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TABLE 4-2

Recognized Binary Compounds of Phosphorus Arranged According to the Periodic Table
(High-temperature compounds not stable at room temperature are shown in brackets)

Li Li_3P, LiP	Be Be_3P_2																	
Na Na_3P, Na_2P	Mg Mg_3P_2																	
K K_3P,	Ca Ca_3P_2	Sc Not investigated	Ti TiP, Ti_3P, Ti_2P, Ti_5P	V VP, V_3P, V_2P, V_5P	Cr CrP, Cr_3P, CrP_2, Cr_2P, Cr_5P	Mn MnP, Mn_3P, Mn_2P, Mn_5P, Mn_3P	Fe FeP, Fe_3P, Fe_2P, Fe_5P	Co CoP_3(?) Co_2P_3(?) CoP Co_2P(?) Co_3P Co_5P(?)	Ni NiP, Ni_5P_2, Ni_3P, Ni_2P, Ni_5P	Cu Cu_3P, Cu_3P_2(?) Cu_2P(?) Cu_3P	Zn Zn_3P_2, Zn_2P_3	Ga GaP	Ge GeP	As As-P	Se P_4Se_3, P_4Se_7	Br PBr, PBr_3	Kr None
Rb Rb_3P,	Sr Sr_3P_2	Y Not investigated	Zr ZrP, Zr_3P $Zr_3P_{0.5}$ Zr_2P	Nb NbP, Nb_3P $NbP_{0.5}$	Mo Mo_3P, Mo_2P Mo_3P	Tc Not investigated	Ru RuP, Ru_2P Ru_3P	Rh RhP, Rh_3P, Rh_2P, Rh_7P Rh_3P	Pd PdP, Pd_3P, Pd_2P, Pd_5P	Ag Ag_3P, Ag_2P, Ag_3P	Cd CdP_2, Cd_3P_2	In InP	Sn SnP, Sn_3P_4, Sn_4P_3	Sb Not (?)	Te Te_3P_2	I P_4I_2, P_2I_4	Xe None
Cs Cs_3P,	Ba Ba_3P_2 BaP_2 Ba_2P_3	La* LaP	Hf Not investigated	Ta TaP, Ta_3P	W WP, W_3P W_2P W_5P	Re Re_3P, ReP_2, ReP Re_2P	Os Os_2P,	Ir IrP, Ir_2P Ir_3P	Pt PtP, Pt_2P_3,	Au Au_3P, Au_2P	Hg Hg_3P_2(?)	Tl TlP, Tl_3P(?)	Pb Pb_3P_4 PbP_2(?)	Bi Not (?)	Po Not investigated	At Not investigated	Rn None
Fr Not investigated	Ra Not investigated	Ac** Not investigated																

Ce CeP	Pr PrP	Nd NdP	Pm Not investigated	Sm Not investigated	Eu Not investigated	Gd Not investigated	Tb Not investigated	Dy Not investigated	Ho Not investigated	Er Not investigated	Tm Not investigated	Yb Not investigated	Lu Not investigated
Th Th_3P_4 ThP	Pa Not investigated	U UP, U_3P_4 U_3P_4(?) U_2P	Np Np_3P_4	Pu Not investigated	Am Not investigated	Cm Not investigated	Bk Not investigated	Cf Not investigated					

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with great accuracy. However, it is given approximately by the following equation:

$$\log p_{mm.} = -7560/T + 13.36 \qquad (4\text{-}27)$$

The electrical resistivity[72] of crystalline black phosphorus is considerably lower than that of the other forms of phosphorus but is still extremely high as compared to the metals. The electrical resistivity of black phosphorus is equal to 0.711 ohm-cm.[3] at 0°C. The resistivity decreases with pressure and temperature, with the temperature coefficient, $(1/R)(dR/dT)$, being equal to $-0.0077/°C$. Since the conductivity of the most metallic form of arsenic is about 2×10^4 times greater than that of phosphorus and the conductivity of graphite is about 500 times greater, black phosphorus should definitely not be considered as a semimetal. The comparison often made between black phosphorus and graphite (which has conducting electrons which can freely move in the direction of the cleavage planes of the crystal) is very misleading in that it implies that black phosphorus also has freely moving electrons, somewhat as in a metal. This is not true.

From a thermodynamic viewpoint, it appears that crystalline black phosphorus is the most stable form of this element.[73] However, α-white phosphorus is usually used as the standard comparison state in tables of thermodynamic data. Black phosphorus is the least reactive of the solid forms of elemental phosphorus. Indeed, it can be sawed and machined with safety and is *completely stable in air. It can be ignited, but with difficulty, with a* match.

THE PHOSPHIDES

Binary Compounds of Phosphorus

A listing is given in Table 4-2 of the relatively well-proven compounds in which phosphorus is combined with one other element. These binary compounds of phosphorus are of three major types: (1) simple molecules, which are readily volatilized; (2) complex polymers, in which the phosphorus atoms alternate with other atoms in a three-dimensional or planar network structure; (3) metalloid compounds, which range in properties from those of the so-called "hard metals" toward those of covalently bonded polymers. Some of the metal phosphides may also exhibit a considerable

[72] P. W. Bridgman, *Proc. Natl. Acad. Sci.*, 21, 109 (1935).

[73] This is based on unpublished entropy measurements by C. C. Stephenson of the Mass. Inst. of Technol., Cambridge, Mass. See the Ph.D. Theses of R. L. Potter (1948), T. G. Maple (1949), and others.

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amount of ionic character in their bonding so as to give salt-like properties to the compound.

Most of the binary compounds of phosphorus with the elements of Groups VIA and VIIA lie in the class of volatile molecular compounds. With respect to its compounds with phosphorus, hydrogen acts as if it were a member of Group VIIA and is not at all similar to the Group IA metals. The only known volatile molecular compound of phosphorus with an element in Group VA is the P_4 molecule (a phosphorus compound of phosphorus). Then there are the high-temperature molecules which show up in spectrographic investigations but are not stable at room temperature. Examples are found in the PH, PO, and PN molecules. These high-temperature molecules are all enclosed in square brackets in Table 4-2.

Most of the binary compounds of phosphorus with the elements of Groups IIIA, IVA, and VA can probably be considered as covalently bonded polymers. In addition, vitreous P_2O_5, the crystalline varieties of P_2O_5 exhibiting a low vapor pressure, and the solid hydrogen phosphide with the empirical formula P_2H exemplify the formation of polymers among the binary compounds of phosphorus with the elements of Groups VIA and VIIA. It should be noted that, generally speaking, binary compounds of phosphorus with the elements of Groups IIIA, IVA, VA, and VIA exhibit un-ionized molecular structures in which the atoms of both elements are covalently bonded to their neighboring atoms.

The term "hard metals" is used to describe a group of very hard substances with metallic character which have the following distinguishing properties: high hardness value, high melting point, good resistance to chemical attack, and high conductivity for heat and electricity. In general, it is found that the borides, carbides, silicides, nitrides, and phosphides—as well as some oxides and sulfides—of the transition metals constitute the class of hard metals.[74] The typical crystal structure of a hard metal consists of an arrangement of the transition-metal atoms often similar to that found in metals (close packing of spheres) with the carbon, nitrogen, phosphorus, or other modifying atoms filling the interstices between the transition-metal atoms. In the case of transition-metal phosphides for which the metal-to-phosphorus ratio (M/P) is equal to or greater than one, the phosphorus atom, which is large with respect to the boron and carbon atoms, causes an expansion of the metal lattice so that the distance between the centers of the transition-metal atoms is increased by about 15% over the distance found in the pure metals. The structure of the transition-metal phosphides for which $M/P < 1$ is not well understood as yet. As a class, however,

[74] G. Hägg, *Ion*, 24, 343 (1953).

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these phosphides appear to be somewhat similar to the lower phosphides in that they exhibit metal-like properties. Presumably, the transition-metal phosphides for which $M/P < 1$ are intermediate between the hard metals and the metalloid polymers—such as silicon, black phosphorus, and aluminum phosphide.

The binary compounds of phosphorus with the metals of Groups IA and IIA are usually described in the literature as being salt-like. Preparations made to date do not have a metallic appearance and, indeed, it is said that Mg_3P_2 is transparent. If phosphorus can exist as a negative ion, it will probably be in these compounds. However, there is no definite evidence available at present as to the amount of ionic character in the bonds between the alkali metal or alkaline earth metal atoms and the phosphorus atoms. Such data should be obtained. The question of the type of bonds existing in the binary compounds of the alkali or alkaline earth metals with boron, carbon, silicon, nitrogen, or phosphorus should be examined by the best modern techniques of structure analysis. The alkali metals, in particular, are usually considered as being ionized in all of their compounds; whereas, carbon and phosphorus, for example, have been shown to be covalently bonded to their neighboring atoms in all cases in which the bond type has really been determined and not simply postulated, as is so often done. Which type of bonding prevails in the binary compounds? Presumably, there is a covalent bond with considerable ionic character. The binary compounds of phosphorus with the elements of Groups VIIA and VIA, as well as the phosphorus nitrides, are described in Chapters 5 and 6. The remaining binary compounds of phosphorus are described in this chapter.

As would naturally be expected, phosphorus does not form compounds with the noble gases. However, there is one report in the literature which indicates that helium is either strongly absorbed or forms an interstitial compound with elemental phosphorus at liquid-air temperatures.[75]

Historical and General Considerations of the Phosphides[76]

In the latter part of the Eighteenth Century, study of the metal phosphides was begun.[77] Since that time, a great deal of work has been done

[74] E. H. Boomer, *Nature*, 115, 16 (1925).

[75] Much of the information given here and in the remainder of this chapter was obtained from R. C. Valman, unpublished manuscript. Also see T. D. Farr, Phosphorus—Properties of the Element and Some of Its Compounds, *T.V.A. Chem. Eng. Rept. No. 8*, U. S. Govt. Printing Office, Washington, D. C., 1950.

[77] B. Pelletier, *Ann. Chim. Phys.* 1, No. 1, 105 (1789); *ibid.*, 13, 109, 132 (1792) [phosphides of precious metals, Pb, Mo, and Sb]; A. S. Marggraf, *Chem. Schrift. (Berlin)*, 1, 12 (1762); B. G. Sage, *Mém. Acad.*, 1779, 210 [copper phosphides].

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TABLE 4-3
Some Typical Phosphides

Other element	Phosphide	Melting point (°C.)	Density (g./cm.)	Color and crystal system	Heat of formation from red P and the metal (kcal.)	Reactions with: Cold H_2O	Hot H_2O	Dilute acids	Dilute bases	Strong oxidizing acids	Strong bases	Alkaline melts
Aluminum	AlP	>1700	2.42	Grey-white, cubic		Mod.	Fast					
Arsenic	AsP			Black crystals		Mod.	Fast					
Beryllium	Be_3P_2		2.24	Brown, cubic		Fast	Fast					
Boron	BP			Maroon powder		No	No	No		Fast	Yes	Yes
Cadmium	CdP_2	ca. 700		Orange-red, pseudocubic		No	No	Slow				
	Cd_3P_2			Steel grey, tetragonal		No	No	No		Yes		
Calcium	Ca_3P_2		2.51	Reddish brown crystals		Fast	Fast					
Carbon	C_3P			Yellowish white amorphous ppt.		No	No	No	No			
Chromium	CrP		5.3	Grey-black, orthorhombic		No		Slow	No	Slow		Yes
	Cr_2P	1515	6.1	Grey-black, tetragonal		No		Slow	No	Slow		Yes
Cobalt	CoP_3		4.26	Grey	−52	No						
	CoP		6.24	Grey, orthorhombic	−30	No						
	Co_2P	1386	6.4	Grey, orthorhombic	−43	No	Slow	Slow	No	Yes		Yes
Copper	CuP_3		4.20	Grey-black	−20	No	Slow	No		Yes		
	Cu_3P_2		6.35	Grey-black		No						
	Cu_3P		6.4	Grey-metallic		No	No	No		Yes		
	Cu_2P	1023	7.15	Steel grey, hexagonal	−32	No	Slow	No		Yes		
Gold	Au_2P_3		8.12	Grey powder		No	No	No		Yes		Yes
Iron	Fe_2P_3		4.95	Grey, orthorhombic	−34	No	Slow	Slow	No	Yes	Yes	Yes
	FeP		6.07	Grey, orthorhombic	−25	No	Slow	Slow	No	Yes	Yes	Yes
	Fe_3P	1370	6.77	Steel grey, hexagonal	−35	No	Slow	Slow	No	Yes	Yes	Yes
	Fe_2P	1166	7.11	Steel grey, tetragonal	−35	No	Slow	Slow	No	Yes	Yes	Yes
Lithium	Li_3P_4	ca. 650		Reddish brown powder		Fast	Fast					
	Li_3P		1.43	Dark colored, hexagonal		Fast	Fast					
Magnesium	Mg_3P_2		2.06	Yellowish grey transparent cubic		Fast	Fast					
Manganese	Mn_3P_2		4.20(?)	Black powder		No						
	MnP	1147	5.34	Grey, orthorhombic		No	Slow			Yes		
	Mn_2P	1327	6.32	Grey, hexagonal		No						
	Mn_3P	1105		Tetragonal								
Molybdenum	MoP_2		5.35									
	MoP		6.58	Grey crystals, hexagonal		No	Slow			Yes		
	Mo_2P		9.07	Steel grey, tetragonal		No	No	No	No			

(continued)

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TABLE 1-3 (*continued*)

Other element	Phosphide	Melting point (°C.)	Density (g./cm.)	Color and crystal system	Heat of formation from red P and the metal (kcal.)	Reaction with: Cold H_2O	Hot H_2O	Dilute acids	Dilute bases	Strong oxidizing acids	Strong bases	Alkaline melts
Nickel	NiP_3		4.19	Steel grey, hexagonal	−33	No						
	NiP_2		4.62	Steel grey, orthorhombic	−30	No						
	Ni_5P_4	1185	5.85	Steel grey crystals	−136	No						
	Ni_2P	1112	7.2	Steel grey, hexagonal	−40	No	No	No	No	Yes		
	Ni_3P_2	1185	7.5	Steel grey	−96	No	No	No	No	Yes		
	Ni_3P	975	7.7	Silvery grey, tetragonal	−48	No	No	No	No	Yes		
Platinum	PtP_2	ca. 1500	9.25	Steel grey, cubic		No	No	No	No	Slow		Yes
Potassium	K_3P_4	ca. 650	ca. 2	Reddish brown		Fast	Fast					
Rhenium	ReP_3		7.30	Grey		No	No	No	No			
	ReP_2		5.83	Steel grey, cubic		No	No	No	No			
	ReP		12.0	Steel grey, cubic		No	No	No	No			
Rhodium	RhP_3		5.10	Steel grey		No	No	No	No	Slow		Yes
	Rh_2P	ca. 1500	9.13	Steel grey, cubic		No	No	No	No	Slow		Yes
	Rh_4P											
Silicon	SiP		ca. 2.4	Light yellow powder		Slow	Yes					
Sodium	Na_3P_4	ca. 650		Reddish brown powder		Fast	Fast					
	Na_3P		1.74	Dark colored, hexagonal		Fast	Fast					
Strontium	Sr_3P_2		2.63	Brown crystals		Fast	Fast					
Tantalum	TaP_2		8.41	Black powder		No						
	TaP		10.9	Black powder, hexagonal		No						
Thorium	Th_3P_4		8.44	Greyish black, cubic		No	No	Slow				
	ThP		8.81	Greyish black, cubic		No	No					
Tin	SnP_3	580		Silvery white		No	Slow	No				
	Sn_4P_3	562		Silvery white		No	Slow	Slow	No	Yes		
	Sn_3P_4	550		Silvery white		No	Slow	Yes	No	Yes		
Titanium	TiP		3.95	Steel grey		No	No	No	No	Slow	No	Yes
	$TiP_{0.88}$			Hexagonal		No						
Tungsten	WP_2		9.17	Black crystals		No	No	No	No	Slow		Yes
	WP		12.3	Steel grey, orthorhombic		No	No	No	No	Slow		Yes
Uranium	UP_2		8.57			No	No					
	U_3P_4		10.0	Greyish black, cubic		No	No	Yes				
	UP		10.2	Greyish black, cubic		No	No					
Vanadium	VP		4.7	Grey, hexagonal		No						
Zinc	ZnP_2	ca. 700	3.0	Orange-red, pseudocubic		No	No	Slow		Yes		
	Zn_3P_2		4.7	Steel grey, tetragonal	−98	No	No	Slow		Yes		
Zirconium	ZrP_2		5.5	Grey		No	No	No	No	Slow	No	Yes
	ZrP			Silvery grey, hexagonal		No	No	No	No	Slow	No	Yes
	$ZrP_{0.99}$			Silvery grey, cubic								

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TABLE 4-3
Some Typical Phosphides

Other element	Phosphide	Melting point (°C.)	Density (g./cm.)	Color and crystal system	Heat of formation from red P and the metal (kcal.)	Reaction with: Cold H_2O	Hot H_2O	Dilute acids	Dilute bases	Strong oxidizing acids	Strong bases	Alkaline melts
Aluminum	AlP	>1700	2.42	Grey-white, cubic		Mod.	Fast					
Arsenic	AsP			Black crystals		Mod.	Fast					
Beryllium	Be_3P_2		2.24	Brown, cubic		Fast	Fast					
Boron	BP			Maroon powder		No	No	No		Fast	Yes	Yes
Cadmium	CdP_2	ca. 700		Orange-red, pseudocubic		No	No	Slow				
	Cd_3P_2			Steel grey, tetragonal		No	No	No		Yes		
Calcium	Ca_3P_2		2.51	Reddish brown crystals		Fast	Fast					
Carbon	C_3P			Yellowish white amorphous ppt.		No	No	No	No			
Chromium	CrP		5.3	Grey-black, orthorhombic		No		Slow	No	Slow		Yes
	Cr_3P	1515	6.1	Grey-black, tetragonal		No		Slow	No	Slow		Yes
Cobalt	CoP_3		4.26	Grey	−52	No						
	CoP		6.21	Grey, orthorhombic	−30	No						
	Co_2P	1386	6.4	Grey, orthorhombic	−43	No	Slow	Slow	No	Yes		Yes

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Copper	CuP_3		4.20	Grey-black	−20	No	Slow	No		Yes		
	Cu_3P_2		6.35	Grey-black		No						
	Cu_2P		6.4	Grey-metallic		No	No	No		Yes		
	Cu_3P	1023	7.15	Steel grey, hexagonal	−32	No	Slow	No		Yes		
Gold	Au_3P_2		8.12	Grey powder		No	No	No		Yes		Yes
Iron	Fe_2P_3		4.95	Grey, orthorhombic	−34	No	Slow	Slow	No	Yes	Yes	Yes
	FeP		6.07	Grey, orthorhombic	−25	No	Slow	Slow	No	Yes	Yes	Yes
	Fe_2P	1370	6.77	Steel grey, hexagonal	−35	No	Slow	Slow	No	Yes	Yes	Yes
	Fe_3P	1166	7.11	Steel grey, tetragonal	−35	No	Slow	Slow	No	Yes	Yes	Yes
Lithium	Li_3P_2	ca. 650		Reddish brown powder		Fast	Fast					
	Li_3P		1.43	Dark colored, hexagonal		Fast	Fast					
Magnesium	Mg_3P_2		2.06	Yellowish grey transparent cubic		Fast	Fast					
Manganese	MnP_3		4.26(?)	Black powder		No						
	MnP	1117	5.31	Grey, orthorhombic		No	Slow			Yes		
	Mn_2P	1327	6.32	Grey, hexagonal		No						
	Mn_3P	1165		Tetragonal								
Molybdenum	MoP_3		5.45									
	MoP		6.58	Grey crystals, hexagonal		No	Slow			Yes		
	Mo_3P		9.07	Steel grey, tetragonal		No	No	No	No			

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TABLE 4-3 (*continued*)

Other element	Phosphide	Melting point (°C.)	Density (g./cm.)	Color and crystal system	Heat of formation from red P and the metal (kcal.)	Reaction with: Cold H_2O	Hot H_2O	Dilute acids	Dilute bases	Strong oxidizing acids	Strong bases	Alkaline melts
Nickel	NiP_3		4.19	Steel grey, hexagonal	−33	No						
	NiP_2		4.62	Steel grey, orthorhombic	−30	No						
	Ni_4P_3	1185	5.85	Steel grey crystals	−136	No						
	Ni_2P	1112	7.2	Steel grey, hexagonal	−40	No	No	No	No	Yes		
	Ni_5P_2	1185	7.5	Steel grey	−96	No	No	No	No	Yes		
	Ni_3P	973	7.7	Silvery grey, tetragonal	−48	No	No	No	No	Yes		
Platinum	PtP_2	ca. 1500	9.25	Steel grey, cubic		No	No	No	No	Slow		Yes
Potassium	K_3P_4	ca. 650	ca. 2	Reddish brown		Fast	Fast					
Rhenium	ReP_2		7.30	Grey		No	No	No	No			
	ReP_3		8.83	Steel grey, cubic		No	No	No	No			
	ReP		12.0	Steel grey, cubic		No	No	No	No			
Rhodium	RhP_3		5.16	Steel grey		No	No	No	No	Slow		Yes
	Rh_2P	ca. 1500	9.13	Steel grey, cubic		No	No	No	No	Slow		Yes
	Rh_3P											
Silicon	SiP		ca. 2.4	Light yellow powder		Slow	Yes					
Sodium	Na_3P_4	ca. 650		Reddish brown powder		Fast	Fast					
	Na_3P		1.74	Dark colored, hexagonal		Fast	Fast					

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Strontium	Sr_3P_2		2.68	Brown crystals		Fast	Fast					
Tantalum	TaP_2		8.41	Black powder		No						
	TaP		10.9	Black powder, hexagonal		No						
Thorium	Th_3P_4		8.44	Greyish black, cubic		No	No	Slow				
	ThP		8.81	Greyish black, cubic		No	No					
Tin	SnP_3	580		Silvery white		No	Slow	No				
	Sn_4P_3	502		Silvery white		No	Slow	Slow	No	Yes		
	Sn_3P_4	550		Silvery white		No	Slow	Yes	No	Yes		
Titanium	TiP		3.95	Steel grey		No	No	No	No	Slow	No	Yes
	$TiP_{0.65}$			Hexagonal		No						
Tungsten	WP_2		9.17	Black crystals		No	No	No	No	Slow		Yes
	WP		12.3	Steel grey, orthorhombic		No	No	No	No	Slow		Yes
Uranium	UP_2		8.57			No	No					
	U_3P_4		10.6	Greyish black, cubic		No	No	Yes				
	UP		10.2	Greyish black, cubic		No	No					
Vanadium	VP		4.7	Grey, hexagonal		No						
Zinc	ZnP_2	ca 700	3.0	Orange-red, pseudocubic		No	No	Slow		Yes		
	Zn_3P_2		4.7	Steel grey, tetragonal	−98	No	No	Slow		Yes		
Zirconium	ZrP_2		5.5	Grey		No	No	No	No	Slow	No	Yes
	ZrP			Silvery grey, hexagonal		No	No	No	No	Slow	No	Yes
	$ZrP_{0.65}$			Silvery grey, cubic								

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in this field; but a number of the formulas which have been given for specific compounds are incorrect. In fact, in reviewing the literature on phosphides, Mellor[28] says "The subject generally wants overhauling, since many of the alleged phosphides hold a precarious position in the list of chemical individuals." Since the publication of Mellor's treatise, a considerable amount of x-ray, phase-diagram, and vapor-pressure work has been carried out which has resulted in a clear definition of the chemical individuality of a number of phosphides. Most of the discussion of phosphides given in this book is based on relatively recent papers; and the reader is referred to Mellor and Gmelin[29] for a more thorough review of the earlier literature.

Nearly all of the elements react with phosphorus, phosphorus vapor, or phosphine at elevated temperatures to form phosphides, the exact formula of which depends on the specific experimental conditions. Generally speaking, there are several different phosphides of each metallic element; although some metals have only one phosphide, and antimony, bismuth, lead, and mercury may not form any phosphides stable under normal conditions. Unlike alloys, the various crystalline species of the metal phosphides exhibit either a specific value of the metal-to-phosphorus ratio or a narrow range of values. In this respect, the phosphides are similar to salts. Some metal phosphides—such as Na_3P, Ca_3P_2, AlP, and Th_3P_4—have formulas which correspond to the classical valency rules; but this is far from common. Thus, the stable alkali metal phosphides exhibit an empirical formula M_2P_5.

The higher phosphides of a given metal usually decompose when heated to give a lower phosphide and phosphorus vapor. The phosphides of the alkali and alkaline earth metals react rapidly with cold water to form hydrogen phosphides (predominantly phosphine), whereas the phosphides of the elements of Groups IIIA, IVA, and VA do not. However, as a rule, these phosphides give hydrogen phosphides by reacting with dilute acids. The phosphides of the transition metals are considerably less reactive, and hot, strong, oxidizing acids or molten alkalies are usually needed to decompose them. Some of the transition-metal phosphides are extremely unreactive and only decompose when heated in strongly oxidizing atmospheres, such as Cl_2 or F_2. Thus, these particular phosphides can be considered as being among the more inert of all substances.

The properties of the binary phosphides are reported in Table 4-3,

[28] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longman's Green & Co., London, 1928, Vol. VIII, pp. 833-66. Also see the various volumes of L. Gmelin, *Gmelin's Handbuch der anorganischen Chemie*, Verlag-Chemie, Weinheim, Germany.

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where the phosphides are arranged in the order of an alphabetical listing of the element combined with the phosphorus. Heats of formation of the phosphide from red phosphorus plus the other element in its thermodynamic standard state are shown in this table when available.

Preparation of Metal Phosphides

The simplest and most generally used method for preparing phosphides is to heat the metal with red phosphorus or phosphorus vapor in a nonoxidizing atmosphere. Hydrogen or carbon dioxide has often been used as a carrier for the phosphorus vapor, and large-scale preparation of some of the phosphides is often achieved by submerging white phosphorus in a bath of the molten metal so that phosphorus vapor is formed, only to be absorbed by the metal melt. In laboratory preparations, the volatile and easily oxidized metals are sometimes covered by a liquid such as paraffin oil while they are being reacted with phosphorus. Lithium chloride and tin phosphide have also been used as protective layers. Naturally, when an element forms several stable phosphides, the proper stoichiometric quantities must be used in the preparation.

In order to bring about the formation of thermally unstable phosphides (generally higher phosphides of a given metal), Biltz and coworkers[29] have used a modification of the procedure whereby phosphorus and the metal are reacted together. According to this technique, the synthesis is carried out at elevated temperatures, up to 1100°C., in an enclosed system using an excess of phosphorus. After heating for the desired length of time, the excess phosphorus is condensed in a slightly cooler portion of the apparatus. Since this reaction technique was first introduced to chemistry by Faraday, the term "Faraday method" may be applied to the procedure, which has been described in considerable detail in the literature.[30] When the reaction is allowed to take place above the boiling point of red phosphorus, considerable pressure may develop depending on the amount of excess phosphorus used, and the procedure is then referred to as the pressure (Druck) technique.

When a metal forms several phosphides, advantage may be taken of the fact that higher phosphides are often thermally unstable. For example, VP_2 has a vapor pressure of 760 mm. at 710°C., whereas VP has a negligible vapor pressure even at 1050°C.[31] Vanadium monophosphide can thus be

[29] W. Biltz and R. Juza, *Z. anorg. u. allgem. Chem.*, 190, 161 (1930).

[30] H. Haraldsen, *Skrifter Norske Videnskaps-Akad., Oslo, Mat. Naturv. Kl.*, 1932, No. 9, 1.

[31] M. Zumbusch and W. Biltz, *Z. anorg. u. allgem. Chem.*, 249, 30 (1941).

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prepared by heating the diphosphide in a vacuum at elevated temperatures. Of course it should be noted that, when the lower phosphides are also unstable, this method may produce a mixture of phosphides and/or the metal. Thermally stable phosphides are sometimes conveniently prepared by heating a higher phosphide with a stoichiometric amount of the metal. Thus, V_2P can be made by heating vanadium with vanadium monophosphide which, in turn, was prepared by decomposing the diphosphide.[31]

Instead of using red phosphorus or phosphorus vapor, phosphine may be passed over the hot metal to make the lower phosphides. In several cases, phosphides have been prepared by reacting the metal chloride with phosphine to give the metal phosphide plus hydrogen chloride vapor. Examples[32] are the formation of WP_5, ZrP_2, and TiP. Reaction of phosphine with solutions of metal salts often gives phosphides which may contain unsubstituted hydrogen. With metal salts the phosphides of which are not very stable, a mixture of phosphides and the metal is often formed. As would be expected, when phosphine reduces the metal salt to the metal, it is simultaneously oxidized to the oxyacids of phosphorus. By using an excess of phosphine, a number of allegedly pure metal phosphides have been made. Preparation of Ag_3P, Cu_3P, Au_3P, Hg_3P, Hg_3P_2, Pb_3P_2, Cd_3P_2, and Cu_3P_2 by this procedure has been reported.[33] White phosphorus reacts in a manner similar to phosphine with solutions of metal salts. However, this reaction is usually not used as a preparative procedure, since the resulting phosphide forms a coating over the phosphorus, when present either in liquid or solid form, which greatly slows down the reaction and can lead to an impure product. A few experiments have been carried out on the reactions between phosphine or phosphorus and the alkali metals in liquid ammonia. However, the initial products are often not normal phosphides but are hydrogen-containing compounds analogous to the amides and imides.

Phosphides can also be made by reducing salts of the oxyacids with carbon, hydrogen, and other reducing agents. Usually phosphates are reduced in this manner at red heat. High-temperature electrolysis of fused sodium phosphates containing oxides or salts of heavy metals has been used to obtain the phosphides of several metals. By controlling the composition of the melt, the temperature, and the current density, different phosphides of a given metal can be produced. Some phosphides, such as W_2P,

[31] L. D. Defacqz, *Compt. rend.*, 130, 915 (1900); *ibid.*, 132, 32 (1901); J. Geweke, *Liebig's Ann.*, 361, 79 (1908).

[32] L. Moser and A. Brukl, *Z. anorg. u. allgem. Chem.*, 121, 73 (1922); A. Brukl, *ibid.*, 125, 252 (1922).

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which cannot be obtained by any other method are made in this manner. This technique has been discussed in two reviews.[34]

Alkali Metal Phosphides

The best-known and well-established phosphides[35] of the alkali metals have the formula M_3P_4, where M stands for Li, Na, K, Rb, or Cs. These phosphides are thermally stable up to temperatures near 650°C. and, as they are usually prepared,[37] exhibit a reddish brown color. They react instantly with water or with moisture in the air to form phosphine.

In addition to the compounds with the formula M_3P_4, lithium and sodium also form compounds having the approximate composition M_3P.[38] When the stoichiometric amounts of sodium or lithium are heated with phosphorus under a layer of lithium chloride, a product having less alkali metal than corresponds to the M_3P composition is obtained. X-ray examinations of these materials showed the presence of a phase which is similar in structure to the known compound Na_3As. No chemical analyses have been made on reliable preparations of Li_3P or Na_3P, and their existence is based wholly on this x-ray evidence. By this same criterion, K_3P, Rb_3P, and Cs_3P do not seem to exist.

As shown in Table 4-4, both Na_3P and Li_3P have crystal structures like the trisodium arsenide (Na_3As) type, so that the comments given below for Na_3P are true for Li_3P, except that the interatomic distances will be different. According to the detailed structure of these crystals, there are two locations for the alkali metal atoms. In one location, each sodium has three neighboring phosphorus atoms surrounding it in the same plane at a distance of 2.88 A. between atom centers. In addition, there are six nearest-neighbor sodium atoms at a distance of 3.24 A. The six sodium atoms are arranged so as to form a trigonal prism with the three neighboring phosphorus atoms being outside the square faces of this prism. The arrangement of nearest-neighbor atoms around this sodium is shown on the next page.

[34] M. C. Neuberger, *Z. Kryst.*, 93, 1 (1936); also see ref. 164.

[35] J. L. Andrieux, *Rev. mét.*, 45, 49 (1948); *J. four élec.*, 57, No. 3, 54 (1948); M. Chéne, *Ann. Chim.*, 15, 187 (1941).

[36] E. Zintl and G. Woltersdorf, *Z. Elektrochem.*, 41, 876 (1935); V. A. Pleskov and M. Monoszon, *Acta Physicochem. U.S.S.R.*, 1, 725 (1935).

[37] [illegible]

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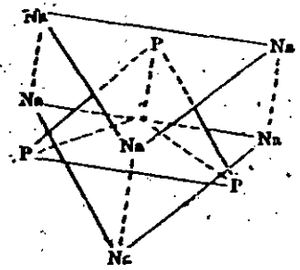
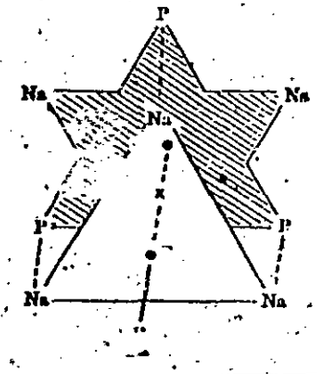


(4-28)

• = central Na atom

In the other location, there are two sodium atoms for each atom in the first sodium location. Each of the sodium atoms in this second location has one phosphorus atom directly below it, at a distance of 2.93 A. There are also three phosphorus atoms forming an equilateral triangle in a plane situated above the sodium atom in question. The Na-P distance in this case is 3.24 A. These four nearest-neighbor phosphorus atoms thus form a distorted tetrahedron about the sodium atom. In addition, the sodium atoms in this location have six nearest-neighbor sodium atoms at a distance of 3.24 A., with a seventh neighboring sodium atom directly above it at 2.93 A. Three of these atoms are in the same plane as the triangle of nearest-neighbor phosphorus atoms but form an equilateral triangle which is rotated 60° from the phosphorus triangle. The other three sodium atoms are also in the form of a triangle, but this triangle lies directly under that formed by the phosphorus and is also below the central sodium atom. The arrangement of nearest neighbors about this sodium is shown below; where the seventh neighboring sodium atom directly above the central one is hidden by the star formed by alternate sodium and phosphorus atoms:

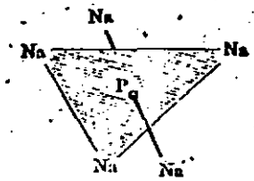


(4-29)

12

In the first position, each sodium atom is surrounded by six other sodium atoms in an arrangement similar to hexagonal close packing of spheres, whereas in the second position the six nearest sodium atoms surround the given sodium atom as in cubic close packing of spheres. In both cases, the sodium atoms are placed with respect to their nearest sodium neighbors in an arrangement which is common to metals. It should be noted that in this structure the Na-Na distances are 12% smaller than in metallic sodium (in which the Na-Na coordination number is 8 instead of 6). For Li_3P, the Li-Li distance is 8% smaller than in the metal.

Each phosphorus atom in Na_3P is surrounded by five nearest-neighbor sodium atoms, with six additional sodium neighbors at a further distance (3.42 A.). Three of the nearest-neighbor sodiums form an equilateral triangle in the center of which lies the phosphorus. The Na-P distance in this case is 2.88 A. Directly above and directly below this central phosphorus are sodium atoms. The Na-P distance for these two sodiums is 2.93 A. Thus, the phosphorus atom in Na_3P has its five nearest-neighbor sodium atoms arranged at the corners of a trigonal bipyramid having the same general geometry as the five halide atoms in the phosphorus pentahalides. This arrangement is shown below:



(4-30)

If the phosphorus covalent radius of 1.1 A. is subtracted from the Na-P distance, a sodium radius of 1.8 A. is obtained. Likewise, if the Na-Na distance observed in Na_3P is divided in half, a sodium radius of 1.6 A. results. The accepted radius for the sodium atom in metals is 1.8 A., whereas its accepted radius in ionic compounds is 1.0 A. Moreover, an extrapolation of covalent radii—such as is given in Figure 2-3—leads to a covalent radius of 1.4 A. for sodium. One can conclude from this that in the Na_3P crystal, the sodium atoms exhibit bonding that is somewhat similar to that found in metals. On the other hand, Na_3P can probably not be considered as an interstitial compound similar to the borides, carbides, nitrides, and phosphides of the transition metals. In these interstitial compounds, the metal-to-metal distance is larger in the phosphide than in the metal, whereas in Li_3P and Na_3P the reverse is true. In other words, the alkali-metal atoms in Li_3P and Na_3P have effectively "shrunk" when the phosphorus atoms

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were introduced. This implies that the metallic bond exhibits appreciable covalent or ionic character in these compounds.

The phosphorus in this compound is surrounded by sodium atoms situated at the corners of a trigonal bipyramid. This means that, if the phosphorus is covalently bonded to its neighboring sodium atoms, the base σ-bond structure corresponds to sp^3d-hybridization. In the phosphorus pentahalides where there is little question about the sp^3d-base structure, the two apical halide atoms are at a slightly greater distance than the other three halides, so that the geometry is the same as in the Na_3P and Li_3P crystals. Although the evidence is far from conclusive, it appears that the phosphorus in Li_3P and Na_3P may be covalently bound to its neighboring atoms and exhibits the symmetry ascribed to sp^3d-hybridization. Because it is thought that the bonds from the phosphorus are primarily covalent with some ionic character, the bonds between sodium atoms are probably part way between metallic and covalent bonds.

The structure of Na_3P was discussed in considerable detail because, if there is any chance that a phosphide ion exists, it probably should be found in binary compounds with the alkali metals. Detailed structure analysis of the two alkali metal phosphides for which x-ray data are available gives no particular support to the concept of phosphide ions. On the other hand, these measurements do not definitely demonstrate that phosphide ions are nonexistent in these crystals. However, the most reasonable interpretation of the data does not support the idea of phosphide ions, and we can probably assume that the phosphorus is connected to its neighboring atoms by bonds which are primarily covalent in character.

Phosphine or phosphorus reacts with the alkali metals in liquid ammonia to give hydrogen gas and solid reaction products which, upon evaporation of the ammonia, are usually found to contain nitrogen. In a recent study[88] it was shown that when lithium, sodium, or potassium in liquid ammonia was titrated with a solution of phosphorus in toluene, there were definite changes in color which were attributed to compound formation. At the start of the titration, the ammonia exhibited a deep blue color due to the alkali metal. As the reaction proceeded, the blue color showing up in the ammonia first changed to a greenish cast, then to a deep yellow-green color, and finally there was a distinct end-point color change to yellow tinged with orange. This definite color change corresponded to Li/P and Na/P mole ratios of 2 and a K/P mole ratio of 1.5. Interpretation of the chemical properties of these solutions indicated that the sodium and lithium phosphides thus formed are derivatives of diphosphine corresponding to the formula,

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M_2PPM_2.[89] However, a solid compound taken from solution and formulated as $Na_2PPNa_2 \cdot 2NH_3$ by Evers and coworkers was later stated by others[90] to be a mixed phosphide-amide having the formula $NaHPPH\text{-}Na \cdot 2NaNH_2$. In reality, there is not much evidence to show that either formula is right; and, in all caution, the compound should probably be written in terms of its empirical composition, *viz.*, Na_2PNH_x where x is probably 3.

When phosphine was passed into a solution of lithium in liquid ammonia at −80°C., the blue solution became yellow-colored in the same way as was found when elemental phosphorus was added to the alkali metal in liquid ammonia.[91] Upon evaporation of the liquid ammonia, a white microcrystalline powder was formed. Measurement of the phosphine absorbed and hydrogen evolved during the reaction showed that 1 mole of PH_3 was taken up per mole of Li to give $^1/_2$ mole of H_2. Reaction of the white microcrystalline powder with water showed that there were 4 moles of NH_3 per mole of Li. This leads to the empirical formula $LiPH_2 \cdot 4NH_3$ for the white powder[91] which reacts vigorously with water to give PH_3 plus a mixture of LiOH and NH_4OH. Upon heating,[92] the compound $LiPH_2 \cdot 4NH_3$ loses first 2 and then 1 mole of NH_3. Removal of the last mole of NH_3 results in the simultaneous loss of approximately $^1/_2$ mole of PH_3 per formula weight of the phosphide. This decomposition takes place at 50°C., leaving a residue having the empirical composition Li_2PH.

When monosodium phosphine, exhibiting the empirical formula $NaPH_2$ is made in liquid ammonia, it is difficult if not impossible to obtain a nitrogen-free solid product. However, this has been accomplished by working in organic solvents.[93] Thus, the purest form of $NaPH_2$ has been made by blowing a vigorous current of phosphine into ether to which was added gradually a solution of triphenylmethyl sodium, $(C_6H_5)_3CNa$, in ether—so that phosphine is always present in excess. The $NaPH_2$ is produced as a pure white flocculent precipitate which ignites spontaneously in air but can be stored indefinitely in an inert atmosphere. In water this compound decomposes instantly into phosphine and sodium hydroxide. When the sodium or potassium compounds $NaPH_2$ or KPH_2 are heated,[92] there is first an evolution of phosphine (at 70°C. for the sodium derivative and at

[89] E. C. Evers, *J. Am. Chem. Soc.*, 73, 2038 (1951); E. C. Evers, E. H. Street, and Shee Lup Jung, *ibid.*, 73, 5088 (1951); E. C. Evers and J. M. Finn, *J. Phys. Chem.*, 57, 559 (1953).

[90] P. Royen and W. Zschunke, *Z. Naturforsch.*, 8b, 777 (1953).

[91] C. Legoux, *Compt. rend.*, 207, 634 (1938).

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TABLE 4-4
Structure of Some Phosphides for Which Adequate X-Ray Data Are Available

Compound	Crystal system	Space group	Formula weights per unit cell	Cell dimensions	Number of atoms surrounding a specified atom at the distances given						Data for the metal in elemental form	Structure prototype[A] and isomorphs	Refs.[B]
Li_3P	Hexagonal	$C6/mmc$	2	$a = 4.264$ $c = 7.579$	P	3 Li_I	2.46 A.	Li_I	3 P	2.46 A.	8 Li at 3.033 A.	Na_3As Li_3As α-Li_3Sb Na_3Bi Na_3Sb K_3Bi K_3Sb K_3As	88 [V, 6-7] [V, 59-60]
						2 Li_{II}	2.53		6 Li_{II}	2.77			
						6 Li_{II}	2.77		2 Li_I	2.79			
						6 P	4.26						
						6 P	4.52						
								2 Li_{II}	1 P	2.53 A.			
									3 P	2.77			
									3 Li_I	2.77			
									3 Li_{II}	2.77			
Na_3P	Hexagonal	$C6/mmc$	18	$a = 4.960$ $c = 8.797$	P	3 Na_I	2.88 A.	Na_I	3 P	2.88 A.	8 Na at 3.708 A.	As above	As above
						2 Na_{II}	2.93		6 Na_{II}	3.24			
						6 Na_I	3.24		2 Na_I	4.40			
						6 P	4.98						
								(2) Na_{II}	1 P	2.93 A.			
									3 P	3.24			
									3 Na_I	3.24			
									3 Na_{II}	3.24			
$LiZnP$	Cubic		4	$a = 5.78$	P	4 Li	2.50 A.	Li	4 P	2.50 A.	See Li_3P and Zn_3P_2	Anti-CaF_2	94 [XIII, 30]
						4 Zn	2.50		6 Zn	2.89			
						12 P	4.25		6 Li	2.89			
								Zn	4 P	2.50 A.			
									6 Li	2.89			
									6 Zn	2.89			

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LiMgP	Cubic	$Fm\bar{3}m$	4	$a = 6.02$	P	(8 or 4) Li_T	2.61 A.	Li_T	4 P	2.61 A.	See Li_3P and Mg_3P_2	Anti-CaF_2 with interstitial atoms
						(12 or 0) Li_O	3.01		(8 or 4) Li_O	2.61		
						4 Mg	2.61		(6 or 0) Li_T	3.01		
						12 P	4.25		6 Mg	3.01		
								Li_O	(8 or 4) Li_T	2.61 A.		
									(12 or 0) Li_O	4.25		
									4 Mg	2.61		
									6 P	3.01		
Mg_3P_2	Cubic	$Ia\bar{3}$	16	$a = 12.01$	P_I	6 Mg	2.6 A.	(6) Mg	1 P_I	2.6 A.	6 Mg at 3.101 A. also 6 Mg at 3.203 A.	Anti-Mn_2O_3. Also an anti-structure to Sc_2O_3, Y_2O_3, In_2O_3
						6 P_{II}	4.0		1 P_{II}	2.3		
						6 P_{II}	4.4		1 P_{II}	2.9		
					(3) P_{II}	2 Mg	2.2 A.		1 P_{II}	3.0		
						2 Mg	2.9		3 Mg	3.2		
						2 Mg	3.0		3 Mg	4.1		
						2 P_I	4.0					
						2 P_I	4.4					
						4 P_{II}	4.0					
						4 P_{II}	4.5					
AlP	Cubic	$F\bar{4}3m$	4	$a = 5.42$	P	4 Al	2.35 A	Al	4 P	2.35 A.	12 Al at 2.858 A.	ZnS, CuCl, CuBr, CuI, BeS, CdS, HgS, BeSe, ZnSe, CdSe, HgSe, BeTe
						12 P	3.84		12 Al	3.84		
						12 Al	4.50		12 P	4.50		

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TABLE 4-4 (*continued*)

Compound	Crystal system	Space group	Formula weights per unit cell	Cell dimensions	Number of atoms surrounding a specified atom at the distances given		Data for the metal in elemental form	Structure prototype[a] and isomorphs	Refs.[b]
GaP	Cubic	$F\bar{4}3m$	4	$a = 5.436$ A.	P: 4 Ga 2.36 A.; 12 P 3.85; 12 Ga 4.51	Ga: 4 P 2.36 A.; 12 Ga 3.85; 12 P 4.51	At 2.44 and at 2.71 A.	As above	102, 103 [II, 76–7,140, 772] [II, 236]
CuP	Hexagonal	$C\bar{1}c$	6	$a = 7.070$ A. $c = 7.135$	(3) P: 2 Cu_{II} 2.28 A.; 2 Cu_{III} 2.33; 2 Cu_{III} 2.41; 2 Cu_{III} 2.50; 2 Cu_{I} 3.23; 2 Cu_{II} 3.73; 2 P 3.96; 4 P 4.47	Cu_{I}: 6 Cu_{III} 2.54 A.; 2 Cu_{I} 3.57; 6 Cu_{III} 4.26; 3 P 3.23 (2) Cu_{II}: 6 Cu_{III} 2.64 A.; 2 Cu_{II} 2.57; 3 Cu_{I} 4.26; 3 P 2.28; 3 P 3.73 (6) Cu_{III}: 1 Cu_{I} 2.54 A.; 1 Cu_{III} 2.57; 1 Cu_{III} 2.62; 2 Cu_{III} 2.64; 2 Cu_{III} 2.73; 2 Cu_{III} 2.78; 1 P 2.33; 1 P 2.41; 1 P 2.50	12 Cu at 2.55 A.		129 [VI, 7–9, 65–7] [VII, 99] [XI, 110]

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Zn_3P_2	Tetragonal	$P4_2/nmc$	8	$a = 8.09$ A. $c = 11.45$	P	2 Zn_{III} 2 Zn_I 4 Zn_{II} 4 P_{III} 4 P_{II} 4 P_{III}	2.35 A. 2.44 2.77 3.96 4.05 4.13	Zn_{II}	2 P_{III} 1 P_{II} 1 P_I 1 Zn_{III} 2 Zn_{III}	2.35 A. 2.44 2.77 3.00 3.07	6 Zn at 2.660 A. Also 6 Zn at 2.907 A.	Cd_3P_2 Zn_3As_2 Cd_3As_2	139 [III, 51–3, 353–7]
Cd_3P_2	Tetragonal	$P4_2/nmc$	8	$a = 8.74$ A. $c = 12.28$	P	2 Cd_{III} 2 Cd_I 2 Cd_{II} 4 P_{III} 4 P_{II} 4 P_{III}	2.55 A. 2.62 2.99 4.28 4.34 4.45	Cd_{II}	2 P_{III} 1 P_{II} 1 P_I 1 Cd_{III} 2 Cd_{III}	2.55 A. 2.62 2.99 3.22 3.33	6 Cd at 2.973 A. Also 6 Cd at 3.287 A.	Zn_3P_2 Zn_3As_2 Cd_3As_2	139 [III, 51–3, 353–7]
ThP_2	Cubic	$Im3d$	4	$a = 8.600$ A.	(4) P	8 Th 3 P 2 P 4 P 6 P	2.98 A. 3.20 3.72 4.24 5.36	(3) Th	8 P 8 Th 4 Th 8 Th	2.98 A. 4.02 5.31 5.88	12 Th at 3.590 A.		144 148
TiP	Hexagonal	$P6_3/mmc$	4	$a = 3.487$ A. $c = 11.65$	P	6 Ti 6 P 6 P	2.48 A. 3.49 3.54	Ti	6 P 1 Ti	2.48 A. 2.91	6 Ti at 2.91 A. Also 6 Ti at 2.95 A.	MoC β-ZrP NbN	149
α-ZrP	Cubic	$Fm3m$	4	$a = 5.27$ A.	P	6 Zr 12 P	2.61 A. 3.73	Zr	6 P 12 Zr	2.64 A. 3.73	6 Zr at 3.17 A. and 6 Zr at 3.22 A.	NaCl	149
β-ZrP	Hexagonal	$P6_3/mmc$	4	$a = 3.677$ A. $c = 12.52$	P	6 Zr 6 P 6 P	2.64 A. 3.68 3.78	Zr	6 P 1 Zr	2.64 A. 3.13	As above	MoC TiP NbN	149
VP	Hexagonal	$P6_3/mmc$	2	$a = 3.18$ A. $c = 6.22$	P	6 V 6 P 6 P	3.41 A. 3.18 3.61	V	6 P 2 V	2.41 A. 3.11	8 V at 2.627 A.	NiAs	149

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TABLE 4-4 (*continued*)

Compound	Crystal system	Space group	Formula weights per unit cell	Cell dimensions	Number of atoms surrounding a specified atom at the distances given		Data for the metal in elemental form	Structure prototype[a] and isomorphs	Refs.[b]
α-NbP	Hexagonal	$P6_3/mmm$	4	a = 3.32 A. c = 6.60	P: 4 Nb 2.35 A.; 4 P 3.32; 4 Nb 3.29; 4 P 3.29 Nb: 4 P 2.35 A.; 4 Nb 3.29; 4 P 3.29	8 Nb at 2.853 A.	α-TaP	149
β-NbP	Hexagonal	$I4_1/a$	4	a = 3.325 A. c = 11.38	P: 4 Nb 2.35 A.; 4 P 3.32; 4 P 3.30 Nb: 4 P 2.35 A.; 4 Nb 3.37	As above	β-TaP	149
α-TaP	Hexagonal	$P6_3/mmm$	4	a = 3.320 A. c = 6.60	P: 4 Ta 2.35 A.; 4 P 3.32; 4 Ta 3.30; 4 P 3.30 Ta: 4 P 2.35 A.; 4 Ta 3.30; 4 P 3.30	8 Ta at 2.854 A.	α-NbP	149
β-TaP	Hexagonal	$I4_1/a$	4	a = 3.330 A. c = 11.39	P: 4 Ta 2.36 A.; 4 P 3.33; 4 P 3.30 Ta: 4 P 2.36 A.; 4 Ta 3.33	As above		149
CrP	Orthorhombic	Pb/nm	4	a = 5.106 A. b = 5.36 c = 3.113	P: 2 Cr 2.25 A.; 2 Cr 2.27; 1 Cr 2.37; 2 P 3.08; 2 P 3.11 Cr: 2 P 2.25 A.; 2 Cr 2.48; 2 P 2.27; 1 P 2.37	8 Cr at 3.492 A.	MnP	149
MoP	Hexagonal	$P\bar{6}m2$	1	a = 3.23 A c = 3.20	P: 6 Mo 2.46 A.; 2 P 3.20; 6 P 3.23 Mo: 6 P 2.46 A.; 2 Mo 3.20	8 Mo at 2.720 A	WC	149
WP	Orthorhombic	$Pbnm$	4	a = 6.219 A. b = 5.717 c = 5.238	P: 2 W 2.38 A.; 2 W 2.43; 1 W 2.55; 2 P 3.18; 2 P 3.24 W: 2 P 2.38 A.; 2 P 2.43; 1 P 2.55; 2 W 2.71	8 W at 2.735 A. In β-form at 2.519 and at 2.816.	MnP	149

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MnP	Orthorhombic	Pbnm	4	a = 5.905 A. b = 5.249 c = 3.167	P	1 Mn 2 Mn 2 Mn 1 Mn 1 P	2.30 A. 2.32 2.22 2.39 2.69	Mn	1 P 2 P 2 P 1 P 1 Mn 1 Mn 1 Mn	2.30 A. 2.32 2.36 2.39 2.69 2.74 2.84	At 2.24 A. and at 2.38 A.	WP	A [III, 17-8, 263-4]
FeP	Monoclinic	C2m2	2	a = 5.85 A. c = 3.45	Pt	6 Fe$_I$ 3 Fe$_{II}$ 2 P$_I$ 6 P$_{II}$	2.56 A. 2.34 3.45 3.67	(3) Fe$_I$	2 P$_{II}$ 2 P$_I$ 2 Fe$_I$ 6 Fe$_{II}$	2.24 A. 2.30 2.63 2.63	In α-Fe at 2.478 A. and in γ-Fe at 2.52 A.	Ni$_2$P	B [II, 15-8, 284-5]
					(2) P$_{II}$	3 Fe$_{II}$ 3 Fe$_I$ 2 P$_{II}$ 3 P$_{II}$ 3 P$_I$	2.19 A. 2.24 3.45 3.49 3.67	(3) Fe$_{II}$	2 P$_{II}$ 1 P$_I$ 6 Fe$_I$ 2 Fe$_{II}$ 2 Fe$_{II}$	2.19 A. 2.34 2.63 3.10 3.45			
FeP$_2$	Orthorhombic	Pnnm	2	a = 2.75 A. b = 4.98 c = 5.66	(2) P	1 P 1 Fe 2 Fe 2 P 4 P 4 P 1 P	2.17 A. 2.24 2.30 2.72 3.15 3.27 3.70	Fe	2 P 4 P 2 Fe 8 Fe	2.24 A. 2.30 2.73 4.01	As above	FeS$_2$ FeAs$_2$ FeSb$_2$	C [III, 310]
RhP	Cubic	Fm3m	4	a = 5.50 A.	P	8 Rh 12 P	2.38 A. 3.89	(2) Rh	4 P 6 Rh	2.38 A. 2.75		Anti-CaF$_2$, Ir$_2$P	148
IrP	Cubic	Fm3m	4	a = 5.54 A.	P	8 Ir 12 P	2.40 A. 3.91	(2) Ir	4 P 6 Ir	2.40 A. 2.77	12 Ir at 2.700 A.	Anti-CaF$_2$, RhP	148

[a] The structure prototypes are in bold face type. These bold face structures have arbitrarily been chosen by crystallographers as comparison standards.

[b] References to *Strukturbericht* and to its successor, *Structure Reports* (issued by the Crystallographic Society) are given in brackets, [ ]. The Roman numeral refers to the volume number and the Arabic numbers to the pertinent pages. Other references denoted by capital letters are the following:

A. K. E. Fylkner, *Arkiv Kem. Mineral. Geol.*, 11B, No 43, 1 (1934).

B. S. B. Hendricks and P. R. Kosting, *Z. Kryst.*, 74, 511 (1930); J. B. Friauf, *Trans. Am. Soc. Steel Treating*, 17, 499 (1930).

C. K. Meisel, *Z. anorg. u. allgem. Chem.*, 218, 360 (1934).

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100°C. for the potassium derivative), followed by release of hydrogen (at 100°C. for $NaPH_2$ and 175°C. for KPH_2). At temperatures around 350°C., some of the alkali metal also distills out of the material to leave as a final product the thermally stable compounds Na_2P_5 and K_2P_5, respectively.

A series of mixed phosphides of lithium and other metals has been reported.[94] The formulas of these phosphides are LiMgP, LiZnP, Li_3AlP_2, Li_3GaP_2, Li_4SiP_3, Li_4GeP_3, and Li_4TiP_3. All of them exhibit a high electrical resistance (specific resistance of pressed pieces > 10^6 ohms) and melt at temperatures greater than 900°C. These mixed phosphides are all colored brown. An x-ray structure study has been interpreted[94] to mean that, in LiZnP, each kind of atom has a fixed position but, in the other compounds, the Li atoms are statistically distributed in the structure. The structural data for LiZnP and LiMgP are presented in Table 4-4.

Alkaline Earth Metal Phosphides

All of the alkaline earth metals form phosphides having formulas predicted by classical valence rules, *viz.* M_3P_2. These compounds can be prepared by reacting[28] the metal with red phosphorus in a sealed tube and subliming away the excess phosphorus or by passing phosphorus vapor[28,96] in a stream of hydrogen over the metal at 750°C. and again volatilizing the excess phosphorus. Calcium, strontium, and barium phosphides have also been made by heating the corresponding phosphate with carbon in an electric arc.[76] Calcium phosphide can also be prepared by heating calcium and red phosphorus together under a layer of petroleum.[76] In a recent report[96] it was claimed that barium and red phosphorus react at temperatures in the range of 400–450°C. to produce a crystalline material having the empirical formula BaP_3. On heating, this substance loses phosphorus in the temperature range of 740–780°C. to form a substance having the empirical formula BaP_2, which, in turn, loses phosphorus at a still higher temperature to form the well-known Ba_3P_2.

All of the alkaline earth sesquiphosphides, M_3P_2, are stable on heating in hydrogen at 750°C. In an inert gas, barium sesquiphosphide is found to be unaffected by heating at 840°C.; calcium sesquiphosphide can be heated as high as 1250°C. without decomposition. However, all of these

[94] R. Juza and W. Schulz, *Z. anorg. u. allgem. Chem.*, 275, 65 (1954).

[96] E. Zintl and Z. Huseman, *Z. physik. Chem.*, 21B, 138 (1933); M. von Stackelberg and R. Paulus, *ibid.*, 22B, 305 (1933).

[76] S. A. Shchukarev, M. P. Morozova, and E. A. Prokofyeva, *Zhur. Obshchei Khim.*,

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phosphides react rapidly with moist air to liberate phosphine. When treated with water, all of the alkali metal phosphides liberate phosphine. At temperatures around 300°C., the alkaline earth sesquiphosphides begin to react rapidly with oxygen, becoming incandescent. Beryllium and calcium sesquiphosphides are reported to exhibit a brown color, while the color of magnesium sesquiphosphide has been reported to range from yellow-green to orange. Barium sesquiphosphide has been described as a black crystalline mass. Magnesium sesquiphosphide is said to be transparent and to have a high electrical resistance (typical nonconductor).

The crystal structures of Be_3P_2, Mg_3P_2, and Ca_3P_2 have been investigated by x-ray,[95,97] and a complete structure analysis has been obtained for the beryllium and magnesium phosphides, as shown for the latter in Table 4-4. Beryllium and magnesium sesquiphosphides exhibit a cubic anti-manganese oxide structure in which there are two slightly different positions for the phosphorus atoms. In Mg_3P_2, each magnesium atom is surrounded by four phosphorus atoms so that it is in the center of a distorted tetrahedron. All four Mg-P distances are different (2.2, 2.6, 2.9, and 3.0 A.), with an average value of 2.7 A. Each magnesium atom is also quite close (3.2 A.) to three other magnesium atoms, which are so arranged that the Mg-Mg axes are 90° apart—in other words, if the given magnesium atom is situated at the corner of a 3.2 A. cube, the three nearest magnesium atoms are at adjacent corners. In magnesium metal, the Mg-Mg distance is 3.20 A. Thus, the Mg-Mg distance in the phosphide is the same as in the metal, but the coordination number of nearest neighbors is three in the phosphide instead of six as in the metal.

In either position, each phosphorus atom is surrounded by six magnesium atoms arranged at the corners of a tetragonal bipyramid. In one position, the Mg-P distances are all the same and equal 2.6 A.; in the other, the phosphorus atom is not centered in the tetragonal bipyramid, so that there are three different Mg-P distances (2.2, 2.9, and 3.0 A.), which average 2.7 A. The distances between phosphorus atoms are all equal to or greater than 4 A., so that the phosphorus atoms can be considered as being isolated from each other. The arrangement of the magnesium atoms around the phosphorus suggests the sp^3d^2 hybridization of the phosphorus. The structures of the alkaline-earth sesquiphosphides probably partake about equally of metallic and covalent character. If it is assumed that a phosphide ion (P^{3-}) is present, its radius would be about 2.0 A.; *i.e.*, 2.6–0.65 A., where 0.65 A. is the accepted ionic radius of Mg^{2+}.

The partial pressure of phosphorus over a mixture of Ca_3P_2 plus cal-

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cium phosphates has been measured.[90] This pressure, given by the following equations, represents the partial pressure of P_4 gas over Ca_3P_2, where the solid residue (Ca?) undoubtedly reacts with the calcium phosphates present to form unspecified reduction products:

$$\log p_{mm.} = -6080/T + 6.104 \quad \text{for } 1473° < T < 1595°\text{K.} \quad (4\text{-}31)$$

and

$$\log p_{mm.} = -7760/T + 7.160 \quad \text{for } 1595° < T < 1773°\text{K.} \quad (4\text{-}32)$$

As is the case with the alkali metals, phosphides (often poorly defined) of the alkaline earth metals can be made by adding phosphorus or phosphine to liquid ammonia containing the metal.[92] Thus, a compound having the empirical formula $Ca(PH_2)_2 \cdot 6NH_3$ is made by reacting phosphine with calcium in liquid ammonia. This substance loses 4 moles of ammonia when put in a vacuum at 0°C. Upon heating in the vacuum, a material with the empirical formula CaHP is formed which, at higher temperatures, decomposes further.

Phosphides of Group IIIA Elements

Boron phosphide, BP, has recently been prepared[100] through the reaction between boron and phosphorus in evacuated silica tubes. It has a cubic structure of the zinc-blend type, with a cube edge of 4.538 A. The B-P distance is 1.964 A., and both elements exhibit four-fold coordination. This means that both atoms have an octet of electrons and exhibit an sp^3 type of hybridization. According to the early work[100] on boron phosphides, BP can be made by heating the addition product $BBr_3 \cdot PH_3$ to 300°C. It can also be prepared by heating one of the boron phosphoiodides, BPI_2 or BPI to about 500°C. in a stream of hydrogen. Boron phosphide is a maroon or black powder insoluble in all solvents which were tested. Boiling water has no action on the phosphide, but it is decomposed by boiling concentrated alkalies with the evolution of phosphine and by steam at 400°C. with the formation of boric acid and phosphine. Dilute or concentrated hydrochloric or sulfuric acids have no action on boron phosphide in the cold. When boron monophosphide is heated to about 1000°C. in a stream of hydrogen,

[90] H. H. Franck and H. Füldner, *Z. anorg. u. allgem. Chem.*, 201, 97 (1932).
[92] C. Legoux, *Compt. rend.*, 209, 47 (1939); *Ann. chim.*, 17, 100 (1942).
[100] S. Rundqvist, paper at the XVIth International Congress of Pure and Applied Chemistry, Paris, 1957; P. Popper and T. A. Ingles, *Nature*, 179, 1075 (1957); H. Moissan, *Ann. chim. Phys.*, 6, No. 7, 296 (1895); *Compt. rend.*, 113, 727 (1891); A. Besson,

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it forms the compound B_4P_3. This compound is even more inert than BP, since it does not burn in an atmosphere of chlorine below a dull red heat and is not attacked by nitric acid. It can be decomposed, however, by molten alkali metal nitrates.

According to Moissan,[100] boron phosphodiiodide, BPI_2, can be prepared by reacting a solution of boron triiodide in carbon disulfide with a similar solution of phosphorus in the absence of moisture. The product BPI_2 is a finely divided dark red powder which melts at about 195°C. and volatilizes in a vacuum at about the same temperature. After sublimation, BPI_2 is obtained as a well-crystallized red product. The compound is very slightly soluble in carbon disulfide and is insoluble in benzene, phosphorus trichloride, and carbon tetrachloride. It is very hygroscopic and decomposes rapidly in moist air. It also decomposes in water giving hydriodic, phosphorous, and boric acids plus some phosphine in the presence of a large amount of water, and these products plus a detectable amount of phosphonium iodide and a yellow precipitate which might be the solid hydride, P_2H, in the presence of little water. When BPI_2 is heated in an atmosphere of hydrogen, boron phosphoiodide, BPI, is formed as a finely divided red powder which is somewhat less hygroscopic than BPI_2. This compound, BPI, volatilizes in a vacuum at 210–250°C. without melting and condenses as orange-yellow crystals. Strong oxidizing acids decompose BPI with the formation of iodine.

Although several aluminum phosphides have been reported,[75] recent investigations[101] indicate that there is only one aluminum phosphide—the monophosphide, AlP. This compound is made by passing phosphorus vapor in a stream of hydrogen over hot aluminum. Pure aluminum phosphide is insoluble in both cold and boiling water but dissolves in dilute hydrochloric acid with the evolution of phosphine. This reaction is one of the best procedures for the preparation of pure phosphine. Hot concentrated oxidizing acids have little effect on AlP, but hot concentrated alkalies liberate phosphine. When aluminum phosphide is subjected to dry hydrogen chloride vapor, the solid phosphorus hydride, P_2H, is formed. At very high temperatures, phosphorus is lost from aluminum phosphide; but vapor pressure data are not available. Heating AlP in air converts it to alumina and aluminum phosphate, $AlPO_4$—apparently some phosphorus is lost as PH_3.

Gallium and indium phosphides, GaP and InP, are quite similar[102] to

[101] W. E. White and A. H. Bushey, *J. Am. Chem. Soc.*, 66, 1606 (1944); E. Montignie, *Bull. soc. chim.*, 1949, 276.

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aluminum phosphide, AlP. These compounds are prepared by heating the elements in stoichiometric proportions in a vacuum. The reaction is slow, and the temperature must be raised to 700°C. to complete it. Unlike aluminum phosphide, the phosphides of gallium and indium dissolve with difficulty in dilute hydrochloric acid. The crystal structures of AlP, GaP, and InP are similar. All of them exhibit a zinc-blend type of structure,[102,103] in which both component elements have four-fold coordination. These compounds are isoelectronic with the elements of Group IVA. In other words, AlP should be very similar to elemental silicon. Thus, in silicon the

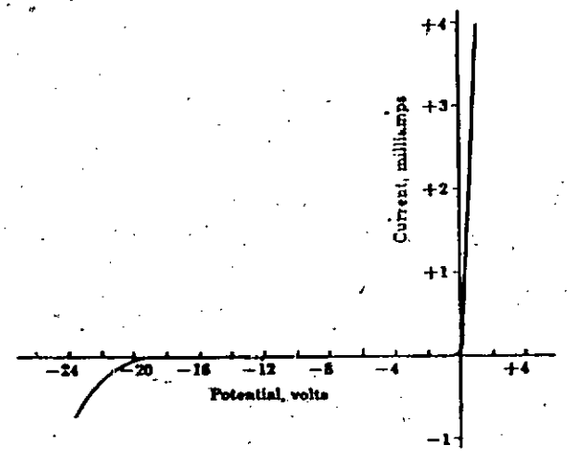

Fig. 4-12. Rectifier curve of a p-conducting crystal of indium phosphide, InP, obtained with point contacts.

individual atoms also exhibit four-fold coordination, and the Si-Si distance is 2.346 A., as compared to an Al-P distance of 2.35 A. in aluminum phosphide. Moreover, in aluminum phosphide, the Al-Al distance is 3.84 A. as compared to 2.858 A. in metallic aluminum. This means that the aluminum atoms, as well as the phosphorus atoms, are distantly separated from like atoms so that there should be essentially no metallic bonding. Like the unreacted elements in Group IVA of the periodic table, the phosphides of the Group IIIA elements are three-dimensional polymers. In these phosphides—as exemplified by AlP—both atoms have an octet of electrons[104] and exhibit an sp^3-type of hybridization.

[102] L. Pacinini, *Gazz. chim. ital.*, 58, 655 (1928); V. Goldschmidt, *Geochem. Vert.*, 8,

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As in the case of the elements of Group IVA, the phosphides of aluminum, gallium, and indium can act as either *p* or *n* semiconductors,[102,105] depending on the kind and level of the impurities. A plot[102] of current *versus* applied potential is given for a *p*-conducting crystal of indium phosphide in Figure 4-12. This curve shows the rectifying characteristics of the crystal. Indium phosphide has also been shown to exhibit transistor properties.[107]

Although the earlier literature[73] claims that thallium phosphides do not exist, a phase study[106] indicates the presence of TlP_3 which melts at about 420°C. This substance tends to dissociate into its constituents at all temperatures, so that a high pressure is necessary for its formation. Another thallium phosphide, Tl_3P, has been reported.[107] It was prepared by heating theoretical amounts of thalium and white phosphorus in a sealed tube at 400°C. Proof that this is a definite compound is lacking.

Phosphides of Group IVA Elements

The best-known carbon-phosphorus compound is the high-temperature molecule, CP, which is known from its band spectrum.[108] The only reference[102] to a phosphorus carbide stable at room temperature is to a reaction product of phosphorus trichloride with acetylene magnesium iodide IMgC≡CMgI. This Grignard reaction product is a yellowish white amorphous precipitate, having the empirical formula PC_4, which was found to be insoluble in ordinary solvents and not attacked by acids or alkalies.

Although no silicon phosphides appear in the older literature,[78] a silicon phosphide having the formula SiP has been demonstrated to exist by vapor pressure studies.[110] This silicon phosphide decomposes according to the following reaction:

$$4\,SiP(s) \longrightarrow 4\,Si(s) + P_4(g) \qquad (4\text{-}33)$$

In the temperature range of 1000-1200°C., the partial pressure of P corresponding to this decomposition is given by the following equation from which a heat of reaction, ΔH, of 72 kcal. was calculated.

$$\log p_{min.} = -15{,}710/T + 13.769 \qquad (4\text{-}34)$$

[105] T. Witmer, *Crystal Rectifiers*, McGraw-Hill Book Co., Inc., New York, 1948, p. 67.
[106] Q. A. Mansuri, *J. Chem. Soc.*, 1927, 2993.
[107] E. Montignie, *Bull. soc. chim.*, 4, No. 5, 295 (1937).
[108] H. Bärwald, G. Herzberg, and L. Herzberg, *Ann. Phys.*, 20, 569 (1934). For more recent discussions, see G. Lovera, *Nuovo cimento*, 9, 541 (1952) and J. W. Linnett, *Trans. Faraday Soc.*, 38, 1 (1942).

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All of the phosphorus can be removed from silicon phosphide by heating in a vacuum at 1000°C. Although it is not thermally stable, silicon phosphide is resistant to oxidation, even at red heat, due to the formation of a protective coating of silicon dioxide. However, as might be expected, it reacts with chlorine at elevated temperatures. Silicon phosphide does not react appreciably with cold water, but it does decompose in boiling water to form phosphine. Only two-thirds of the total phosphorus is given off as phosphine, so that probably either a lower silicon phosphide or the solid phosphorus hydride, P_2H, is formed in the reaction.

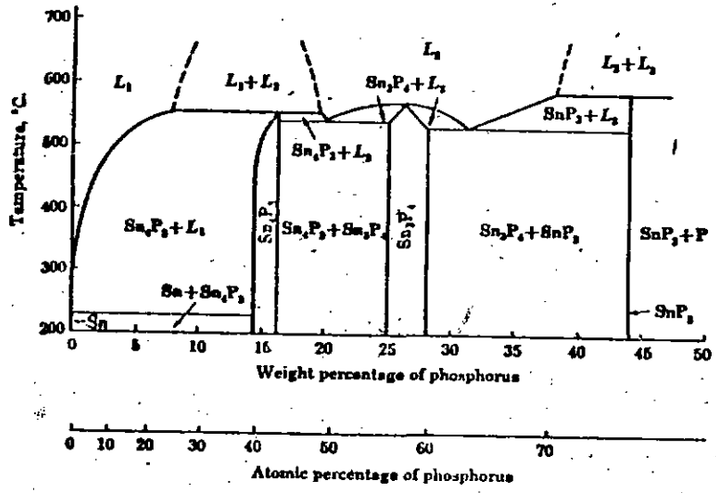

Fig. 4-13. Phase diagram of the tin-phosphorus system.

Although the structure of silicon phosphide has not been determined, it has been shown to have a different x-ray pattern than that of elemental silicon.[110] Silicon phosphide is nonmetallic in character, and the vapor pressure measurements indicate that it is a true compound. A small amount of phosphorus can be dissolved in molten silicon where, upon cooling, it acts as an impurity center with respect to the semiconducting properties of silicon. In this role, phosphorus has been classed as a superior addition agent for silicon,[105] increasing conductivity and producing a good, stable rectifier.

[110] W. Biltz, H. Hartmann, E. W. Wrigge, and F. Wiechmann, *Sitzber. preuss. Akad.*

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Germanium phosphide, GeP, has been made by heating metallic germanium with an excess of phosphorus to temperatures of 400°C. or more in an evacuated tube.[111] X-ray analysis, as well as vapor pressure measurements, show that the reaction product has the formula GeP and is distinct from both elemental germanium and elemental phosphorus. The heat of formation of germanium phosphide from solid germanium and P_4 gas is −37 kcal.

Unlike the phosphides of silicon and germanium, which are probably three-dimensional polymers somewhat similar to the phosphides of aluminum, gallium, and indium, the phosphides of tin are considerably more metallic in character and appear to be related to the phosphides of the alkali and alkaline earth metals and some of the phosphides of the transition metals. The phase diagram[112] of the tin-phosphorus system is given in Figure 4-13, where it can be seen that there are three phosphides, SnP_3, Sn_3P_4, and Sn_4P_3. In this phase diagram both Sn_4P_3 and Sn_3P_4 appear as limited regions of solid solution, whereas SnP_3 exhibits an exact composition. There are three different liquid phases in the tin-phosphorus system—liquids which have limited solubility in each other. This means that in the regions indicated in Figure 4-13 as $L_1 + L_2$ and $L_2 + L_3$, two immiscible liquid layers of melt are present. In the three-phase system, Fe—Sn—P, which has been examined in detail,[113] no mixed phosphides of iron and tin were observed. The effect of adding either iron or phosphorus to tin is to increase the fusion temperature of the alloy rapidly. When tin is added to the iron-phosphorus system, the latter fusion diagram is unaffected up to about 5% tin, except for a slight lowering (about 70°) of the eutectic temperatures.

When tin is reacted with an excess of phosphorus in a sealed tube, SnP_3 is formed. This phosphide is insoluble in hydrochloric acid and, upon being heated in a vacuum at 350°C., loses phosphorus to form Sn_4P_3, which is soluble in HCl.[114] Sn_4P_3 can be separated from tin in alloys containing up to 13% phosphorus by making the alloy the anode in a solution of sodium polysulfide. This causes the tin to dissolve, leaving silver-white crystals of Sn_4P_3. Presumably, the tin monophosphide, SnP, reported in the literature[114] is identical to the compound Sn_3P_4 shown in Fig. 4-13. When this compound is heated to 415°C., it loses phosphorus and forms Sn_4P_3.

[111] M. Zumbusch, M. Heimbrecht, and W. Biltz, *Z. anorg. u. allgem. Chem.*, 242, 257 (1934).

[112] A. C. Vivian, *Inst. Metals Preprint*, 1920, 35 pp.

[113] R. Vogel and G. Swiatoslawski, *Arch. Eisenhüttenw.*, 26, 631 (1955).

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The vapor pressure of phosphorus over the various tin phosphides has not as yet been measured. It is interesting to note that reduction of tin phosphate with hydrogen at 600°C. gives only metallic tin and no tin phosphides.[116]

Because of the low melting point of the tin phosphides (about 550°C.), the ease of formation of the higher tin phosphides under pressure, and the difference in solubilities of SnP_3 and Sn_4P_3 in hydrochloric acid, these compounds can be used in preparing phosphides of other metals. In general, the process is to bring to red heat in an enclosed system a mixture of red phosphorus with a 5% alloy of the desired metal in tin. Any SnP_3 which is formed can be converted to Sn_4P_3 by heating in a vacuum at 350°C. This latter tin phosphide can then be dissolved in hydrochloric acid to leave the phosphide of the desired metal. Nickel, cobalt, and platinum phosphides have been prepared in this way.[116,117]

Molten lead will dissolve up to about 1.5% of phosphorus.[76] Although a lead phosphide of the formula PbP_2 made by reacting white phosphorus and molten lead has been described by several authors,[118] the existence of this compound is considered questionable, since in another study[119] phosphorus and lead were not found to react in elemental form. By combining lead acetate dissolved in ethyl alcohol with phosphine dissolved in alcoholic potassium hydroxide, a black flocculent precipitate having the formula Pb_3P_2 is formed. This precipitate is very unstable and, on standing, decomposes to leave a film of lead on the glass walls of the containing vessel. Water and dilute acids or alkalies react slowly with this product when cold, and rapidly when warm, to give phosphine.

By allowing phosphorus to react with the lead alloys of zinc, cadmium, or mercury for 8–10 days at temperatures ranging from 525 to 610°C., there are produced[120] ternary phosphides exhibiting the general formula $MPbP_{16}$, where M stands for Zn, Cd, or Hg. These compounds all have similar properties. They are stable in air and do not dissolve in water or nonoxidizing mineral acids. These phosphides are all well crystallized and exhibit a grey to silver color, being opaque and having a metallic luster. However,

[116] J. C. Hutter, *Ann. chim. (Paris)*, 8, 450 (1953).
[117] W. Biltz and M. Heimbrecht, *Z. anorg. u. allgem. Chem.*, 237, 132 (1938).
[118] W. Biltz, I. Mathiesen, and F. W. Wrigge, *Z. anorg. u. allgem. Chem.*, 232, 284 (1937).
[119] A. C. Vournasos, *Ber.*, 44, 3269 (1911); A. Stock and F. Golmolke, *ibid.*, 42, 4510 (1909); G. Linck and P. Müller, *ibid.*, 41, 1404 (1908).
[120] A. Granger, *Ann. chim. Phys.* 14, No. 7, 74 (1898); *Contribution à l'étude des phosphures métalliques*, Thesis Univ. of Paris 1899. [illegible]

they do not conduct electricity and have very weak piezoelectric properties. The crystals belong to the tetragonal system and show fibrous cleavage along the *c*-axis. The dimensions of the unit cells of the mercury and cadmium compounds, $HgPbP_{16}$ and $CdPbP_{16}$, are the same, whereas the cell constants of the zinc compound, $ZnPbP_{16}$, are several per cent smaller. From a partial analysis of the x-ray data and the fact that the crystals exhibit fibrous cleavage and contain a large amount of phosphorus, it has been suggested that the structure involves straight chains of interconnected phosphorus atoms directed along the *c*-axis.[120] If this is so, these compounds represent the unusual case of a phosphide in which the phosphorus atoms are not widely separated from each other. In other words, Krebs *et al.* suggest that these compounds are true polyphosphides. Another item of note concerning the compound $HgPbP_{16}$ is that it is stable, although binary compounds of phosphorus with either lead or mercury may not exist or, at least, are difficult to prepare and store.

Phosphides of Arsenic, Antimony, and Bismuth

X-ray and thermal analysis studies[121] show that phosphorus forms only one compound with arsenic, arsenic monophosphide, AsP. This compound, AsP, consists of black leaflets which have the superficial appearance of graphite. Its specific electrical resistance is in the range of 1–10 ohms, only a little higher than that of black phosphorus. Presumably this compound has a structure similar to those of black phosphorus and grey arsenic. In grey arsenic, the atoms are arranged in the same way as in black phosphorus so that the crystal consists of layers in which each arsenic atom has three equidistant nearest-neighbor arsenic atoms at 2.51 A. and then three more neighbors somewhat farther removed.

According to a recent phase diagram study,[122] there are no antimony phosphides. The greatest solubility of phosphorus in molten antimony is 0.85%, which causes a reduction in melting point of the antimony from 630.5 to 612°C.

There also does not seem to be a bismuth phosphide, although there were a few reports of such a substance in the early literature.[75] By passing phosphine into a solution of bismuth trichloride in ether, a black, hygroscopic deposit having the composition PBi_2Br_7 is formed.[123]

[121] W. Klemm and I. von Falkowski, *Z. anorg. Chem.*, 256, 343 (1948).
[122] R. Vogel and D. Horstmann, *Arch. Eisenhüttenw.*, 23, 127 (1952).
[123] A. Cavazzi and D. Tivoli, *Gazz. chim. ital.* [illegible] (1891); [illegible]

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Phosphides of Copper, Silver, and Gold

The well-recognized phosphides of copper, silver, and gold are tabulated below.

	CuP_2		Cu_3P_2	Cu_3P	Cu_3P
AgP_2	AgP_2				Ag_3P
		Au_3P_2			Au_3P

The two best established copper phosphides are CuP_2 and Cu_3P. Metallic copper reacts with phosphorus vapor at high temperatures and pressures to form CuP_2. This compound then decomposes to form Cu_3P according to the following equation.

$$^{12}/_{3}\ CuP_2(s) \longrightarrow {}^{4}/_{3}\ Cu_3P(s) + P_4(g) \qquad (4\text{-}35)$$

In the temperature range from 600 to 800°C., the partial pressure[96,124] of phosphorus vapor, P_4, corresponding to equation 4-35 is given below. At 760°C. the vapor pressure of phosphorus over Cu_3P is immeasurably small. For the following equation, the heat of reaction, ΔH, is 52 kcal.

$$\log p_{mm.} = -11{,}370/T + 13.827 \qquad (4\text{-}36)$$

According to this equation, the partial pressure of phosphorus over a mixture of CuP_2 and Cu_3P is 1 atm. at 765°C. Both CuP_2 and Cu_3P have been observed in a thermal analysis of the copper-phosphorus system.[125] These compounds have also been made by reduction of heated copper metaphosphate by hydrogen.[116] The lower phosphide, Cu_3P, has been prepared by electrolysis[126] of sodium phosphate melts containing copper oxide and by the reaction of excess phosphine on solutions of copper sulfide.[127]

The phase diagram of the copper-phosphorus system has been determined[125,127] up to 15% copper, as shown in Figure 4-14. Beyond 14% copper, corresponding to the phosphide Cu_3P, there is an eutectic between Cu_3P and another higher phosphide. At the left side of the phase diagram, it should be noted that phosphorus dissolves in metallic copper. The maximum solubility of phosphorus in copper is 1.7% at a temperature of 714°C. An x-ray study[128] has been carried out on Cu_3P, and the results are reported in Table 4-4. In this compound, the phosphorus atoms have eight nearest-neighbor copper atoms at 2.3–2.5 A. plus four more at 3.2–3.7 A. The distance of closest approach for the copper atoms to the six nearest copper atoms ranges from 2.54 to 2.64 A., depending on the position of the copper in the lattice. These values should be compared to the Cu-Cu distance of 2.55 A. in metallic copper. Cu_3P possesses a metallic luster, conducts electricity, and is brittle and dense. It is feebly attacked by hydrochloric acid and readily oxidized by air.

[125] H. Haraldsen, *Z. anorg. u. allgem. Chem.*, 240, 337 (1939).
[126] E. Kreutzer, *Z. Physik*, 48, 556 (1928).
[127] M. Chêne, *Compt. rend.*, 214, 977 (1924).
[128] E. Heyn and O. Bauer, *Z. anorg. Chem.*, 52, 129 (1907); D. K. Crampton, H. L. Burghoff, and J. T. Stacy, *Trans. Am. Inst. Mining Met. Engrs.*, 137, 351 (1940).
[129] H. Steenbock, *Ind. Eng. Chem.* [illegible]

The compound Cu_3P has been reported to be obtained by electrolysis of a fused phosphate containing copper oxide.[126] Upon heating, Cu_3P decomposes to form Cu_3P, as would be expected. Since Mn_2P, Fe_2P, and

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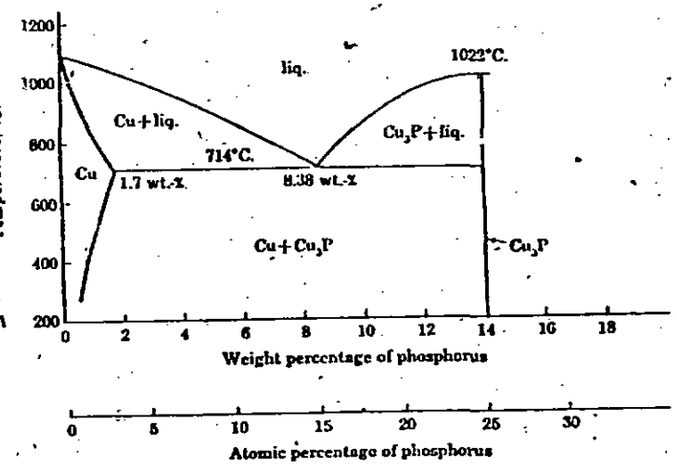

Fig. 4-14. Phase diagram of the copper-rich end of the copper-phosphorus system.

Ni_2P all exist and are isomorphous, it might be expected that Cu_3P would also belong to this isomorphous series. X-ray examination of this compound would help to prove its existence. The compound Cu_2P_2 is said to be formed[75,83] as an intermediate product in the reaction of phosphine with copper salts, either as solids or in solution. In view of the fact that zinc and cadmium form similar compounds, its existence does not seem unlikely. The reactions of phosphine with cupric salts should definitely be reinvestigated. It would also be of interest to study the reactions of cuprous salts with phosphine. In addition to the copper phosphides described here, the earlier literature[75] also refers to a Cu_2P_2 and a CuP.

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pper phosphides are made on a commercial scale. The phase diagrams olving phosphorus, copper, and other metals have been studied to some ent. Thus, the Cu—Sn—P system has had a great deal of work done it.[120] In addition, studies have also been carried out on the following tems: Cu—Fe—P,[120] Cu—Ni—P,[121] Cu—Mn—P,[121] Cu—Cr—P,[121] —Ag—P,[122] Cu—Zn—P,[122] and Cu—Si—P.[123] Because of the use of sphorus in deoxidizing copper and the interest of metallurgists in the ctions between metals and slags, several diverse investigations have also n carried out on the system Cu—P—O.[124]

The silver-phosphorus system has been examined[125] by thermal analysis to only a few per cent phosphorus. An eutectic occurs at a phosphorus tent of about 0.98% by weight and a temperature of 878°C. The maxim solubility of phosphorus in silver is 1.4% at 960°C. As would be ected, the two silver phosphides which contain the most phosphorus ibit relatively high partial pressures of phosphorus. In the case of the er phosphides, there is the stepwise decomposition shown in the follow equations:

$$4\,AgP_3(s) \longrightarrow 4\,AgP_2(s) + P_4(g) \qquad (4\text{-}37)$$

$$2\,AgP_2(s) \longrightarrow 2\,Ag(s) + P_4(g) \qquad (4\text{-}38)$$

partial pressures[80,126] of phosphorus as P_4 over AgP_3 and AgP_2, respec- ly, are given by the following equations, which apply to the temperature ge from 400 to about 550°C. According to these equations, the temper- re at which the partial pressure of P_4 vapor is 1 atm. is 515°C. for AgP_3 551°C. for AgP_2.

$$\log p_{mm.} = -7759/T + 12.726 \qquad \Delta H = 35.5 \text{ kcal.} \qquad (4\text{-}39)$$

$$\log p_{mm.} = -7161/T + 11.566 \qquad \Delta H = 32.7 \text{ kcal.} \qquad (4\text{-}40)$$

J. Voro, *Z. anorg. u. allgem. Chem.*, 213, 257 (1933); L. C. Glaser and H. J. Seemann, *ch. Physik*, 7, 42 (1926); M. Levi-Malvano and F. S. Orofino, *Gazz. chim. ital.*, 41, 97 (1912); D. W. D. Showell, *J. Inst. Metals*, 76, 627 (1950); L. Guillet, *Cuivre et n*, 5, 529 (1932); L. C. Glaser and H. J. Seemann, *Z. tech. Physik*, 7, 90 (1926); N. lakowski, *J. Inst. Metals*, 81, 617 (1953).

R. Vogel and J. Berak, *Arch. Eisenhüttenw.*, 21, 327 (1950); E. Crepaz, *Atti e mem. sci. Padova, Classe sci. fis. mat.* [N.S.], 52, 97 (1936); also see ref. 123.

H. Nowotny and E. Henglein, *Monatsh.*, 79, 385 (1948).

H. Moser, K. W. Fröhlich, and E. Raub, *Z. anorg. u. allgem. Chem.*, 208, 325); K. W. Fröhlich, *Mitt. Forsch.-Insts. u. Probieramt Edelmetalle*, 6, 69 (1932).

W. E. Lindlief, *Metals & alloys*, 4, 85 (1933).

W. Krings, *Z. Metallkunde*, 26, 247 (1934); W. Oelsen, *Z. Erzbergbau u. Metallhütt.* 2, 328, 368 (1949); B. T. Houbten and W. A. Baker, *Metallurgia*, 47, 223 (1953).

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In the similar manner, the gold phosphide, Au_2P_3, loses phosphorus to form Au_2P. The equations for this reaction and for the corresponding pressure of phosphorus vapor, P_4, in the temperature range of 550–700°C. are given below. The heat of the decomposition reaction for Au_2P_3 is 41.7 kcal.

$$^4/_3\,Au_2P_3(s) \longrightarrow {}^4/_3\,Au(s) + P_4(g) \qquad (4\text{-}41)$$

$$\log p_{mm.} = -9126/T + 12.210 \qquad (4\text{-}42)$$

At 705°C., the pressure of P_4 vapor over Au_2P_3 is 1 atm.

With respect to their chemical properties, the silver and gold phosphides are quite similar to the copper phosphides. As is the case with copper salts, solutions of silver or gold salts are found to react with phosphine. In the reaction with silver nitrate, a compound having the composition $Ag_3P \cdot 3AgNO_3$ is first formed[126] as an unstable yellow intermediate. This compound decomposes to give a precipitate of Ag_3P which, in dilute solution, further decomposes into silver and the lower oxyacids of phosphorus. Depending on the concentration, a number of different products can be obtained from the action of phosphine on solutions of silver nitrate. Among these products are the silver nitratophosphide, $Ag_3P \cdot 3AgNO_3$; the silver phosphide, Ag_3P; nitrogen tetroxide; metallic silver; and various oxyacids of phosphorus. Phosphine will react with a large excess of silver salts in water to give a stoichiometric yield of phosphoric acid and metallic silver.[53,110] The same thing is true of auric salts.[127] In the case of the gold salts, the reaction with phosphine usually causes a reduction of the gold to metallic form. However, it is possible to make auric phosphides from phosphine in water.[127]

Phosphides of Zinc, Cadmium, and Mercury

Both zinc and cadmium form two phosphides,[86,103,124,128] ZnP_2 and Zn_3P_2 for zinc and CdP_2 and Cd_3P_2 for cadmium. The orange-red diphosphides are formed by heating the elements in a sealed tube at red-heat. They melt at temperatures in the neighborhood of 700°C. and can be sublimed at this temperature in an atmosphere of phosphorus vapor. However, when heated in a vacuum at 700°C., they decompose to form the lower stable phosphides, M_3P_2. The diphosphides do not react with water. With acids

[126] T. Poleck and K. Thümmel, *Ber.*, 16, 2435 (1883); *Arch. Pharm.* 22, No. 3, 1 (1884). Also see J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Longmans Green & Co., London, 1923, Vol. III, pp. 470–71.

[127] A. Baker and F. L. Usher, *Trans. Faraday Soc.*, 36, 385 (1940).

[128] M. von Stackelberg and R. Paulus, *Z. physik. Chem.*, B28, 427 (1935); P. Jolibois,

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they react slowly to form phosphine. The sesquiphosphides are also stable in water and in cold nonoxidizing acids. The reaction[63] of phosphine with solutions of zinc or cadmium salts gives the lower phosphide, Zn_3P_2 and Cd_3P_2, respectively. The zinc phosphide has been used as a rodenticide, as a result of which some investigations have been carried out on the toxicity of this material.[139]

The phosphides Zn_3P_2 and Cd_3P_2 crystallize in the tetragonal system with eight formula weights per unit cell.[138] These compounds ... iron grey, opaque, and have a metallic luster. They are relatively good conductors of electricity, with the cadmium compound being a better conductor than the zinc. The photoelectric and other semiconducting properties of Zn_3P_2 have been reported in the literature.[140] The diphosphides, ZnP_2 and CdP_2, exhibit a pseudocubic crystal structure which has not been worked out so thoroughly as the structure of the sesquiphosphides.

In Zn_3P_2 and Cd_3P_2, the phosphorus atoms are surrounded by six nearest-neighbor metal atoms, as shown in Table 4-4, and the metal atoms have four nearest-neighbor phosphorus atoms as well as three like atoms at a somewhat larger distance: In Zn_3P_2, the Zn-Zn distances are 3.00 and 3.07 A., as compared to 2.66 and 2.91 A. in metallic zinc. Likewise, in Cd_3P_2, the Cd-Cd distances are 3.22 and 3.33 A., as compared to 2.97 and 3.29 A. in the metal. As is usually the case with the phosphides, the phosphorus atoms are well separated (eight nearest neighbors at 4.0 A.). See Table 4-4 for further details concerning these structures.

Mercury phosphides have not as yet been studied by the methods of physical chemistry. Although there is report[138] of the formation of a mercury phosphide by heating mercury and phosphorus under a layer of paraffin, mercury phosphides have generally not been obtained from a reaction involving the elements. The reaction between phosphine and solutions of mercurous or mercuric salts gives black precipitates containing phosphorus and mercury. The preparation of Hg_3P_2 by this procedure has been reported.[62] There is also a mixed compound which can be written either as $3HgCl_2 \cdot Hg_3P_2$[63] or as $P(HgCl)_3$.[101] Other complex phosphides have been reported.[78] In view of the ease with which mercury forms complex compounds with ammonia, it is not surprising to find that similar compounds are produced with phosphine. The reactions between phosphine and mercury salts should be reinvestigated, using modern technique of structure analysis.

[139] K. Becker and G. A. Hunold, *Pharmazie*, 3, 543 (1948); J. W. Elmore and F. J. Roth, *J. Assoc. Offic. Agr. Chemists*, 26, 559 (1943); G. Dello Iojo, *Folia Med. (Naples)*, 32, 156 (1949).

[140] J. Lagrenaudie, *J. chim. phys.*, 50, 545 (1953).

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Phosphides of Rare Earth and Actinide Metals

Lanthanum, cerium, praseodymium, and neodymium react[141] with phosphorus (violently in the temperature range of 400–500°C.) to form the normal phosphides, MP. With respect to air oxidation, CeP is the most stable, as it can be heated in the open with only slight oxidation. PrP oxidizes slowly in air, whereas LaP is rapidly oxidized. All of these phosphides react with water to liberate phosphine. These rare earth phosphides exhibit a cubic structure of the sodium chloride type, in which both the rare earth and phosphorus atoms have a coordination number of six.[141] The internuclear distances observed in these structures are La-P = 3.01 A., Ce-P = 2.95 A., Pr-P = 2.93 A., and Nd-P = 2.91 A.

Apparently the actinide series of elements most readily forms two types of compounds; M_3P_4 and MP. The known phosphides of this series of compounds are Th_3P_4,[142] ThP,[143] U_3P_4,[144] UP,[144] Np_3P_4,[145] and perhaps U_2P_3.[146] All of these phosphides, with the exception of U_2P_3, are prepared by reaction between the elements, usually under pressure. The U_2P_3 composition was made by passing UH_3 and PH_3 together through a heated tube.

The usual phosphides of the actinide metals—M_3P_4 and MP—exhibit cubic crystal structures. X-ray data on the uranium and thorium phosphides of these compositions have been reported.[142,147] A detailed structure analysis of the Th_3P_4 is presented in Table 4-4. The phosphides, M_3P_4 and MP, exhibit a greyish black color and have a metallic luster. They do not react with water. However, Th_3P_4 and U_3P_4 decompose in cold solutions of hydrochloric acid to liberate phosphine.

In the crystals of Th_3P_4, each thorium atom has eight nearest-neighbor phosphorus atoms at 2.98 A. and eight thorium atoms at 4.02 A. In thorium metal, the Th-Th distance is 11% shorter, being 3.59 A. This expansion of the metal-to-metal distance is typical[74] of the interstitial com-

[141] A. Iandelli and E. Botta, *Atti accad. nazi. Lincei, Mem., Classe sci. fis., mat. e nat.*, 24, 459 (1936); *ibid.*, 26, 233 (1937); *Gazz. chim. ital.*, 67, 638 (1937).

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

[143] K. Meisel, *Z. anorg. u. allgem. Chem.*, 240, 300 (1939).

[144] H. Heimbrecht, M. Zumbusch, and W. Biltz, *Z. anorg. u. allgem. Chem.*, 245, 391 (1941).

[145] I. Sheft and S. Fried, *J. Am. Chem. Soc.*, 75, 1236 (1953).

[146] A. S. Newton, J. C. Warf, F. H. Spedding, D. Johnson, L. D. Johns, R. W. Nottorf,

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pounds which are also known as the hard metals. The phosphorus atoms in Th_3P_4 have six nearest-neighbor thorium atoms at the Th-P distance of 2.98 A. and five phosphorus atoms at 3.20–3.72 A.

Phosphides of Titanium, Zirconium, Vanadium, Niobium, and Tantalum

The recognized phosphides of the metals in Groups IVB and VB are listed below. It should be noted that there are two kinds of "monophosphides"—the α-forms, which are slightly deficient in phosphorus (*e.g.*, $ZrP_{0.90}$), and the β-forms, which appear to correspond exactly to a monophosphide (*e.g.*, ZrP). Generally speaking, the phosphides listed below all lie in the class of hard metals. Recently, the monophosphides in this class have been carefully studied[148] by x-ray; and structural data concerning them are given in Table 4-1.

	β-MP	α-MP			
TiP_2		$TiP_{0.90}$		Ti_2P(?)	
ZrP_2	ZrP	$ZrP_{0.90}$			
VP_2	VP		V_3P_2	V_2P	Zr_2P
NbP_2	NbP	$NbP_{0.90}$			V_2P
TaP_2	TaP	$TaP_{0.90}$			

The diphosphides, MP_2, can be made by heating the metal in a sealed tube with an excess of phosphorus,[61,149] or by passing phosphine over the metal at elevated temperatures.[61] It is very likely that Ti_2P is really Ti_3P since Schönberg showed that it has the Fe_2P structure. Some work has been reported on reacting phosphine and the metal chloride by passing these gases through a hot tube to give either the mono- or diphosphide.[149] When titanium tetrachloride is treated in the cold with phosphine, it forms a yellow crystalline substance which, when heated, decomposes to give phosphine, hydrogen chloride, and some titanium monophosphide, TiP.

The diphosphides decompose to give the monophosphide plus phosphorus vapor according to the following equation.

$$4\,MP_2(s) \longrightarrow 4\,MP(s) + P_4(g) \qquad (4\text{-}13)$$

The partial pressures corresponding to this decomposition have been measured for ZrP_2,[150] VP_2,[61] NbP_2,[151] and TaP_2.[152] The temperatures at which the vapor pressure of phosphorus is 1 atm. are 891°C. for ZrP_2, 711°C.

[148] N. Schönberg, *Acta Chem. Scand.*, 8, 226 (1954).
[149] J. Geweke, *Ann.*, 361, 79 (1908).
[150] E. F. Strotzer, W. Biltz, and K. Meisel, *Z. anorg. u. allgem. Chem.*, 229, 216 (1936).
[151] A. Reinecke, W. Wiechmann, M. Zumbusch, and W. Biltz, [illegible]

for VP_2, and 864°C. for TaP_2. The heats of these reactions, ΔH, are [illegible] kcal., 56 kcal., and 60 kcal., respectively. The equations for the partial pressure of phosphorus vapor as a function of temperature over a mixture of the diphosphide and the monophosphide are given below:

For ZrP_2,

$$\log p_{\text{atm.}} = -10{,}600/T + 11.984 \qquad (4\text{-}14)$$

For VP_2

$$\log p_{\text{atm.}} = -12{,}260/T + 15.281 \qquad (4\text{-}15)$$

For TaP_2

$$\log p_{\text{atm.}} = -13{,}160/T + 14.453 \qquad (4\text{-}16)$$

It is obvious from the above vapor pressure data that a good way to make the monophosphide of these elements is to heat the diphosphide in a vacuum, and this method of preparation has been employed. Depending on the temperature at which the heating is carried out, the α- or β-form of the monophosphide is obtained. Both the α- and β-forms exhibit no measurable vapor pressure of phosphorus at temperatures around 1000°C. The lower phosphides can be prepared directly from the elements.[150] For titanium, the best-known phosphide is the monophosphide, which has been discussed by a number of investigators.[78,153] The other two titanium phosphides have been described only briefly.

A considerable amount of work[85,154] has been done on the preparation of vanadium phosphides, VP and V_2P, by electrolysis of metaphosphate melts containing V_2O_5. The phosphides, NbP and TaP, have also been prepared by this procedure.[154]

The structures of the monophosphides of the Group IVB and VB metals can be classified into four types. One type-group is made up of both the α- and β-forms of NbP and TaP. These four similar structures consist of two-dimensional layers of metal and phosphorus atoms in which both kinds of atoms are surrounded by four atoms of the opposite kind. As is the usual case with the known phosphides, the P-P distances are sufficiently large so that the phosphorus atoms are well isolated from each other. The metal-to-metal distances, both within a layer and between layers, are about 15%

[153] W. [illegible]

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greater than in the pure metals. Presumably, the separate layers are bound together by the same forces which hold metals together.

The three other structure types are represented by (1) TiP and β-ZrP, (2) VP, and (3) α-ZrP. The γ' phase of MoC and Form-I of NbN are isomorphous with TiP and β-ZrP. These structures are typical of the hard metals in that a metal-type lattice is found with the phosphorus atoms in the lattice holes. In TiP and β-ZrP, the mean intermetallic distances are 17% and 14% greater than those observed for the corresponding pure metals. In the isomorphous NbN, the mean intermetallic distance is 6% greater than in the pure metal. Vanadium monophosphide exhibits metal-to-metal distances averaging about 21% larger than in pure vanadium. Although α-ZrP has a sodium chloride type of structure, the metal-to-metal distance is still not very different than in the pure metal, being 17% larger.

Phosphides of Chromium, Molybdenum, Tungsten, Manganese, and Rhenium

The established phosphides of the metals of Group VIB and VIIB are shown below. Except for the fact that triphosphides, MP_3, and the unusual compound W_4P have been reported, this family of phosphides is quite similar to the phosphides of the metals in Groups IVB and VB.

	CrP_2 MoP_2 WP_2	CrP MoP WP	$CrP_{0.90}$ $MoP_{0.4}$	Cr_3P W_3P	Cr_2P Mo_2P	
MnP_3 ReP_3	$Mn_2P(?)$ ReP_2	MnP ReP	Mn_3P_2	Mn_2P Re_2P	Mn_3P	W_4P

Phase diagram studies have been carried out on the chromium-phosphorus[155,156] and manganese-phosphorus[157] systems. In these diagrams the following compounds were found in the composition range studied: Cr_2P, Cr_3P, Mn_3P_2, Mn_2P, and Mn_3P. The systems Cr—Cu—P, Cr—Mn—P, Cr—Fe—P, Cr—Ni—P, Mn—Cu—P, Mn—Fe—P, and Mn—Ni—P have also been investigated.[158] Vapor pressure measurements have been used to demonstrate the existence of a number of phosphides of these particular

[155] R. Vogel and G. W. Kasten, *Arch. Eisenhüttenw.*, 12, 387 (1939).
[156] H. Nowotny and E. Henglein, *Z. anorg. u. allgem. Chem.*, 239, 14 (1938); E. Nowotny, *Naturwiss.*, 26, 631 (1938); also see ref. 132.
[157] J. Berak and T. Heumann, *Z. Metallkunde*, 41, 19 (1950); for earlier work see W. Biltz, F. Wiechmann, and K. Meisel; *Z. anorg. u. allgem. Chem.*, 224, 117 (1937); F. Wiechmann, *ibid.*, 231, 130 (1937); S. Zemczuzny and M. Efremow, *ibid.*, 57, 241

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transition metals. These vapor pressure data show that the diphosphides of the Group VIB and VIIB metals are very similar to the diphosphides of the Group IVB and VB metals—all of which decompose according to equation 4-43.

The temperatures at which the vapor pressure of phosphorus as P_4 equals 1 atm. are 700°C. for CrP_2, about 990°C. for MoP_2, and about 1080°C. for WP_2. For the molybdenum and tungsten phosphides, it must be remembered that there will be some dissociation of the P_4 vapor into P_2 at temperatures around 1000°C. The heats of the reactions corresponding to the equation 4-43 are 39 kcal. for the decomposition of CrP_2, 54.4 kcal. for MoP_2, and 76 kcal. for WP_2. The equations for the partial pressure of P_4 vapor over these phosphides are given below. For CrP_2 in the temperature range of 600–700°C.[158]

$$\log p_{mm.} = -6900/T + 9.829 \qquad (4\text{-}47)$$

For MoP_2 in the temperature range of 800–1000°C.[158,159]

$$\log p_{mm.} = -11{,}900/T + 12.287 \qquad (4\text{-}48)$$

For WP_2 in the temperature range near 1000°C.[159]

$$\log p_{mm.} = -16{,}700/T + 15.210 \qquad (4\text{-}49)$$

Manganese triphosphide loses phosphorus to form manganese monophosphides according to the following equation:[120]

$$2\ MnP_3(s) \longrightarrow 2\ MnP(s) + P_4(g) \qquad (4\text{-}50)$$

At 710°C. the vapor pressure of phosphorus over MnP_3 equals 1 atm., and the heat of the reaction described in equation 4-50 is 54.2 kcal. The partial pressure of P_4 vapor over MnP_3 in the temperature range of 600–700°C. is given by equation 4-51.

$$\log p_{mm.} = -11{,}860/T + 14.948 \qquad (4\text{-}51)$$

The rhenium phosphides exhibit stepwise decompositions, all having measurable vapor pressures.[160] These decompositions are given below, along with the pertinent vapor pressure equations.

$$4\ ReP_3(s) \longrightarrow 4\ ReP_2(s) + P_4(g) \qquad (4\text{-}52)$$

$$\log p_{mm.} = -17{,}060/T + 16.77 \qquad (4\text{-}53)$$

[158] F. E. Faller and W. Biltz, *Z. anorg. u. allgem. Chem.*, 248, 216 (1941).
[159] [illegible]

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$$4\ ReP_3(s) \longrightarrow 4\ ReP(s) + P_4(g) \qquad (4\text{-}54)$$

$$\log p_{mm.} = -14{,}220/T + 13.37 \qquad (4\text{-}55)$$

$$4\ ReP(s) \longrightarrow 2\ Re_2P + P_2(g) \qquad (4\text{-}56)$$

$$\log p_{mm.} = -13{,}780/T + 10.90 \qquad (4\text{-}57)$$

The diphosphides can all be prepared[151,152–162] by heating the metal with excess phosphorus under pressure at high temperatures. Tungsten diphosphide has also been made by reacting WCl_6 with phosphine.[157,162] All of the lower phosphides of chromium and molybdenum, as well as the monophosphides of tungsten and manganese, can be prepared by heating the diphosphides in a vacuum at appropriate temperatures. Details of these experiments can be found in the papers by Biltz *et al.*[158,159,162] These authors found that, in the tungsten system, W_2P, and W_4P could not be prepared thermally. Similar results were found in a study of the ternary system Fe—W—P.[163] On the other hand, W_4P and W_2P were formed[24,164] on a graphite cathode during the electrolysis at 500°C. of sodium and lithium metaphosphates containing tungsten oxide. The compound W_4P is amorphous and undergoes irreversible decomposition at temperatures in the range of 550°C. or higher to form W_2P and α-tungsten. It is believed that W_4P is not directly precipitated on the cathode but owes its formation to the action of the phosphine-hydrogen mixture produced at the cathode. It is interesting to note that chromium forms[165] a carbide, $Cr_{23}C_6$, which is very close in its metal-to-phosphorus ratio to W_4P.

Electrolysis of fused sodium phosphates containing the appropriate metal oxide has also been used to prepare phosphides in this group of compounds.[24,25] As previously stated, W_2P and W_4P are made by this procedure. In addition, CrP, Mo_2P, MoP, WP, Mn_2P, and MnP have been obtained from electrolysis.

Considerable work[166] has been done on the magnetic properties of MnP and MnP_2, which exhibit ferromagnetism as do the boron, antimony, and

[151] S. Helpert and T. Dieckmann, *Ber.*, 47, 780 (1928).
[152] E. Heinerth and W. Biltz, *Z. anorg. u. allgem. chem.*, 198, 181 (1931).
[153] R. Schneider and R. Vogel, *Arch. Eisenhüttenw.*, 26, 483 (1955).
[154] H. Hartmann and J. Orban, *Z. anorg. u. allgem. Chem.*, 226, 257 (1936); H. Hartmann, F. Ebert, and O. Bretschneider, *ibid.*, 198, 116 (1931).
[155] A. F. Westgren, *Farnkontorets Ann.*, 117, 501 (1933).
[156] G. Foex, *Bull. soc. chim. France*, 1949, 157; C. Guillaud, *Compt. rend.*, 223, 110 (1946); A. Smits, H. Gerding, and F. Vermast, *Rec. trav. chim.*, 51, 1178 (1932); R. Forrer, *Compt. rend.*, 194, 697 (1932); L. F. Bates, *Phil. Mag.* 8, No. 7, 714 (1929); S. Hilpert and Th. Dieckmann, *Ber.*, 47, 780 (1914); *ibid.* 44, 2831 (1912); E. Wedekind, *ibid.* 40,

arsenic compounds of manganese. The lower Curie point for MnP_2 lies at 38°C., whereas that for Mn_2P is at 28°C. Throughout the paramagnetic region of temperature, MnP follows the Weiss law and does not exhibit any signs of temperature hysteresis, such as is found with MnAs. As predicted from the Weiss theory, there is a small increase in specific heat at the Curie point.[167] In the paramagnetic state, MnP has a magnetic moment of about 4.4 magnetons which is interpreted to mean that the manganese atoms have each gained an average of one electron from the phosphorus atoms. Measurements of the magnetic moments of the paramagnetic nitrides, phosphides, and arsenides usually show no gain or loss of electrons for the metal atom in the compound as compared to being in the pure metal.

All of the phosphides of chromium, molybdenum, and tungsten are grey-black and exhibit a metallic luster. They conduct electricity and are very inert chemically, *i.e.*, they dissolve with considerable difficulty in oxidizing acids. However, the phosphides of the metals of Group VIB are somewhat less thermodynamically stable (based on heats of formation) than those of the Group IVB and VB metals. This corresponds to the behavior of the nitrides of these metals.[168] The detailed atomic structures of the monophosphides of chromium, molybdenum, tungsten, and manganese have been determined and are reported in Table 4-4. In addition, crystallographic studies on Cr_2P and Mo_2P have shown that these compounds are isomorphous with schreibersite, Fe_2P.

Phosphides of Iron, Cobalt, and Nickel

The phosphides of iron, cobalt, and nickel have probably been more extensively studied than those of any of the other metals. A listing of the accepted phosphides of these metals is given below.

	FeP_4	FeP		Fe_2P		Fe_3P
CoP_3		CoP		Co_2P		Co_3P*
NiP_3	NiP_2	$Ni_5P_4(?)$	Ni_5P_4	Ni_2P	Ni_3P_2	Ni_3P

* Only in solid solution with Ni_3P, Fe_3P, etc.

Phase-diagram studies have been carried out on all three of these groups of phosphides. In the iron-phosphorus system,[169] which is shown in Figure

[167] B. G. Whitmore, *Phil. Mag.* 7, No. 7, 125 (1929).
[168] I. E. Campbell, Ed., *High-Temperature Technology*, John Wiley & Sons, Inc., New York, 1956, p. 171.
[169] N. Konstantinow, *Z. anorg. Chem.*, 60, 405 (1909); F. Weibke and G. Schrag, *Z.*

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4-15, Fe_3P and Fe_2P have been isolated and FeP shows up, although the diagram was not extended to a high enough phosphorus content to reach this compound in pure form. As can be seen from the phase diagram, the

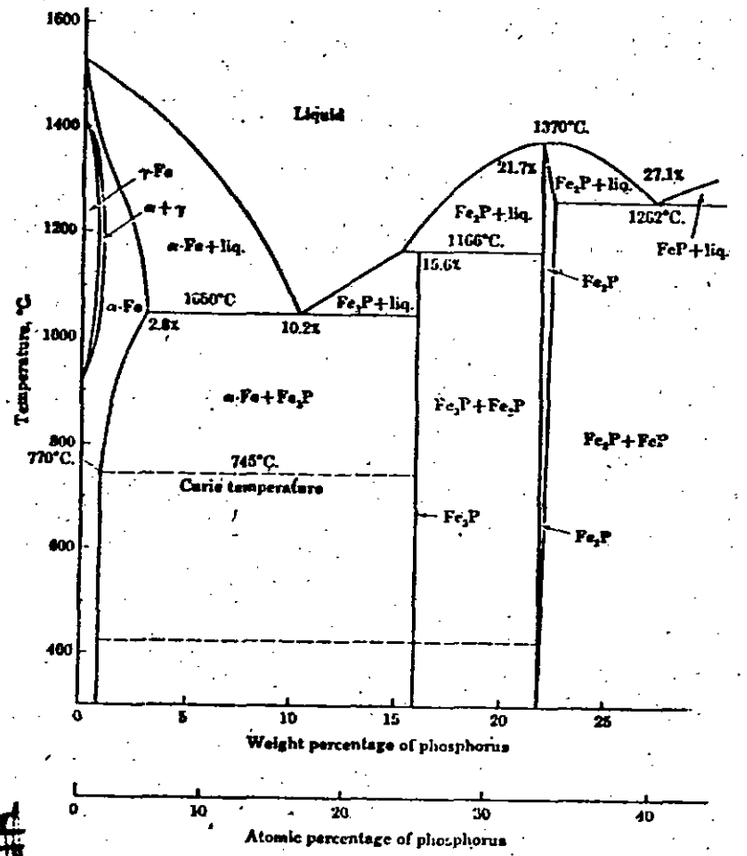

Fig. 4-15. Phase diagram of the iron-phosphorus system.

highest concentration at which phosphorus can be dissolved in solid iron corresponds to 2.8% phosphorus at 1050°C. Below this concentration of dissolved phosphorus, there is an interesting phase change from [illegible]

in the iron. As can be seen in Figure 4-15, the larger amounts of dissolved phosphorus (between about 0.7 and 2.8% phosphorus) prevent the formation of γ-iron. This causes the pure γ-iron to exist in a restricted region—bounded by upper and lower temperature limits of 1400 and 900°C. at 0% phosphorus and a temperature of about 1150°C. at 0.30% phosphorus. This region is called the γ-loop and is of considerable importance in steel making.[170] To the right of the γ-loop in Figure 4-15, there is a crescent-shaped region in which both α- and γ-iron are found. Calculations[170] indicate that at 1150°C., where the crescent is the widest, the $\alpha + \gamma$ region ranges from about 0.30–0.70% phosphorus.

In the phase diagram shown in Figure 4-15, it should be noted that Fe_2P at higher temperatures (around 1000°C.) exists over a small composition range as a solid solution, whereas at lower temperatures the composition of this compound is no longer variable. In the iron-phosphorus system, the solid solution corresponding to a variation in the mole fraction of phosphorus is limited, although substitution of iron by a similar metal, such as vanadium (see Figure 4-19), gives large regions of solid solution. In other words, the iron-phosphorus system exemplifies the general rule that the various metal phosphides correspond to fixed metal/phosphorus mole ratios.

In the cobalt-phosphorus phase diagram[171] which was partially completed (up to 25% phosphorus by weight), only one phosphide, Co_2P, melting at 1386°C., is shown. This phosphide shows a transition from an α- (high-temperature) to a β-form at 920°C. An eutectic occurs at 1022°C. and 16.5% phosphorus.

In the nickel-rich end of the nickel-phosphorus system,[172] three phosphides are found. These are Ni_3P, Ni_5P_2 (which occurs in an α- and a β-form), and Ni_2P. This phase diagram is shown in Figure 4-16. As was the case with Fe_2P, the β-form of Ni_5P_2 exhibits a narrow region of solid solution at the high temperatures where this form is stable.

Vapor pressure measurements have also been carried out on the phosphides of all of these metals, and a typical series of experimental curves is shown in Figure 4-17 for the compounds FeP_2 and FeP.[173] These vapor pressure curves correspond to the following equilibria:

$$4\,FeP_2(s) \longrightarrow 4\,FeP(s) + P_4(g) \qquad (4\text{-}58)$$

$$4\,FeP(s) \longrightarrow 2\,Fe_2P(s) + P_2(g) \qquad (4\text{-}59)$$

[170] H. Schrader and B. N. Bose, *Trans. Indian Inst. Metals*, 6, 104 (1952).
[171] S. Zemczuzny and J. Schepelew, *Z. anorg. Chem.*, 64, 245 (1909).
[172] [illegible]

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The heats of the reactions shown above in equations 4-58 and 4-59 are 67.0 and 80.2 kcals., respectively. It should also be noted that the heat of formation of Fe_2P from iron and red phosphorus is −34.5 kcal. The vapor-pressure equations are given below:

For FeP_2 in the temperature range of 900–1000°C.

$$\log p_{\text{mm.}} = -14{,}650/T + 14.469 \qquad (4\text{-}60)$$

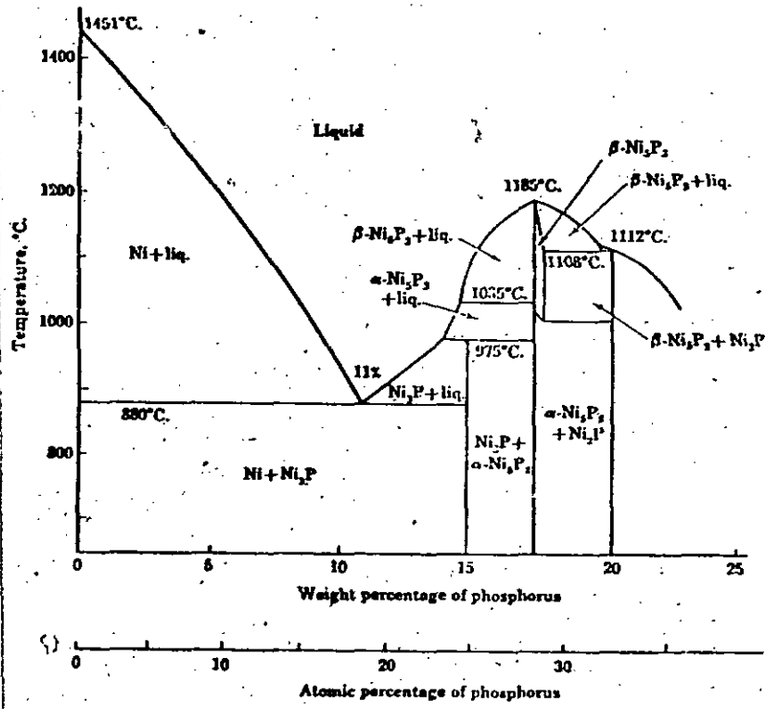

Fig. 4-16. Phase diagram of the nickel-phosphorus system.

For FeP in the temperature range of 1000–1200°C.

$$\log p_{\text{mm.}} = -17{,}540/T + 13.210 \qquad (4\text{-}61)$$

According to equation 4-60 the partial pressure of P_4 vapor reaches 1 atm. at about 990°C.

In the cobalt system, the triphosphide decomposes[174] directly to the monophosphide as shown by the following equation, which has a heat of reaction of 71.6 kcal. The partial pressure of P_4 vapor corresponding to this decomposition is also given below for the temperature range of 900–1100°C.

$$2\,CoP_3(s) \longrightarrow 2\,CoP(s) + P_4(g) \qquad (4\text{-}62)$$

$$\log p_{\text{mm.}} = -15{,}650/T + 14.397 \qquad (4\text{-}63)$$

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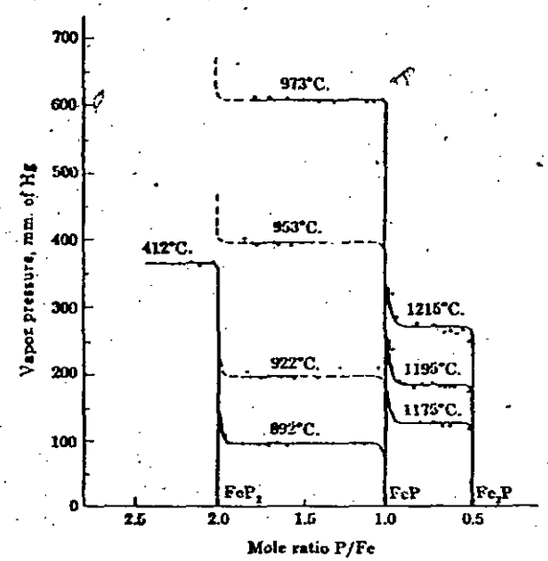

Fig. 4-17. Measured partial pressures of phosphorus over mixtures of iron and phosphorus which were fused together.

In the nickel-phosphorus system a series of stepwise thermal decompositions have been found as shown below.

$$4\,NiP_3(s) \longrightarrow 4\,NiP_2(s) + P_4(g) \qquad (4\text{-}64)$$

$$24/7\,NiP_2(s) \longrightarrow 4/7\,Ni_5P_4(s) + P_4(g) \qquad (4\text{-}65)$$

$$2\,Ni_5P_4(s) \longrightarrow 6\,Ni_2P(s) + P_4(g) \qquad (4\text{-}66)$$

The heats of these reactions are 43, 57, and 63 kcals., respectively, and the temperature at which the partial pressure of P_4 vapor reaches 1 atm. is

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662°C. over NiP_3 and 865°C. over Ni_6P_5. The partial pressures of P_4 vapor corresponding to the three decomposition reactions given above are:

For NiP_3

$$\log p_{mm.} = -9{,}340/T + 12.865 \quad (4\text{-}67)$$

For NiP_2

$$\log p_{mm.} = -12{,}430/T + 14.315 \quad (4\text{-}68)$$

For Ni_6P_5

$$\log p_{mm.} = -13{,}740/T + 14.951 \quad (4\text{-}69)$$

In addition to preparing these phosphides directly from the elements or by decomposing the phosphide with a higher vapor pressure to one with a lower vapor pressure, the cobalt and nickel triphosphides have been made in an interesting manner based on the properties of the tin phosphides.[116,117] In this procedure a 5% alloy of cobalt or nickel with tin is heated with excess phosphorus in a sealed container at 500°C. After cooling, SnP_3 is converted to Sn_3P_4 by heating in a vacuum at 350°C. The latter compound is soluble in hydrochloric acid, so that the more inert cobalt or nickel triphosphide is left behind. In this preparation, formation of a considerable amount of the solid, yellow hydrogen phosphide, P_2H, was noted.[117]

Phosphides of all of these metals have also been made in crystalline form by electrolysis of fused sodium phosphate melts containing the heavy metal oxide. In this way there have been prepared FeP, Fe_2P, Fe_3P, CoP, Co_2P, Ni_2P, Ni_6P_5, and Ni_3P, as well as another nickel phosphide not obtained by other techniques and having an analysis corresponding to Ni_6P_5. In Figure 4-18 a graphical representation is given of the variation of the phosphorus content of the phosphides plated onto the electrode from melts having different Fe_2O_3/P_2O_5 mole ratios. As can be seen from this chart, there is a reasonably wide range of melt compositions which give a pure phosphide. For example, to get pure FeP, the Fe_2O_3/P_2O_5 mole ratio in the bath may be varied from 1/20 to 1/8.

The cobalt phosphide, Co_2P, has not been shown to exist in pure form. In view of the fact that Fe_2P and Ni_2P decompose on melting, this is not surprising. However, small amounts of cobalt are found in schreibersite, which has the general composition $(Fe, Ni, Co)_3P$ with Fe > Ni > Co. This is probably due to stabilization of the Co_2P by the formation of a solid solution with the isomorphous Fe_2P and Ni_2P. However, pure Co_2P has

phosphite on cobalt salts.[178] These same authors also report the formation of Co_2P_3, Co_3P_2, Co_4P, and CoP. In view of the difficulties previously described in studying the reaction of phosphine with metal salts, as well as the instability of some intermediate products made in this way, the formation of unusual cobalt phosphides from aqueous solution using sodium hypophosphite should be viewed with skepticism. However, in spite of these comments, it should be noted that the known nickel phosphides Ni_6P_2 and

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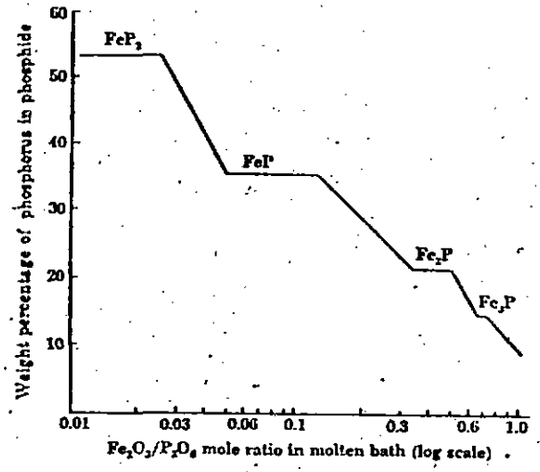

Fig. 4-18. Variation in the composition of the phosphide obtained by electrolyzing a sodium phosphate melt containing Fe_2O_3. The Fe_2O_3/P_2O_5 mole ratio in the melt is plotted against the weight per cent of phosphorus in the phosphide. All data refer to 850°C. except for the upper part of the curve corresponding to FeP_2.

Ni_2P were prepared by the action of sodium hypophosphite on nickel salts.[178] These reactions should be reinvestigated.

If the hypophosphite work is ignored, it is seen that there are more phosphides known for nickel than there are for any other metal. In addition, two of the phosphides, Ni_6P_5 and Ni_6P_2, have rather unusual formulas. Only one other accepted phosphide has the latter formula, and that is the palladium phosphide of the related element palladium. Co_2P_2 has been reported in the older literature,[78] but no recent investigator has found evidence for this compound. An x-ray investigation of these two nickel phosphides, as

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well as the rhodium phosphide having the composition Rh_4P_4 would be of interest. It is possible that Ni_6P_6 and Rh_4P_4 are related to the phosphorus-deficient phases of the "monophosphides" of zirconium, niobium, and tantalum.

All of the phosphides of iron, cobalt, and nickel are grey to grey-black, with a metallic appearance. They conduct electricity, and the lower phosphides are ferromagnetic. They are all insoluble in water and dilute min-

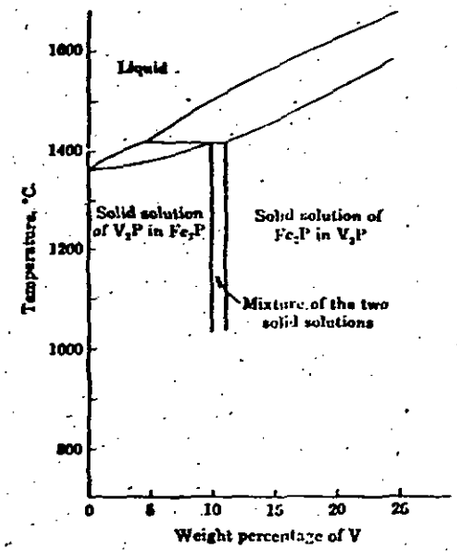

Fig. 4-19. Solid solutions in the Fe_3P-V_3P system, showing one phase identical to Fe_3P although containing vanadium and another phase which is still richer in vanadium.

eral acids but dissolve in hot nitric acid. The magnetic moment of iron in Fe_3P is 14 magnetons—the same as in the neutral atom (unionized Fe).

Structural data on Fe_3P and FeP_2 are reported in Table 4-1. In FeP_2, which has a marcasite type of structure, there are pairs of phosphorus atoms, at a distance of 2.17 A. from each other. This is the same P-P distance that is found in black phosphorus. The pairs of joined phosphorus atoms are also relatively close to each other, with the shortest P-P distance between pairs being 2.73 A. For comparison, in Fe_3P the shortest P-P distance is 3.45 A. The shortest distance between iron atoms [illegible]

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of the other transition metal phosphides—each iron atom has three or fo nearest-neighbor phosphorus atoms, depending on the location of the ir atom; and two-thirds of the phosphorus atoms have six nearest-neighb iron atoms, while one-third have nine nearest-neighbor iron atoms.

Phase-diagram studies have been carried out on a number of ternary sy tems involving iron and phosphorus. Thus, the following systems invol ing phosphorus, iron, and another metal have been investigated either ful or in part: Fe—Co—P,[176] Fe—Ni—P,[166,177] Fe—Cr—P,[156,178] Fe—Mn-P,[156,179] Fe—W—P,[163] Fe—Mo—P,[180] Fe—V—P, Fe—Zn—P,[181] Fe—Cu-P,[130] Fe—Sn—P,[112] Fe—Al—P,[182] and Fe—Sb—P.[183] An interesting tra sition between two solid solutions in the Fe—V—P system is shown i Figure 4-19. This figure again demonstrates that replacement of a give metal in a phosphide by a similar metal gives extended regions of soli solution.

In addition to the systems involving phosphorus, iron, and another meta systems based on iron, phosphorus, and a nonmetallic element other tha phosphorus have also been studied, as shown by the following example which, again, have been only partially investigated in most cases: Fe—P-C,[184,185] Fe—P—C—Si,[186] Fe—P—Si,[187] Fe—P—S,[188] Fe—P—CO,[189] an

[176] J. Berak, *Hutnik*, 18, 6 (1951); *Arch. Eisenhüttenw.*, 22, 131 (1951).

[177] R. Vogel, *Abhandl. Ges. Wiss. Göttingen, Math.-physik. Kl.*, 3, No. 6, 1 (1932); R. Vogel and H. Baur, *Arch. Eisenhüttenw.*, 5, 269 (1931/32).

[178] R. Vogel and G. W. Kasten, *Arch. Eisenhüttenw.*, 12, 387 (1939).

[179] R. Vogel and J. Berak, *Arch. Eisenhüttenw.*, 23, 217 (1952).

[180] R. Vogel and D. Horstmann, *Arch. Eisenhüttenw.*, 24, 369 (1953).

[181] R. Vogel and D. Horstmann, *Arch. Eisenhüttenw.*, 24, 247 (1953).

[182] R. Vogel and H. Klose, *Arch. Eisenhüttenw.*, 23, 287 (1952).

[183] R. Vogel and D. Horstmann, *Arch. Eisenhüttenw.*, 23, 127 (1952).

[184] R. Vogel, *Arch. Eisenhüttenw.*, 3, 369 (1929); E. Scheil, *Mitt. Forsch.-Inst. Ver Stahlwerke A.-G. Dortmund*, 1, 1 (1928); N. S. Konstantinov, *J. Russ. Phys.-Chem. Soc.*, 50, I, 311 (1918).

[185] J. E. Stead, *J. Soc. Chem. Ind. (London)*, 33, 173 (1914); M. Künkele, *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf*, 12, 23 (1930); Y. Yamamoto, *Bull. Inst. Phys. Chem. Research (Tokyo)*, 9, 838 (1930); F. Rogers, *Nature*, 114, 275 (1924).

[186] O. von Keil and R. Mitsche, *Arch. Eisenhüttenw.*, 3, 149 (1929); P. Bardenheuer and M. Künkele, *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf*, 12, No. 3, 33 (1930); *ibid.*, 12, No. 4, 33 (1930).

[187] W. Hummitzsch and F. Sauerwald, *Z. anorg. u. allgem. Chem.*, 194, 113 (1930); F. Sauerwald, W. Teske, and G. Lempert, *ibid.*, 210, 21 (1933); H. Hanemann and H. Voss, *Zentr. Hüttenw. u. Walzwerke*, 31, 245 (1927).

[188] R. Vogel and O. de Vries, *Arch. Eisenhüttenw.*, 4, 613 (1931); also see H. Lofenia

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a small amount of information on the system Fe—P—Si—O.[190] These studies were primarily directed toward a better understanding of steel making as, for example, in the Bessemer process.[191] An interesting phenomenon which has been investigated rather thoroughly is the phosphide eutectic in cast iron.[192] Molten iron containing carbon and phosphorus can congeal as either metastable mixtures of iron plus iron carbide and iron phosphide or as stable mixtures of iron plus graphite and iron phosphide. The ternary phosphide eutectic is found in the former case. In cooling a material such as cast iron, the last of the melt to solidify is the eutectic mixture between Fe, Fe_3P, and Fe_3C. On slow cooling, some of the carbon of the iron carbide diffuses out of the eutectic and forms a fringe of pearlite around the region of the eutectic mixture, but in diffusing into the surrounding solid solution of phosphorus in iron, the carbon precipitates some Fe_3P, which then appears as laminae in juxtaposition to the pearlite. In this manner, fringes consisting of iron saturated with carbon and phosphorus, iron phosphide, and iron carbide are formed.

Due to the action described above and other effects, the phosphorus content of most steels is reduced to about 0.06% or even lower. However, in low-carbon steels, phosphorus is considered as a useful alloying agent, the content of which is intentionally increased.[170] Thus, the tensile and yield strengths of a low-carbon steel are roughly doubled by the addition of 0.9% phosphorus.[193] Use of phosphorus also increases[193] the creep strength of some steels and has a favorable effect[197] on the corrosion resistance of the steel in moist atmosphere. Phosphorus also causes the formation of an adherent scale which prevents steel sheets from sticking together when rolled.

In the commercial manufacture of elemental phosphorus, the iron present in the phosphate ore forms iron phosphides which are known under the generic name of ferrophosphorus. In addition to its formation as a by-product, ferrophosphorus for metallurgical use is sometimes made commercially by reducing phosphate rock in the presence of iron.[194] Commercial ferrophosphorus usually contains about 23-26% phosphorus by weight, corresponding to an impure mixture of Fe_2P and FeP. Most of the ferro-

[190] F. Kocher and W. Oelsen, *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch. Düsseldorf*, 19, No. 9, 109 (1936).

[191] H. Wentrup, *Stahl u. Eisen*, 62, 749 (1942); *Tech. Mitt. Krupp Forschungsber.*, 5, 141 (1942).

[192] E. d'Amico, *Ferrum*, 10, 289 (1912–1913); C. H. Lorig and D. E. Krause, *Metals & Alloys*, 7, 69 (1936).

phosphorus which is produced is employed in iron metallurgy, but there is a considerable literature on the conversion of ferrophosphorus into other products, such as the phosphates or phosphorus sulfides. Since silicon is an undesirable impurity in ferrophosphorus for use in iron metallurgy, methods have been developed for its removal.[195,198]

A typical process[197] for utilizing ferrophosphorus consists of roasting it with soda ash and salt and leaching it in several steps to produce hydroxylapatite, trisodium orthophosphate, lead chromate, and vanadium pentoxide as valuable products. Air oxidation as well as the chlorination of ferrophosphorus has been studied.[198] Oxidation, either chemically or electrically, of ferrophosphorus in concentrated aqueous acids[199,199] and bases[199,200] has also been considered as a means of converting ferrophosphorus into salable products. Fusion of ferrophosphorus with molten NaOH, Na_2CO_3, or NaCl, either alone or as mixed melts, in the presence of air gives sodium phosphates.[196,199,200] An interesting reaction between ferrophosphorus and sodium carbonate in a vacuum to give metallic sodium as one of the products has been described[201] in the patent literature. Instead of sodium salts, ferrophosphorus can be heated with calcium salts, such as limestone, to give calcium phosphates said to be suitable for fertilizers or animal-feed supplements.[196] By heating ferrophosphorus with pyrites, some of the phosphorus is recovered as phosphorus sulfides.[202] A number of other reactions of ferrophosphorus have also been investigated.[196,200]

Phosphides of the Platinum Group Metals

A number of phosphides of the Group VIII elements belonging to the second and third long periods have been reported. Those which have been observed in the course of vapor pressure and x-ray studies are listed here.

[195] B. G. Klugh, U. S. Pat. 2,476,418 (1949, assigned to Monsanto Chem. Co.).

[196] E. L. Newman and L. D. Copeland, Analytical Index of Chemical Engineering Publications, Patents, and Reports, *Tenn. Valley Author. Chem. Eng. Rept. No.* 10, Wilson Dam, Alabama, 1954, pp. 28–31.

[197] L. H. Banning, W. E. Amble, and R. T. C. Rasmussen, *J. Metals*, 5, 423 (1953), also in *AIME Trans.*, 197, 423 (1953); L. H. Banning and W. E. Amble, U. S. Pat. 2,654,655 (1953).

[198] F. A. Henglein and F. Stoeckhert, *Beiheft Z. Ver. deut. Chem.*, No. 27, 24 pp. (1937); *Angew. Chem.*, 50, 389 (1937).

[199] For example, O. Quadent and V. Veelak, *Congr. chim. ind., Compt. rend. 18me congr., Nancy, Sept.–Oct.*, 1938, 592 (1938).

[200] Unpublished Monsanto Research Reports.

[201] [illegible] U. S. Pat. 2,481,266 (1949, assigned to Monsanto Chem. Co.).

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	RuP_2		RuP	Ru_2P			
RhP_3	RhP_2	Rh_4P_5		Rh_2P		Rh_3P	
	PdP_2				Pd_4P_3	Pd_3P	Pd_4P
	OsP_2						
	IrP_2			Ir_2P		Ir_3P	
	PtP_2					$Pt_{20}P_7$	

Rhodium triphosphide can be obtained at 800–900°C. by heating the metal with an excess of red phosphorus in an enclosed system.[203] The diphosphides of the other metals of this series can be prepared in the same way.[204–207]

With the exception of osmium diphosphide, all of the diphosphides, as well as rhodium triphosphide, decompose on heating to form lower phosphides. In this way, the compounds RuP,[207] RhP_2, Rh_4P_5,[203] PdP_2, Pd_4P_3, Pd_3P, Pd_4P,[201] Ir_2P,[206] and $Pt_{20}P_7$[204] (near the Pt_3P composition) can be obtained. On the other hand, osmium diphosphide when heated at temperatures above 1200°C. decomposes to the metal.[127]

Although the compound Rh_4P_5 is unusual, its existence has been demonstrated through vapor pressure studies and x-ray examination.[203] The compound $Pt_{20}P_7$ has been observed in a thermal analysis investigation of the platinum phosphides, and its existence has been confirmed by x-ray examination.[206] The palladium compounds Pd_4P_3, Pd_3P, and Pd_4P were all observed as a result of thermal analysis.[204]

Except for Ir_2P, which is lavender-colored as it has been prepared, all of these compounds are either grey or black—the color being darker the higher the phosphorus content. Ir_2P is very stable, hard, and extremely inert chemically. It has been used as a tip on fountain pens. All of the phosphides of this group of metals are inert toward moist air and do not dissolve in strong aqueous oxidizing agents such as aqua regia or hydrogen peroxide in basic solution. In order to decompose these compounds, it is necessary to use alkali fusions.

In this group of metal phosphides, vapor pressure data have only been obtained on rhodium triphosphide, which decomposes at extremely high temperatures. The equation for this decomposition and the partial pressure computed in terms of P_4 vapor are given by the following equations.

[203] F. Faller, E. F. Strotzer, and W. Biltz, *Z. anorg. u. allgem. Chem.*, 244, 317 (1940).
[204] G. Wichage, F. Weibke, and W. Biltz, *Z. anorg. u. allgem. Chem.*, 228, 357 (1936).
[205] W. Biltz, F. Weibke, E. May, and K. Meisel, *Z. anorg. u. allgem. Chem.*, 223, 129 (1935).
[206] K. H. Sölle, M. Heimbricht, and W. Biltz, *Z. anorg. u. allgem. Chem.*, 243, 297 (1940).

The vapor pressure data apply to the temperature range of 900–1000°C., at which temperatures a correction must be made for the decomposition of P_4 vapor into P_2 vapor.

$$4\ RhP_3(s) \longrightarrow 4\ RhP_2 + P_4(g) \qquad (4\text{-}70)$$

$$\log p_{mm.} = -12{,}850/T + 11.713 \qquad \Delta H = 60\ \text{kcal.} \qquad (4\text{-}71)$$

Like FeP_2, the compound PtP_2 has pairs of phosphorus atoms in its structure. However, PtP_2 exhibits a pyrite-type of crystal structure. X-ray data[147] on Rh_2P and Ir_2P are given in Table 4-4. In both of these structures the phosphorus atoms are coordinated by eight metal atoms which, in turn, are surrounded by four nearest-neighbor phosphorus atoms. The Ir-Ir distance of closest approach is 2.77 A. in Ir_2P as compared to 2.71 A. in metallic iridium.

Embrittlement[208] of the platinum-group metals is caused by small amounts of phosphorus. This is due to the formation at the boundary between platinum grains of the low-melting eutectic (m.p. 588°C.) between platinum and Pt_3P_{20}. Certain alloys of platinum are more resistant to corrosion by elemental phosphorus than pure platinum. Platinum containing 1% gold, as well as an alloy of 96% Pt, 3.5% Ru, and 0.5% Nb, has been found[209] successful for use as corrosion-resistant containers for materials from which small amounts of phosphorus are generated at high temperatures.

[208] A. Jedele, *Z. Metallkunde*, 27, 271 (1935); H. J. Frost, *Chem.-Ztg.*, 65, 14 (1941).
[209] K. W. Kröhlich, *Chem. Fabrik*, 1940, 431; J. S. Streicher, U. S. Pat. 2,384,502 (1945, assigned to the American Platinum Works).

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