Phosphorus

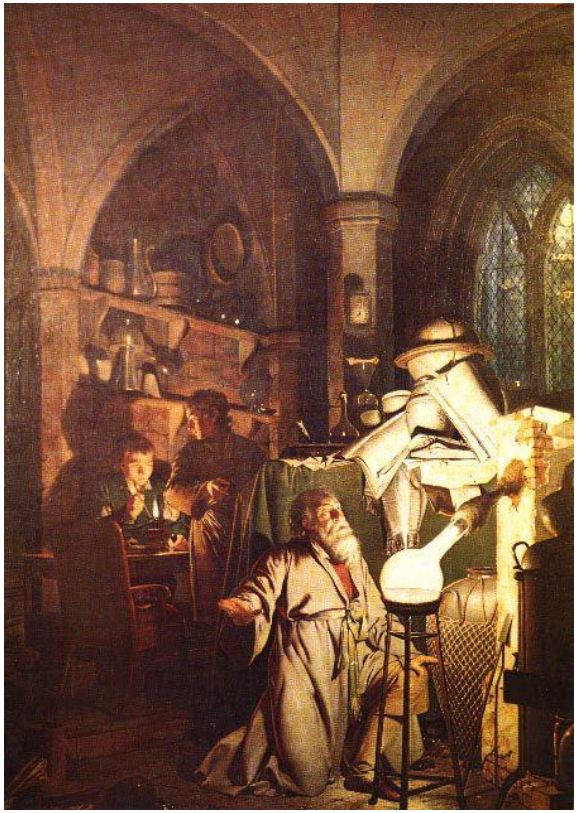
- Phosphorus exists in several allotropic forms: white (or yellow), red, violet and black.

- 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

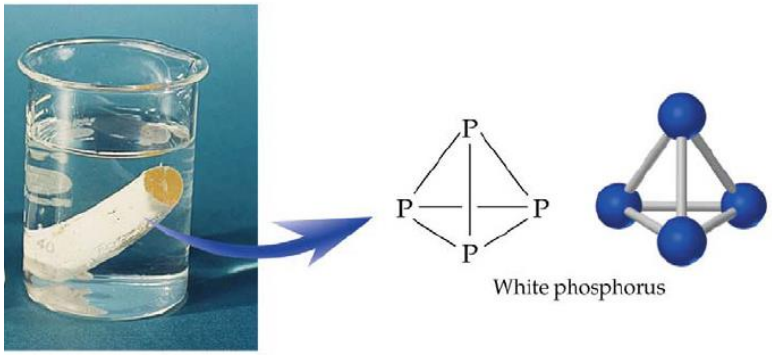
Phosphorus was first isolated in 1669 by Hennig Brand, a German physician and alchemist. Like most chemists of his day, was trying to make gold. He let urine stand for days, boiled it down to a paste, heated this paste to a high temperature, and drew the vapors into water where they could condense - 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.

White Phosphorus

- White phosphorus is composed of P_4 molecules.
- Very poisonous: 50 mg constituting an approximate fatal dose.
- As three phosphorus atoms are involved per tetrahedral surface an anomalously small bond angle of 60 degrees is found in the molecule which is highly strained as a result.
- White phosphorus is especially reactive. It spontaneously ignites in air and must be stored under water. Its affinity for oxygen is so high that it will, nevertheless, burn under water if oxygen is introduced via a tube.



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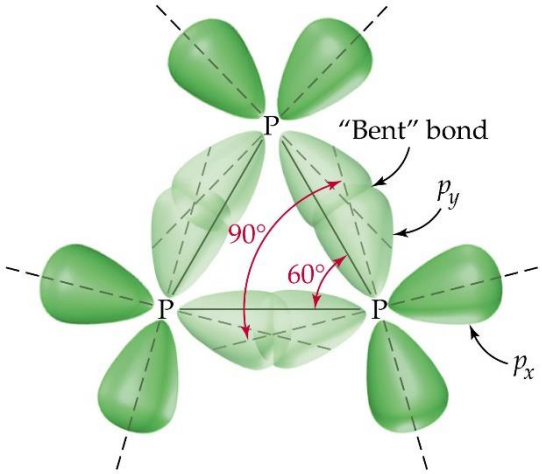
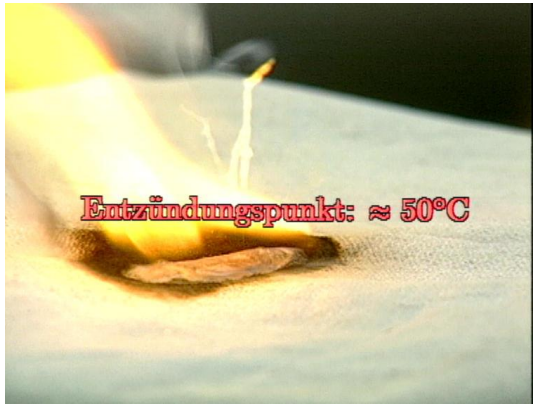


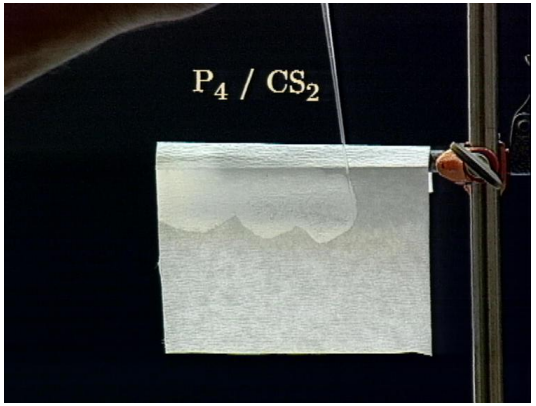
$$P_4 + 5\ O_2 \longrightarrow P_4O_{10}$$

Oxidation of White Phosphorus in Air



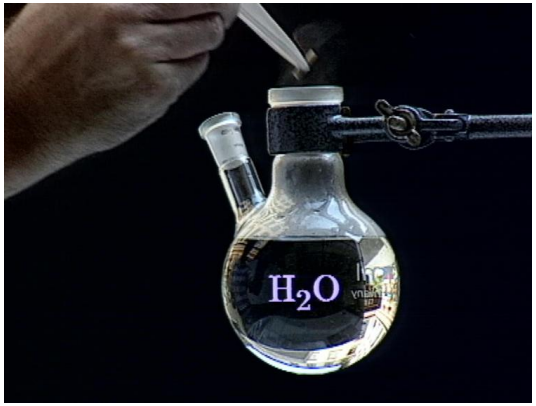
White phosphorus is self-igniting in air. Ignition temperature is dependent upon the surface structure. Phosphorus in compact form self ignites above 50°C. In this experiment, white phosphorus is on a filter paper. It starts to smoke through superficial oxidation. The phosphorus is further heated to 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.

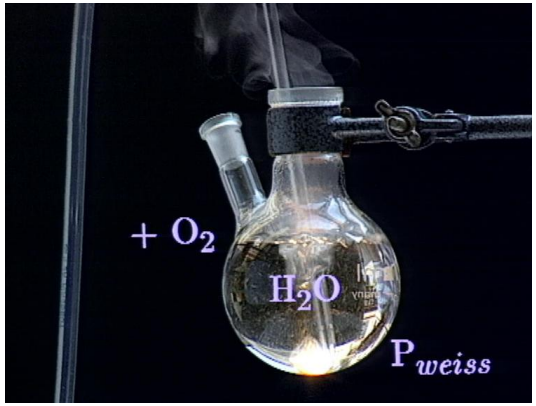
Oxidation of White Phosphorus in Air

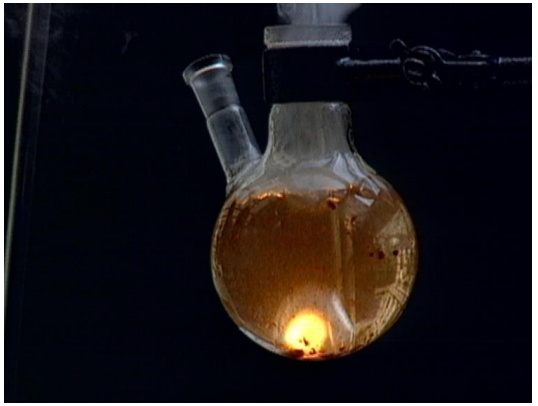


In contrast to the compact white phosphorus, the finely dispersed form burns at room temperature. This finely dispersed white phosphorus with a large surface area can be produced by evaporation of a solution of white phosphorus in carbon disulphide (Bp.: 46°C).

Oxidation of White Phosphorus under Water

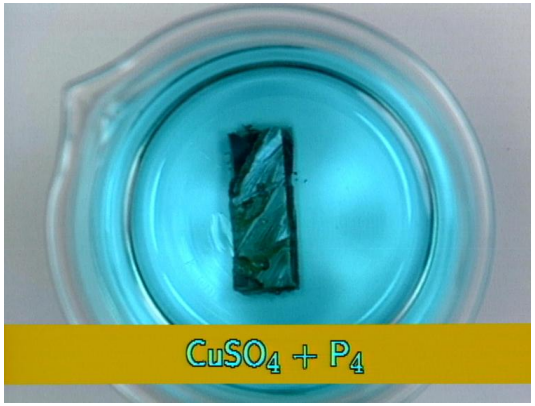


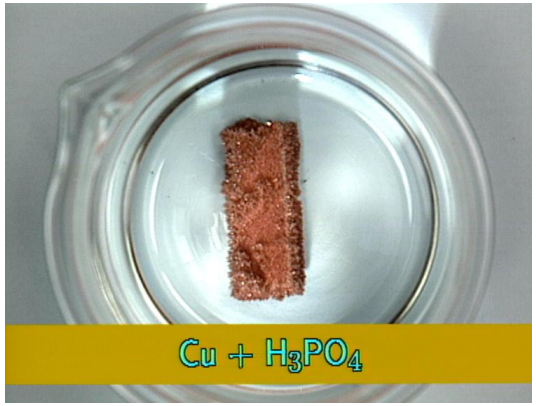


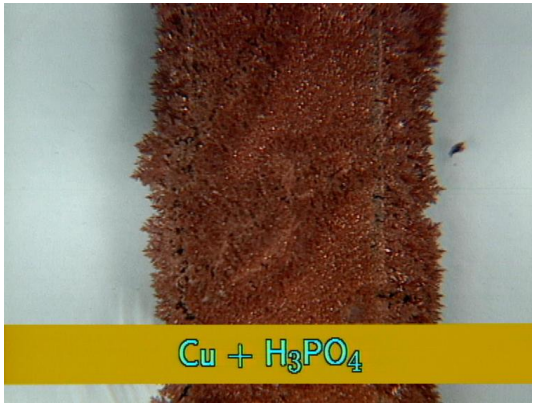


1) A piece of white phosphorus is added to water.
2) Pure oxygen is introduced through a tube.
3) Even under water flames appear from the oxidation.

Precipitation of Copper on White Phosphorus



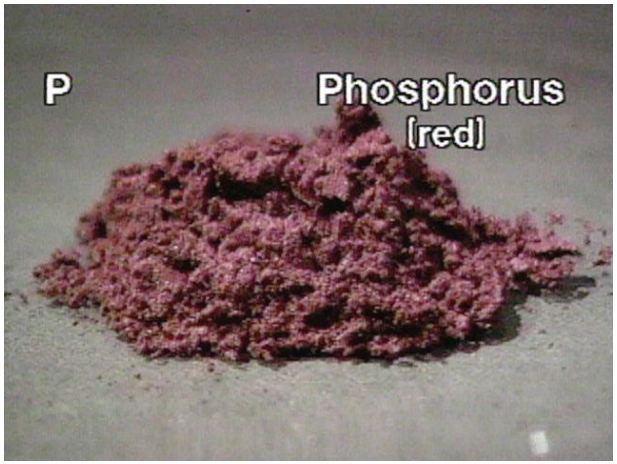




White phosphorus exhibits a high tendency to oxidation, and is therefore a strong reductant. White phosphorus can be added to salt solutions of easily reduced (more electropositive) metals (gold, silver, copper, lead), leading to the precipitation of the elements. The experiment demonstrates the reduction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

Red Phosphorus

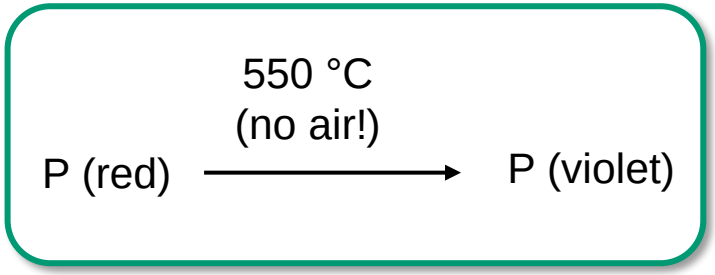
- Amorphous, red phosphorus is formed by heating white phosphorus to 250°C or by exposing white phosphorus to sunlight.
- Red phosphorus is not poisonous and is not as dangerous as white phosphorus.
- Used in safety matches, fireworks, smoke bombs and pesticides.

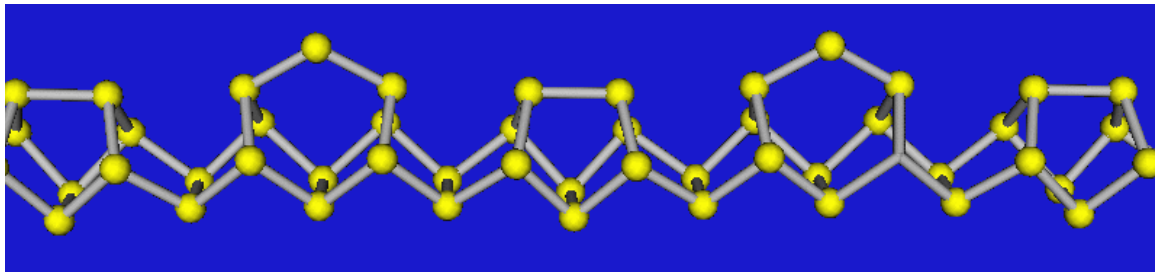


$$P_4 \text{ (white)} \xrightarrow{\sim 250\ ^\circ C,\ \text{(no air!)}} P \text{ (red)}$$

Violet Phosphorus

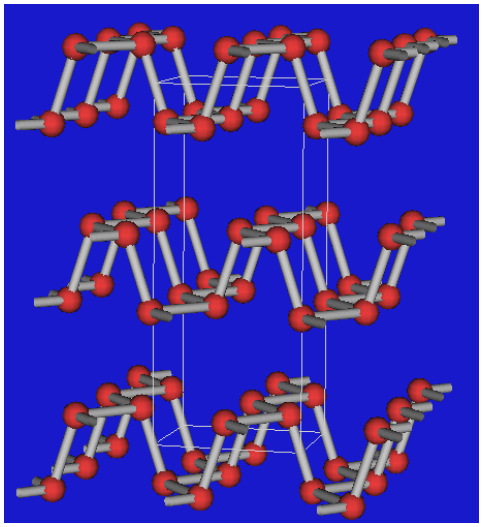
- Violet phosphorus is formed by heating red phosphorus to 550 °C.
- Complicated sheet structure.

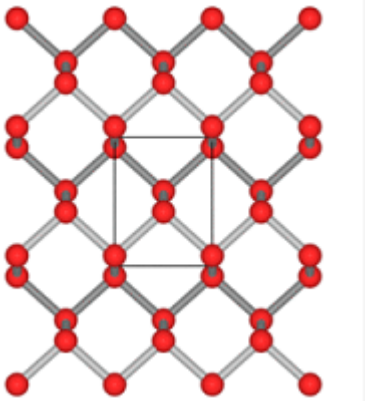




Black Phosphorus

- Black phosphorus is also formed by heating white phosphorus, but a mercury catalyst and a seed crystal of black phosphorus are required.
- Black phosphorus has a sheet structure.
- Black phosphorus is the least reactive form of phosphorus and has no significant commercial uses.

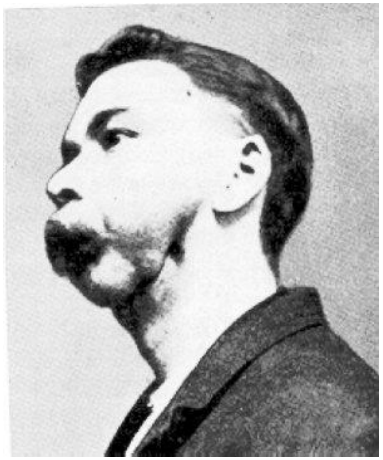




$$P_4 \text{ (white)} \xrightarrow[\text{or}]{\text{200 °C and 12 kbar}\atop\text{380 °C and [Hg]}} \text{P (black)}$$

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 sulfur, 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 !).

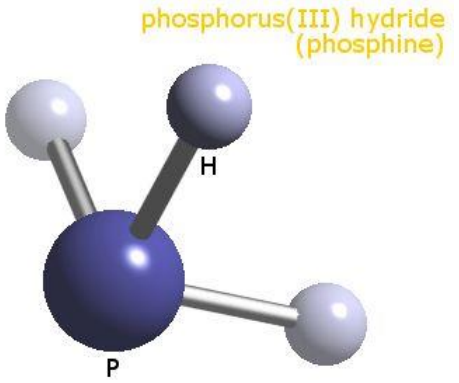


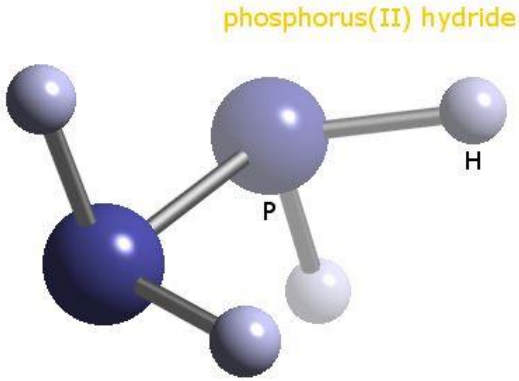
Phosphorus Hydrides

- Phosphine, **PH_3**, is a very reactive poisonous gas. It inflames spontaneously in air and has been described as smelling of both garlic and rotten fish.

- PH_3 is **less basic than NH_3**, as the P-H bond is much less polar. → PH_3 does not form hydrogen bonds and $[PH_4]Cl$ dissociates to PH_3 and HCl.

- **P_2H_4** is a colorless liquid that also inflames spontaneously in air.



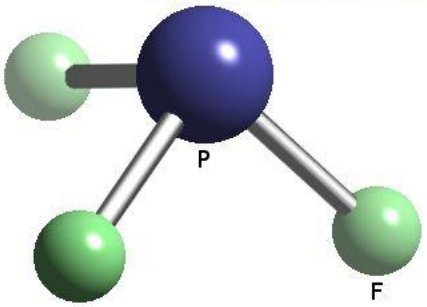


Phosphorus(III) Halides

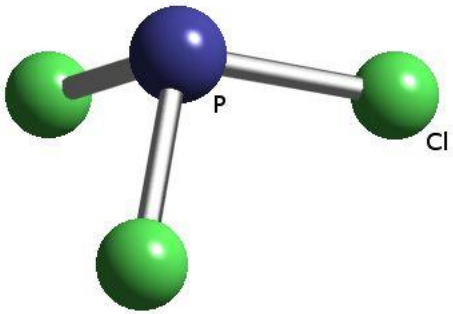
Direct reaction of phosphorus with halogens gives the trihalides if phosphorus is kept in excess.

$$P_4 + 6\ X_2 \longrightarrow 4\ PX_3$$

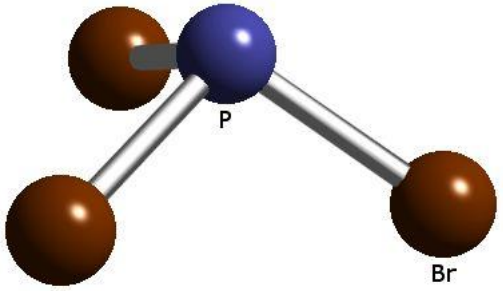
phosphorus(III) fluoride



phosphorus(III) chloride



phosphorus(III) bromide

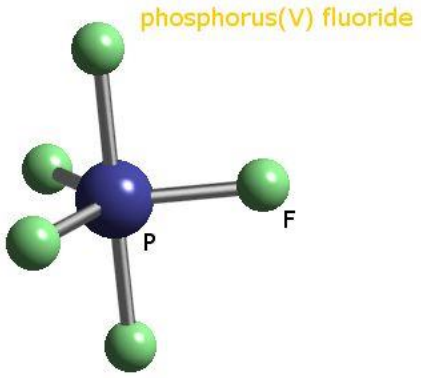


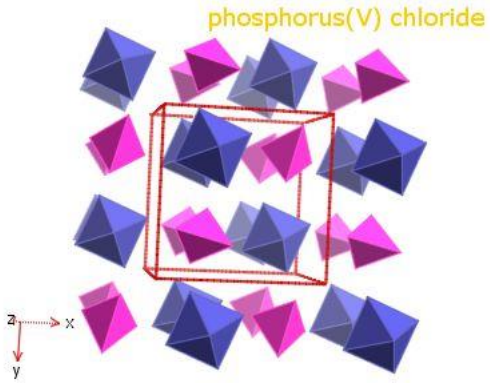
Phosphorus(V) Halides

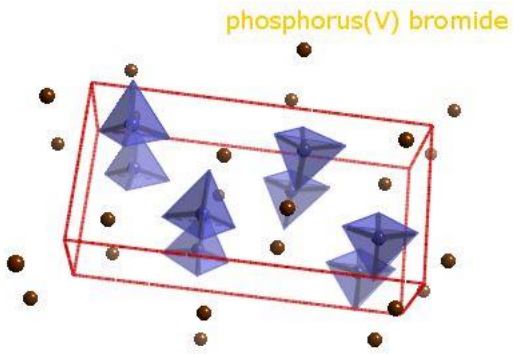
- All PX_5 can be made from the elements.

$$P_4 + 10\ F_2 \longrightarrow 4\ PF_5$$

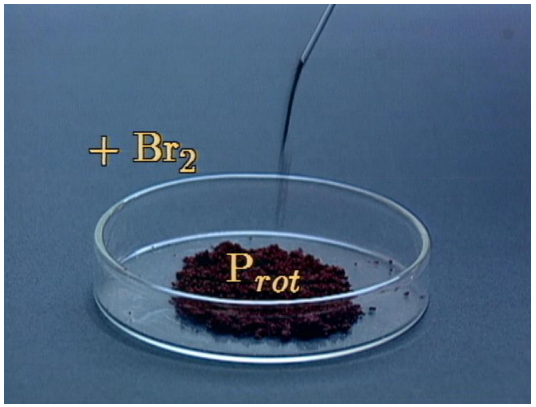
- PCl_5 and PBr_5 are ionic compounds in the solid state: **$[PCl_4]^+[PCl_6]^-$** and **$[PBr_4]^+Br^-$**.

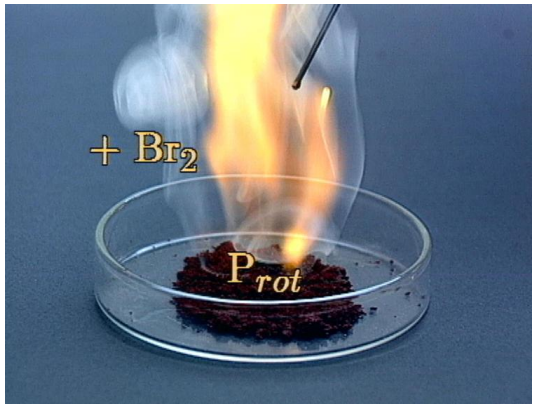






Reaction of Red Phosphorus with Bromine



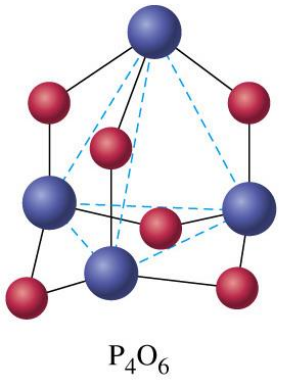


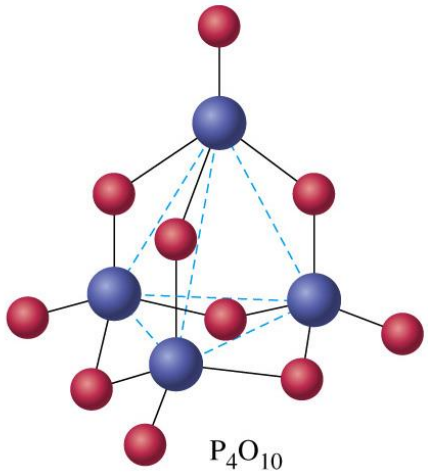
PBr_5 is a crystalline substance with the structure $[PBr_4]^+Br^-$, and degrades into PBr_3 and Br_2 above 84 °C. Upon cooling, the reaction progresses in the opposite direction. During combustion, it is therefore predominantly PBr_3 that is produced, which then reacts further with the bromine vapor during the cooling process.

$$P(red) + 2.5\ Br_2(l) \longrightarrow PBr_3(g) + Br_2(g) \underset{> 84\ °C}{\overset{< 84\ °C}{\rightleftharpoons}} PBr_5$$

Phosphoroxides

- In **P_4O_6**, an O atom is inserted between each pair of P atoms of the basic P_4 structure, leading to a total of six O atoms in the molecule.
- In **P_4O_{10}**, an additional O atom is bonded to each P atom, yielding a total of ten O atoms per molecule.
- P_4O_{10} is an **efficient drying agent**. It hydrolyzes to phosphoric acid.

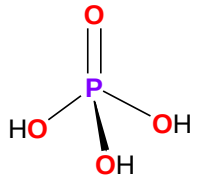


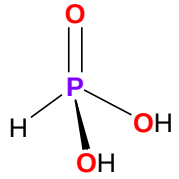


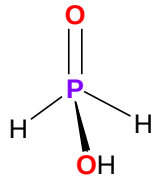
$$P_4O_{10} + 6\ H_2O \longrightarrow 4\ H_3PO_4$$

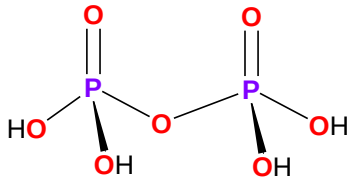
Oxoacids of Phosphorus

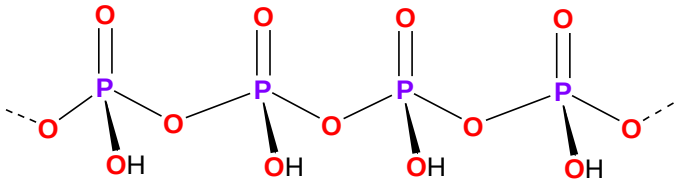
FORMULA	COMMON NAME	ANION
H_3PO_4	Phosphoric acid	Phosphate
H_3PO_3	Phosphonic acid	Phosphite
H_3PO_2	Phosphinic acid	Phosphinate
$H_4P_2O_7$	Diphosphoric acid	Diphosphate
$(HPO_3)_n$	Metaphosphoric acid	Metaphosphate





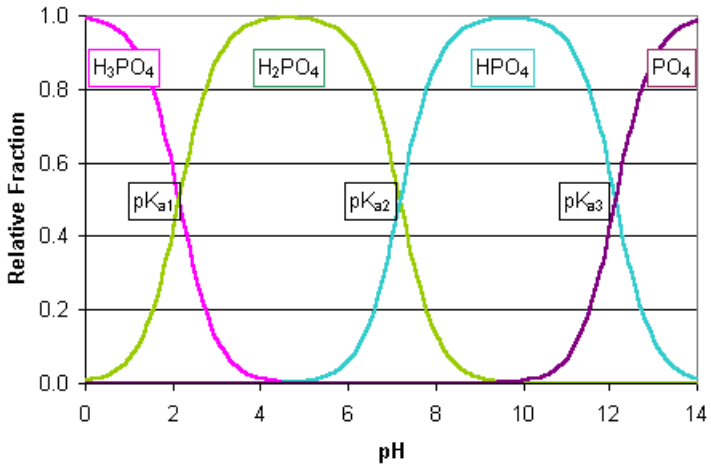






Phosphoric Acid (H_3PO_4)

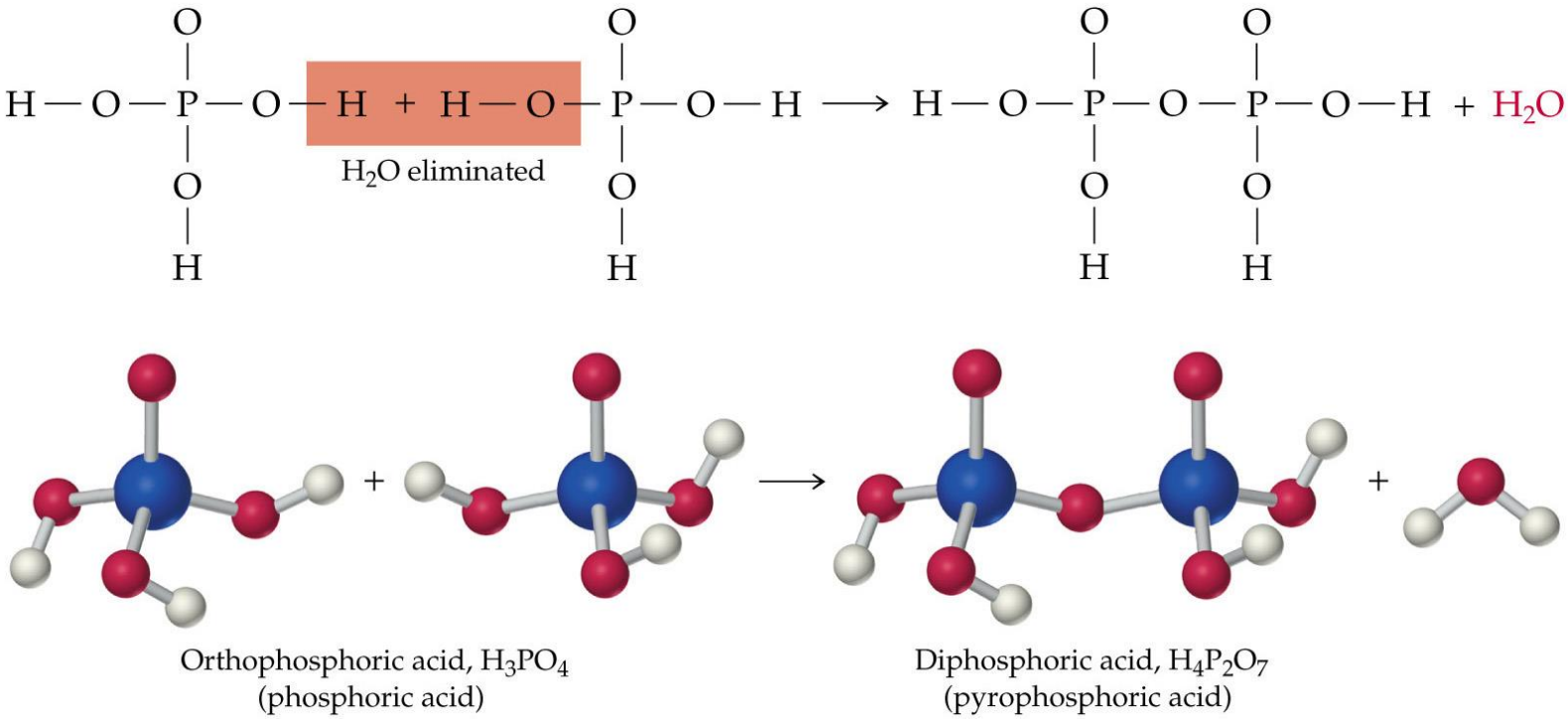
- ~ 80% of H_3PO_4 is used in the **production of** agricultural **fertilizers**.
- The commercial method of preparation is the **addition of sulfuric acid to phosphate rock**.
- Pure phosphoric acid is a white solid that melts at 42 °C to form a viscous liquid.
- In foods and beverages (Coca Cola), phosphoric acid provides an acidic flavor.



Phosphoric acid behaves as a triprotic acid

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \longrightarrow 3\ CaSO_4 + 2\ H_3PO_4$$

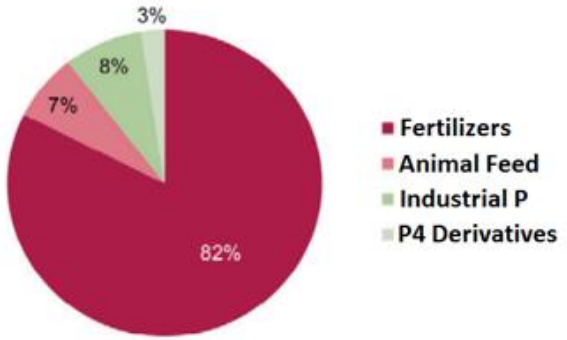
Polyphosphoric Acids



Heating phosphoric acid results in a condensation of the molecules with elimination of water to form dimers, trimers, and higher polymers of phosphoric acid.

Phosphate-Fertilizers

- Phosphate-fertilizers contain calcium or ammonium phosphates.
- Natural **$Ca_3(PO_4)_2$ is not soluble → reaction with sulfuric or phosphoric acid** to make dihydrogenophosphates (60 % of the world production of H_2SO_4 is used that way).
- Ammonium phosphate is formed by reaction of NH_3 with phosphoric acid.



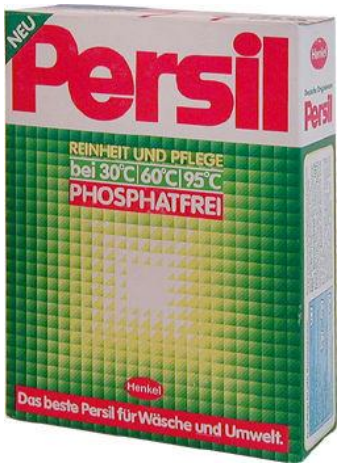
$$Ca_3(PO_4)_2 + 2\ H_2SO_4 \longrightarrow Ca(H_2PO_4)_2 + 2\ CaSO_4$$

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 \longrightarrow 3\ Ca(H_2PO_4)_2$$

$$2\ NH_3 + H_3PO_4 \longrightarrow (NH_4)_2HPO_4$$

Phosphates, Detergents and the Environment

- Sodium triphosphate ($Na_5P_3O_{10}$) was used for years in detergents to complex Mg^{2+} and Ca^{2+} ions (they tend to precipitate with the detergent molecule).
- Excess of phosphates in rivers and lakes is thought to be responsible for the occurrence of eutrophication.
- Most states in North America have banned the use of phosphate in detergents by 1993.



Highly eutrophic water of the New River in London

Phosphorus Shortage

NATIONAL GEOGRAPHIC

SCIENCE | NEWS

Farmers are facing a phosphorus crisis. The solution starts with soil.

Overuse of fertilizer has led to phosphorus shortages and water pollution.

October 2020

The Guardian

Scientists warn of 'phosphogeddon' as critical fertiliser shortages loom

March 2023

SCIENTIFIC AMERICAN

Phosphorus: A Looming Crisis

David A. Vaccari

June 2009

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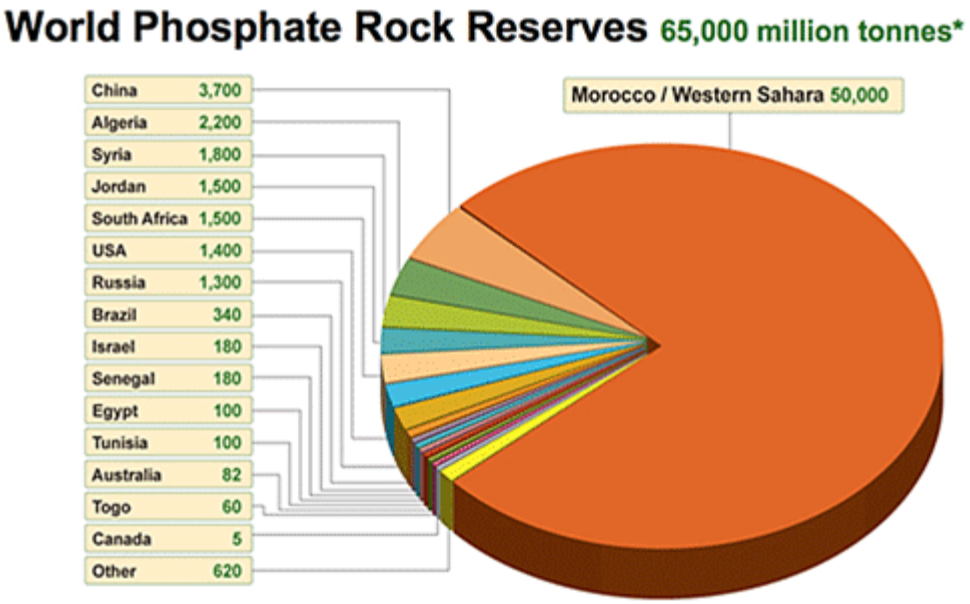
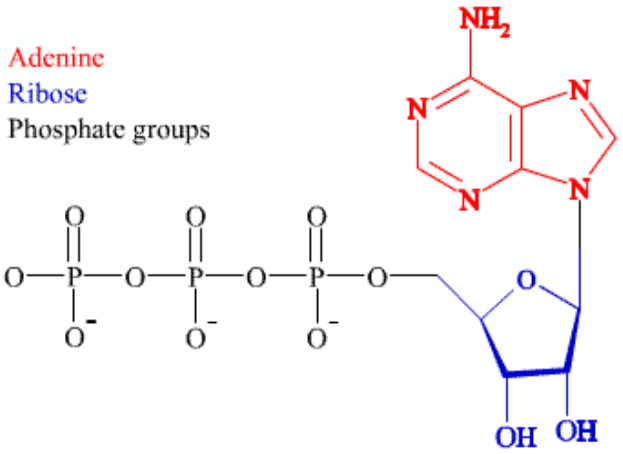


→ link

WORLD RESOURCES FORUM

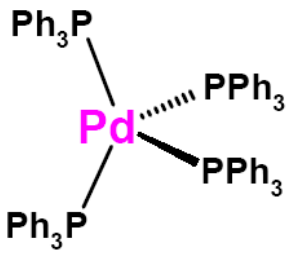
Phosphates and Life

- Most phosphate in animals is found in the form of calcium phosphate in the bones.
- Of the phosphate in the blood, 92 % are organophosphates and only 8 % are simple phosphate.
- The organ richest in phosphate is brain tissue.
- ATP acts as a source of chemical energy. It is produced in our bodies at ~ 1 kg/h !.
- The recommended daily intake of phosphate is 0.8 g but a normal diet supplies 1-2 g per day. Phosphate rich: tuna, salmon, chicken, eggs and cheese (>200 mg per 100 g).

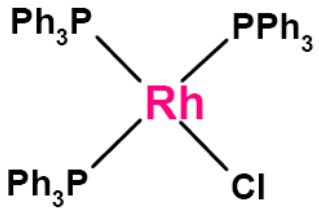


Phosphines (PR_3)

- Phosphines are important ligands in coordination chemistry.
- Are able to stabilize metals in low oxidation states.



Pd^0 catalyst used in C-C coupling reactions

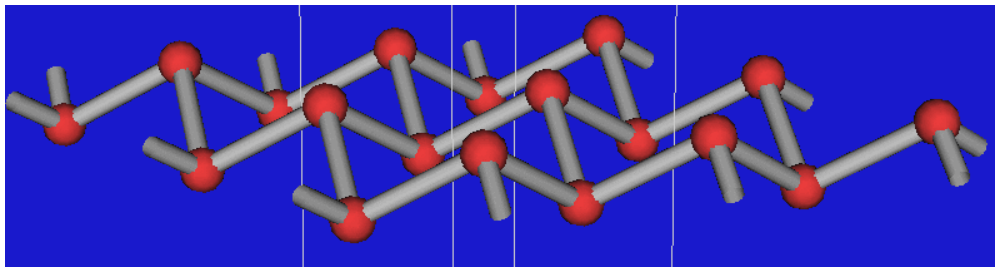


Rh^I catalyst used in hydrogenation reactions

Arsenic

- Arsenic occurs free in nature, but is most often found in the mineral **arsenopyrite (FeAsS)**.

- The thermodynamically most stable form is **metallic (or grey) arsenic with a sheet structure**. At high temperatures, it sublimes to give **As_4 molecules in the gas phase**. If cooled rapidly, you get yellow arsenic (analogous to white phosphorus).



Sheet structure of arsenic (antimony and bismuth are isostructural)

Arsenic(III) Oxide

- Arsenic(III) oxide, **As_2O_3**, is a white, crystalline solid which is formed by oxidation of As in air or by oxidation of As-containing minerals.

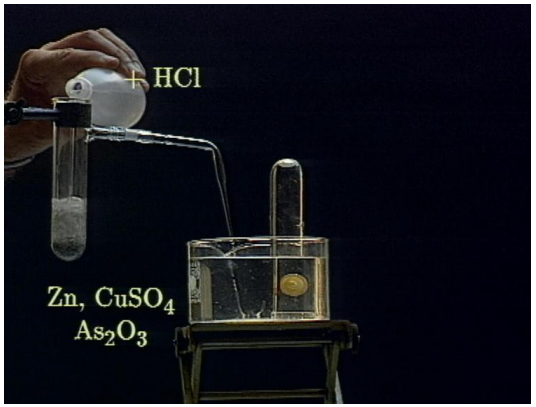
$$4\ As + 3\ O_2 \longrightarrow 2\ As_2O_3$$

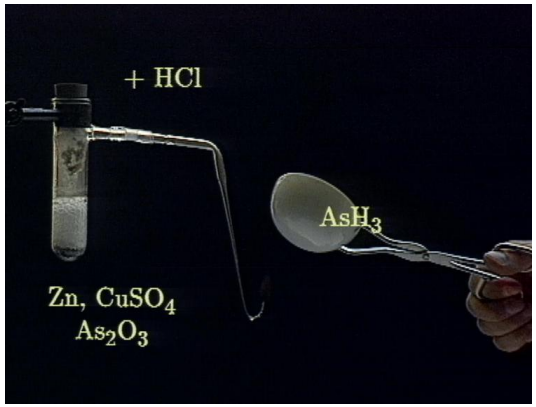
$$2\ FeAsS + 5\ O_2 \longrightarrow As_2O_3 + Fe_2O_3 + 2\ SO_2$$

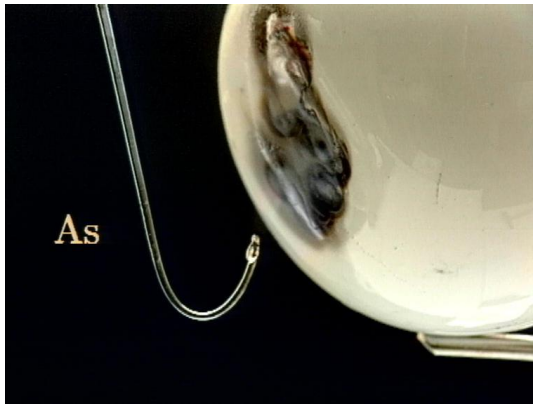
- As_2O_3 is a **highly toxic** with a lethal dose of ~ 0.1 g. Dangerous because tasteless. In the 15th and 16th century, the Italian family of Borgias used arsenic as their favorite poison for political assassinations. Symptoms of arsenic poisoning were difficult to detect, since they could mimic food poisoning.

As_2O_3

Marsh's Test for Arsenic







Strong reducing agents, e.g. Zn / HCl, reduce As_2O_3 to the oxidation state –3 of the arsenic hydride. This can be verified by thermic decomposition .

$$6\ Zn + 12\ HCl \longrightarrow 6\ ZnCl_2 + 6\ H_2$$

$$As_2O_3 + 6\ H_2 \longrightarrow 2\ AsH_3 + 3\ H_2O$$

$$2\ AsH_3 + 1.5\ O_2 \longrightarrow 2\ As + 3\ H_2O \text{ (air deprivation; black mirror)}$$

$$2\ AsH_3 + 3\ O_2 \longrightarrow As_2O_3 + 3\ H_2O \text{ (excess air; white mirror)}$$

Antimony

- A hard, crystalline **semi-metal** which also exists as a grey powder.
- Most important **oxidation states: +3 and +5** with the former being more stable.
- It is sometimes found free in nature, but is usually obtained from the ores stibnite (Sb_2S_3).
- Very pure antimony is used to make certain types of semiconductor devices.
- Antimony compounds are quite toxic although they were used extensively as a medicine in the 16th to 18th century.

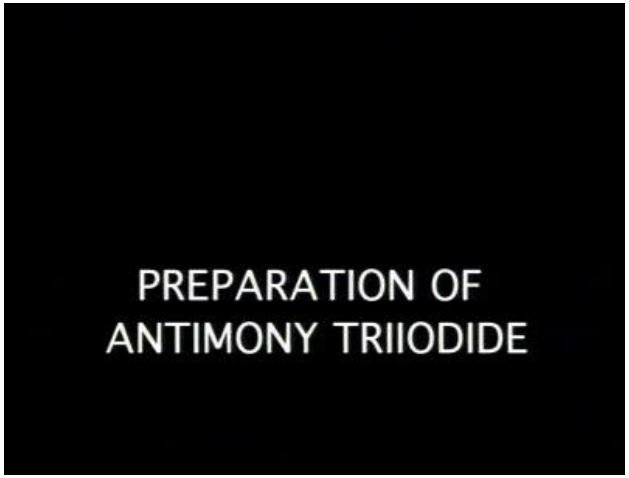
Stibinite, the main source of antimony.

Large crystals of Sb.

Antimony Halides

- With all halides, a compound of the formula **SbX_3** is formed. They are solid compounds at RT.

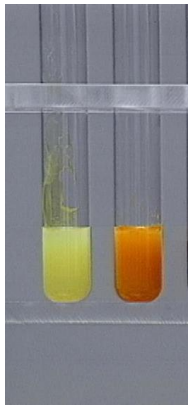
- Pentahalides **SbX_5 are known for X^- = F^- and X^- = Cl^-**.



(Video)

Comparison of As(III) and Sb(III)

Precipitation of yellow As_2S_3 and orange Sb_2S_3 results from the addition of hydrogen sulfide or thioacetamide to hydrochloric solutions of arsenite and antimonite.



$$2\ As^{3+} + 3\ S^{2-} \longrightarrow As_2S_3\ \text{(yellow)}$$

$$2\ Sb^{3+} + 3\ S^{2-} \longrightarrow Sb_2S_3\ \text{(orange)}$$

Bismuth

- Bismuth does occur free in nature and in minerals such as bismite (Bi_2O_3).
- Pure bismuth is a white, brittle metal with a slight pink color.
- Bismuth oxide (Bi_2O_3), a bismuth compound, is used as a yellow pigment in paints and cosmetics. Bismuth oxychloride (BiOCl) is used to make a pigment known as bismuth white.
- Peptobismol® is a suspension of bismuth subsalicylate (BSS) – antibacterial and thickens the gastric mucus.