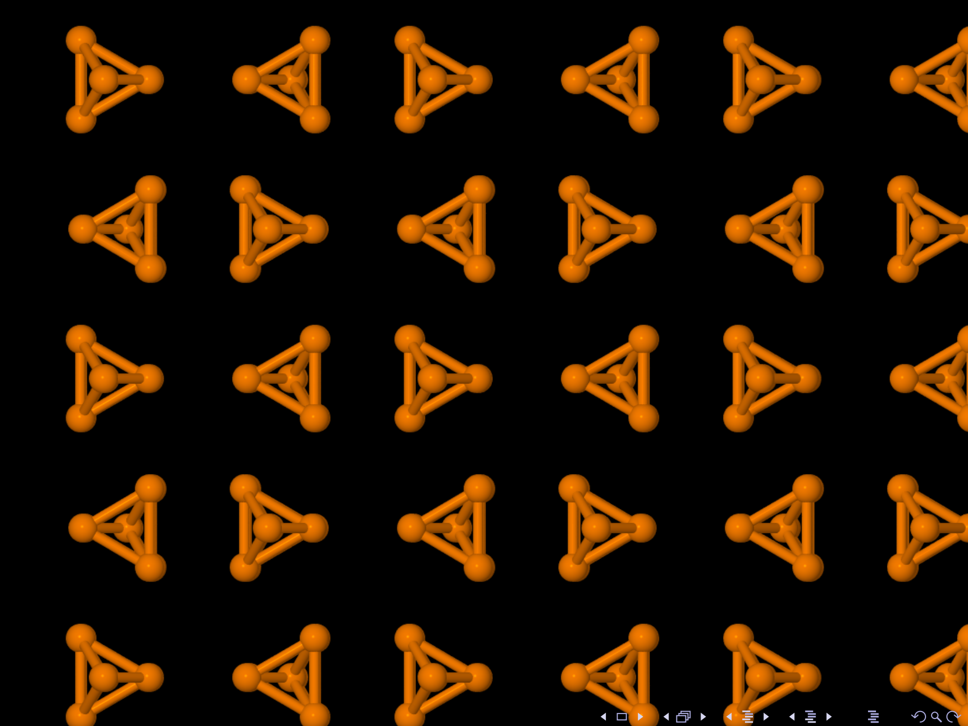


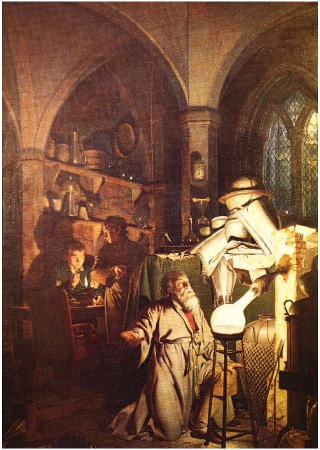
Phosphorus

- Phosphorus exists in several allotropic forms: white (or yellow), red, violet and black.
- Never found free in nature, it is widely distributed in combination with minerals. Phosphate rock, which contains the mineral apatite, an impure calcium phosphate, is an important source of the element.

Apatite
$[Ca_5(PO_4)_3(OH, F, Cl)]$

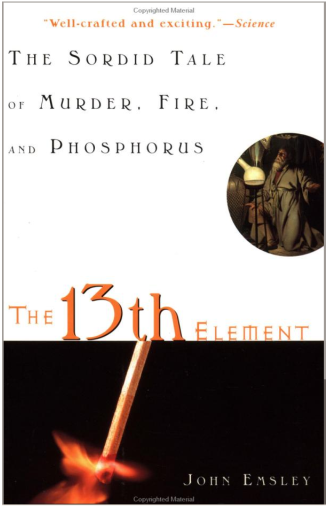
Discovery of Phosphorus

In what is perhaps the most disgusting method of discovering an element, phosphorus was first isolated in 1669 by Hennig Brand, a German physician and alchemist. Like most chemists of his day, was trying to make gold. He let urine stand for days, boiled it down to a paste, heated this paste to a high temperature, and drew the vapours into water where they could condense - to gold. To his surprise and disappointment, however, he obtained instead a white, waxy substance that glowed in the dark. Brand had discovered phosphorus. The word phosphorus comes from the Greek and means "light bearer". Thankfully, phosphorus is now primarily obtained from phosphate rock.

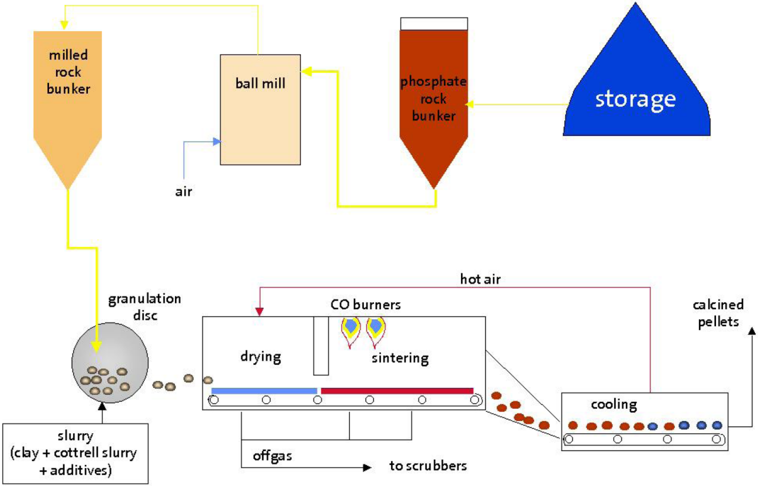


The discovery of phosphorus by Hennig Brand in 1669 - painted by Joseph Wright.

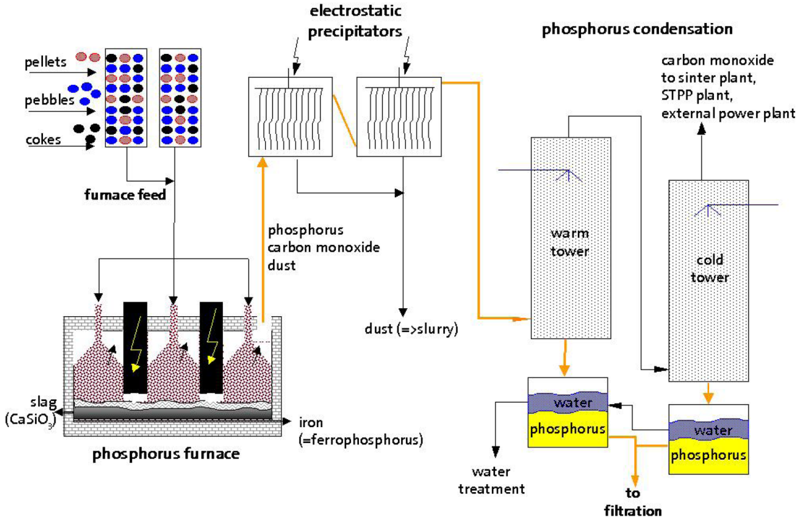
The 13th Element



Industrial Production of Elemental Phosphorus



Industrial Production of Elemental Phosphorus



Oxidation of White Phosphorus in Air

(Vidéo: http://www.cci.ethz.ch)

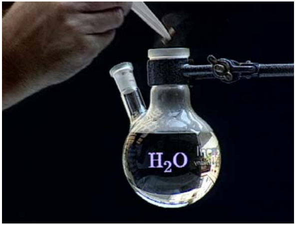
White phosphorus is self-igniting in air. Ignition temperature is dependent upon the surface structure. Phosphorus in compact form self ignites above 50°C. In this experiment, white phosphorus is on a filter paper. It starts to smoke through superficial oxidation. The phosphorus is further heated to its melting point (Fp: 44°C) by the energy released in this superficial oxidation. The melted mass continues to be heated up by the progressing oxidation and after a short period the phosphorus combusts in its entirety.

Oxidation of White Phosphorus in Air

(Vidéo: http://www.cci.ethz.ch)

In contrast to the compact white phosphorus, the finely dispersed form burns at room temperature. This finely dispersed white phosphorus with a large surface area can be produced by evaporation of a solution of white phosphorus in carbon disulphide (Bp.: 46°C).

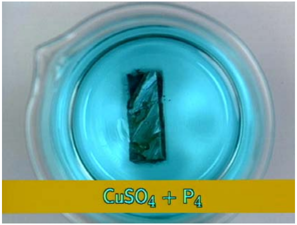
Oxidation of White Phosphorus under Water

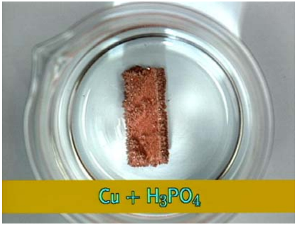


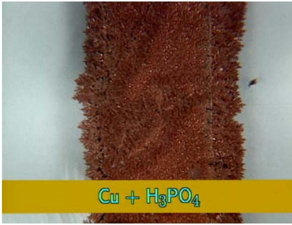
(Vidéo: http://www.cci.ethz.ch)

1) A piece of white phosphorus is added to water.
2) Pure oxygen is introduced through a tube.
3) Even under water flames appear from the oxidation.

Precipitation of Copper on White Phosphorus







(Vidéo: http://www.cci.ethz.ch)

White phosphorus exhibits a high tendency to oxidation, and is therefore a strong reductant. White phosphorus can be added to salt solutions of easily reduced (more electropositive) metals (gold, silver, copper, lead), leading to the precipitation of the elements. The experiment demonstrates the reduction of $CuSO_4$.

$$P_4(s) + 16\ H_2O + 10\ Cu^{2+} \longrightarrow 4\ H_3PO_4 + 20\ H^+ + 10\ Cu(s)$$

Industrial Synthesis of Triphenylphosphine

Chlorine is added and then removed

$$0.25\ P_4 + 1.5\ Cl_2 \longrightarrow PCl_3 \quad (1)$$

$$PCl_3 + 3\ ClC_6H_5 + 6\ Na(molten) \longrightarrow P(C_6H_5)_3 + 6\ NaCl \quad (2)$$

White Phosphorus is Converted to Red at 300 °C

Reference: M. Ruck et al. *ACIE*, 2005, *44*, 7616-7619.

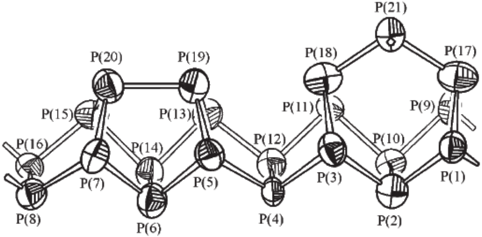


Figure 2. Repeating unit of the tubes in fibrous and in Hittorf's phosphorus (numbering of atoms in analogy to ref. [5]). Thermal ellipsoids enclose 90% probability for atomic displacement. Bond lengths are between 219(1) and 231(1) pm; the mean bond length is 221.9 pm.

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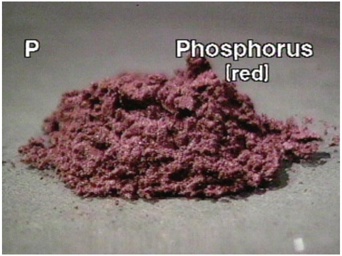
Red Phosphorus

- Amorphous, red phosphorus is formed by heating white phosphorus to 250°C or by exposing white phosphorus to sunlight.
- Red phosphorus is not poisonous and is not as dangerous as white phosphorus, although frictional heating is enough to change it back to white phosphorus.
- Used in safety matches, fireworks, smoke bombs and pesticides.

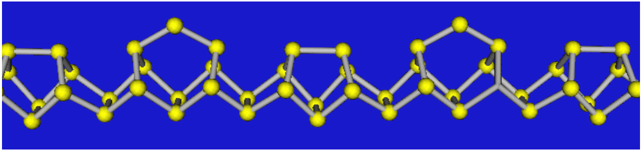


$$P_4 \text{ (white)} \xrightarrow[\text{(no air!)}]{\sim 250\ ^\circ\text{C}} \text{P (red)}$$

Violet Phosphorus

- Violet phosphorus is formed by heating red phosphorus to 550 °C.
- Complicated sheet structure.

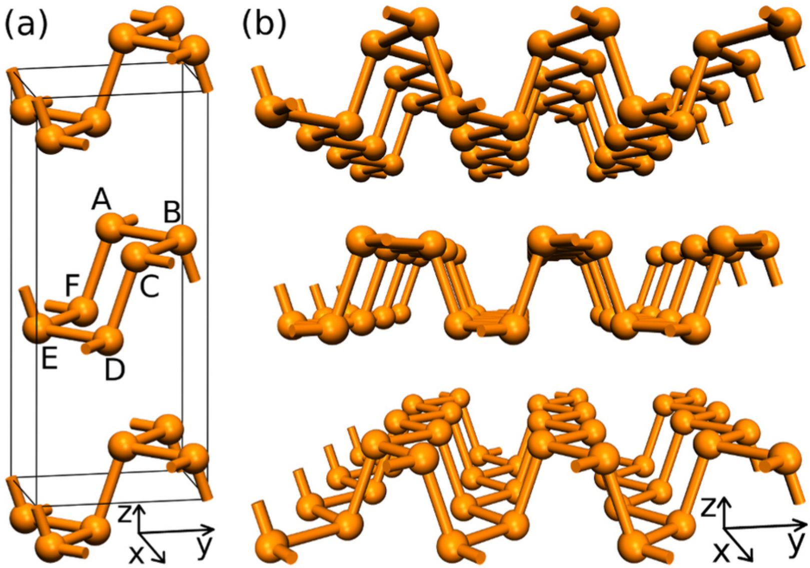
$$\text{P (red)} \xrightarrow[\text{(no air!)}]{550\ ^\circ\text{C}} \text{P (violet)}$$



Phosphorus and Matches

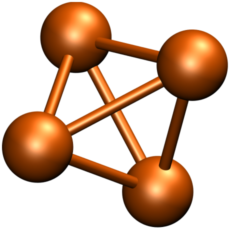
- In 1780 the ‘Ethereal Match’ -- waxed paper tipped with phosphorus, in a sealed glass container -- was produced in France. When the glass was broken the phosphorus ignited and set fire to the paper or string.
- John Walker invented the friction match in 1827. For many years, most friction matches were tipped with a mixture of P_4 and sulphur, and could be struck anywhere.
- After red phosphorus was discovered in 1845, J. E. Lundstrum invented the safety match (P_{red} on the striking surface and $Sb_2S_3/KClO_4$ on the match).
- Workers using P_4 in the manufacture of matches suffered a condition known as ‘phossy jaw’. P_4 was eventually outlawed in matches (1912 !).

Structure and thermoelectric properties: Qin et al. doi:10.1038/srep06946



Why P_4 Rather than P_6 or P_8?

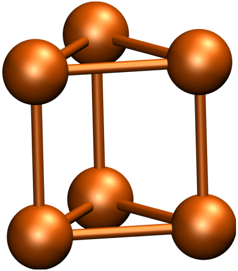
Spherical aromaticity: Hirsch et al. *ACIE*, 2001, *40*, 2834-2838.



HOMO-LUMO gap = 4.95 eV

$(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^4$

satisfies $2(N+1)^2$ rule for both σ and π $(2a_1)$

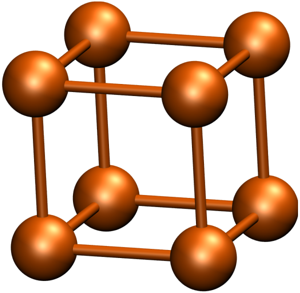


HOMO-LUMO gap = 2.1 eV

$(1a_1')^2(1a_2'')^2(1e')^4(1e'')^4(2a_1')^2(3a_1')^2(2e')^4(2a_2'')^2(3e')^4(2e'')^4$

does *not* satisfy $2(N+1)^2$ rule

$2\ P_6 \longrightarrow 3\ P_4$
$\Delta E = -71$ kcal/mol



HOMO-LUMO gap = 1.33 eV

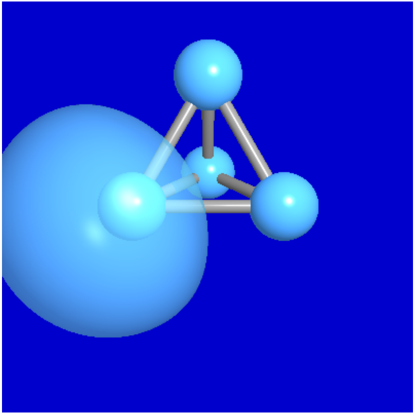
$(1a_{1g})^2(1t_{1u})^6(1t_{2g})^6(1e_g)^4(1a_{2u})^2(2a_{1g})^2(1t_{2u})^6(2t_{1u})^6(2t_{2g})^6$

does *not* satisfy $2(N+1)^2$ rule

$P_8 \longrightarrow 2\ P_4$
$\Delta E = -66$ kcal/mol

Bonding in P_4

P_4 is well-described by a single Lewis structure



- The lone pair has 81% *s* character

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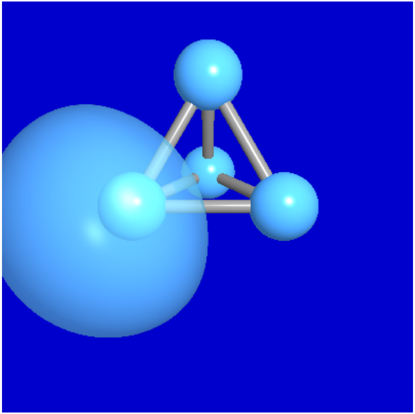

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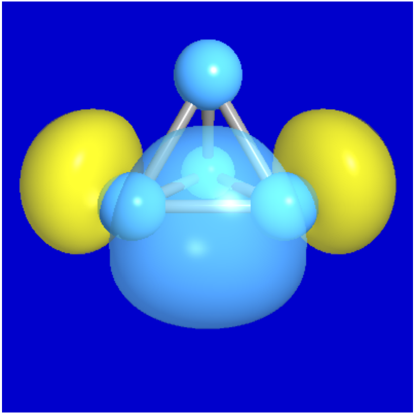

- The bond has 92% *p* character

Bonding in P_4

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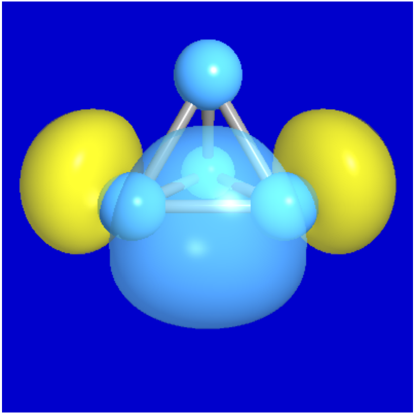
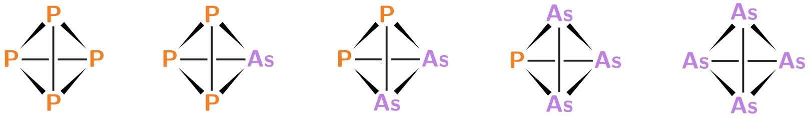


- The bond has 92% *p* character

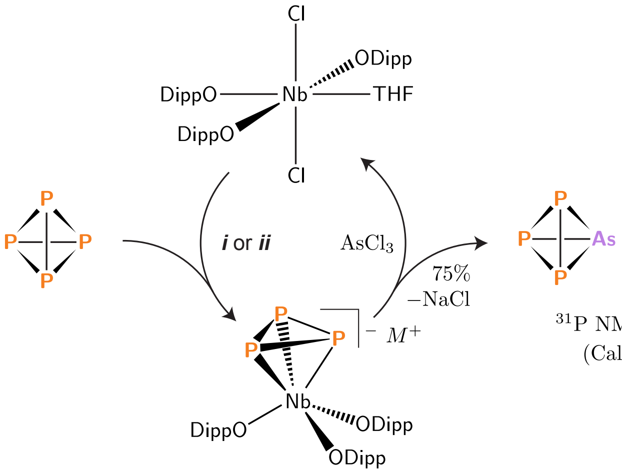
From White Phosphorus to Yellow Arsenic
Bridging the knowledge gap



commodity chemical | ? | ? | ? | *unstable*

Synthesis of AsP_3

Niobium chemistry permitting replacement of one P vertex with As



^{31}P NMR: $\delta = -484$ ppm
(Calcd: $\delta = -482$ ppm)

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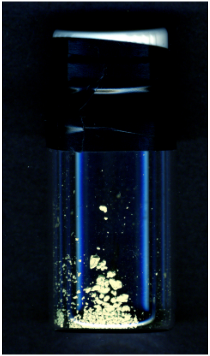
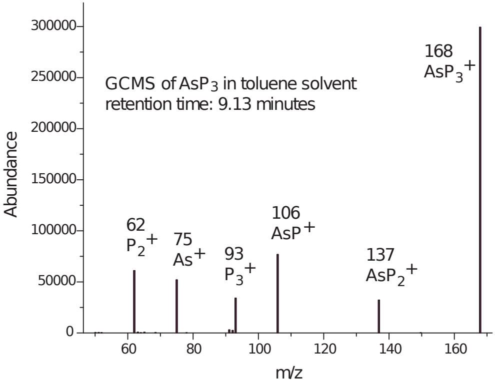
Properties of the AsP_3 Molecule

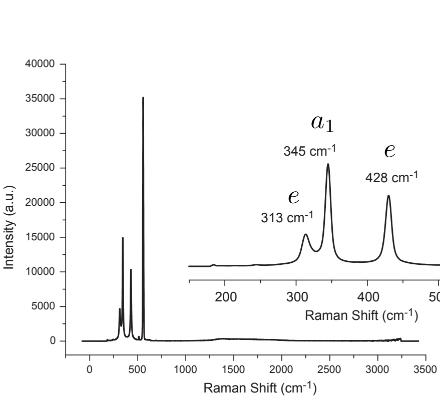
Solid AsP_3 sublimes and melts without decomposition at 71-73 °C





Characterization of AsP_3

Raman spectroscopic data and Ozin's 1970 assignments



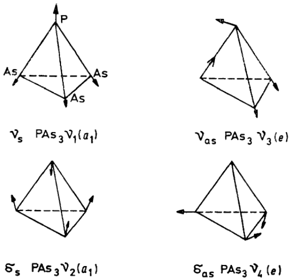
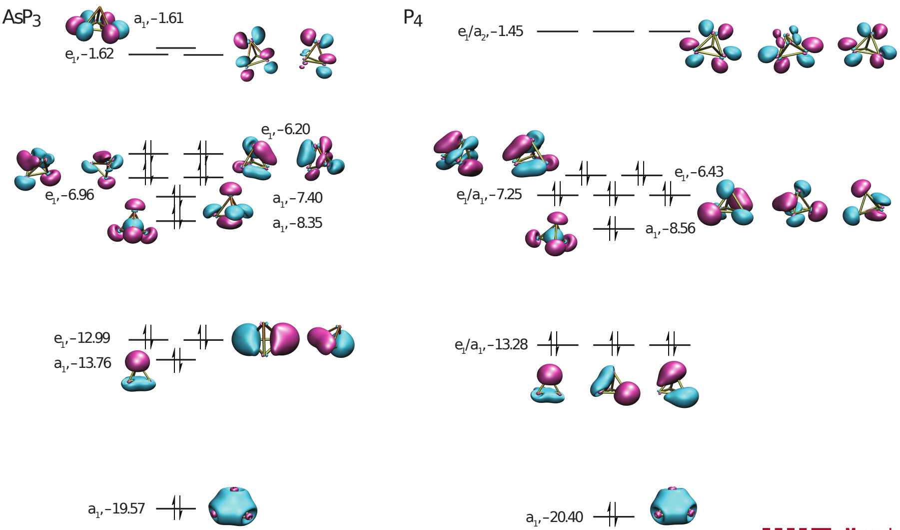
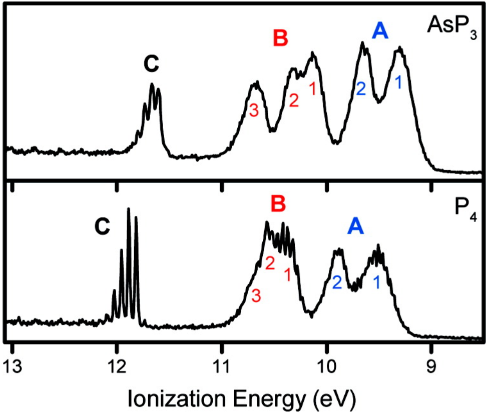


FIGURE 2 Approximate pictorial representation of the symmetry co-ordinates for the $C_{3v}XY_3$; only one of the components of each degenerate mode (ν_3 and ν_4) is shown

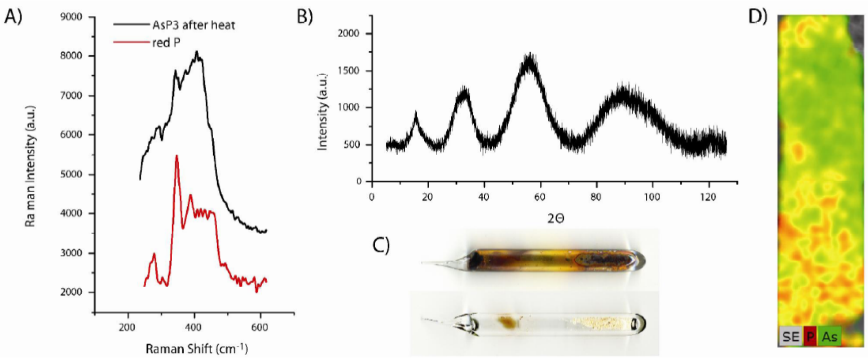

AsP3
a_1,−1.61
e_1,−1.62
e_1,−6.20
e_1,−6.96
a_1,−7.40
a_1,−8.35
e_1,−12.99
a_1,−13.76
a_1,−19.57
P4
e_1/a_2,−1.45
e_1,−6.43
e_1/a_1,−7.25
a_1,−8.56
e_1/a_1,−13.28
a_1,−20.40

Photoelectron Spectra of AsP_3 and P_4

Prof. Dennis L. Lichtenberger and Ashley R. Head (U. of Arizona)



Segregation of the Elements upon Heating
Thermolysis at 300 °C leads to separation of arsenic and phosphorus



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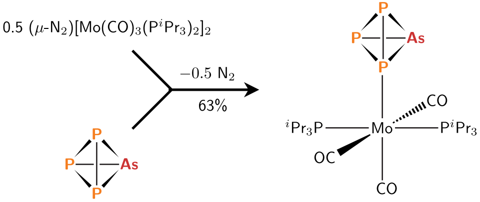
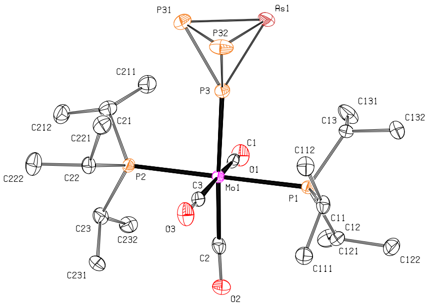
Structure of an AsP_3 Complex

Coordination of AsP_3 to Kubas fragment affords an isolable complex





Book by Dasent

"Compounds whose structures do not offend the simpler rules of valence"

Nonexistent Compounds

COMPOUNDS OF LOW STABILITY

W. E. DASENT
SENIOR LECTURER
DEPARTMENT OF CHEMISTRY
VICTORIA UNIVERSITY OF WELLINGTON, NEW ZEALAND

1965
MARCEL DEKKER, INC.
NEW YORK

- $P_2(g) \rightarrow 2\ P(g)\ \Delta H^\circ = +116$ kcal/mol
- $N_2(g) \rightarrow 2\ N(g)\ \Delta H^\circ = +226$ kcal/mol
- $2\ P_2(g) \rightarrow P_4(s,\ \alpha\text{-mod})\ \Delta H^\circ = -68.5$ kcal/mol
- C, N, and O form stable compounds having π bonds formed from p_π–p_π overlap
- For the heavier congeners (Si, P, etc.) compounds having such π bonds are *much* less common

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Thermodynamic Considerations

Triply bonded P_2 is at a thermodynamic disadvantage

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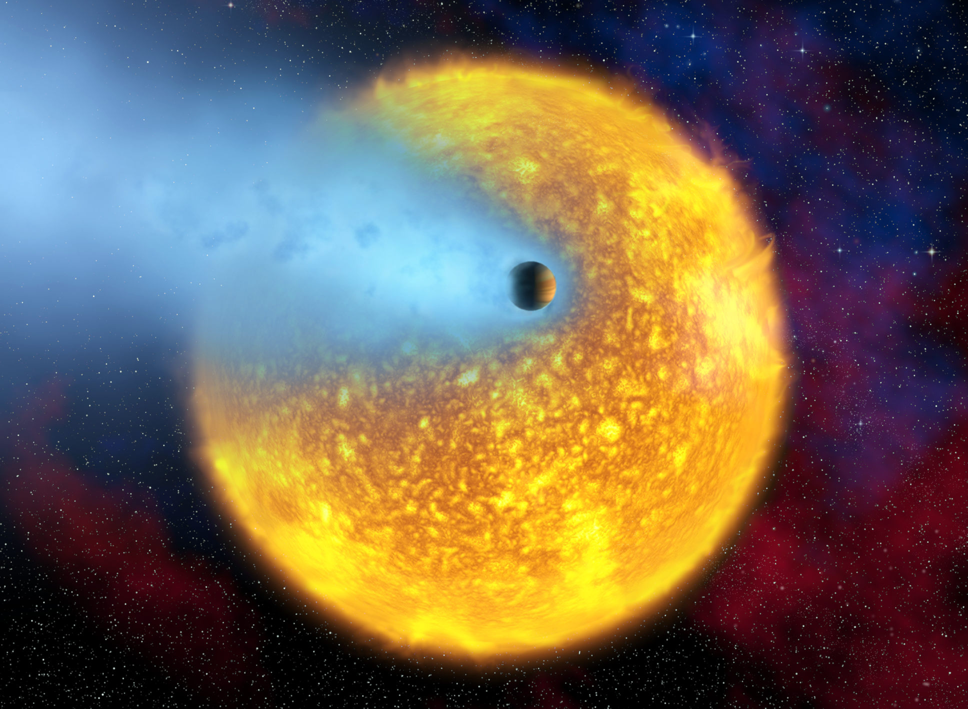
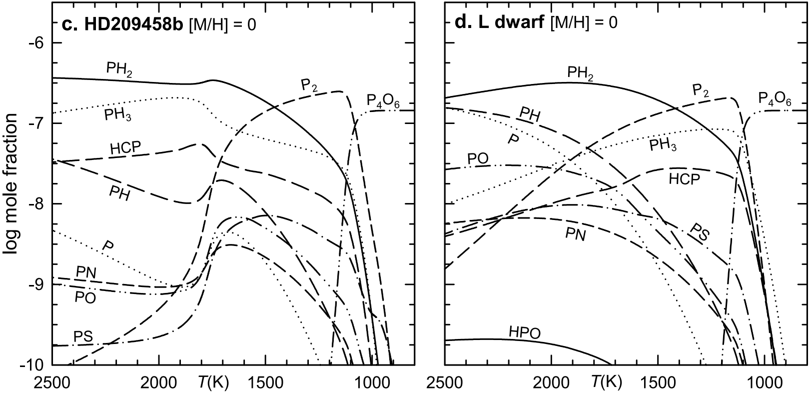
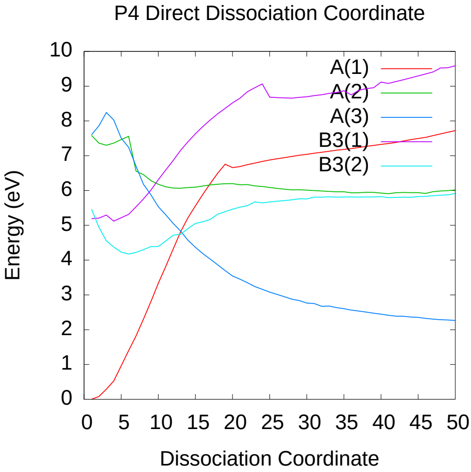


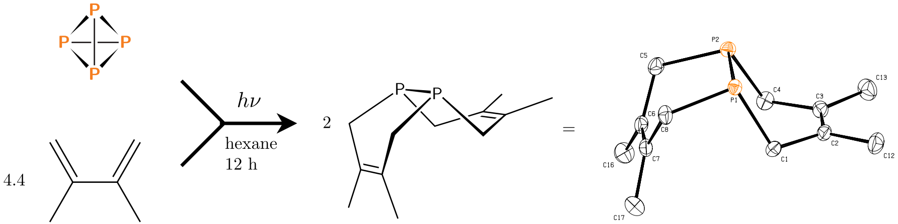


c. HD209458b [M/H] = 0
d. L dwarf [M/H] = 0
log mole fraction
-6
-7
-8
-9
-10
2500
2000
T(K)
1500
1000
PH2
PH3
HCP
PH
P
PN
PO
PS
P2
P4O6
HPO


P4 Direct Dissociation Coordinate
Energy (eV)
Dissociation Coordinate
A(1)
A(2)
A(3)
B3(1)
B3(2)
0
1
2
3
4
5
6
7
8
9
10
0
5
10
15
20
25
30
35
40
45
50

A Simple Synthesis of P_2 Double Diels-Alder Adducts

Daniel Tofan discovers photochemical phosphorus incorporation



^{31}P NMR: $\delta = -53.8$ ppm
colorless crystals (toluene, −35 °C)
150 mg/batch
14% based on P_4 used
34% based on P_4 consumed