tained when the hydrogen atom concentration near the wall was lowered by increasing the path between filament and wall. The necessity for providing a very cold surface and the stability problem were shown by the drastic reduction in reaction product when a bath of $-78°$ was substituted for the $-195°$ bath. These observations lead to the hypothesis that at least the last, if not all, of the reaction steps leading to the formation of the hydride occur at the wall and that the continuous evaporation of aluminum serves the purpose of providing a constantly renewed film surface. However, the data do not eliminate the possibility that this is essentially a gas phase rather than a heterogeneous reaction.

The experimental determination of half-order kinetics for this reaction is in line with similar kinetics that previously were found when hydrogen was dissociated into atoms at a glowing tungsten filament.[6,7] Roberts and Bryce have explained their kinetics in terms of the mechanism of dissociation of hydrogen at the tungsten surface over a temperature range that coincides with the present study. It may thus be reasonably assumed that the rate determining step in the present process is the production of hydrogen atoms at the filament. The geometry of the apparatus supports this conclusion since the probability of hydrogen collisions with the filament is considerably lower than gas phase or wall collisions.

That the hydride formed was a chemical compound rather than physical adsorption of hydrogen was demonstrated by the decomposition kinetics. The activation energy of 14.4 kcal./mole establishes that the bonding is in the class of chemical compounds.[8] A physical desorption process would have an activation energy of approximately 1–2 kcal./mole.[8,9]

It should be emphasized that the composite H/Al ratios in Table I do not necessarily represent the compositions of the hydride molecules because these ratios also include unreacted aluminum atoms and aluminum atoms which resulted from the decomposition of initially formed hydrides. Since aluminum distilled to the wall of the reactor where the surface was constantly covered by successive layers, it is extremely unlikely that all aluminum atoms could react, keeping in mind that covered atoms were lost to the reaction. The drastic reduction in product when the wall bath was at $-78°$, a temperature at which the hydride is normally quite stable, proves that the hydride molecules at the constantly changing surface were exposed to a disruptive environment. This consisted of constant attack by hydrogen atoms with H recombination reactions liberating 103 kcal./mole while hydride molecules with an activation energy for decomposition of 14.4 kcal./mole served as third bodies; in addition radiation and conduction energy was transferred from the glowing filaments. Since a composite value of $H/Al = 1.02$ was achieved under these conditions, it is reasonable to postulate that for the actual hydride, AlH_x, x was greater than unity.[10]

Acknowledgments.—The author gratefully acknowledges the interest and advice of Dr. A. Wheeler, Dr. E. Mishuck and D. Seedman and is indebted to Dr. Seymour Siegel for critically reading the manuscript. The Bureau of Ordnance of the U. S. Dept. of the Navy sponsored this investigation under Contract NOrd-18386.

(6) J. K. Roberts and G. Bryce, *Proc. Cambridge Phil. Soc.*, **32**, 653 (1936).

(7) I. Mochan, *Chem. Abst.*, **36**, 3091 (1942).

(8) S. Glasstone, K. Laidler and H. Eyring, "The Theory of Rate Processes," chapter on Heterogeneous Processes, McGraw-Hill Book Co., New York, N. Y., 1941, and R. Gomer and C. S. Smith, "Structure and Properties of Solid Surfaces," chapter on Chemisorption, Univ. Chicago Press, Chicago, Illinois, 1952.

(9) A. Eucken and W. Hunsmann, *Chem. Abst.*, **34**, 666 (1940).

(10) The instability of AlH_x at ambient temperatures and the fact that the hydride was isolated admixed with surface-active aluminum have made its chemical characterization difficult; for example, both AlH_x and aluminum deposited in the present apparatus react completely with water to liberate H_2.

AZUSA, CALIFORNIA

[CONTRIBUTION FROM THE GENERAL ELECTRIC COMPANY, LAMP DEVELOPMENT DEPARTMENT]

On the Preparation of the Phosphides of Aluminum, Gallium and Indium

BY ARRIGO ADDAMIANO

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The phosphides of aluminum, gallium and indium can be prepared by reaction between those metals and zinc phosphide, Zn_3P_2, in a neutral atmosphere (argon, hydrogen) at about 800–900°. The reactions proceed according to the scheme

$$2Me + Zn_3P_2 \rightarrow 2MeP + 3Zn\uparrow \qquad (Me = Al, Ga, Zn)$$

with formation of the phosphides of the third group elements and evolution of zinc vapors. X-Ray and analytical data are given. The yield of reaction is a maximum for AlP, while some metal is left unreacted in the preparation of GaP and InP.

Introduction

The phosphides of aluminum, gallium and indium all have been prepared by direct synthesis from the elements.[1–7] Of them the least known is perhaps the phosphide of aluminum, while gallium and indium phosphide have been prepared in the form of single crystals[4,5,7] and considered for applications such as electroluminescence and high-temperature rectification. It seemed interesting

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(3) J. W. Mellor, "Inorganic and Theoretical Chemistry," Vol. VIII, Longmans, Green and Co., London, second impression, 1947, p. 845.

(4) G. Wolff, P. H. Keck and J. D. Broder, *Phys. Rev.*, (2) **94**, 753 (1954).

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(6) G. A. Wolff, L. Toman, Jr., N. J. Field and J. C. Clark, *ibid.*, p. 463.

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to prepare these compounds by a method which would avoid the hazards of working with dangerous materials such as phosphorus or phosphine and which would lend itself to continuous production of the phosphides. The reaction between the metals, aluminum, gallium and indium, and a commercially available product, zinc-phosphide, Zn_3P_2, proved satisfactory to this end and will be described here.

Experimental and Results

The general schema of reaction for the preparation of the metal phosphides in question is

$$2Me + Zn_3P_2 \longrightarrow 2MeP + 3Zn\uparrow \qquad (1)$$

where Me = Al, Ga, In. The reaction can be expected to lead to quantitative formation of the phosphides of the third-group elements if the zinc is subtracted from the reaction as soon as it is formed, for instance by sublimation. This can be accomplished by operating at temperatures close to the b.p. of zinc (907°). In fact the b.p. of alumium, gallium and indium are very high (*ca.* 2000°), the sublimation rate of zinc phosphide becomes appreciable only around 1100°,[8] and the melting points of the phosphides of aluminum, gallium and indium[6,9] are above 1000°. In practice a temperature of 800° *circa* proved convenient for the preparation of all three of the phosphides.

Aluminum Phosphide.—Only two papers[1,2] on the preparation of aluminum phosphide have been published in recent years. Although in both cases the direct synthesis from the elements was used, the properties ascribed to the products obtained (such as body color, thermal stability, resistance to attack by water, acids and alkalies, etc.) are entirely different.

The zinc phosphide and aluminum powder used in my experiments were commercial products, from Fisher Scientific Company. The aluminum powder was assumed to be pure: a trace of aluminum oxide and perhaps smaller amounts of other impurities were probably present. As for the zinc phosphide, which was known to contain relatively large amounts of water and other impurities, purification was deemed necessary. This was accomplished by subliming the compound in a stream of argon at 1100°. In agreement with Jolibois[8] it was found that zinc phosphide sublimes undecomposed. The compact mass obtained by sublimation, which often contained beautiful single crystals of zinc phosphide, was reduced once more to a fine powder (minus 200 mesh size), and this powder was used for the preparations.

Weighed amounts of zinc phosphide and aluminum were mixed thoroughly and transferred to a boat of silica or spectrographically pure graphite. The boat was placed in a silica tube and heated for several hours at the desired temperature in a combustion tube furnace. A continuous flow of argon through the silica tube prevented oxidation of the sample and also displaced the evolved zinc vapor.

A stoichiometric mixture of aluminum and zinc phosphide was used for most experiments. In those cases where zinc phosphide was in excess the unreacted zinc phosphide was driven off at the end of the reaction by raising the temperature to 1000–1100° for about 30 minutes.

The reaction products, both those remaining in the boat and those which had condensed downstream on the silica tube, were identified by X-ray diffraction. It was found that between 400 and 600° no reaction occurs. In 6 hr. at 700° incomplete reaction takes place. Five hours at 800–900° results in an almost quantitative formation of aluminum phosphide and zinc. At about 1000° zinc phosphide begins to sublime and its presence in the sublimation products can be detected by X-ray diffraction.

X-Ray powder photographs of different samples of aluminum phosphide are consistent with the existence of a cubic, zinc-blende structure. The measured value of the cell-edge is a_0 = 5.451 Å., in good agreement with an earlier determination by Passerini.[10]

The intensities of the lines, however, were found to be quite different from the data reported by the ASTM File Index. A recalculation of the intensities

$$I_{\text{calcd.}} \propto |F|^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

where $|F|$ = structure factor modulus, p = multiplicity, θ = Bragg angle of reflection, gave good agreement with the experimental values, which are reported in Table I.

TABLE I

X-RAY DATA FOR AlP

(CuK_α radiation, λ_{α_1} = 1.5405 Å.; a_0 = 5.451 Å.)

hkl	sin θ	$I_{\text{obsd.}}$[a]	$I_{\text{calcd.}} \times 10^{-3}$
111	0.245	v.v.s.	866
200	.283	...	3
220	.399	v.s.	568
311	.469	s.	339
222	.489	...	53
400	.565	v.w.	88
331	.616	m.s.	136
420	.632	...	<1
422	.692	m.s.	250
511 + 333	.734	w.	83 + 28
440	.799	v.v.w.	72
531	.836	m.s.	146
600 + 442	.847	...	0 + 44
620	.894	m.s.	157
533	.926	v.w.	95
622	.937	...	64
444	.979	w.	143

[a] v. = very; s. = strong; w. = weak; m. = moderately.

Quantitative analytical data were obtained by measuring the change in weight of the contents of the reaction boats upon reaction. They are consistent with a yield of reaction of 94% or more. Samples of AlP also have been weighed, dissolved through acid attack and the aluminum determined after precipitation by 8-hydroxyquinoline in alkaline media. For a preparation at 850°, for instance, the data are: found Al 46.81%, theor. Al 46.54%.

The body color of aluminum phosphide obtained is pea-green, and its physical and chemical proper-

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(8) P. Jolibois, *Compt. rend.*, **147**, 801 (1908).

(9) J. van den Boomgaard and K. Schol, *Philips Research Repts.*, **12**, 127 (1957).

(10) L. Passerini, *Gazz. chim. ital.*, **58**, 662 (1928).

ties are in agreement with those described by White and Bushey.[1] Thus the substance has a low vapor pressure at 1000°, has a faint smell of phosphine, reacts violently with concd. or dil. HCl, and with explosion with 1:1 H_2SO_4, aqua regia, etc. Some differences, more of a quantitative than of a qualitative nature, were observed, however, in the stability in presence of water and alkalies. It was observed that after some weeks immersion in water samples of AlP still gave the diffraction pattern of the compound together with lines due to products of hydrolysis. Also, alkaline solutions at room temperature attack aluminum phosphide very slowly, without fast development of gases and inflammation of the vapors, as is the case with oxidizing acids. These differences of behavior probably are due to the absence, in the aluminum phosphide prepared from zinc phosphide and aluminum, of free phosphorus and aluminum, which are always present in the products obtained by direct synthesis.

Gallium Phosphide.—The preparation of gallium phosphide is very similar to that of aluminum phosphide. Either pure gallium (99.99% pure), or a Ga–Zn eutectic (m.p. 25°) were used. Difficulties are encountered in obtaining a homogeneous mixture of the metal and zinc phosphide. By long shaking of a mixture of liquid gallium and zinc phosphide, the gallium can be dispersed in the form of minute droplets. However, in the process of heating, large drops of gallium metal form again and these react only on the surface, greatly decreasing the yield of reaction. Occasional shaking of the reaction system helps somewhat but a continuous stirring is recommended. Operating with an excess of zinc phosphide increases slightly the yield of reaction. Zinc phosphide in excess can be separated easily by hydrochloric acid treatment, as gallium phosphide dissolves in hydrochloric acid only with difficulty.

The reaction occurs at 800°, when evolution of zinc vapors becomes appreciable. It is, however, slower than in the case of aluminum phosphide and reaction times of 12–24 hr. are required. Even so not all the gallium metal reacts. What is left unreacted can be separated mechanically and by centrifugation and/or sedimentation techniques. The product obtained after purification is a powder of yellow or yellow-green color, rather than an orange one, probably because of traces of gallium metal still present. The powder pattern of it, however, contains only the lines of gallium phosphide and the intensities are in good agreement with the calculated values, as shown in Table II.

Indium Phosphide.—Pure (99.999%) indium metal and zinc phosphide in excess over stoichiometric requirements, produce InP with low yields after 1–2 days at 700–800°. Excess zinc phosphide can be eliminated by HCl treatment, and much unreacted indium metal is eliminated mechanically, very much as in the case for GaP. The product obtained, a dark gray or black powder, gives the expected X-ray pattern[11] for a substance with zinc-blende structure and cell edge a_0 = 5.87 Å. The relative intensities of the lines agree with the calculated values, though they are at variance with values by Iandelli.[12] Table III contains the relevant X-ray data.

TABLE II

X-RAY DATA FOR GaP

(CuK$_\alpha$ radiation, λ_{α_1} = 1.5405 Å.; a_0 = 5.4504 Å.)

hkl	sin θ	$I_{obsd.}$[a]	$I_{calcd.} \times 10^{-3}$
111	0.245	v.s.	2933
200	.283	v.v.w.	399
220	.399	s.	1688
311	.469	m.s.	1136
222	.489	...	138
400	.565	v.v.w.	281
331	.616	w.	442
420	.632	...	104
422	.692	w.	604
511 + 333	.734	v.w.	281 + 94
440	.799	v.v.w.	225
531	.836	w.	523
600 + 442	.848	...	17 + 111
620	.894	w.	520
533	.926	v.w.	351
622	.937	...	160
444	.979	v.v.w.	425

[a] v. = very; s. = strong; w. = weak; m. = moderately.

TABLE III

X-RAY DATA FOR InP

(CuK$_\alpha$ radiation; λ_{α_1} = 1.5405 Å.; a_0 = 5.8687 Å.)

hkl	sin θ	$I_{obsd.}$[a]	$I_{calcd.} \times 10^{-3}$
111	0.227	v.s.	8952
200	.262	m.s. to w.	2236
220	.371	s.	4931
311	.435	s.	4040
222	.455	v.w.	684
400	.525	w.	791
331	.572	m.s.	1606
420	.587	w.	778
422	.643	m.s.	1694
511 + 333	.682	m.s.	939 + 313
440	.742	w.	579
531	.776	m.s.	1488
600 + 442	.787	w.	98 + 436
620	.830	m.s.	1089
533	.860	w.	777
622	.870	v.w.	471
444	.909	v.v.w.	459
711 + 551	.937	m.s.	1081 + 1081
640	.946	v.v.w.	627
642	.982	s.	6040

[a] v. = very; w. = weak; s. = strong; m. = moderately.

Conclusions

The method just described for the preparation of the phosphides of aluminum, gallium and indium, is relatively simple and danger free. The reactions occur at low temperature and, at least for aluminum phosphide, the yield is the theoretical one.

An interesting feature of the process is also the ease with which excess unreacted zinc phosphide can be eliminated at the end of the reactions, by sublimation in the case of aluminum phosphide, which melts at high temperature but is easily attacked by acids, and by hydrochloric acid treat-

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(11) G. Giesecke and H. Pfister, *Acta Cryst.*, **11**, 369 (1958).

(12) A. Iandelli, *Gazz. chim. ital.*, **71**, 58 (1941). These data contain an absorption correction with $\mu r = \infty$ (private communication).

ment for the phosphides of gallium and indium, which are stable in the presence of non-oxidizing acids.

The X-ray photographs of the products obtained, after purification, contain no lines due to impurities or to phosphides of different composition. Unreacted metals (Al, Ga, In), if present in the end products, are therefore in trace amount concentration. While in preparations on a laboratory scale the zinc obtained in the reactions is not worth saving, a continuous process can be envisaged, in which the zinc is retransformed into zinc phosphide and this reacts again with the third group elements. This possibility makes the process interesting from the standpoint of the industrial production of the phosphides of aluminum, gallium and indium.

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CLEVELAND, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RHODES UNIVERSITY, GRAHAMSTOWN, SOUTH AFRICA]

The Thermal Decomposition of Silver Oxide

BY P. J. HERLEY AND E. G. PROUT

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The results of the thermal decomposition of silver oxide, freed from silver carbonate by preheating at 280° for 3 hr. *in vacuo*, are highly reproducible. Study of the kinetics of the reaction in the range 330–380° has shown that the pressure–time curves over the acceleratory region are represented by the equation $P^{1/2} = kt + c$. Reaction proceeds by the growth of two-dimensional nuclei with an activation energy of 28.3 kcal./mole. The decay stage follows a unimolecular law and the activation energy is 29.6 kcal./mole. Pre-irradiation by ultraviolet light, cathode rays, ^{60}Co γ-rays, thermal neutrons and fast neutrons has no effect on the subsequent thermal decomposition.

The thermal decomposition of silver oxide has been investigated by various workers. Their results show discrepancies between the activation energies, the form of the pressure–time curves and the mathematical relationships describing such plots.

Lewis[1] prepared silver oxide from silver nitrate and barium hydroxide (or sodium carbonate). The oxide was heated in oxygen at atmospheric pressure at 320–350°. The decomposition, in the case of the first specimen (Merck silver oxide), was preceded by very long induction periods. None of the prepared specimens showed this property. In all cases the equation

$$dx/dt = kx(1 - x) \qquad (1)$$

where x is the fractional number of moles of silver oxide decomposed, was obeyed. The activation energy for the reaction was 31.8 kcal./mole.

Hood and Murphy,[2] using a similar procedure, confirmed the results of Lewis. The integrated form of equation 1

$$\ln x/(1 - x) = kt + c \qquad (2)$$

was applicable.

Pavlyuchenko and Gurevich[3] prepared silver oxide in darkness, and in the presence of air, by adding an aqueous solution of KOH to an aqueous solution of $AgNO_3$ at 5°. They obtained complex pressure–time curves and a low activation energy of 10.2 kcal./mole. Decomposition was carried out *in vacuo* in the relatively low temperature range of 118–220°.

Benton and Drake[4] decomposed silver oxide prepared by the combination of silver and oxygen. The decomposition temperature was 150° lower than that of Lewis and the activation energy was 35–36 kcal./mole.

Averbukh and Chufarov[5] decomposed silver oxide on a spring balance. The rate of decomposition for a constant degree of dissociation was determined and an activation energy of 29.0 kcal./mole was calculated.

Garner and Reeves[6] repeated the preparations of Lewis and decomposed the oxide at 300–330° in vacuum. The pressure–time plots showed no induction period but gave a maximum rate at the beginning of the reaction. The curves were irregular and not of an autocatalytic type. As well, specimens of silver oxide were annealed in oxygen at 28–38 atm. for 8–10 days at 200–300° to yield a dense coarsely crystalline oxide which decomposed *in vacuo* to yield sigmoid curves for the pressure–time plots. The autocatalytic relation of Lewis was not valid, but it was considered that the plots were described by the power law

$$P^{1/3} = k_1t + c_1 \qquad (3)$$

It was not possible to determine the activation energy in the usual manner due, presumably, to the irreproducibility of results from sample to sample. Instead split runs on the same specimen of oxide at different temperatures were performed. The activation energy for the reaction was 45.6–46.2 kcal./mole.

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(3) M. M. Pavlyuchenko and E. Gurevich, *J. Gen. Chem., U.S.S.R. (Eng. Transl.)*, **21**, 511 (1951).

(4) A. F. Benton and L. C. Drake, THIS JOURNAL, **56**, 255 (1934).

(5) B. D. Averbukh and G. I. Chufarov, *Zhur. Fiz. Khim.*, **23**, 37 (1949).

(6) W. E. Garner and L. W. Reeves, *Trans. Faraday Soc.*, **50**, 254 (1954).