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Preparation and Properties of Thorium Monophosphide, ThP_{1-x}, and Phase Studies of the Partial System Th–ThP[1]

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Thorium monophosphide, ThP_{1-x}, has been prepared by three methods: by direct reaction between the elements over the temperature range 1400–1850°, by thermal degradation of Th_3P_4 over the temperature range 1100–2400°, and by solid state reaction between the various combinations of thorium, Th_3P_4 and ThP_{1-x}. Chemical analysis was used for thorium and phosphorus to determine the compositions of the samples. The phase relationships in the condensed partial system Th–ThP have been investigated by X-ray powder diffraction and mass spectrometric techniques. The only phosphide found in this composition range is the ThP_{1-x} phase which is coexistent with phosphorus-saturated thorium metal over the temperature range 1000–2000°. No intermediate phase could be detected. Thorium monophosphide, which crystallizes in the NaCl-type structure, was found to have an existence range of $ThP_{0.96}$ to $ThP_{0.55}$ at 1000°, with lattice parameters of 5.840 and 5.830 Å., respectively, at 26° for the boundary composition. Within the existence range the lattice parameter appears to be a linear function of composition. Evidence is given that at high temperatures the phosphorus-rich phase boundary in coexistence with Th_3P_4 shifts to a lower, and the thorium rich phase boundary to a higher, P/Th ratio. Thorium monophosphide is a blue substance with high chemical resistivity and a melting point of >2400°.

Introduction

In the system thorium–phosphorus two compounds have been reported by Strotzer, *et al.*,[4] Th_3P_4 and a subphosphide, ThP_n, that could, however, not be obtained free of thorium dioxide and Th_3P_4. The correct formula for the ThP_n phase was obscured by the presence of these other phases. These authors estimated the phosphorus-rich boundary as $ThP_{0.87}$ on the basis of chemical analysis of grains of ThP_n that could be separated under microscopic examination of a product containing Th_3P_4 and thorium dioxide. X-Ray investigations by Meisel[5] show that Th_3P_4 has a body-centered cubic structure of the $D7_3$ type with the space group $T_d{}^6$ and that ThP_n is face-centered cubic with a possible NaCl(B1)-type structure.

Tensiometric analysis of Th_3P_4 by Gingerich and Efimenko[6] showed that Th_3P_4 vaporizes incongruently by decomposition into the solid monophosphide and gaseous phosphorus and that the monophosphide has a broad homogeneity range estimated as $ThP_{0.9}$–$ThP_{0.7}$.

In this paper the preparation and properties of thorium monophosphide, ThP_{1-x}, and the study of the partial system Th–ThP are presented. In particular, methods suitable for the preparation of thorium subphosphide which require high-temperature techniques under inert conditions will be reported. The extent of the existence range of the ThP_{1-x} phase and its boundary compositions at 1000° were investigated by X-ray powder diffraction. In addition, mass spectrometric techniques were used for the study of the change in boundary compositions with temperature.

Experimental

(A) **Starting Materials.**—The thorium metal used was crystal bar prepared by the iodide process and obtained from Metal Hydrides, Inc., Beverly, Mass. The following certified spectrochemical analysis was supplied with the bars with the elemental impurities given in p.p.m.: Bar No. 93: B, 1; Si, 3; Mg, 3; Fe, 3; Cu, 4; Ti, 1; Al,2. Bar No. 96: B,7; Si, 13; Pb, 7; Mg, 4; Fe, 4; Ni, 27; Cu, 27; O_2, 86. Semiconductor grade (5N) red phosphorus was obtained from L. Light and Co., Ltd., Colnbrook, Bucks, England. As typical impurities in p.p.m.: C, <3; and others, total, <5, were quoted by the manufacturer. Thorium powder used in some preparations was made by forming the hydride from crystal bar thorium and purified hydrogen gas at 400° followed by degassing *in vacuo* at 900°.

(B) **Containers.**—Tungsten boats or crucibles were used for containers in most experiments, but thoria crucibles were also used in some Th_3P_4 preparations.

Although compact tungsten and phosphorus vapor reacted, the reaction was only superficial. At lower temperatures the reaction is most likely controlled by slow diffusion of phosphorus through a surface layer of tungsten phosphide; at higher temperatures, because of the low stability of tungsten phosphides, the reaction was confined to solid solution formation of phosphorus in tungsten. From semiquantitative tests the solubility of phosphorus in tungsten appears to be very small.

(C) **Synthetic Methods.**—Because of the high affinity of thorium and phosphorus to oxygen all heat treatments were performed under inert conditions.

(1) **Preparation of Th_3P_4.**—For the preparation of Th_3P_4 the elements were combined by the conventional Faraday method.[4] In this method the reactants are contained inside a sealed evacuated Vycor or fused silica tube that is kept at two different temperatures. The side of the tube containing the tungsten boat with the thorium metal was held at a convenient reaction temperature (800–1000°). The end containing the phosphorus was kept at 400° to provide a phosphorus pressure of about 1 atm. The reaction took several days to weeks. This method was found to lead ultimately to the formation of Th_3P_4 provided that sufficient or excess phosphorus is present; otherwise, some thorium remains unreacted and trace amounts of the subphosphide phase may be formed at the reaction layer.

(2) **Preparation of Thorium Monophosphide, ThP_{1-x}.**—Thorium monophosphide samples and equilibrated phase mixtures for

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[2] Battelle Memorial Institute, Columbus, Ohio.

[3] Part of this investigation has been performed as part of an M.S. thesis by D. W. Wilson. Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

[4] E. F. Strotzer, W. Biltz, and K. Meisel, *Z. anorg. allgem. Chem.*, **238**, 69 (1938).

[5] K. Meisel, *ibid.*, **240**, 300 (1939).

[6] K. A. Gingerich and J. Efimenko, "Thermodynamics of Nuclear Materials," International Atomic Energy Agency, Vienna, 1962, pp. 477–486.

values of $0 < x < 1$ in ThP_{1-x} were prepared by several high-temperature methods.

The high temperatures were generated by radiofrequency induction, with a 10-kw. Lepel generator at a frequency of 450 kc. The samples were maintained at temperatures constant to ±20° by a constant power setting of the generator. Temperature was measured by means of a calibrated disappearing filament-type optical pyrometer, which was used to observe a black-body hole in the top or bottom of the graphite block holding the crucible. In this way, black-body conditions were simulated. Temperature corrections were made for the intensity loss through the Pyrex top of the reaction tube and the mirror. To check the reliability of these corrections, the melting point of thorium was determined by heating thorium in 10° increments in a tungsten container and examining the powdered metal for melting. Melting was observed to occur at 1770 ± 10° after corrections were made, which is in agreement with the reported value[7] of 1755 ±10°.

(a) **High-Temperature Faraday Synthesis.**—The Faraday method[4] was modified for use up to 1850° utilizing induction heating. With induction heating the Vycor mantel is not heated to the reaction temperature as in the standard Faraday method; however, the cool end of the reacting tube was maintained at 400° by an auxiliary heater to maintain a constant phosphorus pressure. The experimental arrangement is shown in Figure 1. The tungsten crucibles which contained the samples were placed inside a graphite tube for support and better coupling conditions with the field produced by the induction coil. The containers, susceptor, and shields were inserted into a 38-mm. diameter Vycor tube and evacuated and sealed.

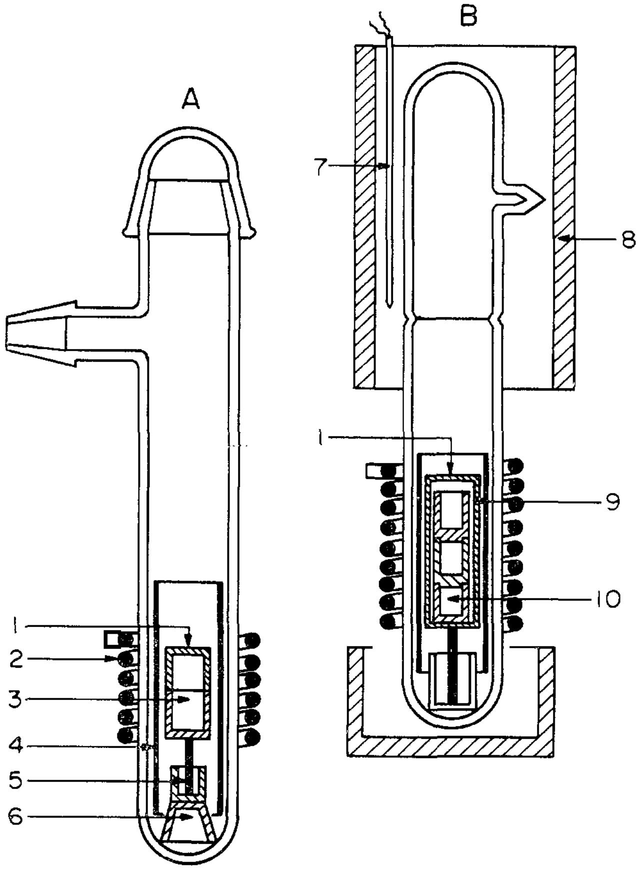

Figure 1.—Reaction tubes for thorium phosphide synthesis with induction heating: A, attachment for thermal degradation of Th_3P_4; B, apparatus for Faraday method; 1, black-body hole; 2, induction coil turns; 3, tungsten Knudsen cell; 4, ceramic tube heat shield; 5, tantalum support rod; 6, ceramic supports; 7, thermocouple; 8, 400° furnace; 9, graphite susceptor; 10, tungsten crucibles.

Faraday experiments were made with crystal bar and powdered thorium over the temperature range 1400–1850°. The crystal bar reacted very slowly at temperatures below 1700°. Five grams of crystal bar, treated for 3 days at 1600°, was found to take up all the phosphorus in a 1:1 atomic ratio but to contain a large amount of Th_3P_4 with the rest mainly metal. Some of the ThP_{1-x} phase was present on the surface of the bar. The same heat treatment using thorium powder instead of crystal bar gave the ThP_{1-x} phase and traces of Th_3P_4 using all the phosphorus (1:1). The lattice parameter of the cubic ThP_{1-x} phase resulting from the powdered thorium was 5.8345 ± 0.0003 Å. Powdered thorium at 1650° produced similar results. At 1850° the thorium powder and phosphorus reacted in a 1:1 ratio to give ThP_{1-x} and a small amount of Th_3P_4, but the lattice parameter of the ThP_{1-x} phase was 5.8340 ± 0.0002 Å.

The high-temperature modification of the Faraday method described in this investigation was not used to prepare single-phase thorium monophosphide samples. It is, however, considered to be a valuable tool for the preparation and phase studies involving high-melting metal compounds with reactive nonmetals of relatively high volatility. Its principal advantage appears to be that it permits synthetic work at temperatures high enough for attainment of equilibrium within a reasonable time period.

(b) **The Thermal Degradation of Th_3P_4.**—Th_3P_4 was degraded by heating at temperatures from 1000 to 2400° with continuous removal of evaporating phosphorus by pumping. The pumping system consisted of a PMC-720 4-in., three-stage oil diffusion pump backed by a mechanical pump. Pressures of the order of 4×10^{-6} mm. were consistently obtainable. The apparatus used in the degradation was of Vycor and is shown in Figure 1. The tungsten crucible containing a weighed sample rested on a pedestal of tantalum rod, inserted in zirconia crucible. The tungsten crucible was essentially a Knudsen cell with a comparatively large orifice which served as a black-body hole. A zirconia or alumina tube surrounding the Knudsen cell served as a radiation and heat shield.

It was possible to operate continuously below 2000° for several hours. Above this temperature, the Vycor softened from excessive heating, and, therefore, the reaction setup was only used for short periods of time. The ThP_{1-x} phase was not melted at temperatures that were in excess of 2400°. The composition of the end product was determined by weight loss, assuming all to be due to phosphorus loss, or by chemical analysis.

The degradation method was found useful as a means of preparing larger subphosphide samples for experimental use. High-purity homogeneous samples of the ThP_{1-x} phase were made by degradation of Th_3P_4 above 1500° for several hours. Below this temperature the reaction did not produce a single-phase sample unless the heat treatment was extended to longer periods of time. Degradation at 1850° for 12 hr. followed by degradation at 2000° for 2 hr. produced a sample analyzed as $ThP_{0.68}$ with a lattice parameter 5.8330 ± 0.0003 Å. This composition is the lowest phosphorus content obtained by direct degradation of Th_3P_4.

(3) **The Pellet Method.**—For the study of the phase relationships in the composition range Th–ThP, samples of a defined P/Th atomic ratio were prepared by annealing mixtures of the appropriate phases at the desired temperature in the form of pressed pellets.

For the study of the composition range Th–$ThP_{0.75}$, 325 mesh thorium powder and 325 mesh $ThP_{0.75}$ were mixed in an agate mortar and pressed inside the inert gas box into a pellet. For samples with an atomic P/Th ratio larger than 0.75 phase mixtures of $ThP_{0.75}$ and Th_3P_4 were used. Other pellets in the range of bulk composition $ThP_{0.90}$ to $ThP_{1.10}$ were made from samples obtained by degrading Th_3P_4 to the intermediate compositions, but under conditions such that the sample contained both phases. These degradations of the Th_3P_4 were carried out in the temperature range 1100–1300° for short periods of time,

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(7) P. Chiotti, *J. Electrochem. Soc.*, **101**, 567 (1954).

up to 1 hr., and the resulting bulk composition was determined from the weight loss.

The heat treatment of the pellets was begun by holding the temperature at 600° for several hours and then raising the temperature slowly to the final temperature, at which the pellets were annealed for at least 1 day and up to several days. The pellets treated at or below 1000° were contained in tungsten boats and sealed in Vycor tubes under vacuum. At the end of each heat treatment they were quenched by dropping the Vycor tube into water. Above 1000°, where induction heating was used, the pellets were placed in a tantalum cup lined with tungsten sheet. The cup was inserted in a graphite tube which served as a susceptor. In these heat treatments the same reaction vessel was used with a running pump as in the degradation experiments. At the end of the heat treatment the samples were quenched by turning off the power of the induction generator.

(D) **Mass Spectrometry.**—The experimental conditions used for the mass spectrometric investigation of thorium phosphides have been described previously.[6] The interpretation of mass spectrometric data for determining terminal compositions of compounds with a marked range of composition has been shown elsewhere.[8]

At all temperatures more than 95% of the ionic species originating from the thorium phosphide sample were either P^+ or P_2^+. At temperatures below 1400° P_2^+ was by far the predominant primary species.[6] From the analysis of the ionization efficiency curve, P_2^+ was identified as a primary species, originating from P_2. Approximately 10% of the primary P_2 are fragmented by 55-e.v. electrons, to produce P^+.[9] The ion intensity measured at any stage of the thermal decomposition was correlated to the corresponding P/Th ratio of the solid by correlating the total weight loss of the sample to the total ion intensity–time integral of the P^+ and P_2^+ observed. The weight loss of the sample was corrected for the loss due to thorium-containing species. The fragmentation pattern of the phosphorus species was considered. The influence of P_4 was neglected because its concentration in the vapor, when observed, was always less than 1 vol. %.

(E) **X-Ray Diffraction.**—Room-temperature X-ray diffraction patterns were taken with a 114.6-mm. Straumanis-type camera and Cu Kα radiation. The exposure times were usually 12 hr. A 57.3-mm. camera was used in many cases for qualitative studies and phase identification, which reduced the exposure times to 3 hr. For the precision lattice parameter determinations, the 114.6-mm. camera was used exclusively. The samples were 325 mesh powders sealed in Lindemann glass capillaries of 0.03 mm. diameter. A Norelco X-ray diffractometer was also used to examine samples for the phases present and for the examination of relative intensities of peaks within a given sample.

For the determination of the lattice parameters a, the 2θ values that did not resolve the Cu Kα radiation into α_1 and α_2 components were assigned d values using a Cu Kα wave length of 1.5418 Å., which is the weighted average of the Cu Kα_1 (1.54050 Å.) and Cu Kα_2 (1.54434 Å.). The lattice parameters were determined by making use of the α_1 reflections and the Nelson–Riley[10] graphical extrapolation function.

Most of the samples gave diffraction patterns with well-defined α_1–α_2 splitting in the high-angle region. The α_1 lines of known *hkl* were used to evaluate the lattice parameters on the IBM 7074 computer. The computer program carried out Cohen's[11] least-squares treatment. Where the α_1–α_2 splitting was defined, the lattice parameter was determined to within about 0.5 part per ten thousand. When the samples were in the two-phase regions the reliability of the lattice parameter determinations is limited by the necessary choice of low-angle lines to carry out the measurements, and the precision drops to about 2 parts per ten thousand. All lattice parameters correspond to a temperature of 26 ± 3°.

(F) **Chemical Analysis.**—The composition of the thorium phosphide samples could be calculated from the weight gain or loss by assuming the weight change to be due to the addition or loss of only phosphorus. The absence of extra lines on a diffraction pattern was used to verify the absence of impurity phases. The most likely impurity that could be picked up in the course of preparation is oxygen. A comparison of diffraction patterns with the chemically analyzed samples indicated that thorium dioxide lines were visible when the sample contained as little as 1% of thorium dioxide.

Chemical analysis was carried out to determine both the thorium and phosphorus contents of the samples. The detailed procedure has been described elsewhere.[12]

Dissolution of phosphides in concentrated nitric acid and potassium permanganate yielded a small amount of yellow residue identified by X-ray diffraction as thorium dioxide and estimated to be less than 2 wt. % of the starting material. Control experiments on the analytical method indicated that thorium determinations were consistently low by 0.5 rel. %, and phosphorus values were between 0 and 1 rel. % too low. Taking into account the systematic errors, the atomic ratio P/Th in the composition range $ThP_{0.5}$–$ThP_{1.33}$ could be determined within ±0.02. Contamination of the samples with tungsten from the containers was shown to be negligible by spectrochemical analysis of a thermally degraded Th_3P_4 sample.

Results and Discussion

(A) **Preparation.**—In Table I the conditions under which various thorium monophosphide samples were prepared by thermal degradation of Th_3P_4 and the results of chemical and X-ray diffraction analysis of the products are given.

The X-ray diffraction patterns of the products of degradation experiments performed at 1300° or at a lower temperature show that the Th_3P_4 phase was still present. In all X-ray film patterns with the exception of that for sample No. D-6 one or several of the strongest reflections of thorium dioxide could be observed.

A noteworthy characteristic of all products of the degradation of Th_3P_4 was that the lattice parameter of the ThP_{1-x} phase usually varied between 5.833 and 5.834 Å., and the X-ray films of the samples showed well-resolved back-reflection lines even when Th_3P_4 was present.

For the samples for which a chemical analysis was available, the P/Th ratio of the ThP_{1-x} phase agreed with that calculated from the weight loss of Th_3P_4 under the assumption that no impurities are present, within ±0.02. From the difference to 100% of the sum of the analytical values for thorium and phosphorus estimates as to the amount and influence of impurities can be made. Considering that each the phosphorus and thorium values tends to be 0.5 rel. % too low, and excluding sample D-5, this difference is 1 ± 0.7 wt. %. Most likely this difference is due to insoluble ThO_2 as evidenced from X-ray diffraction analysis of the ThP_{1-x} samples and from the observation and identification of the insoluble residue of ThP_{1-x} samples. From this it can be deduced that under the experimental conditions applied no thorium oxyphosphides are formed and

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(8) K. A. Gingerich in "Advances in Mass Spectrometry," Vol. III, Institute of Petroleum, London, in press.

(9) K. A. Gingerich, *J. Phys. Chem.*, **68**, 768 (1964).

(10) J. B. Nelson and D. P. Riley, *Proc. Phys. Soc.* (London), **57**, 166 (1945).

(11) M. U. Cohen, *Rev. Sci. Instr.*, **6**, 68 (1935).

(12) D. W. Wilson and K. A. Gingerich, *Anal. Chem.*, in press.

Table I

Samples Prepared by the Thermal Degradation of Thorium Phosphides under High Vacuum

		Degradation		Description of the product				
Sample	Starting[a] material	Time, hr.	T, °C.	Wt. % by anal. Th	Wt. % by anal. P	Formula[b] ThP_n	Phases present[c] (in addition to ThP_{1-x})	ThP_{1-x} lattice parameter, Å.
6A	Th_3P_4 (6)	6	1275			$ThP_{0.87}$ (W)	ThO_2, Th_3P_4	5.834
6B	Th_3P_4 (6)	6	1175			$ThP_{0.92}$ (W)	ThO_2, Th_3P_4	5.834
6C	$ThP_{0.92}$ (6B)	5	1300			$ThP_{0.85}$ (W)	ThO_2	5.833
12	Th_3P_4 (B-3)	12	1700	89.45	9.08	$ThP_{0.76}$ (C)	ThO_2	5.8334 ± 0.0005
13	Th_3P_4 (B-3)	12	1850	90.20	8.19	$ThP_{0.68}$ (C)	ThO_2	5.8330 ± 0.0003
		2	2000					
D-1	Th_3P_4 (B-4)	5	2000	89.46	8.95	$ThP_{0.75}$ (C)	ThO_2	5.8331 ± 0.0004
D-5	Th_3P_4 (B-5)	5	1200	86.30	10.58	$ThP_{0.92}$ (C)	Th_3P_4, ThO_2	5.8341 ± 0.0005
D-6	Th_3P_4 (B-5)	2	1200	86.92	11.61	$ThP_{1.00}$ (C)	Th_3P_4	5.8343 ± 0.0004

[a] The notations for the Th_3P_4 starting materials refer to Table 1 of the thesis by D. W. Wilson.[3] [b] W means that the formula was arrived at by the weight loss method. [c] As determined by the presence of lines on the X-ray power pattern.

that the possible formation of tungsten–thorium–phosphorus alloys must be negligible. The latter has been supported for a degraded sample by spectrochemical analysis, in which within the detection limit of 100 p.p.m. no tungsten was found. It can also be deduced that if part of the oxygen present is dissolved in the thorium monophosphide, its amount must be below 1 atomic %.

It should be noted that a thorium dioxide content of 1% corresponds to an oxygen content of only 0.12%. In similar high-temperature preparations involving a highly reactive transition metal the oxygen content of the product is rarely specified by the investigators and is assumed to be frequently higher. Nevertheless, in the course of preparing thorium monophosphide samples in the two-step process described the oxygen content has increased from the 100 p.p.m. level to approximately 1000 p.p.m. for the purest samples. Such an oxygen pickup may be due to diffusion of air through the Vycor walls during the extended heat treatment, to degassing of Vycor walls, containers, and heat shield during preparation, and to a possible oxygen pickup by the red phosphorus prior to its use.

The starting materials for the pellet preparations were chemically analyzed for thorium and phosphorus. The Th_3P_4 was of composition $ThP_{1.33}$. No ThO_2 was detected by X-ray diffraction analysis in the powdered thorium and in Th_3P_4. The $ThP_{0.75}$ sample (D-1 in Table I) was estimated to contain less than 1.7% ThO_2, and its X-ray pattern contained two very weak low-angle lines attributed to ThO_2. The X-ray patterns of subsequent pellets did not contain these lines, probably due to the dilution factor and increase in background on the films. The oxygen impurity of the pellets was estimated, therefore, to be less than 0.2%.

(B) **Phase Studies in the Region Th–ThP_{1-x}.**—In all samples prepared by the pellet method at 1000° the ThP_{1-x} phase was present (see Table II). The lattice parameter of this phase was found to change with bulk composition over the range $ThP_{0.6}$ to $ThP_{0.9}$, indicating a broad range of existence for this phase. Compositions richer in thorium in the bulk formula which were equilibrated at either 1000 or 1400° were found to give a constant lattice parameter of a 5.830 ± 0.001 Å., indicating coexistence of this phase with another condensed phase. In compositions with P/Th atomic ratios smaller than 0.5, this phase appeared to be thorium metal. All X-ray diffraction lines in pellets prepared at 1000 or 1400° could be attributed to either metallic thorium or the ThP_{1-x} phase. This indicates that no additional phase exists in this temperature and composition region.

Table II

Lattice Parameters and Compositions for ThP_n Pellets Annealed at 1000°

Pellet no.	Composition	Lattice parameter, Å., for ThP_{1-x} phase	Phases present
	Pellets Made by Annealing Th + $ThP_{0.75}$		
1	$ThP_{0.30}$	5.8302 ± 0.0012	Th, ThP_{1-x}
2	$ThP_{0.38}$	5.8298 ± 0.0014	Th, ThP_{1-x}
3	$ThP_{0.50}$	5.8300 ± 0.0010	Th, ThP_{1-x}
4	$ThP_{0.55}$	5.8300 ± 0.0010	ThP_{1-x}
4a	$ThP_{0.55}$	5.8302 ± 0.0005	ThP_{1-x}
5	$ThP_{0.59}$	5.8320 ± 0.0002	ThP_{1-x}
6	$ThP_{0.67}$	5.8331 ± 0.0005	ThP_{1-x}
7	$ThP_{0.61}$	5.8313 ± 0.0005	ThP_{1-x}
8	$ThP_{0.65}$	5.8316 ± 0.0004	ThP_{1-x}
	Pellets Made by Annealing $ThP_{0.75}$ + Th_3P_4		
9	$ThP_{0.83}$	5.8363 ± 0.0003	ThP_{1-x}
10	$ThP_{0.85}$	5.8374 ± 0.0003	ThP_{1-x}
11	$ThP_{0.90}$	5.8379 ± 0.0004	ThP_{1-x}
12	$ThP_{0.95}$	5.8390 ± 0.0007	ThP_{1-x}
	Pellets Annealed from Degraded Th_3P_4 samples		
13	$ThP_{0.98}$	5.8400 ± 0.0010	ThP_{1-x}, Th_3P_4
14	$ThP_{1.00}$	5.8398 ± 0.0007	ThP_{1-x}, Th_3P_4
15	$ThP_{1.11}$	5.8398 ± 0.0012	ThP_{1-x}, Th_3P_4

The diffraction lines of thorium metal were visible on some X-ray films, but they never appeared strong or well-resolved; thus, the effect of phosphorus on the lattice parameter of thorium metal could not be determined. When the pellets were pulverized in the agate mortar, some small particles were found to be soft and malleable. These were, no doubt, thorium that may have sintered into larger masses from the powder, or may they have formed by eutectic melting of the thorium.

In order to obtain information on the extent of the two-phase region a series of pellets heat treated at 1400° was analyzed by means of the diffractometer for the relative amounts of the two phases present. The poor resolution of the thorium and the possibility of poor sampling because of sintered thorium are effects that would be of less hindrance in X-ray analysis by the diffractometer.

The diffractometer pattern of thorium is characterized by an intense peak at $2\theta = 30.5°$. The ThP pattern has two peaks at nearly equal intensity at $2\theta = 30.7°$ and $2\theta = 26.5°$. The diffractometer patterns of a phase mixture of ThP_{1-x} with traces of thorium metal showed the presence of the thorium by changing the relative intensities of the two ThP_{1-x} peaks. This is because of the overlap of the thorium peak with the ThP_{1-x} peak at $2\theta = 30.7°$. The relative intensities of these peaks were measured by counting the areas under the peaks and the intensity ratios ThP_{1-x}/Th obtained. These intensity ratios for each composition are plotted *vs.* composition in Figure 2.

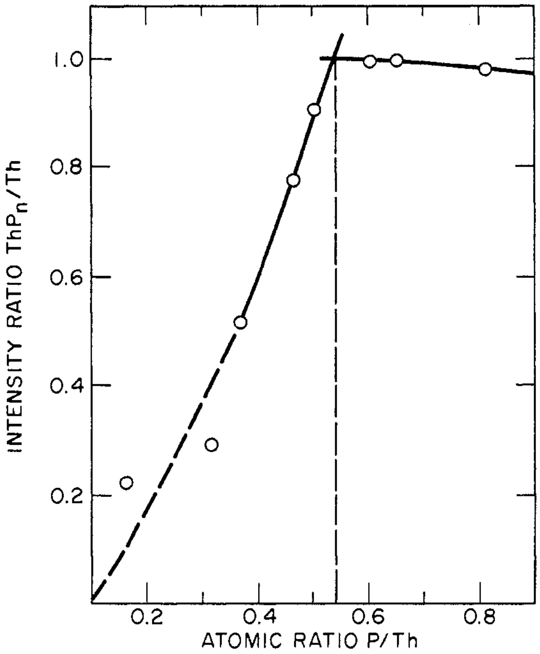

Figure 2.—X-ray intensity–composition relation for $Th-ThP_{1-x}$ mixtures annealed at 1400°.

Extrapolation of the two curves that represent the single-phase and two-phase areas to a point of intersection results in a composition of $ThP_{0.54}$ which thus represents the boundary of the ThP_{1-x} phase at 1400°. The accuracy of the P/Th ratio for this terminal composition is estimated to be 0.54 ± 0.04. Extension of the line in the two-phase area indicates that a zero intensity ratio occurs at $ThP_{0.1}$ rather than at the origin. This could be interpreted that the thorium in equilibrium with $ThP_{0.54}$ has about 10 atomic % phosphorus dissolved in it; but, in view of the large scatter observed in Figure 2 for the dotted part of the curve, this is a highly qualitative conclusion. Taking in addition the observed ductility of the thorium metal particles into account, the solubility of phosphorus is estimated to be considerably smaller than 10 atomic %.

An indication of a solubility of phosphorus in liquid thorium metal at 2000° has been found in the mass spectrometric study of a $Th-ThP_{1-x}$ mixture.[13] Preliminary evaluation of the partial pressure of primary thorium observed over this sample shows that it is considerably lower than the vapor pressure of liquid thorium metal calculated from data given by Stull and Sinke.[14] The observation of primary thorium in the saturated vapor above this two-phase mixture also indicates that liquid thorium and ThP_{1-x} coexist at 2000°.

(C) The Thorium Monophosphide Phase, ThP_{1-x}. (1) The Existence Range of the ThP_{1-x} Phase at 1000°. —The existence range of the ThP_{1-x} phase at 1000° was determined by the parametric method from samples prepared by the pellet method. The lattice parameters are listed in Table II. In Figure 3 they are plotted as a function of P/Th ratio in the bulk sample. From Figure 3 it can be seen that within the accuracy of measurement there is linear change of lattice parameter with composition starting with the composition $ThP_{0.55}$ up to $ThP_{0.96}$. At P/Th ratios larger than 0.96 the lattice parameters were constant at $a = 5.840$ Å., and at P/Th ratios smaller than 0.55 they were constant at $a = 5.830$ Å.

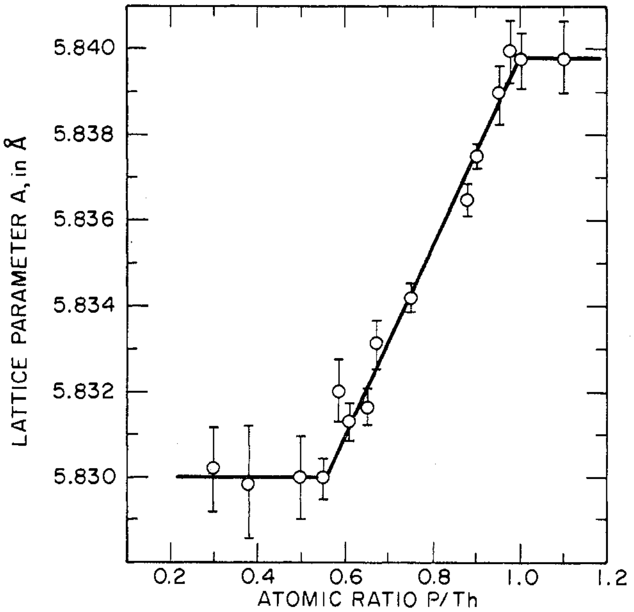

Figure 3.—Lattice parameter–composition relation for the ThP_{1-x} phase at 1000°.

It was observed that the lines on films corresponding to samples with the two phases were not as sharp as those of samples within the single phase region, although the pellets were annealed for at least 3 days and in several cases 14 days. This is reflected in the lower accuracy of the lattice parameters as seen from Figure 3 and Table II. In order to check the influence of annealing time, two new pellets, no. 7 and 8, were prepared and annealed for 3 weeks, and the contents of pellet no. 4 were pressed and annealed for 3 additional weeks (no. 4a). The resultant X-ray patterns were of a much

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(13) K. A. Gingerich, unpublished work.

(14) D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D. C., 1956, p. 206.

better quality in the back-reflection region, and the lattice parameters were easily determined from the α_2 lines by the usual technique. These results would indicate that equilibrium has been attained in the samples by increasing the time of the heat treatment. The lattice parameters obtained from these latter pellets with respect to the parameter–composition relationship are in agreement with the earlier ones. The apparent deviation of the lattice parameter of sample no. 5 ($ThP_{0.59}$) is probably due to incomplete equilibration.

From the evidence given in Figure 3 the ThP_{1-x} phase extends at 1000° between the compositions $ThP_{0.55\pm0.03}$ and $ThP_{0.96\pm0.03}$, excluding the ideal P/Th ratio of unity that would be expected from a compound that crystallized with NaCl-type structure.

(2) The Influence of Temperature on the Existence Range of ThP_{1-x}. **(a) The Phosphorus-Rich Boundary Composition.**—Preliminary conclusions with respect to the change in the phosphorus-rich boundary composition of thorium monophosphide can be drawn from the Faraday synthesis experiments at high temperature. As shown above the high-temperature Faraday synthesis of thorium and phosphorus in an atomic ratio of 1:1 always produces Th_3P_4 in addition to the ThP_{1-x} phase. The small amount of ThP_{1-x} and the unreacted crystal bar thorium observed after 3 days at 1600° obviously show that under these conditions equilibrium between the condensed phases was not attained. With thorium powder, however, all metal had reacted. The larger reaction surface area and the thinner product layers involved apparently lead to a much more rapid attainment of equilibrium between the condensed phases, and it may be assumed that the amount of Th_3P_4 observed in the products of synthesis from powdered thorium metal and the composition of the ThP_{1-x} phase correspond closely to true equilibrium conditions.

As a result the boundary composition of the ThP_{1-x} phase which is coexistent with the Th_3P_4 phase can be obtained from its lattice parameter, using the established parameter–composition relationship shown in Figure 3. The lattice parameter $a = 5.8345 \pm 0.0003$ Å. obtained for 1600° corresponds to a boundary composition $ThP_{0.77\pm0.04}$, and the lattice parameter $a = 5.8340 \pm 0.0002$ Å. obtained for the sample prepared at 1850° would indicate a boundary composition of $ThP_{0.73\pm0.3}$. These results show that there is a significant shift in the phosphorus-rich boundary composition of the ThP_{1-x} phase with increasing temperature.

Additional evidence for such a shift is obtained from mass spectrometric evidence. Part of a sample of $ThP_{0.92}$ (no. 6B in Table I) that passed through a 325 mesh sieve was degraded in the Knudsen effusion–mass spectrometer assembly to $ThP_{0.90}$, as determined from the weight loss. Prior to the degradation in the mass spectrometer, the sample contained a trace of Th_3P_4 as evidenced from the X-ray diffraction pattern. In the product $ThP_{0.90}$, no Th_3P_4 could be detected, while no measurable change of lattice parameter was observed for the ThP_{1-x} phase.

The functionality observed between the P_2^+ ion intensity (which at constant temperature is proportional to the corresponding P_2 partial pressure) and the P/Th bulk ratio of the sample indicates a boundary composition of $ThP_{0.91}$ for 1340 ± 40°.[13] This conclusion would require equilibrium between the solid and gaseous phases. An uncertainty in this value rests in the accuracy of the knowledge of the P/Th ratio at the beginning of the experiment, which is estimated to be ±0.03.

(b) The Thorium-Rich Boundary Composition.—Evidence with respect to the influence of temperature on the thorium-rich phase boundary of the ThP_{1-x} phase can be obtained from X-ray diffraction experiments. As shown above, the boundary composition for the thorium-rich terminal solid solution of the ThP_{1-x} phase at 1000°, as determined by the parametric method, is at $ThP_{0.55\pm0.03}$. The boundary composition obtained for 1400° by the phase disappearance method was found to be $ThP_{0.54\pm0.04}$. Within the experimental error of the methods used, there appears to be no difference in this boundary composition at 1000 and 1400°, respectively.

Evidence for a possible temperature shift in the boundary composition at higher temperatures can be derived from thermal degradation experiments. Experiments at 2000° which were carried out in the attachment to the induction heating generator produced samples with a bulk composition, $ThP_{0.68}$ and $ThP_{0.75}$, respectively (see Table I), with lattice parameters that are consistent with the parameter–composition relationship shown in Figure 3. Considering the extreme conditions of thermal degradation one may assume that these compositions are near the phase boundary or, in the case of $ThP_{0.68}$, perhaps, are already within the two-phase region, indicating a considerable shift in the boundary composition toward higher phosphorus content.

More evidence for such a shift can be obtained from the thermal degradation of Th_3P_4 in the Knudsen effusion–mass spectrometer assembly, in which the thorium-rich boundary composition was reached at a composition $ThP_{0.68}$.[6]

The small amount of residue from the mass spectrometric investigation did not permit a chemical analysis. However, the lattice parameter of the residue, $a = 5.8340$ Å., as redetermined, indicates that the P/Th ratio is within the limits 0.69–0.75 (see Figure 3), in fair agreement with the value of 0.68. The unknown degree of the possible contamination of the residue by the tantalum liner used in the mass spectrometric investigation may add to an uncertainty in the lattice parameter. The result for the boundary composition from the mass spectrometric investigation is also consistent with the results of the thermal degradation experiments using induction heating.

The combined observations concerning the temperature influence on the existence range of the ThP_{1-x} phase presented in this section show that this existence range narrows considerably at higher temperatures and may extend at temperatures near 2000° from approximately $ThP_{0.7}$ to $ThP_{0.75}$.

(3) **Comparison of Properties with Related Phases.**—There is little information available to make a comparison of the existence ranges and properties of the monophosphides, monosulfides, etc., of inner transition metals that are known to crystallize in the rock salt type structure, since most of these compounds have only been qualitatively investigated. In many cases extensive existence ranges may have been overlooked.

Eastman,[15] *et al.*, however, report that there may be a homogeneity range in ThS of several atomic per cent. They observed a difference in lattice parameter when ThS was found in the presence of the neighboring phases. In the presence of thorium, the ThS phase gave a cubic lattice parameter of $a = 5.681$ Å., but in the presence of Th_2S_3 the lattice parameter was $a = 5.673$ Å. The authors hesitated in drawing conclusions because they found one sample that contained both ThS and Th_2S_3 that gave $a = 5.690$ Å. for the ThS phase. Since the authors do not describe the detailed heat treatment of these samples, it is difficult to judge their results critically. But it may be that the lattice parameters which approximately represent the boundary compositions, obscured due to serious nonequilibrium conditions in the samples, are 5.673 to 5.690 Å. This would mean a change of 0.30% or more in lattice parameter for thorium monosulfide, as compared with 0.17% for the existence range at 1000° for thorium monophosphide.

The properties of thorium monophosphide are compared in Table III with those of some other inner transition metal phosphides and sulfides of rock salt structure. The properties of the sulfides were obtained from the papers by Eastman and co-workers.[15,16] The properties of thorium monophosphide and uranium monophosphide have been observed in this investigation; those of CeP are taken from Hansen[17] and the melting point of UP has been received in private communication.[18]

TABLE III

A COMPARISON OF PROPERTIES OF SOME INNER TRANSITION METAL PHOSPHIDES AND SULFIDES OF ROCK SALT STRUCTURE

	CeS	ThS	US	CeP	ThP	UP
a, Å.	5.778	5.683	5.484	5.91	5.830	5.600
M.p., °C.	2450	>2200	>2000	...	>2400	2530
Magnetic susceptibility $\times 10^{-6}$ e.m.u.	2140	Diamagnetic	4180	...	0.5	Paramagnetic
Color	Brass	Silver	Gray	...	Blue	Gray-black
Dissolution in acid	Rapid	Slow	Slow	...	Very slow in concd. HNO_3	Slow in concd. HNO_3

The melting points of the phosphides are comparable with and possibly higher than those of the corresponding sulfides. The color sequence in these compounds might be a useful property for interpreting the electronic structures of those compounds. Noteworthy is the higher stability of uranium and thorium phosphides against chemical attack as compared with the corresponding sulfides. The relation of magnetic susceptibilities to the nature of bonding will be discussed elsewhere.[19]

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(15) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, *J. Am. Chem. Soc.*, **72**, 4019 (1950).

(16) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, *ibid.*, **72**, 2248 (1950).

(17) M. Hansen, "Constitution of Binary Alloys," 2nd Ed., McGraw-Hill Book Co., New York, N. Y., 1958.

(18) Y. Baskin, Argonne National Laboratory, private communication, 1964.

(19) D. W. Wilson and K. A. Gingerich, to be published.