally. Corrections for fragmentation and double ionization were considered. The intensity of U^+ ion was corrected for the effect of oxygen content according to equation (2). For the ionization cross section of the phosphorus monomer the value of 13.8 as given by Otvos and Stevenson(8) was used. For the phosphorus dimer, the value 21.8

was estimated. A value of 37.5 was derived for the cross section of uranium on the basis of congruency of vaporization according to equation (1) using the cross section of the phosphorus monomer as a standard.

In Figure 1 the logarithm of the vapor pressure of each species over uranium monophosphide is presented as a function of the reciprocal of absolute temperature. The derived average values for partial molal heats of vaporization in kilocalories per mole, at 2000° K, are as follows: $\Delta\bar{H}\ (U) = 131.69 \pm 2.25$; $\Delta\bar{H}\ (P) = 119.94 \pm 2.63$; $\Delta\bar{H}\ (P_2) = 105.46 \pm 1.66$ where the uncertainties represent standard deviations. From these values a heat of vaporization, $\Delta\bar{H}^{o}$ [vap] in kilocalories per mole of uranium monophosphide is obtained as 184.42 ± 3.08 for the reaction (1) when $x = 2$ and 251.63 ± 4.88 when $x = 1$. The temperature dependence of the partial pressures over the temperature range of investigation is linear within the limits of experimental errors and can be expressed by the following equations:

$$\log p_{(atm)}\ [P] = \frac{-26211}{T} + 6.4107 \pm 0.0216$$

$$\log p_{(atm)}\ [P_2] = \frac{-23046}{T} + 4.2550 \pm 0.1036$$

$$\log p_{(atm)}\ [U] = \frac{-28778}{T} + 7.795 \pm 0.0687$$

Also included in Figure 1 is the calculated vapor pressure of uranium.(9) Due to the different temperature dependences of the uranium pressures of solid uranium monophosphide and liquid elemental uranium, the uranium dissociation pressure of uranium monophosphide will become equal to that of elementary uranium at 2600° K. This implies that above 2600° K the vaporization of uranium monophosphide becomes incongruent and can be expressed by equation (1) and equations (4) and (5):

(4) $UP_{(s)} = U_{(l)} + \frac{1}{x} P_x$ $(x = 1 \text{ or } 2)$

(5) $U_{(l)} = U_{(g)}$

The congruency of the vaporization below 2600° K may need to be modified to account for a deviation from stoichiometry that increases at high temperatures (4). Indications of this in our work are supported by the decrease in lattice parameter from 5.589 ± 0.001 to 5.584 ± 0.001Å of uranium monophosphide during vaporization and by the observation that there is a slight decrease in total vapor pressure and a decrease in the partial pressure ratio of phosphorus monomer and uranium as the vaporization proceeds. Possible secondary reactions with the container materials have not been considered in the evaluation. From the extrapolation of the total pressure to one atmosphere, a boiling point of uranium monophosphide of 3890° K can be predicted. For uranium mononitride the decomposition temperature is approximately 3110° K(10). As compared with uranium monosulphide (2), the total vapor pressure of uranium monophosphide in our temperature range is lower by a factor between three and ten. Uranium monophosphide thus appears to be a refractory material of high stability. This stability against vaporization and the apparent congruency of the vaporization process, add to its potential usefulness as a nuclear fuel material at high temperatures. The similarity in vaporization behavior and density, and the expected similarity in thermal expansion may make it a promising additive to uranium dioxide base nuclear fuel elements.

We would like to thank Mr. D. W. Wilson for the synthesis and x-ray analysis. This work was supported by the U. S. Atomic Energy Commission.

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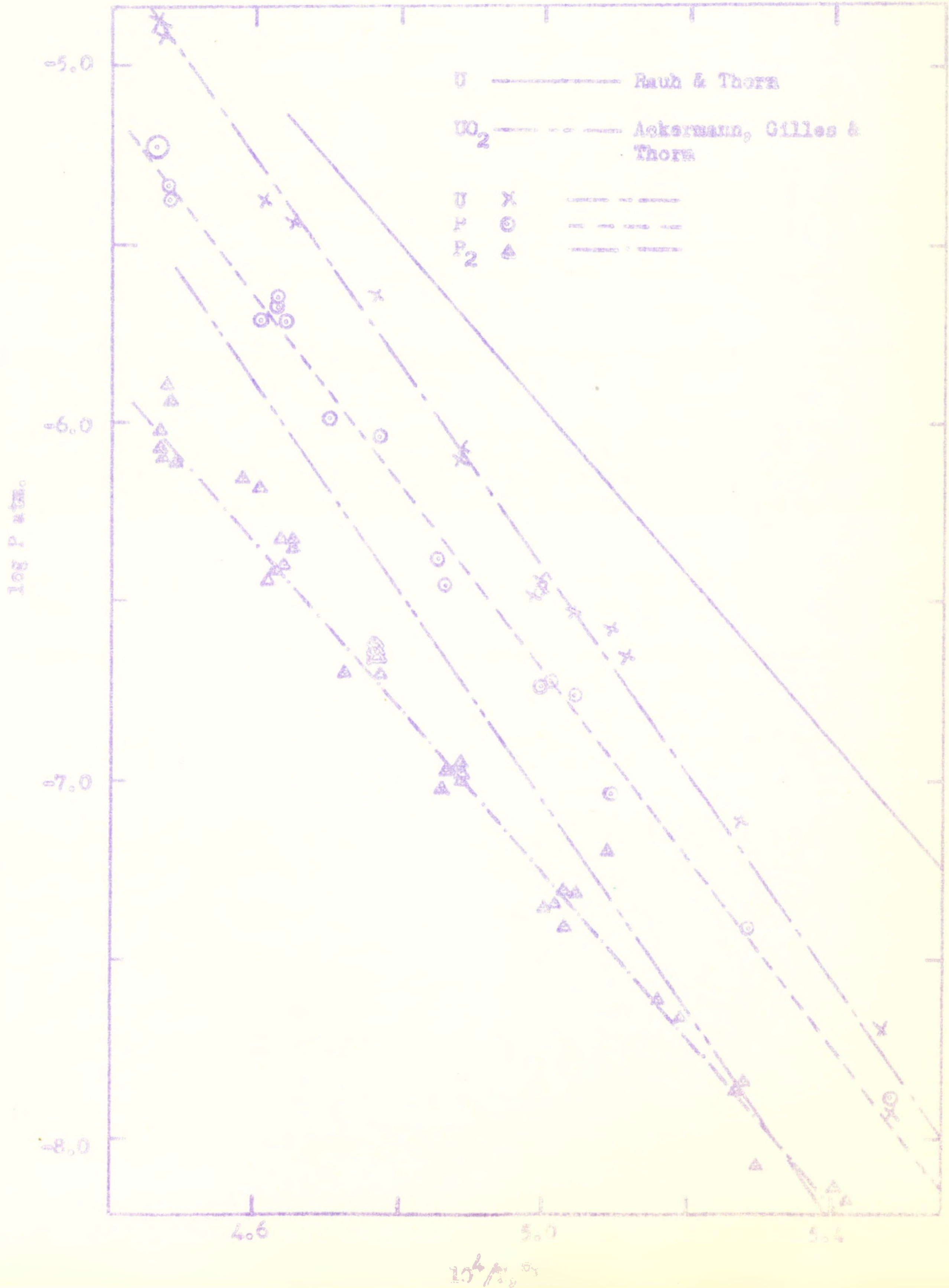
Figure 1

Variation of partial pressures of gaseous species over UP as a function of temperature for Series I.



Paper 2

PRASEODYMIUM—GROUP V COMPOUNDS I:

VAPORIZATION BEHAVIOR AND NONSTOICHIOMETRY OF PrP, PrAs, PrSb and PrBi*

by

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* Revised form of a paper presented at the Third Rare Earth Conference in Clearwater, Florida, April 21-24.

Abstract:

The vaporization of the praseodymium-group V compounds PrP, PrAs, PrSb and PrBi has been studied by the Knudsen effusion method in combination with a mass spectrometer. No vapor species containing both praseodymium metal and a group V element have been observed, with the possible exception of Pr_2P. The vaporization of the praseodymium-group V compounds occurs by decomposition into the respective group V element and a condensed praseodymium rich phase, that is, incongruently. The following approximate heats of dissociation for the reaction

$$\frac{1}{x} PrZ_{y(s)} = \frac{1}{x} PrZ_{y-x(s)} + Z_{(g)} \qquad (Z = As,\ Sb \text{ or } Bi)$$

were obtained from the second law treatment:

$\Delta H_{1800° K} = 124$ kcal for the arsenide, $PrAs_{0.82}$

$\Delta H_{1670° K} = 114$ kcal for the antimonide $PrSb_{0.85}$

$\Delta H_{1530° K} = 98$ kcal for the bismuthide $PrBi_{0.8}$

The ion intensities were related to approximate vapor pressures. According to these, the stability of the compounds decreases with increasing atomic number of the group V element. From the ion intensity variation with composition, it could be derived that all compounds exhibit broad ranges of homogeneity that are possibly temperature dependent.

Introduction:

This paper is the first in a series concerning praseodymium-group V compounds, and describes the vaporization behavior and its relation to the phase equilibria in the solid. It also gives some preliminary information concerning the thermodynamic properties of the compounds under discussion.

Rare earth metal compounds and yttrium with group V elements are expected to be of considerably higher thermal stability than the corresponding group III-V compounds with indium or gallium as metal components. This is expected from the greater difference in electronegativity between the constituents which results in a greater bond polarity and thus bonding strength in the respective compounds, and from the comparison of corresponding compounds with other non-metals. The expected higher thermal stability makes them of interest as potential semi-conductor and thermoelectric materials for high temperature applications. With these potential applications in view, the vaporization of the praseodymium-group V compounds PrP, PrAs, PrSb and PrBi has been studied mass spectrometrically in order to identify the various species produced and to obtain thermodynamic data of the processes involved. The crystal structure of these compounds is of the NaCl (B1)-type(1). No thermodynamic data appear to be present in the literature for these compounds.

Experimental:

The samples used for the mass spectrometric investigation were prepared by reaction of the elements in an evacuated sealed fused silica tube. The praseodymium metal used contained less than 0.1% of other rare earths, 0.13% of oxygen and 0.03% of nitrogen. The purity of the group V elements was better than 99.99%. The praseodymium metal was contained in either tantalum or tungsten boats. The group V element was placed directly in the quartz tube. The composition of the products was obtained from the weight gain of the metal as determined after the synthesis. Chemical reaction between tantalum and arsenic, or antimony, respectively, was accounted for in the determination of the composition. The praseodymium to bismuth ratio of the praseodymium bismuthides was, in addition, determined by volumetric analysis. Chemical analysis indicated 0.30, 0.40 and 0.35 percent weight of oxygen and ≤ 0.05, ≤ 0.05, and ≤ 0.05 of nitrogen for the arsenide, antimonides and bismuthides, respectively. These impurities were accounted for by assuming that oxygen was present as Pr_2O_3 and nitrogen as PrN. The bulk compositions can be expressed by the following formulae: $PrP_{1.0}$, $PrAs_{0.95}$, $PrSb_{0.9}$, $PrSb_{1.0}$, $PrBi_{0.9}$ and $PrBi_{1.0}$. For the mass spectrometric investigation, the samples needed to be exposed in air for a short period of time. The phosphide was exposed to air for a longer period of time. As a result, it took up more oxygen and nitrogen than the other compounds.

For the mass spectrometric investigation, a 60° sector, 12 inch radius, first order directional focusing instrument at the National Bureau of Standards was used. The powdered samples were placed in liners made of thoria, ThO_2, for the antimonide, $PrSb_{0.9}$, of tantalum for the bismuthide, $PrBi_{1.0}$, and of tungsten for the antimonide, $PrSb_{1.0}$, and the phosphide and inserted into a tungsten Knudsen effusion cell. For the arsenide and for $PrBi_{0.9}$ a tantalum cell and a tungsten liner was used. Free molecular flow conditions were maintained during effusion measurements. The temperature was measured by a Pt vs. Pt/10% Rh thermocouple which was inserted into a hole at the bottom of the cell and by optical pyrometer which could be focussed into a black body hole in the bottom or in the side of the cell. The molecular beam was ionized with 55 eV electrons. The ions were detected with an electron multiplier and the ion current was recorded automatically. The variation of ion intensity of a particular species was observed as a function of temperature and time. The effusing species were distinguished from background ions by moving a shutter across the molecular beam. The composition at any stage of the investigation was derived from the starting composition by correlating the intensity-time integral of all species observed to the total weight evaporated.(2)

Mode of Vaporization:

The vaporization of praseodymium-group V compounds has been investigated over a temperature range of 950-2200°K and over varying ranges of compositions.

No molecular species containing both Pr and Sb, As, or Bi, respectively, were observed under the experimental conditions. Only in the case of praseodymium phosphide a species with the same mass number as dipraseodymium monophosphide, Pr_2P was observed. The intensity of this ion was of the order of 1/1000 of that of the PrO^+ ion. In a later experiment under similar conditions this observation could not be confirmed. With the possible exception of dipraseodymium monophosphide, it can be concluded that the ratio of $Z_{(g)}:PrZ_{(g)}$ (Z being either P, As, Sb or Bi) is more than 1000:1 at the highest temperatures in each particular experiment. At the higher temperatures, the ionic species PrO^+, Pr^+, and N_2^+ appeared, originating probably from the oxygen and nitrogen impurities. In the case of the phosphide, praseodymium monoxide even became the predominant vapor component at 2200°K. It is assumed that the presence of these impurities does not influence the thermodynamic properties of the praseodymium-group V phase investigated, with the possible exception that it may form solid solutions with oxygen or nitrogen at the highest temperatures.

The vaporization of praseodymium-group V compounds occurs incongruently over the whole range investigated by decomposition into gaseous group V element and into a more praseodymium-rich condensed phase according to the equation:

$$(1)\quad \frac{1}{x}\,PrZ_y\ (s) = \frac{1}{x}\,PrZ_{y-x}\ (\ell \text{ or } s) + Z_{(g)}$$

where Z is either P, As, Sb or Bi and may be a mixture containing dimers and tetramers in case of P, As, and Sb.

Phase Analysis:

An interesting result of this investigation is that all praseodymium-group V compounds appear to have a wide range of homogeneity. The extent of the homogeneity range as derived from the vaporization behavior corresponds to approximately $PrZ_{0.9}$ - $PrZ_{1.0}$. The determination of the exact boundary compositions appears to be complicated for the following reasons: (a) The sensitivity of a chemical analysis is limited. (b) Impurities are present. (c) Lattice parameters either are not sensitive or only very slightly sensitive to compositional change within the homogeneity range for these phases. (d) There is some evidence that for the arsenide and phosphide the praseodymium-rich phase boundary is temperature dependent. The formation of solid solutions of the NaCl-structure type that are deficient in non-metal content also explains the observation that, in some binary systems between rare earth elements M and elements of Group V or Group VI, a MX phase with NaCl structure which is deficient in X is obtained by direct reaction of the elements.(3)

In the following section the changes in ion intensities of the group V elements with temperature and composition are discussed for each compound in terms of phase relationships in the solid.

Praseodymium bismuthides: For the praseodymium bismuthide, $PrBi_{1.0}$ the ion intensity of Bi^+ at constant temperature decreased at first rapidly until approximately 0.5 atomic percent of bismuth was lost. Thereafter, the ion intensity of Bi^+ decreased at a slower rate until a composition of approximately $PrBi_{0.9}$ was reached, and then remained constant within the precision of measurement upon further decomposition. From the Gibbs phase rule, it may be concluded that in the original praseodymium bismuthide sample a small amount of a phase with a higher bismuth content was present. After the complete decomposition of this small amount, only one phase of approximate composition $PrBi_{1.0}$ was present in the solid. Upon further decomposition the partial pressure of bismuth decreased as the bismuth content within the homogeneity range of this phase decreased, until the phase boundary of the praseodymium-rich end of the phase was reached at an approximate composition of $PrBi_{0.9}$. Further loss of bismuth then yields a new more praseodymium-rich second phase of unidentified composition which coexists with the cubic $PrBi_{1-x}$ phase; hence, the constant vapor pressure was observed. These observations in turn suggest that true equilibrium conditions between vapor phase and solid were prevailing and that the rate of diffusion within the solid is rapid as compared with the rate of vaporization of bismuth. Otherwise, the constant intensity would not be observed in the later stage of decomposition.

For the sample with the composition $PrBi_{0.9}$ the ion intensity of Bi^+ was independent of composition over the range $PrBi_{0.9}$ - $PrBi_{0.85}$. From this observation it can be concluded that in this sample two phases were present from the beginning, and that the praseodymium-rich boundary composition of the $PrBi_{1-x}$ phase corresponds to an x of approximately 0.1 or less.

Praseodymium antimonide: As starting materials $PrSb_{0.9}$ and $PrSb_{1.0}$ were used. For the sample $PrSb_{0.9}$, the ion intensity of Sb^+ at constant temperature was decreased until a composition of about $PrSb_{0.89}$ was reached. The ion intensity of Sb then remained constant upon further evaporation, thus showing that the starting composition was close to the praseodymium-rich phase boundary. The sample $PrSb_{1.0}$ showed a similar intensity-composition relationship as the $PrBi_{1.0}$ sample, thus indicating a homogeneity range for the PrSb phase that extends between the approximate phase boundaries $PrSb_{1.0}$ and $PrSb_{0.9}$.

Praseodymium arsenide: For the arsenide $PrAs_{0.95}$, a similar vaporization behavior was observed as for $PrSb_{0.9}$. In the early stages of decomposition, at any temperature, the intensity of As^+ decreased constantly until the composition $PrAs_{0.91}$ was reached. Further decomposition to $PrAs_{0.83}$ effected only a slight decrease in ion intensity. This slight decrease might be an instrumental characteristic or a slight effect of a diffusion barrier. Since it is much less pronounced than in earlier stages of the decomposition, it is assumed that for the temperature 1860° K the phase boundary for the $PrAs_{1-x}$ phase is reached at a composition corresponding to $PrAs_{0.91}$ and that further decomposition yields a second phase with lower arsenic content. After heating at a composition $PrAs_{0.82}$ to 1950° K, a new decrease in ion intensity was observed for the As^+ ion upon further decomposition. This can be interpreted as indicating a single arsenide phase in the solid at this higher temperature. The most reasonable interpretation would be that the homogeneity range for the $PrAs_{1-x}$ phase is, at high temperatures, temperature dependent and extends to lower arsenic content in the solid.

Praseodymium phosphide: The vaporization of praseodymium phosphide was investigated over a temperature range from 1100 - 2200°K and a wide composition range. The phosphorus content of the starting sample was slightly higher than corresponds to the formula $PrP_{1.0}$. X-ray analysis of the final residue showed that the PrP_{1-x} phase was still present. In the first stage of decomposition, a constant ion intensity of P_2^+, the principal vapor component, was observed at constant temperature, indicating the presence of a second phase of higher phosphorus content. After loss of less than two atomic percent of phosphorus, a strong decline in P_2^+ ion intensity with decreasing phosphorus content in the solid was observed, indicating a homogeneity range. At a temperature of 1500° K and a composition of between $PrP_{0.9}$ and $PrP_{0.85}$ a two-phase region was apparently reached. Based on similar observations as explained for the praseodymium arsenide, the phosphorus content of the praseodymium-rich boundary appears to decrease slightly at 1800° K and more significantly at 2000° K.

The observations in the case of $PrAs_{1-x}$ and PrP_{1-x} that, at higher temperatures, the range of homogeneity increases towards higher Pr contents are of a preliminary nature. Detailed further studies in order to determine the exact temperature dependence of the range of homogeneity will be necessary. The application of the mass spectrometric method for determination of phase boundaries at high temperatures is particularly valuable in cases where the temperature conditions cannot be preserved by quenching. In the case of PrP and PrAs it was observed that diffusion effects appear to be present, but that the decline in intensity due to diffusion barriers was much less pronounced than the decline attributed to the activity change of Z as a function of composition within the homogeneity range. A limitation for this method arises where diffusion-controlled vaporization complicates the interpretation of the ion intensity-composition relationship.

Heats of dissociation:

After reaching a constant intensity at compositions corresponding to the formulae $PrAs_{0.9}$, $PrSb_{0.9}$ and $PrBi_{0.9}$, the variation of the ion intensities I, for the species As^+, Sb^+, and Bi^+, respectively, was determined and was found to be reversible over the whole temperature range measured (1670-1930° K for the arsenide, 1430-1820° K for the antimonide, and 1340-1720° K for the bismuthide). This indicates that equilibrium conditions prevailed, assuming a vaporization coefficient of approximately one. From the reversible ion intensity-temperature relationship, the following average enthalpies of dissociation for the reaction were obtained from the van't Hoff equation

$$d \ln Kp \ / \ d \ln \frac{1}{T} = -\Delta H_T \ / \ R$$

$$\Delta H_{1800° K} = 124 \pm 2.5 \text{ kcal for the arsenide } PrAs_{0.82}$$

$$\Delta H_{1670° K} = 114 \pm 1.0 \text{ kcal for the antimonide } PrSb_{0.85}$$

$$\Delta H_{1530° K} = 98 \pm 1.0 \text{ kcal for the bismuthide } PrBi_{0.8}$$

The uncertainties given are standard deviations. The absolute deviations are probably larger due to possible errors in temperature measurement. These enthalpies of dissociation might also be influenced by a possible change in the boundary composition of the PrZ_{y-x} phase with temperature. An increase of the homogeneity range would reflect in too low enthalpy values. This influence is probably largest for the arsenide.

Dissociation Pressures:

The dissociation pressures p_Z of Z are at constant temperature T directly proportional to the ion intensity I according to $p = I\ T/S$ where the sensitivity, S, designates an apparatus constant that can be determined by vaporizing a weighed amount of the sample under investigation or of a known amount of a standard material, such as silver, the vapor pressure of which is well known. The change in partial pressure of Bi within the homogeneity range as a function of composition is illustrated in Table I for the praseodymium bismuthide.

It appears that the dissociation pressures at the composition $PrZ_{1.0}$ are of the same order of magnitude for PrP, PrSb and PrBi. Within the homogeneity range the decrease in dissociation pressure as a function of composition is greater as the atomic weight of the group V element is lower. The relative stabilities of the PrZ_{1-x} phase at the praseodymium-rich boundary is illustrated by the values of the ratio Z^+/PrO^+ assuming that the partial pressure of PrO is in the first approximation a function of temperature only and is not influenced by the presence of PrZ. The values for the ratios are 10 for Bi at 1650° K, 4 for Sb at 1750° K, 1 for As at 1700° K and 0.2 for P at 2000° K. From this it is concluded that the relative stabilities of the respective compounds increase in the given order: $PrBi_{1-x}$, $PrSb_{1-x}$, $PrAs_{1-x}$, PrP_{1-x}.

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Table I - Relation between composition x in $PrBi_{1-x}$ and ion intensity I at 1250° K.

No.	x in $Pr\ Bi_{1-x}$	I (Relative Scale)
1	0.015	850
2	0.02	680
3	0.04	180
4	0.08	10
5	0.15	1

Paper 3

VAPORIZATION OF TRANSITION METAL PHOSPHIDES[†*]

by

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The vaporization of selected transition metal phosphides has been studied jointly with Dr. J. Efimenko of the National Bureau of Standards by means of a Knudsen effusion - mass spectrometer assembly[1-4]. This instrument[**] permits the simultaneous determination of the composition of the gaseous phase, the pressure of each of the gaseous species and the variation of each pressure with temperature and composition of the solid.

Included in the investigation were the monophosphides of molybdenum, tungsten, niobium, tantalum, titanium, zirconium, hafnium, praseodymium, and uranium, as well as trithorium tetraphosphide and the thorium subphosphide.

All of these phosphides but uranium monophosphide vaporize by decomposition into gaseous phosphorus and a condensed phase with lower phosphorus content. Uranium monophosphide vaporizes primarily by decomposition into gaseous uranium and phosphorus. No gaseous species containing both metal and phosphorus atoms were detected with the possible exception of Pr_2P.

The phosphorus ion intensities were measured as a function of temperature and composition and related to the respective partial pressures by means of silver calibration.[5]

From the investigation of the phosphorus dissociation pressures as a function of composition of the condensed phase, it was found that thorium

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[†] Short discussion paper, presented at the International Symposium of High Temperature Technology, September 8-11, 1963, Asilomar, California.

[*] Work supported by the U. S. Atomic Energy Commission under contract no. AT(30-1)-2541 with the Pennsylvania State University.

[**] HT instrument, 12" radius, 60° magnetic sector, Manuf. Nuclide Corp., State College, Pa.

subphosphide and praseodymium phosphide exhibit at the temperature of investigation broad ranges of homogeneity ($ThP_{0.9 - 0.7}$ and $PrP_{1.0 - 0.9}$) while β-ZrP and TiP appear to have small ranges of homogeneity. No homogeneity range could be detected for MoP, WP, α-ZrP and Th_3P_4. It may be noted here that a Knudsen effusion-mass spectrometer assembly is probably one of the most powerful tools for the study of solid solution composition ranges at high temperatures - one of the underdeveloped areas mentioned in Professor Searcy's paper - which has so far been very little used for this purpose.

From the investigated temperature dependence of the phosphorus dissociation pressures that correspond to the metal-rich boundary composition of the respective phosphide, the partial molal free enthalpies of P_2 dissociation at 2000° K, ΔG^o_{2000} (P_2) were computed. The following values in kilocalories were obtained for the phosphides $ThP_{0.7}$, UP, α-ZrP ($ZrP_{0.92}$), $TiP_{0.94}$, $NbP_{0.94}$, MoP, Th_3P_4 and WP: 68.0, 64.7, 51.8, 25.8, 13.8, 2.2, 2.1 and -2.1 respectively. Although these are preliminary results, they give an indication of the stabilities and stability trends among the phosphides investigated. The stability of HfP was found to be comparable to that of $ThP_{0.7}$ and UP, that of $PrP_{0.9}$ was found to be between that of UP and α-ZrP and the stability of TaP was found to be comparable to that of α-ZrP. The phosphides from thorium subphosphide through α-zirconium monophosphide and tantalum monophosphide are new oxygen-free refractory materials of high thermal stability that deserve consideration of their usefulness for special high temperature applications.

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Paper 4

STABILITY AND VAPORIZATION BEHAVIOR OF GROUP IV - VI TRANSITION METAL MONOPHOSPHIDES*°

by
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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 existance 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 vapor above the condensed phase were P, P_2 and P_4. In the temperature range from 1000 to approximately 1800° K, diatomic phosphorus was the major species. At higher temperature monatomic phosphorus also became an important vapor 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 vapor phase at the temperatures and pressures investigated is at least 100 - 1000 times less than that of the major vapor 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 vapor and a solid phase of lower phosphorus content.

$$(1)\quad \frac{z}{x}\,MP_{1-\delta} = \frac{z}{x}\,MP_{1-\delta-x} + P_z$$

where $0 < x < 1-\delta$ and z is either 1, 2 or 4; δ is approximately 0.04 for TiP 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 subphosphides 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 1700° K. No indication for a homogeneity range was found for MoP, WP, and α-ZrP.

The ion-intensities of P_2^+ were correlated to vapor 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, $\overline{\Delta G}_T^{\,o}\ P_2$. The results are listed in Table I for 1000°K, 1500°K and 2000° K. Also included is the temperature range over which the experimental

TABLE I: PARTIAL MOLAL FREE ENTHALPIES OF P_2 - DISSOCIATION FOR SELECTED TRANSITION METAL MONOPHOSPHIDES

Compound	Temperature Range of Pressure Measurement in °K	$\overline{\Delta G_T^\circ}$ $[P_2]$ in Kcal/mole P_2		
		1000°K	1500°K	2000°K
$TiP_{0.94}$	1295 - 1705	55.8	40.8	25.9
$ZrP_{0.92}$	1770 - 2120		66.8	51.1
$NbP_{0.95}$	1200 - 1450	55.4	34.0	12.7
MoP	1190 - 1450	54.3	28.3	
WP	950 - 1250	36.7	17.3	

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 vapor with the tantalum effusion cell. From the possible observations, it can be estimated that, at 2000°K, the stability of tantalum monophosphide is comparable to 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 ($ThP_{0.7}$)[4] and uranium monophosphide.[5] The results presented in Table I 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 the third transition period.

A comparison of the stability of the group 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 group IV and V compounds because of the strong dependance 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 group 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 significently 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 1000°C make tungsten metal a promising oxygen-free container material for the more stable phosphides.

The author gratefully acknowledges the courtesy of the National Bureau of Standards for the use of the mass spectrometer in this investigation. He is also indebted to Dr. J. Efimenko for his interest in the project.

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** HT instrument, 12" radius, 60° magnetic sector, Manufacturer - Nuclide Corporation, State College, Pennsylvania.

† Letter to the Editor, _Nature_, London, submitted October 15, 1963.

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Does not include photograph.

Jager 5

A STUDY OF THE PHOSPHIDATION OF ZIRCONIUM [†] [*]

by

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[*] This paper has been prepared in March 1963, for submission to the <u>Journal of the Electrochemical Society</u>

Abstract

The direct interaction between phosphorus vapor at 1 atm. and zirconium metal has been studied over the temperature range from 500 - 1100°C. At first, the reaction layer being less than 1 μ thick, only subphosphide of the probable composition Zr_3P is formed. Further phosphidation yields the hexagonal monophosphide ZrP, besides traces of subphosphide. The rate of reaction is small between 500 - 700°C and increases rapidly above 700°C. At 1000°C it is a linear function of time for reaction layers less than 0.05 mm thick. This indicates that possibly due to cracks in the brittle phosphide layer, the phosphidation takes place always at a fresh metal surface. A non-identified black phase containing zirconium and possibly phosphorus was vapor-deposited on the walls of the reaction tubes.

Introduction

It has been reported(1,2) that films of Co, Cr, or Ni-phosphide plated on metals such as Mo, Ti, and Zr exhibit good oxidation protection. The plated films strongly adhere to the metal surface after heat treatment under inert conditions. It has been suggested that the adherence of the films is partially due to secondary reactions taking place at the interface between the phosphide film and the metal base. During the heat treatment between 600 - 1100°C the phosphorus is thought to diffuse from the phosphide film into the base metal forming phosphides therein.

In the present paper the direct interaction between phosphorus vapor and some transition metals is discussed. The phases formed at the surface of the metals are investigated and the rate of reaction is studied as a function of temperature and time. Special emphasis is put on the reaction between phosphorus and zirconium, but some experiments were also carried out with titanium and tantalum.

In the zirconium - phosphorus system three compounds have been reported by Strotzer _et al._(3): a zirconium diphosphide of the idealized composition ZrP_2, a zirconium monophosphide ZrP and a subphosphide of the possible composition Zr_3P. Schoenberg(4) reported two modifications of the monophosphide, the hexagonal β-ZrP with TiP (B_i) - type structure and the cubic α-ZrP with NaCl (B1) - type structure. Irani and Gingerich studied the compositional and temperature transformation $\alpha\text{-ZrP} \rightleftarrows \beta\text{-ZrP}$ and explain it by a model(5).

Experimental Procedure

The Faraday method of evacuated sealed silica tubes was adopted for this investigation. The tubes were placed in a gradient furnace, the cool end containing the phosphorus at 400°C. According to data by Stull and Sinke (6) the phosphorus partial pressure at 400°C is of the order of 1 atm. The temperature of the metal sample was varied from 500 - 1000°C. Temperature control was effected by a simple on-off controller which allowed for temperature oscillations of ± 5°C. The temperature gradient at the hot end was within the same limits. For sample temperatures above 1000°C induction heating was used. There the temperature was read through an optical pyrometer. The accuracy of the pyrometer temperature reading was ± 15°C.

Red phosphorus, microanalytical grade refluxed in NaOH and washed was reacted with zirconium rolled sheet 0.005" thick[1], and with zirconium high purity bar[2]. Some preliminary experiments were also carried out with titanium[3] and tantalum rolled sheet[4].

After reaction the bulk composition of the sample was calculated from the total weight gain and expressed as formula MP_x with reference to the total amount of the metal.

Results and Discussion

At 900°C and approximately 1 atm. of phosphorus vapor the rate of reaction of zirconium is less than that of titanium but more than that of tantalum. The titanium sheet crumbles upon phosphidation while the zirconium sheet retains its original shape. After 64 h at 900°C titanium and zirconium sheets had both completely reacted with phosphorus vapor yielding $TiP_{0.93}$ and $ZrP_{1.01}$ respectively. At the same time tantalum showed only a minor reaction. The average composition of the tantalum sheet was $TaP_{0.03}$.

The rate of reaction between zirconium and phosphorus was further investigated at different temperatures as shown in Table I and Figure 1.

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[1] Zirconium Metals Corporation of America
[2] Courtesy of the U. S. Bureau of Mines
[3] Titanium Metals Corporation of America
[4] Fan Steel Metallurgical Corporation

Table I Rate of reaction of zirconium rolled sheet 0.005" thickness with phosphorus vapor at different temperatures and 1 atm of phosphorus vapor pressure

Sample No.	Heating Time	Sample Temperature	Bulk Formula
1	24 h	500°C	$ZrP_{0.06}$
2	24 h	700°C	$ZrP_{0.08}$
3	24 h	800°C	$ZrP_{0.23}$
4	24 h	900°C	$ZrP_{0.57}$
5	24 h	900°C	$ZrP_{0.72}$

Each of the samples in Table I has been heated to the indicated temperature for the same period of time. Below 700°C the rate of reaction is very small, above 700°C it becomes increasingly larger. At approximately 1000°C the sheets are expected to phosphidize completely within 24 hours.

Fully phosphidized samples as well as the sample Nos. 3, 4, and 5 in Table I yield the x-ray diffraction pattern of the hexagonal zirconium monophosphide, β-ZrP.

Sample No. 1 exhibits lines of a second phosphide phase besides the diffraction pattern of metallic zirconium. In the x-ray diagram of sample No. 2 lines of this second phosphide phase, of the hexagonal monophosphide, and of metallic zirconium are present. Apparently, this second phosphide phase is formed only as an intermediate step to the formation of the monophosphide. It can be detected only in the immediate vicinity of the reaction interface.

To check this point more carefully, zirconium bar sample Nos. 6

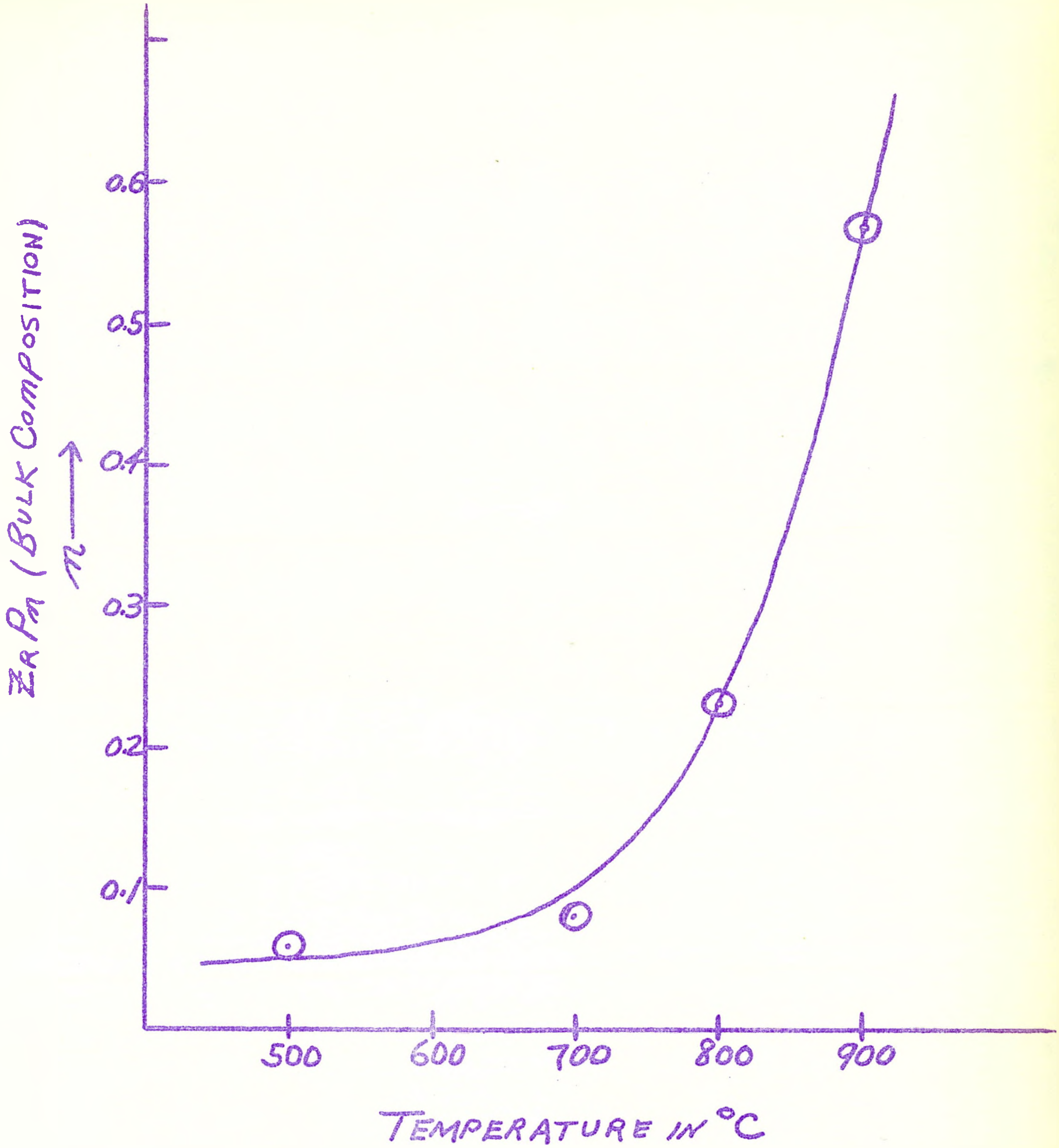

Figure 1

Rate of phosphidation of zirconium sheet 0.005" thickness at different temperatures. Heating time 24 hours, phosphorus vapor pressure approximately 1 atm.

and 7 were phosphidized at 720°C for 24 hours and 3 days respectively. The weight increase of sample No. 6 was 1.2 mg, for sample No. 7 was 5.4 mg. Knowing the total surface of the zirconium bar sample, the thickness of the reaction layer can be estimated. Assuming an approximate density of the phosphide layer of 5.5 g/cm^3 (value given by Schoenberg for β-ZrP), the thickness of the reaction layer would be 0.6 and 2.5 μ respectively.

The results of the x-ray investigation of sample No. 6 are summarized in Table II. Besides the strong lines of α-Zr only lines of the unknown phosphide phase are found. No lines of the monophosphide are detected from sample No. 6.

To check whether the unknown phosphide is identical with the diphosphide or subphosphide reported by Strotzer et al.(3) the published data were re-evaluated. Unfortunately, Strotzer et al. did not publish any d-spacings. They only plotted schematic graphs of the powder diagram on an arbitrary scale. A graphical evaluation of those patterns lead to the conclusion that the unknown phosphide found in sample No. 6 is identical with the subphosphide reported by Strotzer et al. The re-evaluated data of Strotzer's subphosphide are included in Table II.

Table II Diffraction pattern of sample No. 6 with lines of α-Zr and a subphosphide

Line No.	D-spacing	Arbitrary intensity	α-Zr met.	Subphosphide	Literature data (3)
1	2.80	7	x		--
2	2.62	9		x	--
3	2.58	18	x		2.59
4	2.47	off scale	x		2.50
5	2.42	2		x	2.42
6	2.36	2		x	2.36
					2.32
7	2.12	2		x	2.12
8	2.03	4		x	2.03
					1.98
					1.96
9	1.903	34	x		1.89
10	1.866	3		x	1.86
					1.81
11	1.687	2		x	( )
12	1.621	5	x		( )
13	1.530	3		x	( )
14	1.467	56	x		( )

-- No lines published by Strotzer *et al.*

( ) Strotzer's *et al.* data not evaluated.

All lines of the phosphide phase coincide with subphosphide lines except line No. 2 which is the strongest line in the present pattern.

This line, however, is located rather close to a strong zirconium line. Since Strotzer *et al.* reportedly did not have a pure subphosphide pattern, but a mixture of subphosphide, monophosphide and metallic zirconium, it is possible that they overlooked this one strong line for lack of resolution. Strotzer *et al.* also give as subphosphide lines three lines that might be zirconium lines or coincide with them.

The question is now whether by prolonged reaction at the same low temperature the subphosphide layer can be significantly increased in thickness. For this purpose sample No. 7 was reacted for three days, yielding, as mentioned above, a reaction layer of approximately 2.5μ thickness. The x-ray pattern of sample No. 7 indicates, however, that the hexagonal monophosphide has begun to form. As Table III shows β-ZrP lines are found besides a few remaining subphosphide lines and α-Zr lines.

Table III Diffraction pattern of sample No. 7 with lines of zirconium, α-Zr, subphosphide and monophosphide, β-ZrP

Line No.	D-spacing	Arbitrary intensity	-Zr	Subphosphide	-ZrP
1	3.16	9			x
2	2.85	2	x		
3	2.64	11		x	
4	2.54	16			x
5	2.48	15	x		
6	2.03	14		x	
7	1.91	9	x		
8	1.85	9			x

Table III cont'd.

Line No.	D-spacing	Arbitrary intensity	α-Zr	Subphosphide	β-ZrP
9	1.49	3			x
10	1.37	13	x		
11	1.35	3	x		

More samples were phosphidized at higher temperatures. The phosphide layer quickly becomes so thick that the lines of the underlying metallic zirconium do not come through any more. However, in some cases the strongest subphosphide lines are still detectible. While it was originally thought that the subphosphide layer forms only at the very interface between phosphide layer and metal, this last observation seems to indicate that the subphosphide is partly present in the bulk of the monophosphide layer.

Another possible explanation would be that cracks opening in the phosphide layer, as the one shown in Figure 2, expose the ZrP - Zr interface and thus, permit the x-rays to penetrate. However, no α-Zr lines were found as one should expect in such cases.

The samples were also examined microscopically in polarized and non-polarized incident light. For this purpose polished sections were prepared. It was difficult to polish the thin and rather brittle phosphide layer in direct contact with the softer zirconium metal; there was always a slight step at the reaction interface which made the observation of a thin layer between the metal and the bulk monophosphide extremely difficult. Only after applying special techniques, Ni-plating of the sample and embedding it in glass fiber reinforced resin, it was possible to obtain a satisfactory polish.

Figure 2

Crack formed in the phosphide layer alter the shape of the reaction interface (polarized incident light, LEITZ MM 5 Planoobjective 32, total magnification 360x).

No intermediate layer could be detected with normal incident light, nor at first, with polarized light. Later efforts to obtain a still better polish gave the following results: in polarized incident light a small rim can be seen between the thick monophosphide layer and the base metal. This rim is clearly less birefringent than the monophosphide layer. The thickness of the rim is in the order of 1 - 2 μ, as shown in Figure 3.

Before the improvement of the polishing technique permitted the observation of the thin rim at the interface, a microprobe tracing was made across the contact area. The analyzing electron beam had a cross section of not more than 2 μ. No stepwise decrease of the zirconium, nor stepwise increase of the phosphorus signal was, however, observed during a continuous scan across the boundary of the interface from zirconium to zirconium phosphide.

Rate of Reaction

If the reaction at the interface is diffusion controlled, the rate of reaction is expected to decrease with increasing thickness of the phosphide layer formed. To check this, a series of zirconium bar samples was reacted in phosphorus vapor of approximately 1 atm. at nearly 1000°C for various lengths of time. The results are summarized in Table IV and Figure 4.

Figure 3

Subphosphide layer at the reaction interface $Zr - ZrP_{hex}$ (polarized incident light, LEITZ MM 5, Planoobjective 80x total magnification 1000x). Slight blurriness of the photomicrograph is due to the long exposure time of 60 minutes.

Table IV Rate of reaction between zirconium metal and phosphorus vapor at different lengths of time

Sample No.	Length of exposure in days	Temperature of Zr-bar in °C	Temperature of P in °C	Weight increase of Zr-bar in mg.
8	3	1010	380	46.2
9	4	1037	380	56.2
10	5	1010	380	73.2
11	7	1037	380	94.5
12	9 3/4	1037	380	105.4

The reaction first proceeds as a linear function of time. Only after approximately six days of reaction the rate of reaction slows down, e.g., after the reaction layer has reached an average thickness of 0.05 mm. This result seems to indicate that, at least at the beginning, the reaction is not diffusion controlled, but that it takes place freely at an always fresh surface. This means that the phosphorus has always easy access to the metal surface. It is possible that the diffusion of phosphorus through the phosphide layer is effected with great ease due to the presence of the subphosphide phase forming kinds of diffusion channels. The other explanation, which seems more probable, is that cracks opening in the phosphide layer expose always fresh metal surface to the phosphorus vapor.

This explanation is supported by the microscopic observation that the phosphide layer appears shattered by numerous cracks and that the interface bulges inwards at those places where major cracks occur. In fact, the outline of the samples changes in the course of reaction, as shown in Figure 2, due to a considerable difference in density between the phosphide and the metal.

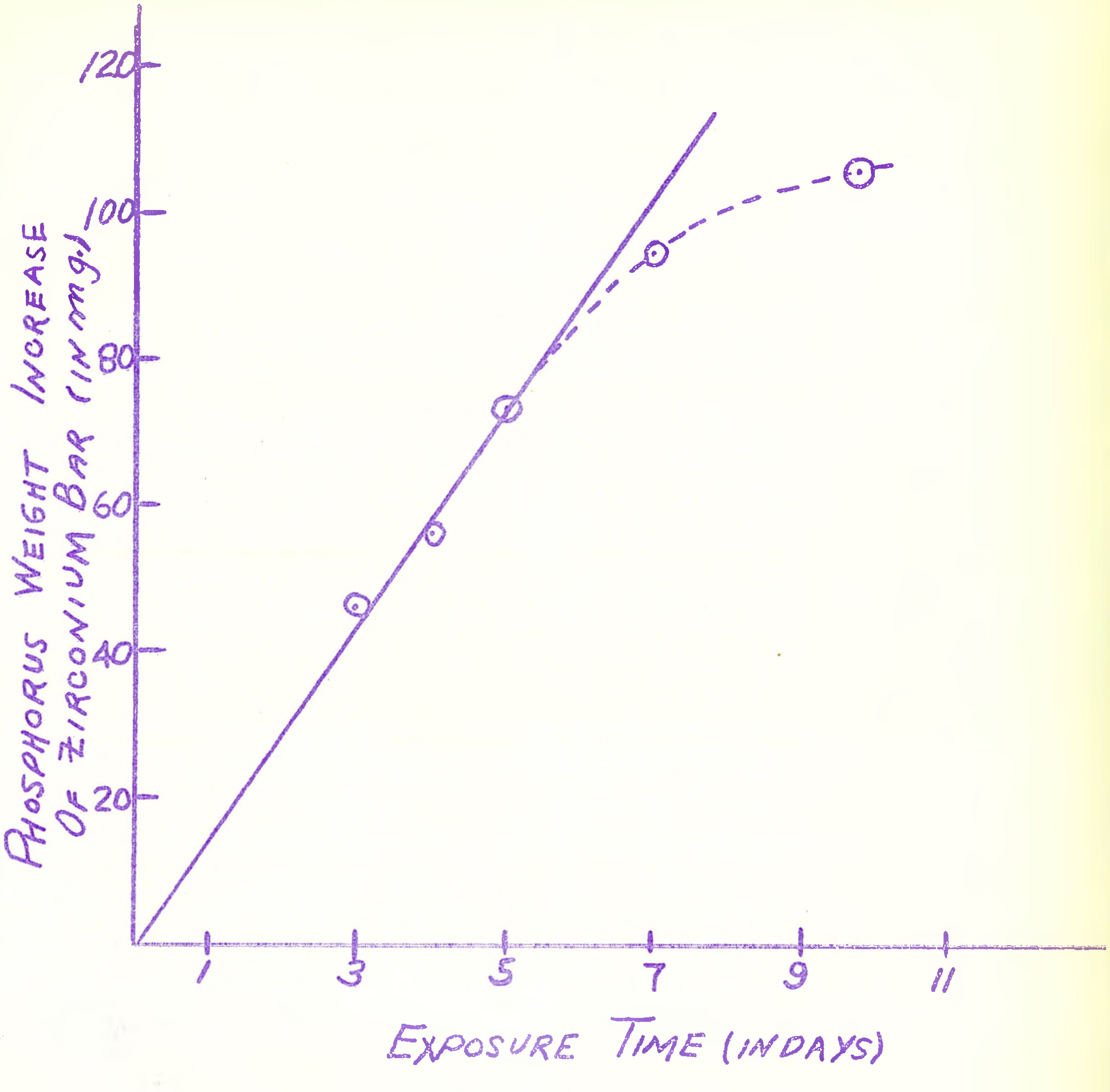

Figure 4

Rate of phosphidation of zirconium bar samples of constant surface area. Reaction temperature at about 1000°C, phosphorus vapor pressure approximately 1 atm.

Vapor Deposit

An unexplained observation was made each time zirconium metal was heated to temperatures above 700°C in a phosphorus vapor atmosphere of approximately 1 atm. In the hot zone of the sealed silica tubes a black deposit spread evenly over the inside walls. This film adhered well to the glass and could be removed only by scratching with a spatula. Its thickness generally increased with increasing reaction time, indicating a continuous process taking place throughout the length of reaction. If the deposit became so thick that the sample inside could hardly be seen, fine flakes would appear that lay loosely on the bottom of the tube.

The film did not dissolve in aqua regia after 24 hours. It was possible to collect enough samples to make an emission spectrographic analysis. The result showed that zirconium is present in the film. Phosphorus could not be detected which, however, does not necessarily mean that phosphorus is not present since the phosphorus lines in an emission spectrogram are weak and partially coincide with lines from the carbon electrode. The chemical behavior, insolubility in aqua regia, indicates that the film is not metallic zirconium but possibly a phosphide phase since zirconium phosphides, too, are not attacked by aqua regia.

This observation of a vapor deposited zirconium phosphide film is puzzling since no volatile phase is known in the Zr-P system. According to Strotzer et al. the diphosphide decomposes upon heating into monophosphide and phosphorus, but no evaporation of a zirconium containing phase has been reported for so low temperatures. In a mass spectrometric study of the vapor species above the zirconium monophosphide no phosphorus containing zirconium species could be observed in the vapor phase below 1800°C(6).

Nowotny(8) finds it possible that the vapor deposit contains zirconium silicide since under the experimental conditions gaseous SiO could have formed by reaction between SiO_2 and the zirconium metal. Yet, this possibility still would not account for the transport of zirconium to the wall of the reaction tube. The latter may be due to a cycling process via a volatile halide which might be formed due to traces of halogen possibly present in the zirconium metal or silica tube.

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Paper 6

VAPORIZATION BEHAVIOR AND PHOSPHORUS DECOMPOSITION PRESSURES OF TUNGSTEN MONOPHOSPHIDE

by

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Abstract

The vaporization of tungsten monophosphide, WP, has been studied by Knudsen effusion techniques in combination with a mass spectrometer. The major vapor species was P_2 with a small amount of P_4. No tungsten-containing species was observed. At 1000° C tungsten monophosphide vaporizes by decomposition into gaseous phosphorus and tungsten metal saturated with phosphorus. No range of homogeneity was observed for WP. An average molal enthalpy of decomposition, $\Delta H_{1100^\circ K}$, of 75.66 ± 1.06 kcal per mole of P_2 (g) was obtained from a second law treatment for the composition range $WP_{0.96}$ - $WP_{0.65}$, where the uncertainty represents the standard deviation. The temperature dependence of the P_2-decomposition pressure was found to be linear over the temperature range from 950° K - 1250° K and can be expressed by the equation:

$$\log p_{atm} [P_2] = \frac{-16534}{T} + 8.501 \pm 0.111$$

Introduction

The system tungsten-phosphorus has been included as part of a program in which the high temperature properties of the most thermodynamically stable transition metal phosphides are investigated[1-4]. These phosphides are expected

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[1] K. A. Gingerich and J. Efimenko, Thermodynamics of Nuclear Materials, International Atomic Energy Agency, Vienna, 1962, p. 477.

[2] K. S. Irani and K. A. Gingerich, J. Phys. Chem. Solids 24, 1153, (1963).

[3] K. A. Gingerich, P. K. Lee and J. Efimenko, to be published in Nature, Nov. 23 issue.

[4] K. A. Gingerich, to be published in Nature, Nov. 30 issue.

to form with the inner transition metals and the d-block transition metals of groups III - V. Preliminary experiments have shown that compact tungsten metal shows little tendency to react with phosphorus and that it forms phosphides of relatively low stability. For these reasons, and because of its high melting point, tungsten metal has been found to be a suitable oxygen-free container which may be used for more stable transition metal phosphides during preparations and property measurements at high temperatures. In order to predict and to understand possible interactions of tungsten with gaseous phosphorus and with other transition metal phosphides, the vaporization behavior of tungsten phosphides has been studied and vapor pressures have been measured in order to obtain thermodynamic properties of the processes involved.

The system W-P has been studied by tensimetric and x-ray powder methods by Faller <u>et</u>. <u>al</u>.[5] According to these authors only WP and WP_2 occur as intermediate phases. The phosphorus decomposition pressures of WP could not be determined by these authors because they were too low. They succeeded, however, in degradating WP in vacuum to metallic tungsten at 1050° C. Schönberg,[6] Bachmeyer <u>et</u>. <u>al</u>.[7] and Rundqvist[8] have confirmed that WP has the MnP (B31)-type structure and have determined the unit cell dimensions.

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[5] F. E. Faller, W. Biltz, K. Meisel and M. Zumbusch, <u>Z. Anorg. Allgem. Chem.</u> <u>248</u>, 209 (1941).

[6] N. Schönberg, <u>Acta Chem. Scand.</u> 8, 226 (1954).

[7] K. Bachmeyer, H. Nowotny and A. Kohl, <u>Monatsh. Chem.</u> <u>86</u>, 39, (1955).

[8] S. Rundqvist, <u>Acta Chem. Scand.</u> <u>16</u>, 287 (1962).

According to Rundqvist and Lundström[9] WP_2 has the orthorhombic MoP_2 - type structure with the possible space group *C m c* 2_1. These authors also report that the compositions of the monophosphide, WP and of the diphosphide, WP_2 correspond closely to stoichiometry and that there are no indications of extended homogeneity ranges. The existence of W_3P is still controversial. Hsu *et. al.*[10] prepared W_3P by fused salt electrolysis below 900°C and reported its x-ray diffraction powder data. After heating W_3P to 1050°C and quenching it, it was found to be disproportionated into W and WP. Other authors [5,9] were unable to prepare W_3P by direct synthesis.

In the present investigation, the vaporization of tungsten monophosphide, WP, has been studied by Knudsen effusion techniques in combination with a mass spectrometer in order to identify the various species produced and to obtain thermodynamic data for the reaction involved. Preliminary results have already been reported.[4]

Experimental

As starting material, a monophosphide produced by fused salt electrolysis[10] was used. For the mass spectrometric studies a 60° sector, 12-inch radius, first order, directional focusing instrument manufactured by Nuclide Analysis Associates, Inc. was used. The sample was placed directly into a tungsten Knudsen cell which had an orifice area of 1.52×10^{-2} cm^2 and a Clausing factor of 0.71. The ratio of the orifice area to the geometrical surface area of the sample was less than 1:88. The temperature was measured by a Pt vs Pt/10% Rh thermocouple which was inserted into a hole at the bottom of the cell. The heating was by radiation from a single tungsten ribbon that was arranged in a concentric spiral around the Knudsen cell. Due to the thermocouple arrangement

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[9] S. Rundqvist and T. Lundström, *ibid.* *17*, 27 (1963).

[10] S. S. Hsu, P. N. Yocom and T. C. C. Cheng, Interim Report from December, 1953-July, 1955, Contract N6ori-071 (50), Office of Naval Research, Dept. of Navy.

and the fact that the sample was placed directly in the tungsten effusion cell, the temperatures reported should have given the sample temperature accurately within a few degrees. The molecular beam was ionized with 55 eV electrons. The ions were detected with an electron multiplier and the ion current was recorded automatically. The variation of ion intensity of a particular species was observed as a function of temperature and composition. Species effusing from the Knudsen cell were distinguished from background species by placing a shutter into the beam periodically.

Results and Discussion

The vaporization of tungsten monophosphide, WP, was investigated over a temperature range of 950 -1300° K and an approximate composition range of WP - $WP_{0.1}$. The following ionic species were observed in the effusing vapor: P^+, P_2^+, and P_4^+. No P_3^+, nor any species containing tungsten and phosphorus could be detected. From the experimental conditions under which the check for tungsten-containing species was carried out, it can be concluded that their concentration is less than 1/1000 of that of the phosphorus vapor concentration in equilibrium with the solid. The appearance potentials of P^+ and $P2^+$ were found to be 13.4 eV and 9.2 eV, respectively, on a relative scale; but they show that P_2^+ is a primary species and P^+, a secondary one. If one considers the shift in electron energy scale to lower values by a factor of approximately 0.9 as derived from the ratio 9.2/10.2 of the measured value for P_2 to the accepted value, the appearance potential for P^+ becomes 14.9 eV. Taking this shift into account, the difference between the appearance potentials of P^+ and P_2^+ is 4.7 eV, which is in fair agreement with the dissociation energy of P_2 of 5.0 eV.[11] This shows, in addition, that P^+ is primarily produced by fragmentation of P_2, most likely by the reaction

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[11] Herzberg, Ann. Physik Lpz. 15 677 (1932).

(1) $P_2 + e^- = P^+ + P + 2e^-$

Additional proof that the P^+ ion is produced by fragmentation of P_2 can be derived from the observation that, over the whole temperature range of investigation, the ion intensity of P_2^+/P^+ had a constant value of 10. The contribution to the P^+ intensity from the fragmentation of P_4 is considered to be minor, because the ion intenisty of P_4^+ is, under experimental conditions, less than that of P_2^+ by a factor of 20 to 30. Because of the low intensity of P_4^+, its appearance potential was not measured. It is assumed that the parent of P_4^+ ion is P_4. In Figure 1, the ionization efficiency curves for P^+ and P_2^+ are represented. Analysis of these ionization efficiency curves shows further that the concentration of primary monatomic phosphorus was too low to be detected.

The observed ion intensity of P_2^+ was independent of composition and a reversible function of temperature over the composition range $WP_{0.96}$-WP_{65}. This indicates that equilibrium conditions were prevailing and that the rate of effusion out of the Knudsen cell was smaller than the rate of diffusion of phosphorus through the phase formed on each individual grain by the decomposition of WP. In checking the reversibility of the ion intensity with temperature, it was observed that the largest source of error was the slowness in attainment of temperature equilibrium. The attainment of temperature equilibrium after each change in temperature was tested by reaching constant temperature and constant intensity. The constancy in temperature as indicated from the thermocouple reading was reached somewhat earlier than the constancy in ion intensity, which is assumed to be due to the low thermal conductivity within the powdered sample. As a result, vapor pressure values which were obtained while raising the temperature are, on the average, slightly lower, as are those obtained during cooling.

The general observation that the ion intensity of P_2^+ is reversible with temperature is modified by observations made in the initial and final stages of the tensimetric analysis of WP in this investigation. Although thermal equilibrium was attained, a set of intenisty data obtained in the composition range $WP-WP_{0.96}$ at the beginning of the experiment shows values that are too low. A possible explanation is that in the early stage of vaporization a fraction of the phosphorus vapor reacted with the tungsten effusion cell to form a solid solution of phosphorus in tungsten. This process would have to occur at a more rapid rate than the rate of vaporization of WP. As the rate of phosphorus take-up by the tungsten cell falls markedly below that of the vaporization of WP, the equilibrium pressure observed in the Knudsen cell corresponds closely to the equilibrium pressure of the WP phase. In the later stage of vaporization, while at a constant high temperature and high ion intensities, a decrease in the ion intensity with decreasing phosphorus content of the solid was observed for the composition range $WP_{0.65}$-$WP_{0.1}$. This is illustrated in Figure 2, in which the relation between the logarithm of the P_2-partial pressure and composition at 1300°K is represented. Two possible interpretations are suggested for this observation: (a) It may be because of kinetic effects such as a diffusion barrier caused by the tungsten coat formed on each WP grain that becomes larger as the coat grows in thickness, or to a bulk diffusion barrier that becomes more pronounced as the rate of vaporization increases. (b) It may indicate the presence of a homogeneity range of a condensed phase with lower phosphorus content, the phosphorus-rich boundary of which has a phosphorus activity similar to that of WP. X-ray analysis of the final product showed that it consisted largely of metallic tungsten. Additional very weak lines observed on an overexposed film were analysed for WO_2, W_4O_9, $W_{18}O_{19}$, $W_{20}O_{28}$, β-W_2C and WC by comparison with the corresponding ASTM data and for W_3O, W_3P and WP by comparison with the corresponding x-ray diffraction patterns. They could not be identified with any of these substances. It was, however, possible to attribute all but one of these additional lines to the most intense tungsten reflections for Cu-K_β and Fe-K_α radiation, respectively. The fact that no WP could be detected would indirectly support explanation (b). It is, however, more likely that so little WP was left that it was not visible by x-ray diffraction and that explanation (a) accounts for the observed decrease in ion intensity. In support of this, the standard deviation is shown in Figure 2 by the vertical line on the curve, indicating that the effects discussed above are small and of the order of the standard deviation. If explanation (b) were to hold, a much larger intensity decrease with change in composition as well as the appearance of a new phase on the x-ray diffraction pattern would be expected.

The fact that the end product was largely tungsten metal and that there was no significant abrupt change in ion intensity at any composition covering the range WP-$WP_{0.1}$ indicates that there is no stable phase existing between WP and W above 1000° C. Thus above 1000° C, WP vaporizes incongruently by decomposition into gaseous phosphorus and tungsten metal according to the equation

$$(2)\quad \frac{2}{a}\,WP = \frac{2}{a}\,WP_{1-a} + \frac{2}{x}P_x$$

where $a < 1$ and x is either 2 or 4.

For the composition range $WP_{0.96}$ - $WP_{0.65}$ over which the ion intensity of P_2^+ was independent of composition, the variation of ion intensity I of P_2^+ has been determined as a function of temperature over the temperature range from 950-1250°K. From the reversible ion intensity-temperature relationship, the average molal enthalpy of decomposition ΔH_{1000}, for reaction (2) with $x = 2$ was obtained from a second law treatment of the dependence of the dissociation pressure upon temperature and is expressed by the equation

$$(3)\quad \Delta H_{1100} = 75.66 \pm 1.06 \text{ kcal/mole } P_{2(g)}$$

The uncertainty given represents the standard deviation. The accuracy is probably lower because of a possible temperature gradient between the position of the thermocouple and the location of the sample.

The ion intensities of P_2^+ were correlated to vapor pressures through an external silver calibration.[12,13] The difference in electron multiplier efficiencies of Ag^+ and P_2^+ were determined separately. Corrections for fragmentation and double ionization were considered. For the relative ionization cross section of Ag the value give by Otvos and Stevenson[14] was used. For the cross section of P_2, a value of 21.8 was estimated with reference to the cross section of 13.8 for P by considering the geometrical shape of the molecule. The Clausing factor for the geometry of the cell orifice was taken into account.[15] The results are represented in Figure 3 and in Table I. The temperature dependence of the P_2-partial pressures over the temperature range 950-1250°K and the composition range $WP_{0.95}$-$WP_{0.65}$ is linear within the limits of experimental error and can be expressed by the following equation:

$$(4) \quad \log P_{(atm)}\ P_2 = \frac{-16.534}{T} + 8.501 \pm 0.111$$

The rather large standard deviation reflects in part the influence of the observations made during the initial and final stages of the investigation into the region selected for the computation of vapor pressures. In the selection of ion intensity values, the main consideration was attainment of temperature equilibrium. Possible slight deviations from temperature equilibrium are, however, included in the standard deviation since the values used correspond to three different temperature cycles. An additional source for the large standard deviation comes from the observation of a possible reaction

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[12] W. A. Chupka and M. G. Inghram, *J. Phys. Chem.* *59*, 100 (1955).

[13] M. G. Inghram, W. A. Chupka and R. F. Porter, *J. Chem. Phys.* *23*, 2159 (1955).

[14] J. W. Otvos and D. P. Stevenson, *J. Am. Chem. Soc.*, *78*, 546 (1956).

[15] S. Dushman and J. M. Lafferty, *Scientific Foundation of Vacuum Technique*, Second Edition, John Wiley and Sons, Inc., 1962, p. 94.

of phosphorus vapor with the tungsten cell. As indicated earlier, this effect appeared to be most pronounced at the very beginning of the investigation, but it is estimated to have continued to the extent indicated by the dotted line in Figure 2 for the composition region $WP-WP_{0.65}$. Reaction of part of the phosphorus would make the pressures reported too low. A systematic error in addition to that reflected in the standard deviation may be because of the change in sensitivity of the instrument during the one-week period between the silver calibration and the investigation of WP. Additional experiments have shown, however, that the sensitivity fluctuation of the mass spectrometer-Knudsen cell assembly over a one-year period was within 30 per cent. An additional systematic error would arise from a vaporization coefficient α which is considerably less than unity. The ratio of orifice to sample area applied in this investigation would require a vaporization coefficient less than 10^{-2} before it would influence the vapor pressure values markedly. That a low value of α must be considered as a possibility is apparent from estimates by Lewis and Myers[16] for the vaporization of ion phosphides where α is estimated to be between 4×10^{-5} and 6×10^{-2}.

Acknowledgments

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The author gratefully acknowledges the courtesy of the National Bureau of Standards for the use of the mass spectrometer in this investigation. He is also indebted to Dr. J. Efimenko for his interest in the project, to Mrs. C. O. Krishna for her help in the mass spectrometric work and to Dr. G. Eulenberger for the x-ray analysis of the residue.

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[16] G. Lewis and C. E. Myers, J. Phys. Chem. 67, 1289 (1963).

TABLE I

Mass spectrometric vaporization data for $WP_{0.95-0.65}$

K	$10^4/T$	$I(P_2^+)$ arbitrary units	p_{atm} (P_2)	$-\log p_{atm}$ (P_2)
992	10.079	13.9	5.85×10^{-9}	8.233
969	10.320	6.50	2.67×10^{-9}	8.573
949	10.535	3.45	1.39×10^{-9}	8.868
948	10.553	3.20	1.29×10^{-9}	8.891
1026	9.751	50.9	2.22×10^{-8}	7.655
1051	9.516	116.1	5.18×10^{-8}	7.286
1065	9.394	167.7	7.58×10^{-8}	7.121
1065	9.390	169.5	7.66×10^{-8}	7.116
1096	9.123	398	1.85×10^{-7}	6.732
1192	8.388	5590	2.83×10^{-6}	5.548
1187	8.423	5290	2.67×10^{-6}	5.574
1220	8.200	20610	1.07×10^{-5}	4.972
1219	8.202	20600	1.07×10^{-5}	4.972
1153	8.672	3890	1.90×10^{-6}	5.720
1152	8.685	3850	1.87×10^{-6}	5.739
1085	9.217	631	2.91×10^{-7}	6.537
1085	9.214	658	3.03×10^{-7}	6.518
1026	9.747	57	2.48×10^{-8}	7.605
1183	8.457	8820*	4.43×10^{-6}	5.354
1219	8.206	20100*	1.04×10^{-5}	4.993
1182	8.643	6330*	3.18×10^{-6}	5.498
1148	8.711	2330*	1.14×10^{-6}	5.945
1096	9.124	549*	2.55×10^{-7}	6.539

Table I (Cont'd) Mass spectrometric vaporization data for $WP_{0.95-0.65}$

K	$10^4/T$	$I(P_2^+)$ arbitrary units	P_{atm} (P_2)	$-\log p_{atm}$ (P_2)
1054	9.491	128*	5.73×10^{-8}	7.242
1027	9.740	54.3*	2.37×10^{-8}	7.626
1262	7.925	41800	2.24×10^{-5}	4.650
1262	7.923	41700	2.23×10^{-5}	4.651

The sequence of data corresponds to decreasing phosphorus content in the solid.

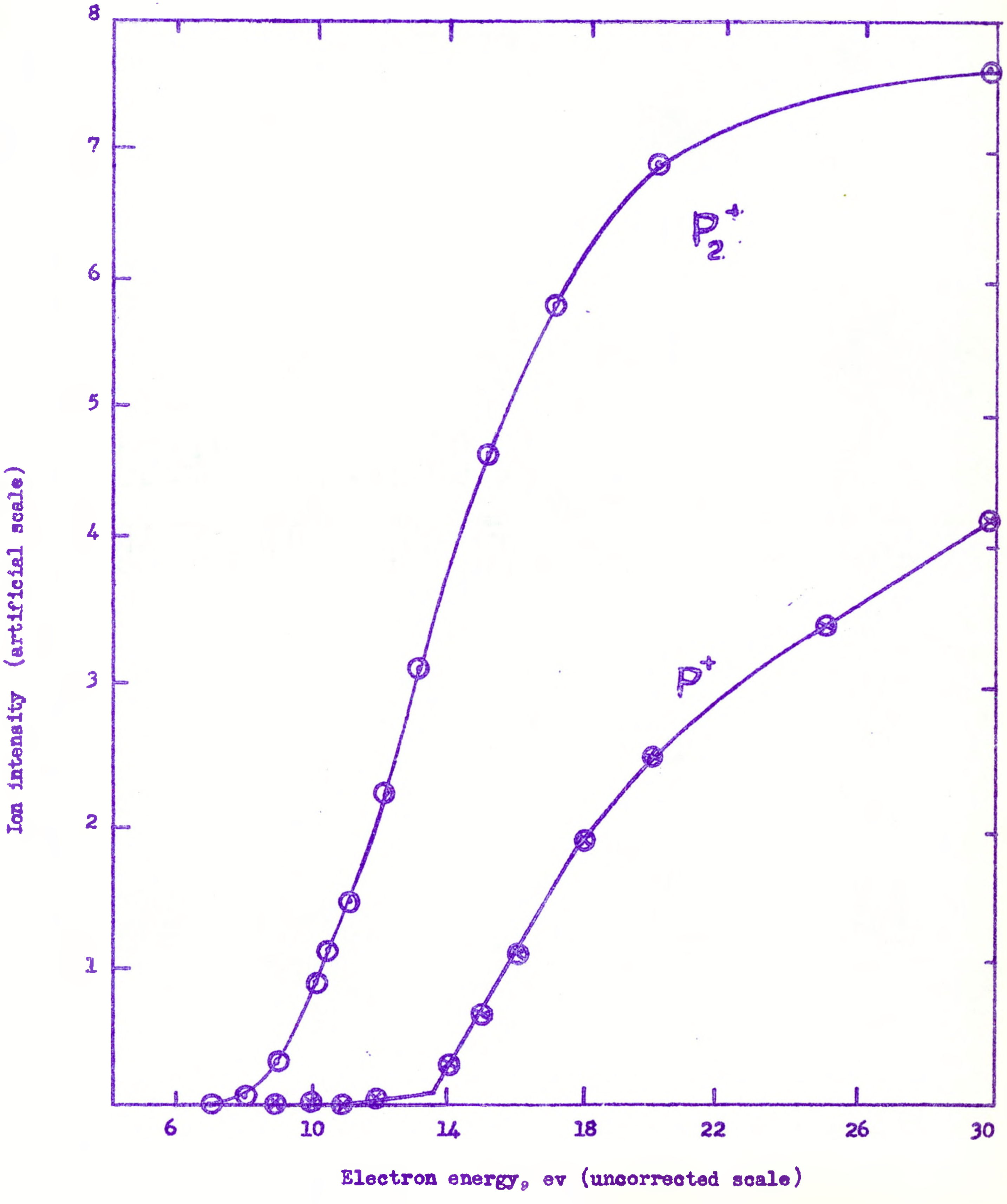
* refers to values which were measured as I(P) and converted to $I(P_2)$ by multiplication by 10.

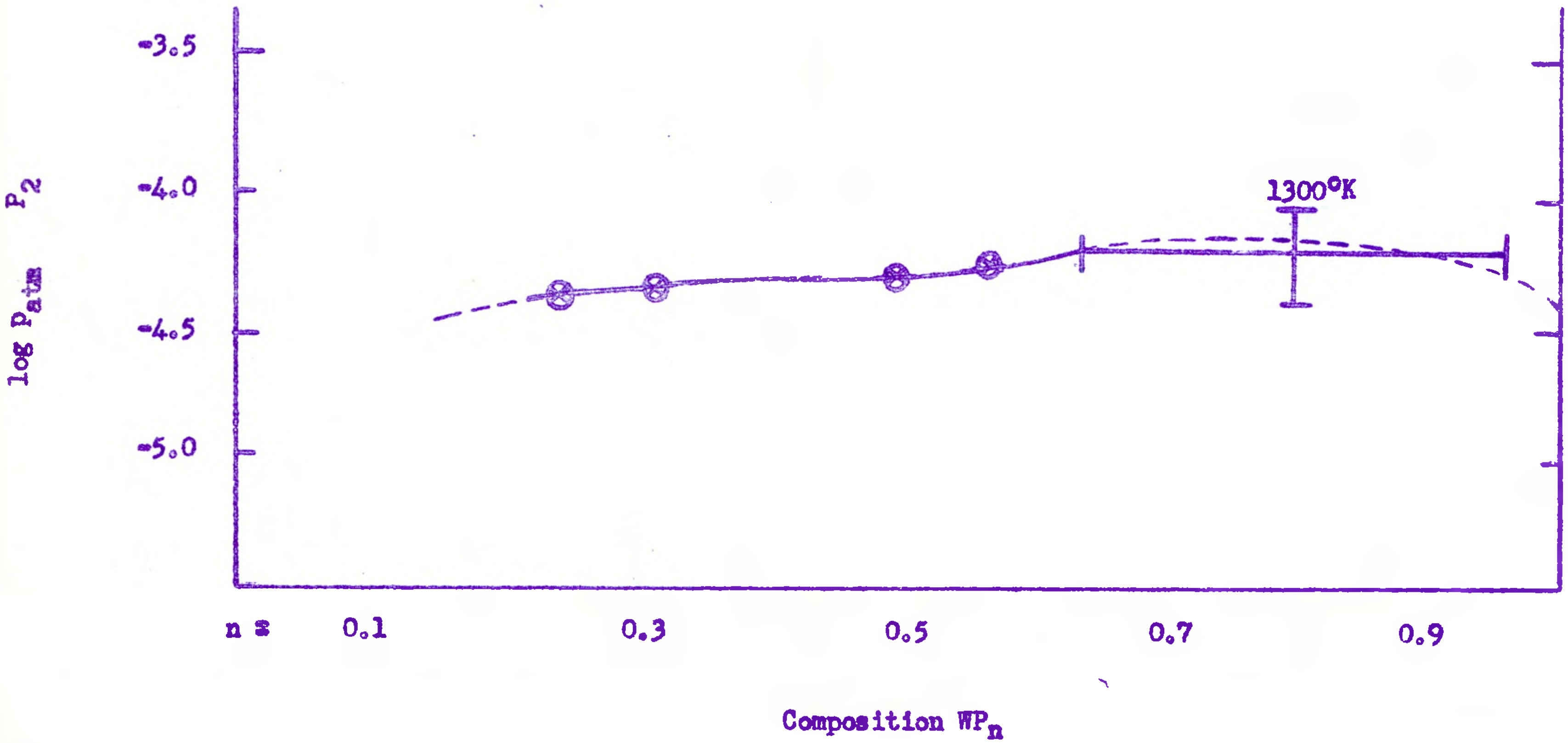
Figure Captions

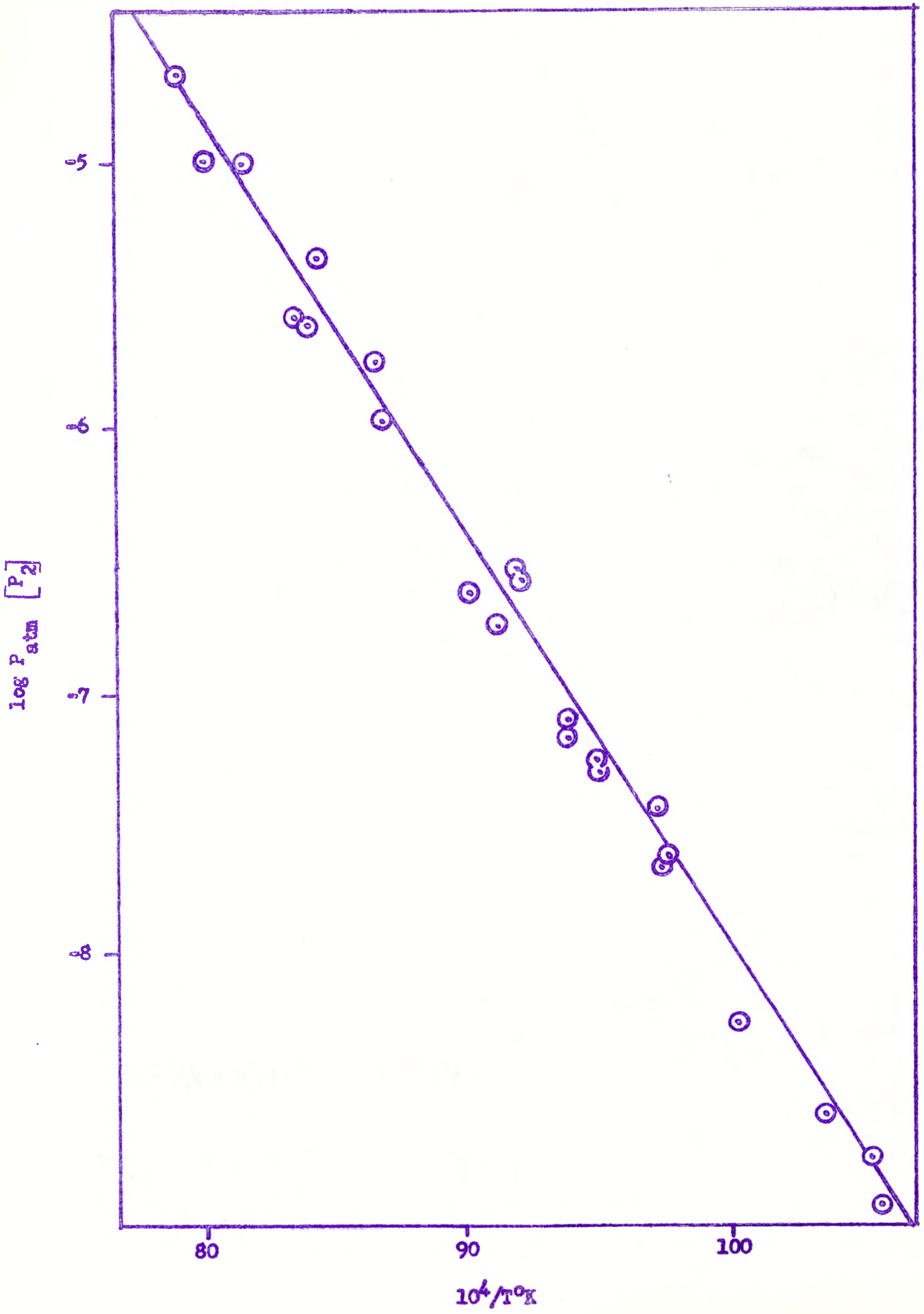
Fig. 1 - Ionization efficiency curves for P^+ and P_2^+ observed over W-WP.

Fig. 2 - P_2-decomposition pressures as a function of composition in the system W-WP at 1300° K.

Fig. 3 - Second law plot for the reaction: $\frac{2}{a}\,WP = \frac{2}{a}\,WP_{1-a} + P_2$


8
7
6
5
4
3
2
1
Ion intensity (artificial scale)
6
10
14
18
22
26
30
Electron energy, ev (uncorrected scale)
P_2^+
P^+


-3.5
-4.0
-4.5
-5.0
log P$_{atm}$ P$_2$
1300°K
n = 0.1
0.3
0.5
0.7
0.9
Composition WP$_n$



-5
-6
-7
-8
log P_{atm} $[P_2]$
80
90
100
$10^4/T^oK$

Paper 7

MASS SPECTROMETRIC STUDY OF THE VAPORIZATION OF URANIUM MONOPHOSPHIDE[*][†]

by

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Abstract

The vaporization of uranium monophosphide, UP, and its mixtures with uranium oxide, UO_2, have been investigated by Knudsen effusion techniques in combination with a mass spectrometer.

The vaporization of UP occurs by decomposition according to:

$$(1)\quad UP_{(s)} = U_{(g)} + \frac{1}{x} P_{x(g)} \qquad (\text{ x either 1 or 2})$$

If UO_2 is present approximately in equimolar ratio with UP the principal reaction is according to:

$$(2)\quad UP_{(s)} + UO_{2(s)} = 2\ UO_{(g)} + \frac{1}{x} P_{x(g)} \qquad (\text{x either 1 or 2})$$

The partial pressures of P, P_2 and U over UP have been obtained from the silver calibration for the temperature range of 1750 - 2250°K as follows:

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[*] This work was supported under A. E. C. Contract No. AT (30-1) -2541.

[†] This report was prepared in October, 1963. It is a revised form of the first part of a paper that has been presented at the Symposium on Thermodynamics and Thermochemistry in Lund, Sweden, July 18-23, 1963.

$$\log p_{atm}\,[P] = \frac{-26211}{T} + 6.6743 \pm 0.0683$$

$$\log p_{atm}\,[P_2] = \frac{-23046}{T} + 4.5188 \pm 0.1097$$

$$\log p_{atm}\,[U] = \frac{-28677}{T} + 7.9313 \pm 0.0709$$

From the second law treatment the heat of vaporization kcal. per mole of UP is obtained for reaction (1) as 183.96 when $x = 2$, and 251.17 when $x = 1$.

Vapor pressures derived from other methods, such as (a) from known dissociation energy of P_2 and thermodynamic functions of P and P_2, and (b) from the amounts of sample evaporated are discussed.

Introduction

In the search for new oxygen-free refractory materials, the vaporization behavior of thorium phosphides had been studies by means of the Knudsen effusion method in combination with a mass spectrometer(1), and it was found that the subphosphide of thorium, $ThP_{0.7}$, possesses high thermodynamic stability(1) which is comparable to that of uranium monosulphide, US.(2) In analogy to uranium monosulphide, and thorium subphosphide, it was expected that uranium monophosphide, UP, also possesses potentially high thermodynamic stability and possibly, as does uranium monosulphide, vaporizes congruently. The expected congruency of vaporization would eliminate the complication of diffusion barriers as were found in the

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1. K. A. Gingerich and J. Efimenko, "Thermodynamics of Nuclear Materials", International Atomic Energy Agency, Vienna, 1962, p. 477.

2. E. D. Cater, E. G. Rauh, and R. J. Thorn, Chem. Phys., 35, 608 (1961).

vaporization of thorium phosphides and thus permit investigation of all the variables and parameters that influence the accuracy of the determination of partial pressures of vaporizing components by using the Knudsen effusion-mass spectrometer method. Preliminary results of this investigation were reported earlier.(3) Also included in this investigation was a mixture of UP with UO_2 in order to investigate the influences of oxygen contaminent which is usually present in the prepared sample on the the vaporization process.

Three compounds were shown to exist in the U-P system in a systematic tensiometric and x-ray analysis(4), namely UP, U_3P_4 and UP_2. Up has the NaCl (B 1) type structure with a = 5.600 Å(5,6); U_3P_4 the cubic Th_3P_4 (D 7_3) type structure with a = 8.21_3 Å(5) and UP_2 the tetragonal Cu_2Sb (C 38) type structure with a = 3.800 Å, c = 7.762 Å and c/a = 2.043(7).

The phosphorus dissociation pressures of UP_2 were investigated and a single value for the dissociation pressure of U_3P_4 was also given (4 mm Hg at 1185° C) (4). No thermodynamic properties of uranium mono-

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3. K. A. Gingerich, P. K. Lee, and J. Efimenko; Nature to be published.

4. M. Heimbrecht, M. Zumbusch, and W. Biltz; Z. anorg. Chem., 245, 391 (1941).

5. M. Zumbusch; Z. anorg. Chem., 245, 402 (1941).

6. R. E. Rundle, and N. D. Baenziger; U. S. Atomic Energy Comm. Report, CC-1778 (1944). Quoted from J. J. Katz and Robinowitch, "The Chemistry of Uranium", Part I, p. 241, McGraw-Hill Book Company (1951).

7. A. Iandelli; Chem. Abstr., 47, 11062 (1953).

phosphide appeared in the literature. Only a melting point of 2730° C has been reported.(8)

Experimental Methods

The uranium monophosphide used in the mass spectrometric investigation was prepared by direct reaction of uranium metal sheet of 0.01 inch thickness from A. D. Mackay Inc. and Semiconductor grade phosphorus from L. Light and Co., Ltd., using the Faraday method. The uranium was contained in a tungsten boat located at one end of a sealed, evacuated quartz tube. At the other end of the sealed tube was placed a fused quartz vial containing red phosphorus. The uranium and phosphorus were maintained at temperatures of 900° C and 400° C respectively for two weeks. The compound U_3P_4 formed was then thermally degraded to monophosphide, UP, in a high vacuum at about 1400° C. The final product was ground to pass 325 mesh and then used as the starting sample for the mass spectrometric experiments. Chemical analysis showed that it contained 0.38 % oxygen. An x-ray diffraction pattern gave the lattice parameter of 5.589 ± 0.001 Å and showed a trace amount of UO_2.

The mass spectrometer used was a 60° sector, 12-inch radius, first-order directional focusing instrument manufactured by Nuclide Analysis Associates Inc., which was similar to that used by Chupka and Inghram(9). A tantalum Knudsen effusion cell with covers having an orifice of three different sizes was used. The orifice areas were 2.24×10^{-3}, 8.17×10^{-3},

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8. Y. Baskin; Reported in the 65th annual meeeting of the Am. Ceramic Soc., April, 1963.

9. W. A. Chupka and M. G. Inghram; J. Phys. Chem., 59, 100 (1955).

and 3.02 x 10^{-2} cm^2 with a corresponding Clausing factor of 0.685, 0.676, and 0.668, respectively. The fitting of cover and body of the Knudsen cell was machined precisely in order to minimize secondary effusion leaks. The sample itself was contained in a tungsten liner which was placed inside the effusion cell. The lower limit of the ratio of the geometrical surface area of sample to the area of the effusion orifice, at the beginning of the experiment was 253, 69.4 and 18.8 respectively. The cell was heated by two concentric tungsten filaments placed in parallel, around the cell. Temperatures were measured by a Leeds and Northrup optical pyrometer which was calibrated by the U. S. National Bureau of Standards. Temperature readings were made on a black body hole in the bottom of the cell, and corrections for window and prism were added. The black body hole was a threaded hole with a depth to radius ratio of 10. Using the emmissibity values for tantalum form Allen *et. al.*(10), the effective emissibity of the black body hole according to Williams(11) was estimated to be more than 0.998.

The ion intensities of different species observed in the vapor phase were recorded as a function of temperature and time. The operating conditions were the following: accelerating potential 3 kV, electron voltage 55 eV, emission current 0.3 ma. The multiplier efficiency for the various ions was determined experimentally. The beam focusing was adjusted to maximum intensity. The appearance potential and ionization

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10. R. D. Allen, L. F. Glaser, P. L. Jordan; *J. Appl. Phys.*, *31*, 1382 (1960).

11. C. S. Williams; *J. Am. Opt. Soc.*, *51*, 567 (1961).

efficiency were measured for various species. The sensitivity of the mass spectrometer was determined by calibration with silver. In addition to the runs with pure uranium monophosphide, one run was made in which approximately equimolar mixtures of UP and UO_2 were used.

Results and Discussion

The vaporization of uranium monophosphide, UP, was investigated over the temperature range from 1750-2250° K. During its vaporization, the major primary ion species observed and measured were U^+, P^+, P_2^+, and UO^+. In the mixture of $UP-UO_2$, UO_2^+ was also a major ion species. In no case was gaseous UP observed. In an experiment (series II) during which 90% of the uranium monophosphide sample was evaporated, the x-ray diffraction pattern of the residue left in the tungsten liner after vaporization showed that the lattice parameter shifted from 5.589 ± .001Å to 5.584 ± .001Å and showed only the lines of UP. The lines of UO_2 could no longer be detected. On the basis of these observations, it appears that UP vaporizes congruently over the temperature range of investigation. It was then assumed that the vaporization process was mainly according to the following reaction:

$$(1)\quad UP_{(s)} = U_{(g)} + \frac{1}{x} P_{x(g)} \qquad (x = 1 \text{ or } 2)$$

The fact that the small amount of oxygen in the uranium monophosphide sample shows as UO_2 in the x-ray pattern indicates that UO_2 is coexistent with UP in the solid at 1400° C and that the formation of solid solution does not occur to an appreciable extent. Ackermann, Gilles and Thorn(12) reported the vapor species over UO_2 and suggested that $UO_{2(g)}$ is the predominant species at 1600-2000° K. Ackermann and Thorn(13) tabulated and computed the thermodynamic properties of gaseous uranium and uranium oxides from their observations(12,14) and the mass-spectrometric data of DeMaria <u>et</u>. <u>al</u>.(15). All the oxides except $UO_{2.00}$ vaporize incongruently, and the composition of the vapor is considerably more oxygen-rich than the condensed phase. Any of the oxides with O/U ratio ≥ 2 will ultimately yield $UO_{2.00}$ when heated in a system in which the vapor can escape. At compositions of O/U ≤ 2 the composition of the vapor is predominantly $UO_{(g)}$ and $U_{(g)}$. Thus, the oxygen impurity in the UP sample was assumed to react according to:

(2) $UP_{(s)} + UO_{2(s)} = 2\ UO_{(g)} + \frac{1}{x} P_x$ $\qquad (x = 1 \text{ or } 2)$

or (3) $UO_{2(s)} = UO_{2(g)}$

and (4) $U_{(g)} + UO_{2(g)} \rightleftharpoons 2\ UO_{(g)}$

Since combination of reactions (1), (3), and (4) gives reaction (2), and UO_2 is a minor component in the UP system, only reactions (1) and (2) are considered. The observations that no UO_2 could be detected in the residue and that the UO^+ ion intensity decreased in relation to the

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12. R. J. Ackermann, P. W. Gilles and R. J. Thorn; <u>J. Chem. Phys.</u>, <u>25</u>, 1089 (1956).

13. R. J. Ackermann and R. J. Thorn; "<u>Thermodynamics of Nuclear Materials</u>", p. 445, International Atomic Energy Agency (1962).

14. R. J. Ackermann and R. J. Thorn; <u>Progress in Ceramic Science</u>, I, Chap. 2, Pergamon Press (1961).

15. G. DeMaria, R. P. Burns, J. Drowart and M. G. Inghram; <u>J. Chem. Phys.</u>, <u>32</u>, 1373 (1960).

U^+ ion intensity as the vaporization progressed reveal that reaction (2) is preferred to (1). The appearance of the UO_2^+ ion resulting from the approximately equimolar mixture of UP-UO_2 in this investigation is contributed to reaction (3).

The measured appearance potentials of the observed species over the UP-UO_2 mixture are selected and presented in Figures 1-3. In each case the measured ion intensity was corrected for background. Analysis of the ionization efficiency curves for U^+ yields a distinct break in all measurements at 13.0, 13.4, 13.4, and 13.75 eV. The corresponding appearance potential for primary U^+ is 4.2, 5.25, 4.96 and 5.0 eV. The average difference between these two sets of values is 8.5 eV which is contributed to the dissociation energy of UO and shows that a large fraction of the U^+ observed results from fragmentation of UO. The value of 8.5 eV for the dissociation energy is higher than the approximate value of 7.6 eV given by Ackermann and Thorn$^{(13)}$. By considering the crudeness of the method used for the estimation and uncertainty in the literature value the agreement is fair enough to support the above conclusion. The relative amount of primary U^+ species to the total U^+ intensity including those produced by fragmentation was found to be 31.2 to 31.7% at 2100° K and 20.8 to 22.3% at 1956° K. Combining these values with ion intensities of U^+ and UO^+ at the same temperatures, the extent of fragmentation of UO was then found to be 8.99 to 10.93%. The average value of 10% was used in the later correction of the ion intensity of U^+ for fragmentation of UO. The appearance potentials of UO^+ and UO_2^+ were found to be approximately 4.2 eV and 4.9 eV respectively. The relatively low value of these appearance potentials is evidence that the UO^+ and UO_2^+ are being formed by simple ionization of UO gas and UO_2 gas, respectively, rather than by dissociative ionization of other species.

The ion intensities of doubly and triply ionized species were also measured in the series with the $UP-UO_2$ mixture. The relative intensity ratio to the corresponding singly-charged species at the same temperature was found to be U^{++}/U^{+} 0.4335; U^{+++}/U^{+} 0.0238; UO^{++}/UO^{+} 0.0349; UO_2^{++}/UO_2^{+} 0.0093; and P^{++}/P^{+} 0.0766. Among the uranium-containing species, only the double ionizations of U^{++} are significant and need be taken into consideration for the correction of ion intensity of U^{+}. From the relative amount of primary U^{+} to total U^{+} and the measured amount of U^{++}/U^{+}, a value of about 0.7 is then estimated for the ratio of U^{++} to the primary U^{+}, and used in the correction of the U^{+} intensities. This value seems rather high.

For the correction of the ion intensity of phosphorus monomer, P^{+}, it was found in earlier experiments that 10% of P_2 was fragmented to P at 55 eV. Furthermore, it was assumed that the formation of P_2^{++} is half as efficient as that of P^{++} by analogy with antimony.(16)

The corrected ion intensities were correlated to vapor pressure through silver calibration(17). A weighed amount of silver which was placed together with the sample in the tungsten liner from the effusion cell and a pressure calibration made in the usual way. The sensitivity oß the mass spectrometer was obtained for each geometry of effusion orifices. The data is presented in Table I. The extent of double ionization of silver was also measured at 55 eV, an average factor of 0.023 related to the singly-charged Ag^{+} was found, and taken into

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16. K. A. Gingerich and J. Efimenko; unpublished work.

17. M. G. Inghram, W. A. Chupka and R. F. Porter; J. Chem. Phys., 23, 2159 (1955).

consideration. The ionization potential of silver and phosphorus were taken from Moore(18), and the ionization potential of P_2 was assumed to be the same as that of P.

For the evaluation of absolute vapor pressure of each species over the UP sample, further information about the relative ionization cross sections, σ, and differences in electron multiplier efficiencies, s, of the vapor species in question are needed. The relative ionization cross sections of P^+ and Ag^+ were taken from Otvos and Stevenson(19). For P_2^+, instead of estimation from rule of additivity, a geometric mean factor considering the molecular shape was added in relation to the ionization cross section of P^+. A value of 55.7 was also estimated for U^+ from Otvos and Stevenson. The relative multiplier efficiencies for the various ions were determined experimentally, and a summary is presented in Table II, in which, for comparison, is also included the multiplier efficiency of P_2^+, P^+ and Ag^+ taken from an independent investigation of tantalum monophosphide which was performed between series II and III of this investigation. In Series IV the ion intensities were high enough to make a thorough measurement, thus the data are more reliable and were chosen for the computation of the vapor pressures for all species.

The mass spectrometric data of the gaseous species, U^+, P^+ and P_2^+ for Series I and the corresponding partial pressures of U^+, P^+ and P_2^+ over solid uranium phosphide are listed in Table III. The results are

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18. C. E. Moore; NBS Circular 476 (1949).

19. J. W. Otvos, and D. P. Stevenson; J. Am. Chem. Soc., 78, 546 (1956).

shown in Figure 4. The derived average values for partial molal heat of vaporization in kcal per mole at 2000° K are as follows:

$$(5)\quad \Delta\bar{H}\ (U) = 131.23 \pm 2.25$$

$$(6)\quad \Delta\bar{H}\ (P) = 119.94 \pm 2.63$$

$$(7)\quad \Delta\bar{H}\ (P_2) = 105.46 \pm 1.66$$

where the uncertainties represent the standard deviations. From these values H^{o}_{2000} vap in kcal per mole of UP is obtained as 183.96 for the reaction (1) when $x = 2$, and 251.17 when $x = 1$. The temperature dependence of the partial pressures over the temperature range of investigation is linear within the limits of experimental errors, and can be expressed by the following equations:

$$(8)\quad \log p\ (\text{atm})\ [P] = \frac{-26211}{T} + 6.6743 \pm 0.0683$$

$$(9)\quad \log p\ (\text{atm})\ [P_2] = \frac{-23046}{T} + 4.5188 \pm 0.1097$$

$$(10)\quad \log p\ (\text{atm})\ [U] = \frac{-28677}{T} + 7.9313 \pm 0.0709$$

The total vapor pressure over uranium monophosphide as derived from the summation of partial pressures within the temperature range of investigation can be expressed by the equation:

$$(11)\quad \log p\ (\text{atm})\ [\text{total}] = \frac{-26917}{T} + 7.4033$$

Also included in Figure 4 is the calculated vapor pressure of pure uranium(20), and the total vapor pressure over uranium phosphide. Because

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20. E. G. Rauh and R. J. Thorn; J. Chem. Phys., 22, 1414 (1954).

of the different temperature dependences of the uranium pressures of $UP_{(s)}$ and $U_{(\ell)}$, the uranium partial pressure of UP will become equal to the vapor pressure of elementary uranium at 2400° K by direct extrapolation. This would imply that above 2400° K, neglecting the possible solubility of phosphorus in liquid uranium metal, the vaporization of UP becomes incongruent and can be expressed by reaction (1) and reactions (12) and (13)

$$(12) \quad UP_{(s)} = U_{(\ell)} + \frac{1}{x} P_x \qquad (x = 1 \text{ or } 2)$$

$$(13) \quad U_{(\ell)} = U_{(g)}$$

In fact the temperature at which the vaporization becomes incongruent would be lowered by the formation of a solid solution of phosphorus in liquid uranium metal.

The congruency of the vaporization below 2400° K may also need to be modified to account for a deviation from stoichiometry that apparently increases at high temperatures(8). Evidence of such a deviation from stoichiometry in this work is supported by the decrease in lattice parameter from 5.589 ± 0.001 Å at 1400°C to 5.584 ± 0.001 Å at 2000° C of the UP sample during vaporization and by the observations that there were slight decreases in total vapor pressure and in the p_P/p_U ratio as the vaporization proceeded. The secondary reactions with the container material which are discussed below may, however, also contribute to the latter observation. From the extrapolation of the total pressure to one atmosphere, a decomposition point of 3828° K for UP could be predicted on the same assumption of neglecting the phosphorus solubility in liquid uranium metal. Such an effect would actually lead to a significant decrease of the decomposition temperature, as was demonstrated in the U-UN system.(21)

An alternative approach is to calculate partial vapor pressures of monomeric and dimeric phosphorus at each temperature from the known dissociation energy of P_2(22) and the free energy functions of the phosphorus vapor species.(23) Table IV gives the typical results computed from the equilibrium constant of dissociation of P_2 and the experimental ratio of partial pressure of P to P_2 obtained from equations (8) and (9) at the corresponding temperature. The computed values are lower than the values from the silver calibration, and the discrepancy increases with temperature. The discrepancy is probably due to the uncertainties in the estimation of relative ionization cross sections and expecially due to possible temperature gradients in the effusion cell, since the sample is located near the black body hole at which the temperature was measured, whereas the temperature for which the P_2/P equilibrium is measured corresponds to the average temperature within the effusion cell. A deviation factor smaller than unity implies that the average temperature within the cell is higher than the temperature of the black body hole in the bottom of the cell. The increase in deviation factor from 1800° to 2200° K suggests, in addition, an increase of this temperature gradiant with increasing temperature.

The other independent approach is to evaluate the partial vapor pressures through the total weight loss of the sample during vaporization.

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21. J. Bugl, and A. A. Bauer; Reported at the Basic Science Division Meeting of the American Ceramic Society, October 1963.

22. Herzberg; Ann. Phys. Lpz., 15, 677 (1932).

23. R. L. Potter and V. N. DiStefano; J. Phys. Chem., 65, 849 (1961).

The intensity of each main species vaporized as a function of time was integrated as in the silver calibration, corrections for relative multiplier efficiencies and relative ionization cross sections were added. For UO, the rule of additivity was applied to estimate the ionization cross section relative to that of U. The amount of UO_2 evaporated according to equation (2) was determined to be 6.4 and 9.7 mole per cent for Series I and II, respectively, in the total weight of sample vaporized. This corresponds to 0.76 and 1.15 weight per cent of oxygen respectively, which represent the upper limit of oxygen content in the respective starting material because of the preferred decomposition of oxygen as UO. The weight loss of UP was corrected for the amount of UO_2 and was separated into the weight of P and U assuming the stoichiometry of UP. The sensitivities of each species calculated from the corresponding weight loss are presented in Table V, in which are also included those sensitivities obtained from the respective silver calibration, and the deviation factors between the two methods. The vapor pressure derived from the weight loss of uranium monophosphide is higher by one order of magnitude than that derived from the silver calibration in Series I, but in Series II the vapor pressures only differ from a factor of five for uranium and three to two for phosphorus. In Series IV the vapor pressures of phosphorus are even lower than the corresponding pressures obtained from the silver calibration. A possible explanation would be that a smaller portion of the uranium monophosphide vaporized did effuse through the Knudsen cell as compared with silver. This might be due to the vapor species of monomeric and dimeric phosphorus and uranium reacting with the tantalum cell and or have a relative higher rate of leakage through the lid and walls of the cell as compared with silver at the respective temperatures of measurements. The trend that the deviation decreases from Series I to IV reflects that a larger fraction of the vapor reacted with the cell in Series I and II and thus rendered the cell partially saturated, so that further reaction was at least slowed down. The differences among the individual deviation factors within each run might be due to the relative difference in the rate of reaction with the cell or of possible diffusion through the wall of the cell.

The observation in Series IV that the amount of phosphorus evaporated appears to be larger by a factor of five as that amount of phosphorus contained in the evaporated sample, is most likely due to the decomposition of the solid solution of phosphorus in the tantalum effusion cell as mentioned before. The evidence is reflected by the observation of the intensity ratio of P^+/UO^+ which increased drastically from 1/3 at 2000°K to approximately 20 at a temperature around 2300°K at the last stage of vaporization in Series IV. For checking this point, the amount of phosphorus that reacted with the effusion cell in the experiments prior to series IV was computed on the basis of weight loss and deviation factors listed in Table V and compared with the amount of excess phosphorus observed in Series IV. In this computation one run of the investigation of tantalum phosphide in the same effusion cell between Series II and III was also included. The amount of phosphorus evaporated in Series III was less than one per cent of that evaporated in Series IV and can, therefore, be neglected here. It was found that the amount of phosphorus taken up by the effusion cell prior to Series IV was the same within the limits of determination (2 per cent larger) as the amount in excess of the phosphorus evaporated from the UP-UO_2 mixture in Series IV. This computation also supports the explanation for the reaction between vapor and effusion cell and the trend of deviation factor in Table V.

We feel that in this investigation the vapor pressures obtained from the silver calibration are the most reliable ones. The loss of sample by preferred reaction with or diffusion through the tantalum cell does not significantly influence the actual pressure inside the cell, as obtained from the silver calibration, since the fraction of sample reacted is of order magnitudes smaller as the ratio of the inside surface of the cell to the effusion orifice. The true equilibrium vapor pressure would be only slightly higher if the reaction of part of the sample with the cell is taken into account.

A possible evaporation co-efficient smaller than unity would also reflect in too-low values for the measured vapor pressures. That the vaporization co-efficient is probably less than one is suggested from Table IV according to which the vapor pressures obtained from Series II and IV are somewhat lower than those in Series I. Because a very small area ratio of orifice to sample was used in Series I, the effect of a low evaporation co-efficient is estimated to be within the experimental error, therefore the vapor pressures measured were assumed to be approximately the equilibrium pressure for the evaluation of enthalpies and vapor pressure equations.

Acknowledgements

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Table I: Sensitivity of mass spectometer for different Knudsen cell geometries from silver calibration.

SERIES	I	II	III	IV*
Orifice Area, $cm^2 \times 10^3$	2.24	8.17	30.2	30.2
Clausing factor	0.685	0.676	0.668	0.668
Silver evaporated, mg	1.04	0.45	1.14	0.90
Integral, volt-min	500.1	226.72	550.25	395.95
Sensitivity, $\frac{amp}{atm} \times 10^{-4}$	1.0705	4.038	14.13	12.18

* UP - UO_2 mixture.

Table II: Summary of experimental multiplier efficiencies in units of 10^{-5}.

SPECIES	Ag^+	p^+	P_2^+	U^+	UO^+	UO_2^+
Series I	5.79	23*	----	17*	25*	----
Series II	----	14*	----	14*	19*	----
Series III	4.74	----	----	----	----	----
Series IV	4.72	12.7	14.1	9.06	9.72	10.8
Others**	4.67	13.1	14.8			

* Values highly uncertain due to low sensitivity of straight collector reading.

** On TaP sample investigated between series II and III.

Table III: Mass spectrometric data and partial pressures of gaseous species over UP. Orifice area: 2.24 x 10^{-3} cm^{-2}.

No.	T, °K	$10^4/T$, °K	$I_{obs.}$	$I_{corr.}$	P_{atm} x 10^{-7}	-log P_{atm}
			Species U^+			
			Orifice area: 2.24 x 10^{-3}	cm^{-2}		
51	2045	4.89	0.920	1.672	8.59	6.0659
54	2048	4.883	0.866	1.574	8.10	6.0916
63	2148	4.655	3.800	6.864	37.0	5.4312
71	2237	4.470	13.20	23.84	134.0	4.7829
86	2234	4.476	12.21	21.88	122.8	4.9108
103	1983	5.043	0.335	0.600	2.99	6.5242
104	1897	5.272	0.073	0.130	0.62	7.2091
109	1822	5.488	0.015	0.027	0.12	7.9115
110	2007	4.983	0.371	0.660	3.33	6.4781
115	2000	5.000	0.390	0.693	3.48	6.4578
116	2000	5.000	0.404	0.718	3.61	6.4425
117	2096	4.771	2.454	4.363	22.98	5.6387
124	2165	4.619	5.250	9.335	41.71	5.3798
125	1961	5.099	0.310	0.551	2.72	6.5661
128	1956	5.113	0.255	0.453	2.23	6.6521
129	1827	5.474	0.025	0.045	0.204	7.6898
			Species p^+			
48	2056	4.864	0.420	0.406	6.395	6.1942
49	2056	4.864	0.435	0.422	6.648	6.1773
62	2153	4.645	2.22	2.185	36.03	5.4434

Table III, Cont'd (1)

No.	T, °K	10^4/T, °K	$I_{obs.}$	$I_{corr.}$	Patm x 10^{-7}	-log Patm
70	2241	4.462	6.45	6.391	109.7	4.9598
85	2230	4.484	4.95	4.938	84.34	5.0740
90	2230	4.484	4.71	4.677	79.88	5.0976
91	2169	4.610	2.19	2.177	36.16	5.4417
96	2125	4.706	1.164	1.156	18.82	5.7255
97	2059	4.857	0.504	0.496	7.82	6.1068
102	1983	5.043	0.215	0.215	3.26	6.4865
106	1892	5.285	0.0474	0.0492	0.71	7.1474
107	1823	5.485	0.0171	0.0178	0.25	7.6107
112	1996	5.010	0.230	0.228	3.48	6.4579
114	2002	4.995	0.221	0.218	3.38	6.4714
119	2095	4.773	1.068	1.159	16.99	5.7697
120	2158	4.634	2.511	2.492	41.19	5.3852
121	2156	4.638	2.355	2.334	38.54	5.4141
127	1961	5.099	0.1155	0.1124	1.68	6.7734

Species P_2^+

37	1780	5.618	0.0075	0.0085	0.0655	8.1831
38	1782	5.612	0.005	0.0057	0.0437	8.3593
39	1845	5.420	0.014	0.0158	0.127	7.8969
41	1894	5.28	0.0285	0.0322	0.267	7.5740
42	1900	5.263	0.027	0.0305	0.254	7.5959
43	1927	5.189	0.0486	0.0549	0.411	7.3862
44	1939	5.157	0.048	0.0542	0.459	7.3381
45	1981	5.048	0.0918	0.1038	0.901	7.0454
46	1989	5.028	0.0924	0.1044	0.909	7.0412

Table III, Cont'd (2)

No.	T, °K	10^4/T, °K	I_{obs}	I_{corr}	P_{atm} x 10^{-7}	-log P_{atm}
47	2046	4.887	0.208	0.2351	2.103	6.6771
50	2056	4.864	0.194	0.2193	1.972	6.7051
55	2048	4.883	0.101	0.2159	1.933	6.7139
56	2048	4.883	0.190	0.2147	1.924	6.7158
57	2097	4.769	0.425	0.4803	4.403	6.3563
58	2097	4.769	0.420	0.4747	4.350	6.3615
59	2093	4.778	0.411	0.4645	4.250	6.3716
60	2148	4.655	0.804	0.9087	8.535	6.0688
61	2156	4.638	0.800	0.9042	8.522	6.0695
65	2148	4.655	0.765	0.8646	8.119	6.0905
66	2180	4.578	1.20	1.3562	12.93	5.8884
67	2172	4.604	1.164	1.316	12.49	5.9034
68	2229	4.486	2.13	2.407	23.46	5.6298
69	2229	4.486	1.968	2.224	21.68	5.6640
73	2237	4.470	1.563	1.767	17.28	5.7625
79	2237	4.470	1.41	1.594	15.59	5.8072
80	2237	4.470	1.401	1.583	15.49	5.8100
84	2227	4.490	1.317	1.489	14.49	5.8388
92	2164	4.621	0.632	0.714	6.76	6.1701
95	2117	4.724	0.355	0.401	3.71	6.4304
98	2057	4.861	0.1725	0.195	1.75	6.7561
101	1988	5.030	0.0741	0.084	0.73	7.1392
105	1888	5.297	0.017	0.019	0.16	7.8030
108	1818	5.501	0.005	0.006	0.044	8.3593
111	1993	5.017	0.0846	0.096	0.84	7.0783
113	1999	5.002	0.084	0.095	0.83	7.0805
118	2095	4.773	0.357	0.404	3.69	6.4324

Table III, Cont'd (3)

No.	T, °K	10^4/T, °K	$I_{obs.}$	$I_{corr.}$	$P_{atm} \times 10^{-7}$	-log P_{atm}
122	2156	4.638	0.691	0.781	7.36	6.1329
123	2160	4.629	0.667	0.754	7.12	6.1476
126	1965	5.089	0.030	0.139	1.19	6.9231

Table IV: Calculated partial vapor pressure of phosphorus from dissociation constant.

$$P_{2(g)} = 2P_{(g)}$$

$$K_p = p^2_P / p_{P2} = (p_P/p_{P2})\, p_P = (a)\,(p_P)$$

a = Experimental pressure ratio of p_P to p_{P2}.

$T^{\circ}K$	Dissociation Constant (23) $K_p \times 10^9$	Experimental Pressure, atm. x 10^9 P		Calculated Pressure, atm. x 10^9 P		Deviation Factor $p_{P\,calc.}/p_{P\,expt.}$
		P	P_2	P	P_2	
Series I						
1800	6.14	13.0	5.18	2.45	0.98	0.18
2000	170	370	98.9	45.5	12.1	0.12
2200	2600	5750	1100	497	95.5	0.086
Series II						
2075	503	520.0	170.1	164.9	54.0	0.32
2237	4074	3906	443.2	462.4	52.5	0.12
Series IV						
1800	6.14	4.23	4.57	6.61	7.12	1.56
2000	170	140	39.6	48.1	13.61	0.343
2200	2600	2448	659	672.7	181	0.275

Table V: Comparison of Sensitivities from Internal Calibration and Silver Calibration in units of atm./volt.

Species:	P^+	P_2^+	U^+
Series I			
From Silver Calibration	7.66×10^{-10}	4.37×10^{-10}	2.51×10^{-10}
From Weight Loss	3.38×10^{-9}	2.77×10^{-9}	3.22×10^{-9}
Deviation Factor	4.41	6.33	12.82
Series II			
From Silver Calibration	1.66×10^{-10}	9.63×10^{-11}	6.66×10^{-11}
From Weight Loss	3.86×10^{-10}	3.18×10^{-10}	3.31×10^{-10}
Deviation Factor	2.33	3.29	4.96
Series IV			
From Silver Calibration	5.49×10^{-11}	3.47×10^{-11}	2.21×10^{-11}
From Weight Loss	1.43×10^{-11}	1.18×10^{-11}	5.98×10^{-11}
Deviation Factor	0.22	0.34	2.71

List of Figure Captions

Figure 1

Ionization efficiency curves for uranium observed over UP-UO_2 mixture at different emission currents and temperatures.

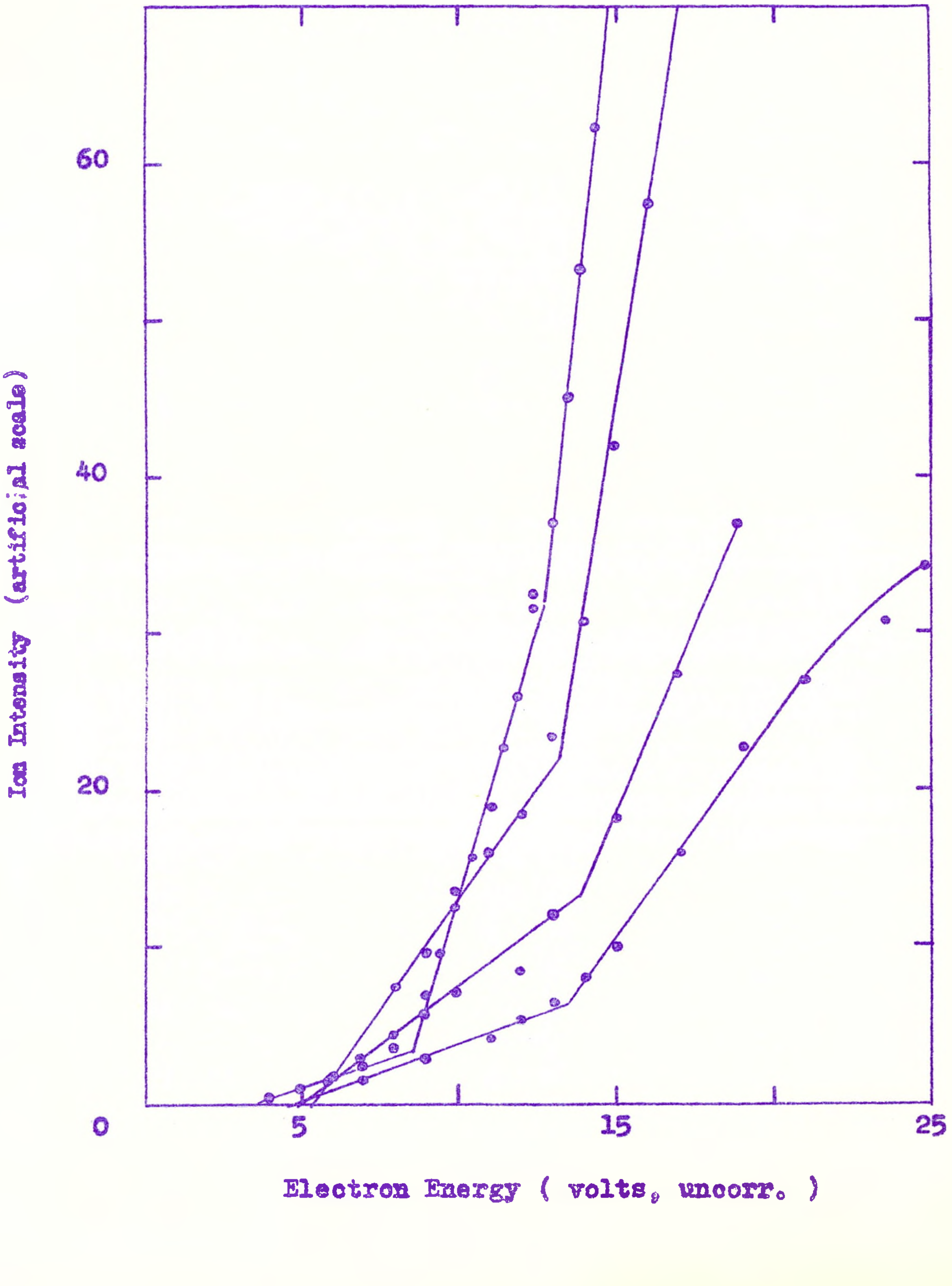


Figure 2

Ionization efficiency curves for singly charged uranium containing species observed over UP and UP-UO_2 mixtures.

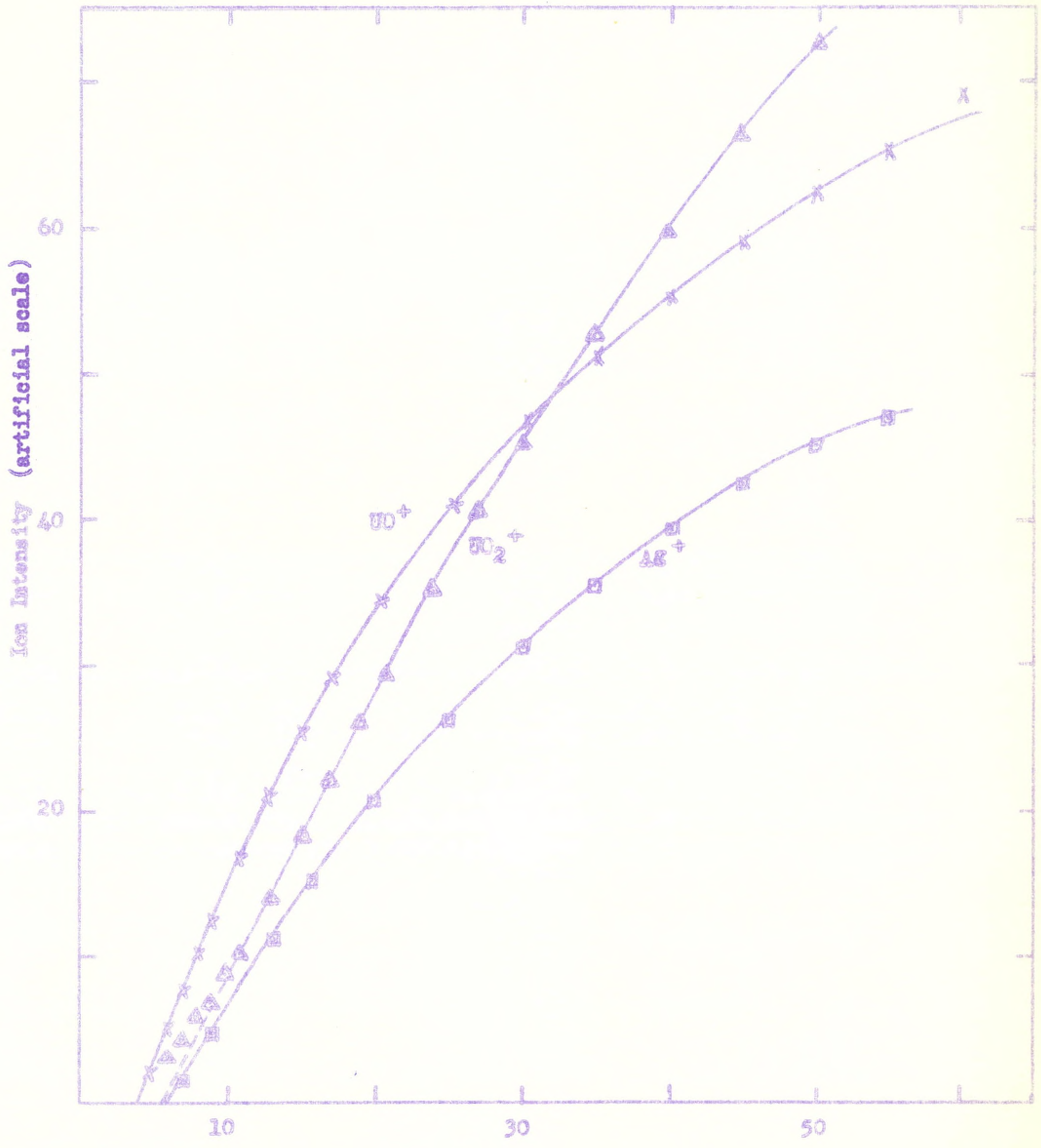


Figure 3

Ionization efficiency curves for doubly charged uranium containing species observed over UP and UP-UC_2 mixtures.

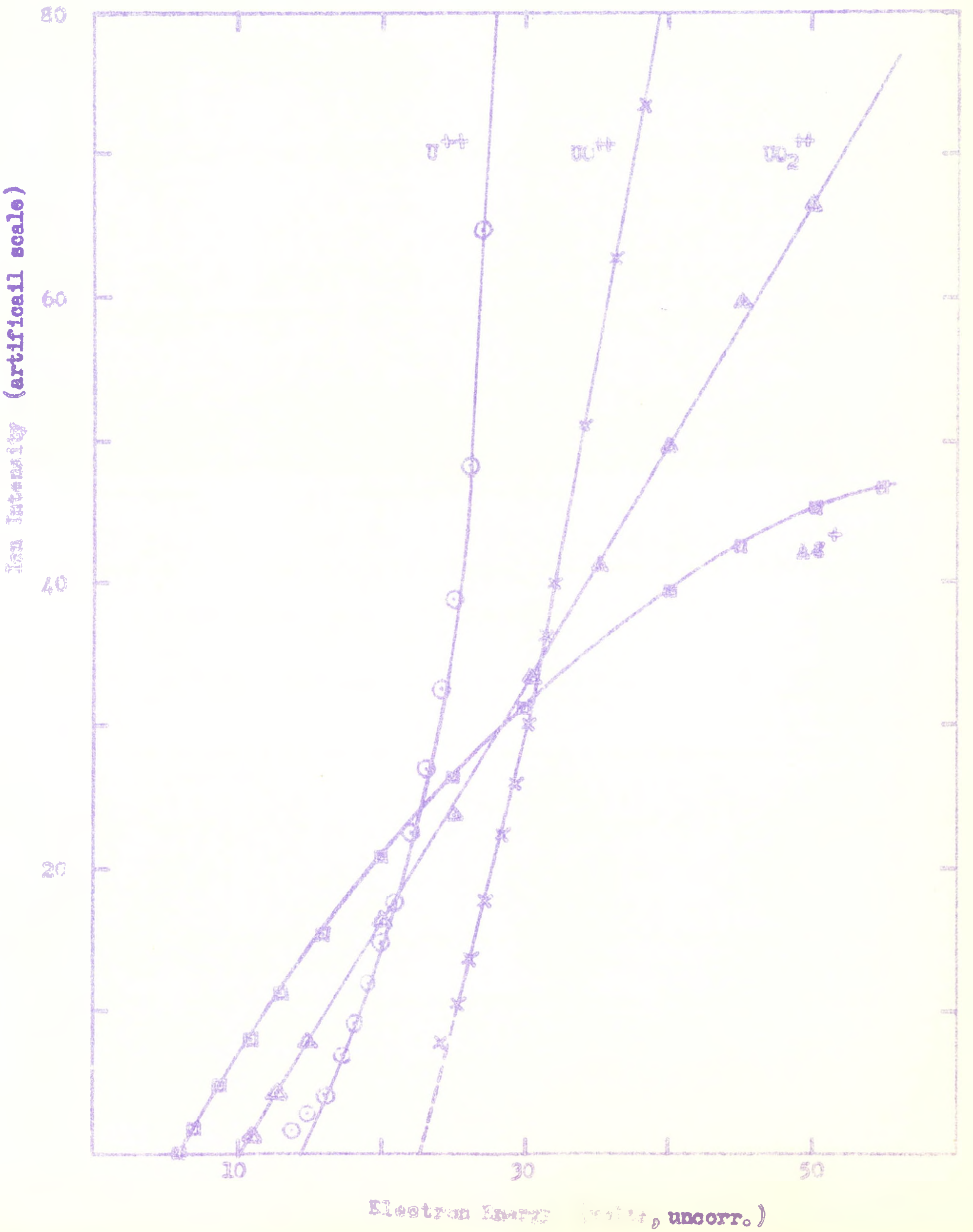
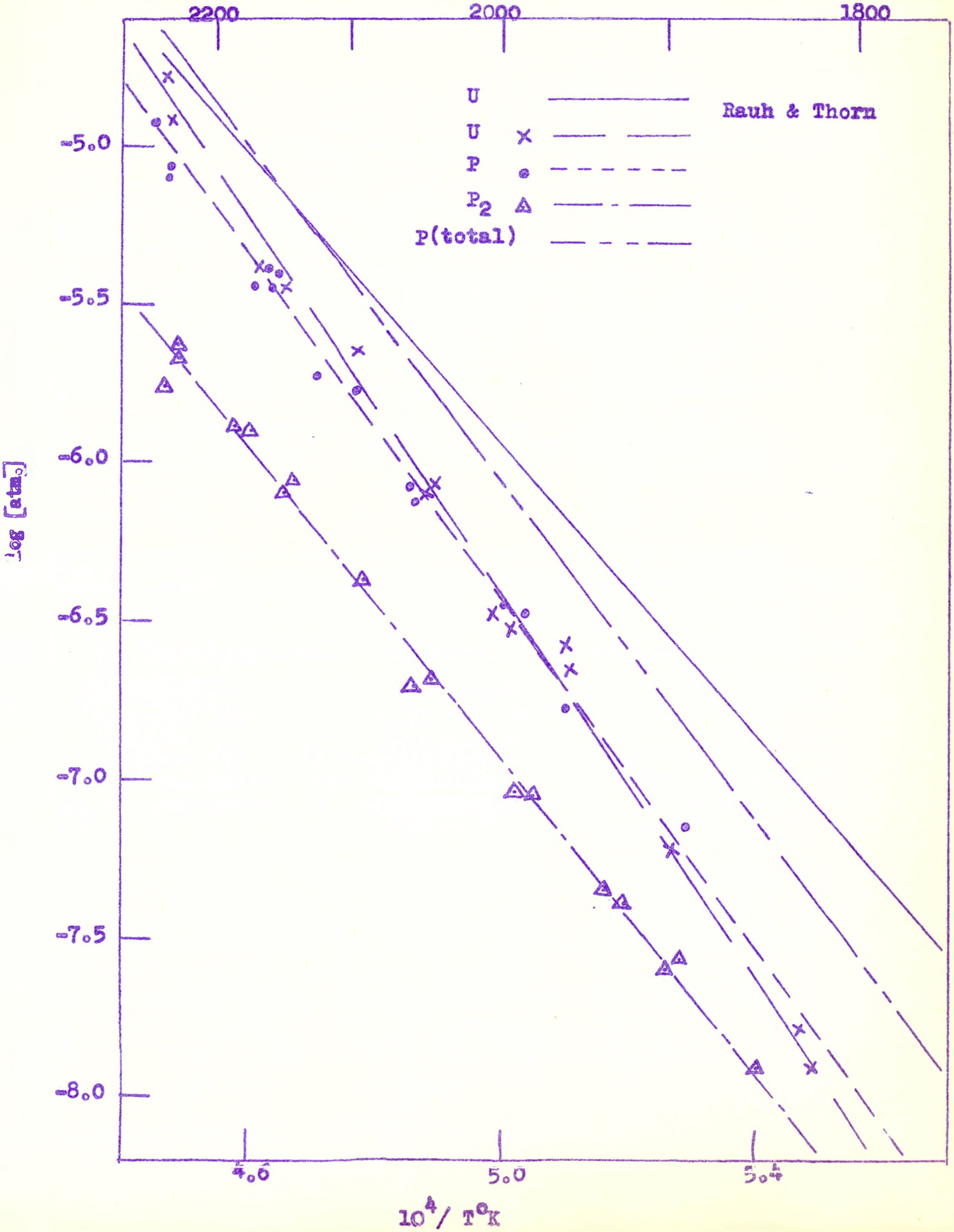


Figure 4

Variation of partial pressures of gaseous species and total pressure over UP as a function of temperature for Series I.



Paper 8

NOTES ON MASS SPECTROMETRIC STUDY OF UP - UO_2 SYSTEM* **

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by

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After we studied the vaporization of uranium monophosphide, UP, with the Knudsen effusion mass spectrometer setup, one additional run was made with a mixture of uranium monophosphide - uranium dioxide of approximately equimolar quantities. The purpose of this experiment was to investigate the function of oxygen contaminent in UP on vaporization, since the oxygen contaminent is usually present in the prepared uranium monophosphide sample.

The experiment conditions were the same as those reported in uranium monophosphide. The mainly gaseous species observed were P^+, P_2^+, U^+, UO^+ and UO_2^+. As indicated earlier, the main reactions involved were believed to be the following:

(1) $UP_{(s)} = U_{(g)} + \frac{1}{x} P_{x(g)}$ (x = 1 or 2)

(2) $UP_{(s)} + UO_{2(s)} = 2\ UO_{(g)} + \frac{1}{x} P_{x(g)}$ (x = 1 or 2)

(3) $UO_{2(s)} = UO_{2(g)}$

During this run, the ion intensities were high enough and a thorough measurement of multiplier efficiencies of the observed species was made and reported in the paper on uranium monophosphide. (1) From the analysis of appearance potentials, we got that 10% of UO was fragmentized to U^+ and O. By considering the same bond energy between U and O in UO and UO_2, we

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** Second part of paper submitted for discussion at the Symposium on Thermodynamics and Thermochemistry in Lund, Sweden, July 18-23, 1963 assumed that 10% of UO_2 was also fragmentized into UO^+ and O under the same ionization voltage. These corrections were then applied to correct the ion intensities of U^+, UO^+ and UO_2^+ respectively.

For correction of ion intensities of phosphorus species, P^+ and P_2^+, the same assumptions and procedures were followed as that in the UP system.

The ionization cross section for U was estimated as 55.7 from Otvos and Stevenson.(2) For UO and UO_2 the rule of additivity was applied in relation to U.

The ion intensities were correlated to vapor pressure through silver calibration associated in this experiment. The mass spectrometric data and the partial vapor pressures of the gaseous species observed over UP - UO_2 mixture are tabulated in Table I. Since the partial pressures of P, P_2 and U have been included in the discussion of UP system as Series IV, we only present the results of UO and UO_2 in Figure 1. The derived average values for partial molal heat of vaporization in kcal. per mole at 2000° K are as follows:

$$(4) \quad \Delta \bar{\bar{H}} \ (P) = 125.16 \pm 2.60$$

$$(5) \quad \Delta \bar{\bar{H}} \ (P_2) = 122.96 \pm 1.51$$

$$(6) \quad \Delta \bar{\bar{H}} \ (U) = 124.59 \pm 4.20$$

$$(7) \quad \Delta \bar{\bar{H}} \ (UO) = 118.50 \pm 4.13$$

$$(8) \quad \Delta \bar{\bar{H}} \ (UO_2) = 130.23 \pm 5.64$$

Where the uncertainties represent the standard deviations. From these values ΔH_{vap} in kcal. per mole of UP is obtained as 186.08 for reaction (1) when $x = 2$, and 249.76 when $x = 1$. These only differ from those obtained from the pure UP by 2.12 and 1.41 kcal., respectively. The temperature is linear within the limits of experimental errors, and thus can be expressed by the following equations:

$$(9) \quad \log p_{atm} [P] = \frac{-27351}{T} + 6.6812 \pm 0.0518$$

$$(10) \quad \log p_{atm} [P_2] = \frac{-26871}{T} + 6.0328 \pm 0.0579$$

$$(11) \quad \log p_{atm} [U] = \frac{-27227}{T} + 6.6217 \pm 0.0672$$

$$(12) \quad \log p_{atm} [UO] = \frac{-25896}{T} + 6.0327 \pm 0.0801$$

$$(13) \quad \log p_{atm} [UO_2] = \frac{-28459}{T} + 6.8203 \pm 0.0993$$

Because we used the largest effusion orifice in this experiment, the partial vapor pressures of P, P_2 and U are lower than those in Series I of UP system where the smallest orifice was used, but are approximately fallen into the same line as Series II of UP system$^{(3)}$ where the medium orifice was used. In the later case, the explanation would be that some phosphorus re-evaporated from the shield. The evidence is indicated from the analysis of shutter profiles of the gaseous species, which is summarized in Table II. About 2.1 to 8.7% of phosphorus was contributed to the shield re-evaporation, thus the obtained partial vapor pressures of P and P_2 are rather high.

The heat of sublimation of UO_2 according to reaction (3) is obtained as 130.23 ± 5.64 kcal at 2000° K, which is in fair agreement with comparison to the data of 137 kcal at 2000° K given by Rehn and Cefola$^{(4)}$ and 137.1 ± 1.7 kcal at 1800° K given by Ackermann, Gilles and Thorn.$^{(5)}$ Also included in Figure 1 is the calculated vapor pressure of UO_2.$^{(5)}$ Our pressure data for UO_2 is lower than that given by Ackermann et al by a factor of less than 2. As we employed a large effusion orifice, the equilibrium pressure should be a little higher than the measured pressure.

Table III gives the total ion intensity-time integrals of all gaseous species over UP - UO_2 mixture. The oxygen content in Up - UO_2 mixture was calculated to be 6.673% by weight. This corresponds to a mole ratio of UP to UO_2 in the original sample of 0.44 to 0.56, respectively. The relative ion intensity ratio of U : UO : UO_2 was, at the average temperature of 2100° K, found to be 1 : 9.49 : 3.31 which is comparable to the ratio of the same species in an approximately equimolar mixture of U and UO_2 that gives 1 : 10 : 1 at 1910° K observed by Achermann, Rauh and Thorn$^{(6)}$ and 1 : 13 : 1.7 observed by DeMaria et al.$^{(7)}$ Because there was more UO_2 in our system, the relative ion intensity of UO_2 observed is higher.

From the above arguments, we are primarily convinced that the function of oxygen impurities present in uranium monophosphide sample is reacted with UP on vaporization according to reaction (2), and in a mixture of UP and UO_2 when the mole ratio of UP and UO_2 is in equimolar, or UO_2 is in higher proportion, the reactions (2) and (3) would be occurred simultaneously and independently during the vaporization process.

REFERENCES:

1. See the author's paper, "Mass spectrometric Study of the Vaporization of Uranium Monophosphide", submitted for discussion in this meeting.

2. Otvos, J. W., and Stevenson, D. P., J. Am. Chem. Soc., 78, 546 (1956).

3. See Figure 5 of Reference (1).

4. Rehn and Cefola, Atomic Energy Commission Document CK-1240 (Jan. 1944), quoted from Reference (5).

5. Ackermann, R. J., Gilles, P. W., and Thorn, R. J., J. Chem. Phys., 37, 2693 (1962).

6. Ackermann, R. J., Rauh, E. G., and Thorn, R. J., J. Chem. Phys., 37, 2693 (1962).

7. DeMaria, G., Burns, R. P., Drowart, J., and Inghram, M. G., J. Chem. Phys., 32, 1373 (1960).

TABLE I: Mass spectrometric data and partial pressures of gaseous species over UP - UO_2

Orifice Area: 3.02×10^{-2} cm.^{2}

no.	T, °K	10^4/T, °K	I_{obs}	I_{corr}	$P_{atm} \times 10^{-7}$	-log P_{atm}
			Species P^+			
47	1958	5.107	0.855	0.685	0.74	7.1332
48	1958	5.107	0.858	0.691	0.743	7.1293
49	1877	5.328	0.203	0.158	0.16	7.7997
63	1824	5.482	0.076	0.056	0.056	8.2479
73	1906	5.247	0.399	0.311	0.33	7.4874
74	1913	~~[illegible]~~ 5.227	0.395	0.310	0.33	7.4872
88	1992	5.020	1.737	1.445	1.48	6.8294
89	2029	4.929	2.780	2.238	2.49	6.6031
90	2030	4.926	2.733	2.190	2.44	6.6123
91	2031	4.924	2.830	2.285	2.55	6.5936
102	2063	4.847	3.490	2.729	3.09	6.5098
103	2088	4.789	6.070	4.875	5.59	6.2526
110	2136	4.682	10.80	8.831	10.36	5.9846
111	2138	4.677	9.69	7.701	9.04	6.0437
112	2138	4.677	10.11	8.108	9.52	6.0214
			Species P_2			
27	1951	5.126	0.263	0.298	0.202	7.6953
28	1950	5.118	0.285	0.322	0.22	7.6619
45	1958	5.107	0.265	0.299	0.204	7.6910
46	1958	5.107	0.261	0.295	0.20	7.6977
51	1873	5.339	0.064	0.072	0.047	8.3287
52	1878	5.325	0.064	0.072	0.047	8.3270
61	1824	5.477	0.026	0.029	0.017	8.7632
62	1824	5.477	0.026	0.029	0.018	8.7284
64	1824	5.477	0.044	0.049	0.031	8.5065
65	1723	5.804	0.004	0.0044	0.0026	9.5795
66	1725	5.797	0.0035	0.004	0.0024	9.6247
67	1760	5.682	0.0086	0.0097	0.0059	9.2259
68	1766	5.663	0.008	0.009	0.0055	9.2562
69	1759	5.685	0.0082	0.0093	0.0057	9.2467
70	1835	5.450	0.039	0.044	0.028	8.5521
71	1840	5.435	0.037	0.042	0.027	8.5683
72	1908	5.241	0.134	0.152	0.0995	8.0019
75	1913	5.227	0.126	0.142	0.0945	8.0247
86	1992	5.020	0.452	0.511	0.353	7.4519
87	1992	5.020	0.446	0.504	0.349	7.4574
92	2029	4.929	0.828	0.936	0.660	7.1870
93	2031	4.924	0.824	0.931	0.657	7.1826
94	2031	4.924	0.859	0.971	0.685	7.1642
101	2057	4.861	1.185	1.339	0.957	7.0192
104	2105	4.751	1.818	2.055	1.503	6.8230
105	2102	4.757	1.858	2.100	1.533	6.8145
113	2132	4.690	3.04	3.346	2.545	6.5943

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TABLE I: cont

No.	T, °K	$10^4/T$, °K	I_{Obs}	I_{corr}	$P_{atm} \times 10^{-7}$	$-\log P_{atm}$
			Species U^+			
30	1951	5.126	0.438	1.457	0.628	7.2019
32	1951	5.126	00.409	1.361	0.587	7.2317
41	1951	5.126	0.396	1.319	0.568	7.2454
42	1951	5.126	0.367	1.121	0.483	7.3161
43	1962	5.097	0.380	1.265	0.548	7.2611
44	1961	5.099	0.390	1.298	0.562	7.2499
53	1878	5.325	0.089	0.287	0.119	7.9237
54	1877	5.328	0.089	0.288	0.120	7.9223
59	1824	5.482	0.030	0.098	0.039	8.4034
76	1913	5.227	0.186	0.601	0.254	7.5953
84	1989	5.028	0.616	1.952	0.858	7.0667
85	1992	5.020	0.622	1.972	0.867	7.0617
95	2033	4.919	1.113	3.527	1.584	6.8002
100	2059	4.857	1.66	5.261	2.393	6.6211
106	2101	4.760	2.469	7.825	3.631	6.4399
			Species UO^+			
31	1951	5.126	[illegible]	4.118	1.55	6.8108
38	1951	5.126	2.81	3.741	1.40	6.8526
39	1951	5.126	2.806	3.736	1.40	6.8533
40	1951	5.126	2.759	3.683	1.38	6.8592
55	1877	5.328	0.61	0.783	0.28	7.5485
58	1820	5.491	0.208	0.263	0.092	8.0355
77	1916	5.219	1.300	1.687	0.62	7.2064
83	1988	5.030	4.17	5.497	2.096	6.6786
96	2030	4.926	7.69	10.064	3.39	6.4055
99	2060	4.854	10.89	14.52	5.76	6.2399
107	2103	4.755	16.56	22.1	8.94	6.0486
115	2137	4.680	24.51	33.87	13.9	5.8564
116	2137	4.680	26.13	35.66	14.7	5.8339
			Species UO_2			
33	1951	5.126	0.6885	0.7650	0.242	7.61708
34	1951	5.126	0.6944	0.7716	0.244	7.61350
36	1951	5.126	0.6335	0.7039	0.222	7.65345
37	1951	5.126	0.624	0.6933	0.219	7.65975
56	1877	5.328	0.1113	0.1237	0.037	8.42527
57	1829	5.467	0.0362	0.0402	0.012	8.92482
78	1916	5.219	0.2544	0.2827	0.0876	8.05735
79	1916	5.219	0.2567	0.2852	0.088	8.05360
80	1916	5.219	0.260	0.2889	0.0895	8.04798
81	1977	5.058	0.880	0.9778	0.313	7.50487
82	1989	5.028	0.893	0.9922	0.319	7.49594
97	2030	4.926	1.518	1.687	0.554	7.25641
98	2055	4.866	2.445	2.717	0.903	7.04422
108	2103	4.755	3.89	4.322	1.57	6.80410
109	2136	4.682	7.02	7.800	2.53	6.59636

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TABLE II: Analysis of Shutter Profiles

Time	Temp, °K	Species	Intensity scale	Description
8:02	2137	UO	10 mv.	Completely regular, whole background is only 1.2/89 or 1.35% of total intensity
8:13	2130	U	10 v.	Completely regular, whole background is only 0.2/42 or 0.47% to 0.6/42 or 1.43%
9:00	1950	P^+	3 v.	Regular profile, background intensity is 17.5/76 or 23% of total intensity and maintains evenly over the whole range.
9:26	2104	P_2^+	10 v.	Profile almost regular. Background is 6/58 or about 10% of total intensity on one side and 10/58 or about 17% of total intensity on the other side, indication some shield reevaporization occurred. Correction factor 48/52= 0.92
11:48	2096	P^+	10v.	Rather regular profile. Background intensity 4.2/54.8 or 7.7% of total intensity, and slightly drops on the later side, no shield re-evaporization.
1:32	2211	P^+	30v.	Same profile as 11:48. Background intensity is 3.8/67.1 or 5.65%. Very little shield re-evaporization, (about 1.5/63.3 or 2.1%
2:31	2253	P^+	10 v.	Background intensity 5/94.5 or about 5.3% of total intensity on one side, to 5.7/94.5 or about 6% of total on the other side. Shield re-evaporization less than 3/89.5 or 3.35%.
2:54	2285	P_2^+	30 v.	Background 5.8/27.6 or 24 % of total intensity on one side of 6.6/27.6 or about 24% of total intensity on the other side. Shield re-evaporization less than 1.7/21.8 or 8.7%.

TABLE III. Total intensity-time area of gaseous species over UP-UO_2

Weight Loss 29.56 mg.

Species	P^+	P_2^+	U^+	UO^+	UO_2^+
Area, volt-min.	5856	1448	1652	11049	2897.4
Area, corr.*	5666.8	1626.3	971.4	9217.5	3219.3
Relative ratio			1.0	9.45	3.31

* Corrected for fragmentation and double ionization

Fig. 1

Variation of partial pressures of gaseous UO and UO_2 over $UP-UO_2$ as a function of temperature.