PHOSPHORUS

References

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PH_3, phosphine, gas, colrl., toxic, evil-smelling, m.p. −134, b.p. −88, infl. 150°, $\Delta H = +5$, v. strong Red agent, sol. in H_2O 20 vol %, $\mu = 0.58$; mol.: trig. pyramid, P—H 1.42, ∠HPH 93 (p^3); · **5.75 H_2O** (8 : 46), clathrate

$PH_4^+ + H_2O \underset{K=10^{-29}}{\overset{H^+}{\rightleftharpoons}} PH_3 + H_2O \underset{K=10^{-29}}{\rightleftarrows} H_3O^+ + PH_2^-$

v. weak donor

PR_3, strong donors

$[Ni(PH_3)_4]$; $[Co(N_2)(PR_3)_3]$

P_2H_4, diphosphine, liq., colrl., m.p. −99, b.p. 63, struct. analogue of N_2H_4, P—P 2.22, P—H 1.45, ∠HPH 94 and 99, dihedral ∠74 (*trans-* and *gauche-* isomers), infl. at 20° (as impurity in PH_3), does not react with ac.; · ***n*** **H_2O**, clathrate [15]

$(PH)_n$, solid, yel., does not react with ac. and alk.; $\xrightarrow{400°} P_4 + PH_3$

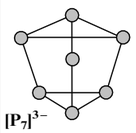
Phosphonium salts $[PH_4]X$
cr., colrl.
$[PH_4]ClO_4$, expl.
PH_4Hal ⇄ $PH_3 + HHal$ (g.) subl. *t*
PH_4Cl −28
PH_4Br 38
PH_4I 80 (b.p.), 18 (m.p.)
v. strong Red agent; $+H_2O \longrightarrow PH_3 + HHal$; cation: tetrahedron ($sp^3$), P—H 1.42

MPH_2, dihydrophosphides, cr., colrl., self-igniting ↓ 100° vac. (−PH_3)
Na_2PH
MAI$(PH_2)_4$; $SiF_3(PH_2)$ [15]

Ca_2PI; Ca_3PI_3, struct.: cation vacancies, octahedra $[CaP_3I_3]$ and $[CaP_2I_4]$, Ca—P 2.83, Ca—I 3.41 and 3.27 [12]

Phosphides M_3P_x

Salt-like [1]	Covalent	Metal-like
		m.p.
Li_3P; Na_3P; Na_2P_5 (m.p. 650)	**BP**↓, dec. >2000, does not sol. in ac. and alk., diamond-like struct.	**Ti_3P** —
K_2P_5; Ba$[P_5]_2$; Rb$_4[P_6]$, struct.: $[P_5]$ and $[P_6]$ planar rings, P—P 2.20	**AlP**, dec. 2000, + $H_2O \longrightarrow PH_3$ (sphalerite-like struct. (ZnS))	**TiP** 1580 with dec., struct.: NaCl type
Na_3P_{21}; Ba$_3[P_7]_2$, anion: cluster	**InP**↓, dec. 1070	**Cr_3P** —
K_4P_3; K_5P_4, anions: chains	**GaP**↓, m.p. 1467	**CrP** 1600
Mg_3P_2; Ca_3P_2 $+O_2$ – infl.,	**AsP**↓, dec. 750	**Fe_3P** 1200 with decomp.
Zn_3P_2; Cd_3P_2 $+H_2O \longrightarrow PH_3 + ...$	**ScP; YP; LaP**, struct.: NaCl type	**Fe_2P** 1356
Cu_3P↓; **CuP_2**↓, insol. in HNO_3 (*t*)	LnP + $H_2O \longrightarrow PH_3$ + ...	**FeP** — ferromagn.
$P(HgCl)_3$↓ $\xrightarrow{H_2O}$ PH_3 + $HgCl_2$		**FeP_2** —
		UP; U_3P_4
		Rh_2P; Ir_2P, *anti*-CaF_2 type struct. Conductors (TiP) or semiconductors (CrP); chem. inert (activity raises with decreasing P content); sol. in Na_2O_2 melts



$[P_7]^{3-}$

Dielectrics or semiconductors (M = Mg, Ca, Zn, In, Ga, As)
KZnP, $CaZn_2P_2$, struct.: layers of $[ZnP_{4/4}]$ tetrahedra Zn—P 2.49 [22]

P^0 3*s* ↓↑ 3*p* ↓ ↓ ↓ 3*d* **E.N.** 2.1

P_4, wh., soft, waxy (yel. due to P_{red} and As impurities), m.p. 44, b.p. 257, sol. in CS_2, NH_3, SO_2, toxic, infl. 40°. Struct.: mol. P_4 – tetrahedron, P—P 2.21, ∠PPP 60, P CN 3. Strain in the tetrahedron is responsible for high reactivity of P.
α-, cub., *a* = 18.51, *d* = 1.83 ↓ < −76.4°
β-, tricl., *a* = 11.45, *b* = 5.50, *c* = 11.26, *α* = 71.8, *β* = 90.4, *γ* = 71.6, *d* = 1.94, in $[P_4]$ P—P 2.17 [34]

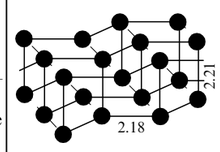
250°, $p > 5 \cdot 10^7$ Pa (I_2; Na; *hν*-UV, X-ray)

P_m, red, insol. in CS_2, nontoxic, infl. 240°, subl. 429, *d* = 2.2–2.4, mol.: chains of various lenghts, P CN 3, P—P 2.24, ∠PPP 102
450° ↓
Hittorf phosphorus, 6 modifications (tricl., tetrag., cub.), struct.: chains of P_8 grs., struct. analogues of As_4S_4, P—P 2.22, ∠PPP 101

550°

P_n, blk., subl. 453, m.p. ≈ 1000°/18 · 10^8 Pa, *d* = 2.69, thermodynamically stab., non-react., infl. 400°, (*a* = 3.31, *b* = 4.38, *c* = 10.50) – corrugated layers in rhomb. struct., P—P 2.18, ∠ PPP 99, graphite-like semiconductor
↓ 83000·10^5 Pa

P, met., rhombohedral, As-type struct., *a* = 3.52, *α* = 57.4, P—P 2.38, *d* = 3.56,
↓ 124000 · 10^5 Pa
cub., struct. analogue of Po, *a* = 2.38, *d* = 3.83



Liq., P_4 280°
Gas P_4 1000° P_2 2000° P [P≡P], P—P 1.90, el. analogue of N_2

Tetraphosphorus complexes $[MCl(P_4)(PR_3)_2]$, M = Rh, Ir [2]

P_4O, polymer

$[R_4N][Ru_4(CO)_{12}(\mu_3\text{-PO})]$, cr., stab. [38]

P_2O_3, phosphorous anhydride, cr., wh., m.p. 24, b.p. 175, $\Delta H = -1640$ (for P_4O_6), sol. in org. solvs. In gas, solns and one of modifications: P_4O_6 dimers. In mol.: 4 *ψ*-tetrahedra [:PO_3], bounded by common vertices, forming "large tetrahedron" [P_4]. In other modifications: polymers of $[PO_4]$ tetrahedra

$M_6P_6O_{12} \cdot n\,H_2O$, M = Rb, Cs, Ba/2, **hexametaphosphites**, anion: chair [31]

$Mn_2H_{11}P_5O_{15} \cdot 4\,H_2O$
$MnH_{10}P_4O_{12} \cdot H_2O$
$Mn_3H_6P_4O_{12} \cdot 1.5\,H_2O$ [16]

$H_4P_2O_5$ = $H_2[H_2P_2O_5]$, di(pyro)phosphorous ac., needles, colrl., m.p. 38, dec. 130

$H_4P_2O_4$ = $H_2[H_2P_2O_4]$

$H[OPH(O)—PH_2]$ [23]

$[P_8]^{2+}(HSO_3F)_2^-$
$[P_4]^{2+}(HSO_4)_2^-$, colrl. (known only in soln.), $[P_8]^{2+}$, bl., $[P_4]^{2+}$, colrl., diamagn. ions [3]

Ba$[H_2P_2O_4]$↓

$M_2[H_2P_2O_5]$, pyrophosphites
$Na_2H_2P_2O_5$; $ZnH_2P_2O_5$, anion: 2 tetrahedra with common vertex [11]

$M_3[HP_2O_5]$, diphosphites
$Na_3HP_2O_5 \cdot 3\,H_2O$

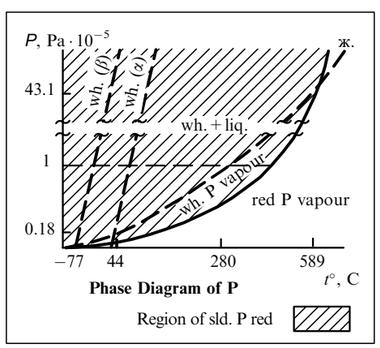
H_3PO_2 = $H[H_2PO_2]$, hypophosphorous ac., cr., colrl., hyg., m.p. 27, *K* = 10^{-1}, sol. in alc., eth.;
50° ⟶ PH_3 + H_3PO_3, v. strong Red agent (in conc. soln. only, *t*) [19]

H_3PO_3 = $H_2[HPO_3]$, phosphorous ac., cr., colrl., hyg., m.p. 74, dec. 200, $K_1 = 10^{-2}$, $K_2 = 10^{-7}$, sol. in H_2O, alc.; mol.: distort. tetrahedron;
H_3PO_3 (cr.) $\xrightarrow{t}$ $PH_3 + H_3PO_4$; strong Red agent (< H_3PO_2; reacts slowly, *t*), at 20° not reacts with HNO_3
$H_2[HPO_3]$ ⇄ $P(OH)_3$;
$P(OR)_3 \xrightarrow[(RHal)]{} (RO)_2P(=O)R$ (Arbuzov rearrangement)

$M[H_2PO_2]_n$, hypophosphites
$NaH_2PO_2 \cdot H_2O$ [19]
KH_2PO_2; $NH_4H_2PO_2$
$Mg(H_2PO_2)_2 \cdot 6\,H_2O$
$Ba(H_2PO_2)_2 \cdot H_2O$
$Ca(H_2PO_2)_2$, readily sol. in H_2O [cf. $CaHPO_4$ and $Ca_3(PO_4)_2$], anion: distort. tetrahedron, P—O 1.52

MH[HPO_3], hydrogen phosphites
$NaH_2PO_3 \cdot 2.5\,H_2O$, m.p. 42, dec. 100
KH_2PO_3; $Zn(H_2PO_3)_2$, anion: distort. tetrahedron, P—O 1.51 [11]

$M_2[HPO_3]$, phosphites [31]
$Na_2HPO_3 \cdot 5\,H_2O$, m.p. 53, dec. 120
K_2HPO_3; $MgHPO_3 \cdot 6\,H_2O$
Ag_2HPO_3↓, wh.; **$CaHPO_3$**↓; **$CrHPO_3 \cdot 2\,H_2O$**, $\xrightarrow{t}$ $M_3PO_4 + PH_3 + P + ...$
$[HPO_3]^{2-}$ – distort. tetrahedron, P—O 1.52, P—H 1.29
$(NH_4)_3[P(Mo_6O_{21})] \cdot 10\,H_2O$↓, yel.



* See notes to p. 58.