Lecture 11.
Chemical properties of elements from VA group.

Part II. Phosphorus, Arsenic, Antimony, Bithmuth.

Main questions of the lecture:

1. Natural resources and allotropic modifications of phosphorus

2. Compounds of phosphorus

3. Compounds of arsenic, antimony, and bithmuth

4. The usage of compounds of elements from VA group in pharmaceutical analysis and medicine

Natural resources

Phosphorus, in contrast to nitrogen, exist in nature only as a part of compounds.

Minerals:

$Ca_5(PO_4)_3(F/Cl/OH)$ – fluoro-, chlor-, or hydroxyapatite.

Comparison between bonds of phosphorus and nitrogen

Bond	Energy, kJ/mol	Bond	Energy, kJ/mol
N—H	389	P— H	322
N—O	230	P—O	360
N—C	334	P—C	272

Production:

$$Ca_3(PO_4)_2 + 5C + 3SiO_2 \overset{1500°C}{=} 3CaSiO_3 + 5CO + 2P$$

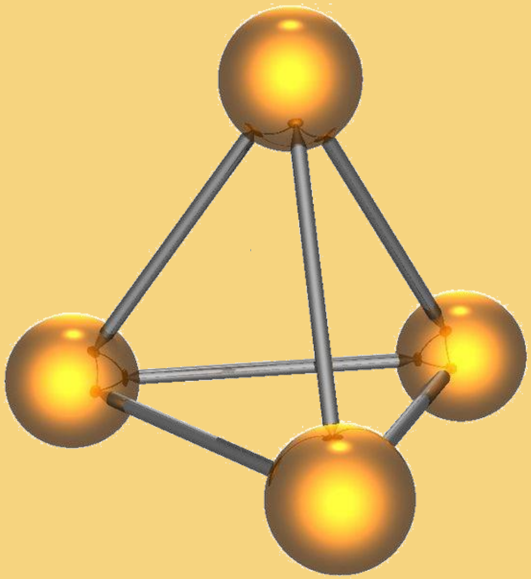
Allotropic modifications of phosphorus

White, red, and black

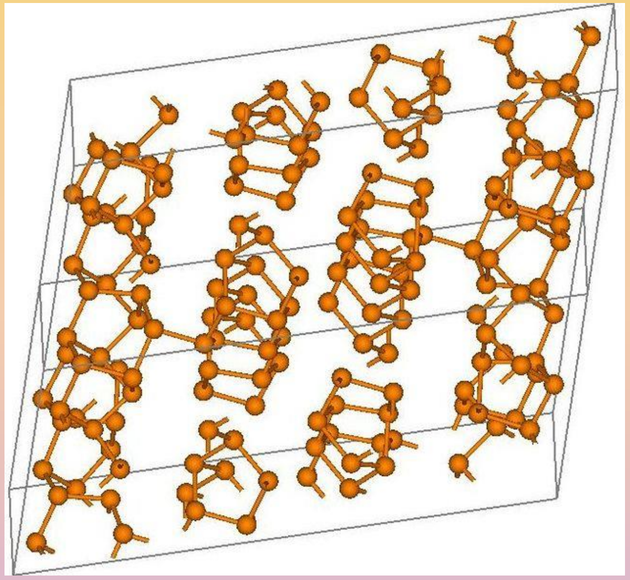
«Yellow» phosphorus

White (P_4)	Red (P)	Black (P)
Molecular compound	Amorphous substance	Has agraphite-like atomic crystal lattice
Garlic odor	Has no odor	Has no odor
$t_{melting} = 44\ ^oC$	$t_{melting} = 593°C$ Under pressure	$t_{melting} \approx 1000°C$
t combustion 50^{o}C	t combustion > 250^{o}C	t combustion > 400^{o}C
Insoluble in water, soluble in carbon sulfide	Insoluble neither in water, nor in carbon sulfide	Insoluble neither in water, nor in carbon sulfide
Produces a light (chemiluminiscence)	Doesn’t produce a light	Doesn’t produce a light
Poisonous (lethal dosage is 50 - 150 mg), burns a skin	It is not poisonous, doesn’t burn a skin	It is not poisonous

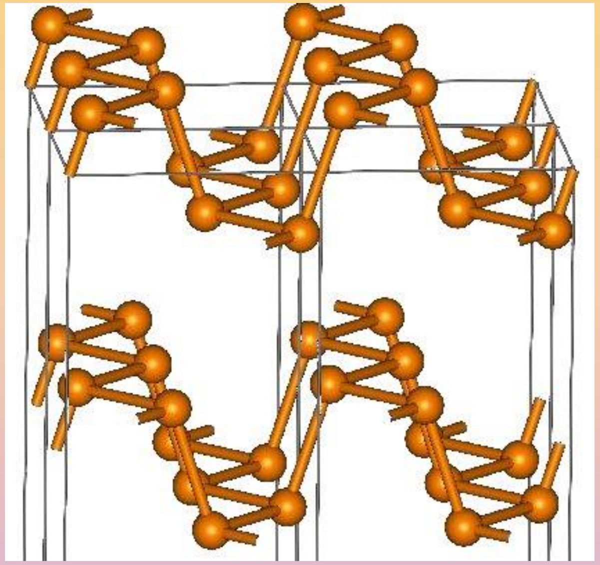
White phosphorus



In the **P_4 molecule** the valence angle (60°) is not equal to the angle at which 3 p-orbitals are situated (90°), as well as sp^3 orbitals (109°). As a result, the molecule is very instable.



Red phosphorus



Black phosphorus

Chemical properties

Phosphorus reacts with many substances, and more frequently plays a role of a **reducer:**

$$4P + 5O_2 = 2P_2O_5;$$

$$2P + 3S = P_2S_3;$$

$$2P + 3Cl_2 = 2PCl_3;$$

$$P + 5HNO_3 = H_3PO_4 + 5NO_2 + H_2O$$

Chemiluminiscence

The burning of white phosphorus in water

As an oxidizer phosphorus can react with metals:

0 -3

$3Ca + 2P = Ca_3P_2$

$3Mg + 2P = Mg_3P_2$

Phosphides of s-elements are decomposed by water:

$Mg_3P_2 + 6H_2O = 3Mg(OH)_2 + 2PH_3\uparrow$

Phosphine burns down immediately after its formation:

$2PH_3 + 4O_2 = P_2O_5 + 3H_2O$

Production of phosphine:

$$P_4 + 3KOH + 3H_2O = PH_3 + 3KH_2PO_2$$

Production of calcium phosphide

Hydrolysis of calcium phosphide

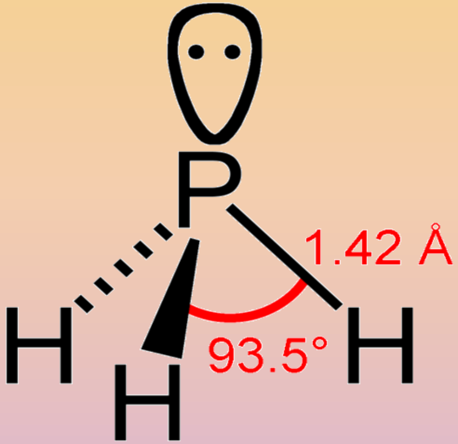
Phosphine PH_3 is a poisonous gas with a garlic odor that is a strong reducer

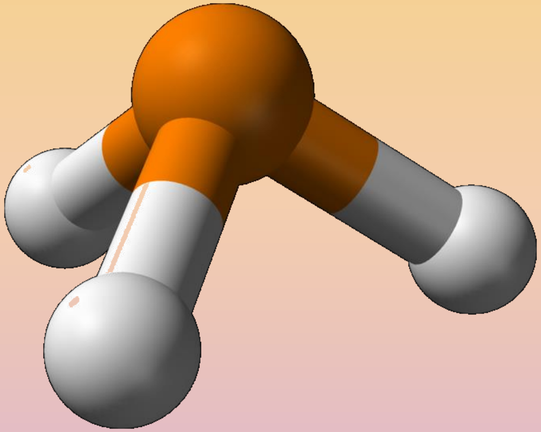
It burns spontaneously in the open air:

$$\mathbf{2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O}$$

Basic properties of phosphine are weaker than those of ammonia. Phosphine cannot react with water and form $\mathbf{PH_4^+}$. Salts of phosphonium are known.

$\mathbf{PH3 + HI = PH_4I}$ (phosphonium salts)





Compounds with phosphorus in positive oxidation states

Phosphorus can make compounds like PHal_3 and PHal_5 with halogens (except PI_5).

Hydrolysis of halides

$$\mathbf{PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl}$$

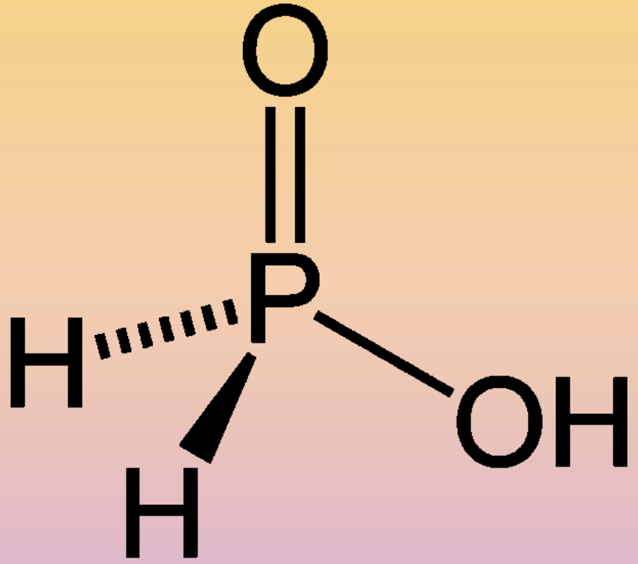
$$\mathbf{PCl_5 \rightarrow PCl_3 + Cl_2 \quad (t > 300\ °C)}$$

In hot water hydrolysis is irreversible:

$$\mathbf{PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl}$$

Phosphorus usually demonstrates such positive oxidation states as **+1, +3, +5.**

There is just one hydrogen atom able to form a cation in **hypophosphorous acid H_3PO_2**. So, it is a monoprotic acid.



$pK_a = 1.2$

Production:

$$2P_4(\text{white}) + 3Ba(OH)_2 + 6H_2O \rightarrow 2PH_3 + 3Ba(H_2PO_2)_2$$

$$Ba(H_2PO_2)_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + 2H_3PO_2$$

The salts are called **- hypophosphites**. They are soluble and water, but they are unstable in a basic medium.

$$2Na(PH_2O_2) + 3NaOH \rightarrow Na_2(PHO_3) + Na_3PO_4 + 3H_2\uparrow$$

P_4O_6

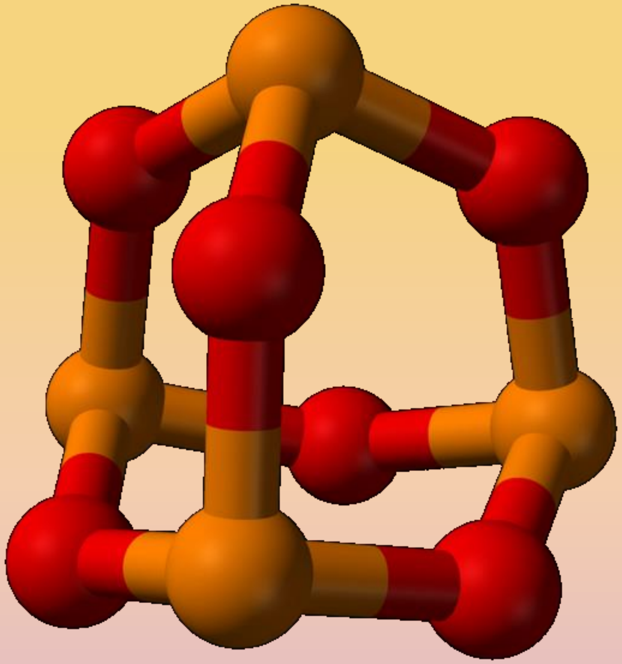
The simplest formula is **P_2O_3**

P_4O_6 has a melting point at room temperature

$t_{melting} = 22.5°C$

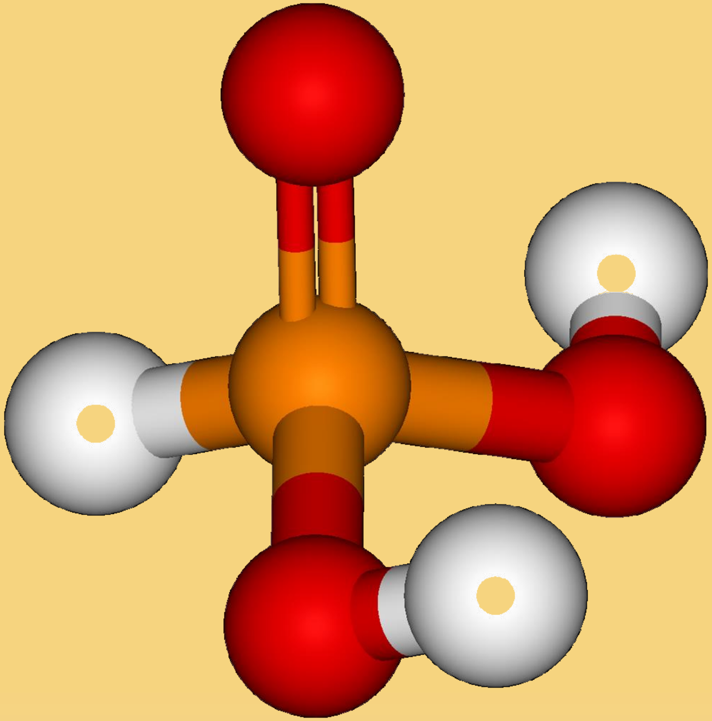
Production:

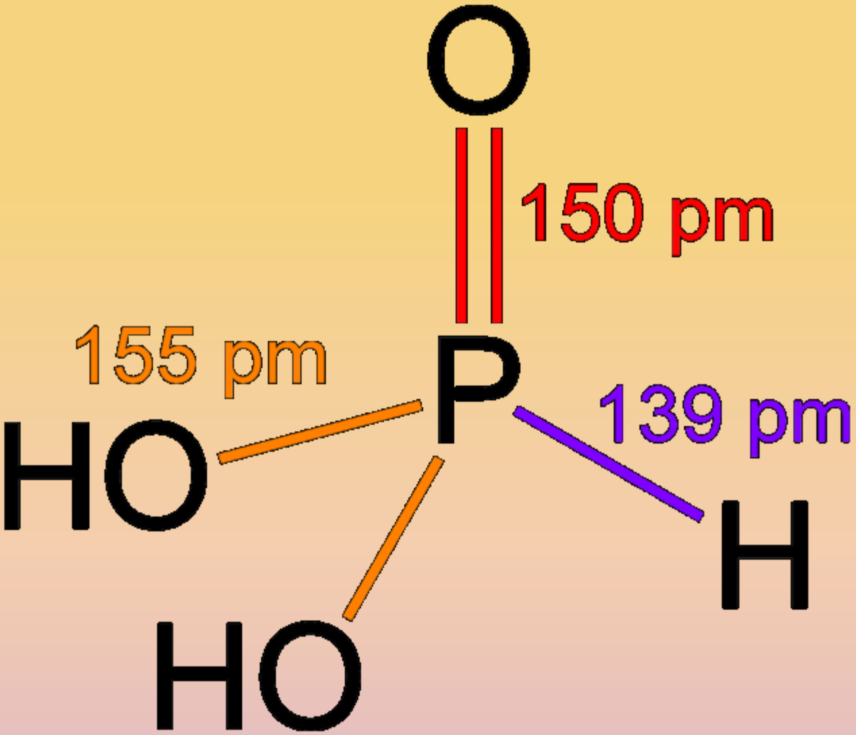
$$4P + 3O_2 = P_4O_6$$



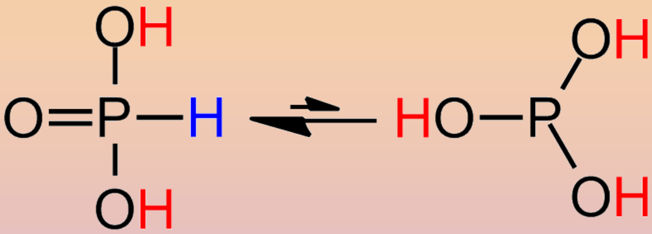
$$P_4O_6 + 6H_2O = 4H_3PO_3$$

Phosphorous acid





$pK_{a1} = 1.3$
$pK_{a2} = 6.7$



H_2PHO_3 H_3PO_3

Sodium phosphite - Na_2HPO_3
Sodium hydrogenphosphite - NaH_2PO_3

$H_2[HPO_3]$

$$P_2O_3 + 4NaOH = 2Na_2HPO_3 + H_2O$$

$$4H_3PO_3 = PH_3 + 3H_3PO_4 \text{ (t ,°C)}$$

$$HgCl_2 + H_2[HPO_3] + H_2O = H_3PO_4 + Hg\downarrow + 2HCl$$

$$H_3PO_3 + Cl_2 + H_2O = H_3PO_4 + 2HCl$$

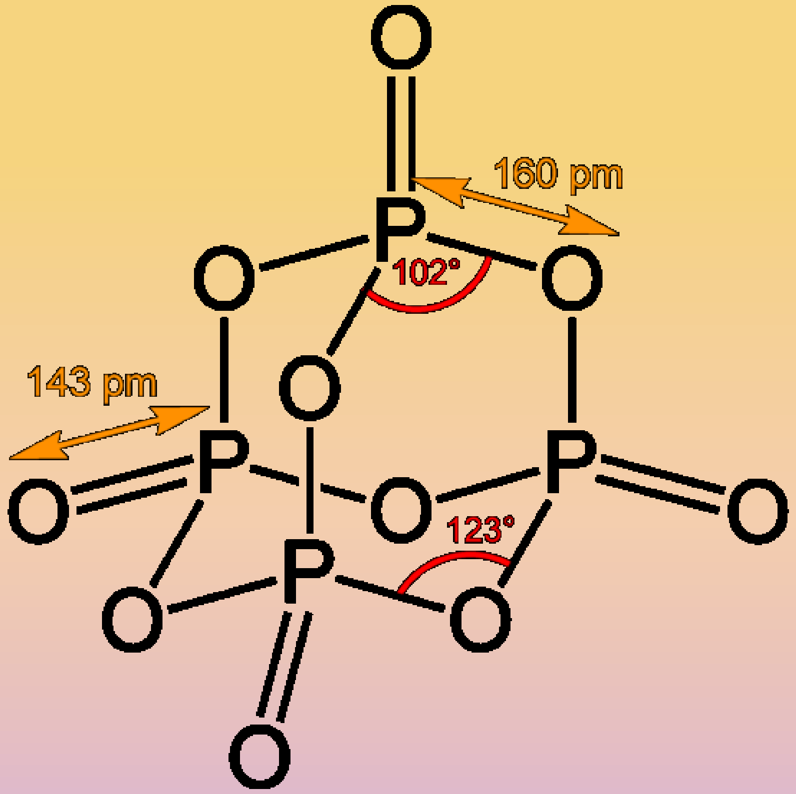
P_4O_{10}

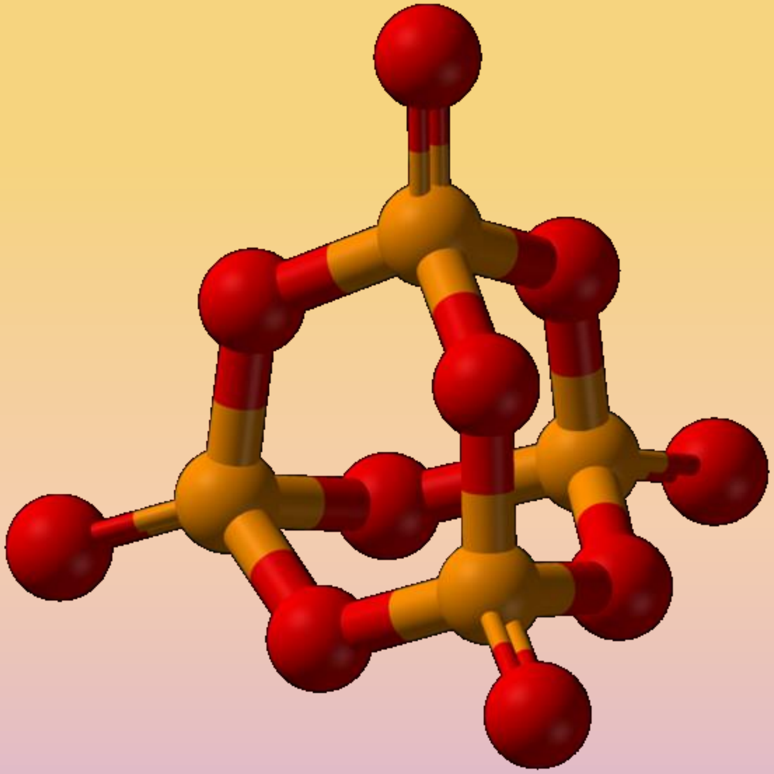
The simplest formula is P_2O_5

$$4P + 5O_2 = P_4O_{10}$$

$$P_2O_5 + H_2O = 2HPO_3$$

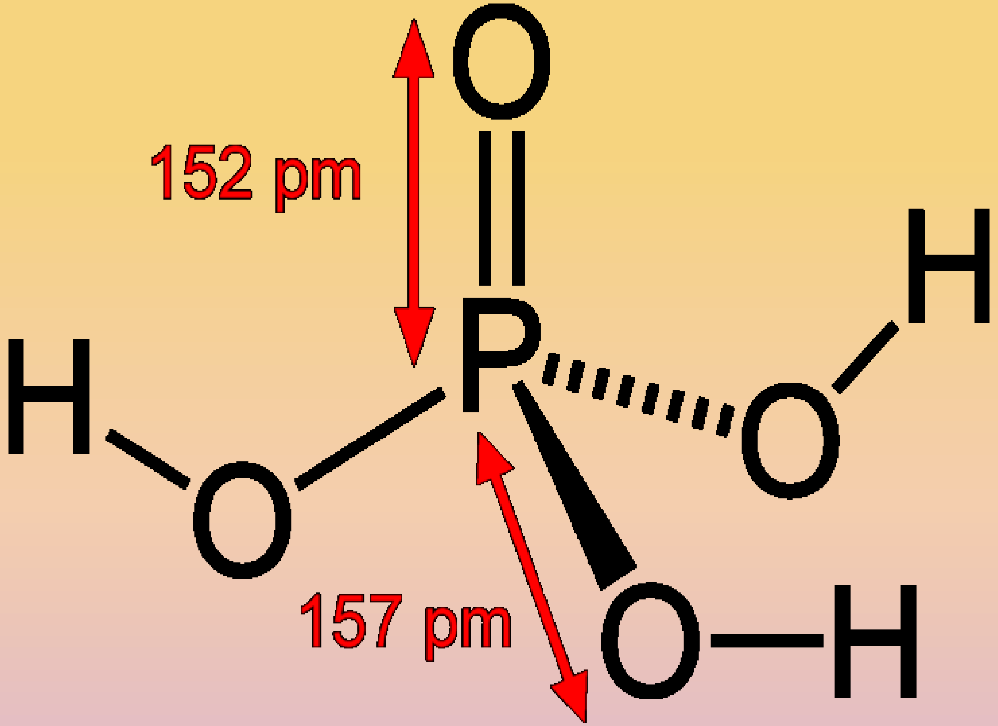
(metaphosphoric acid)

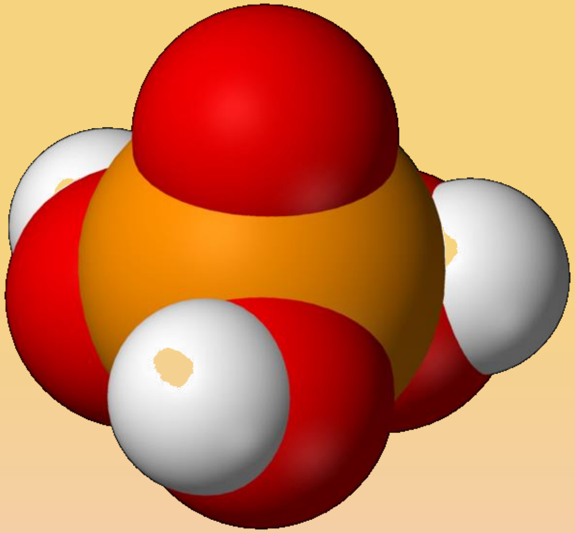




$$HPO_3 + H_2O = H_3PO_4$$

Orthophosphoric acid





H_3PO_4 – is a white solid substance

Production:

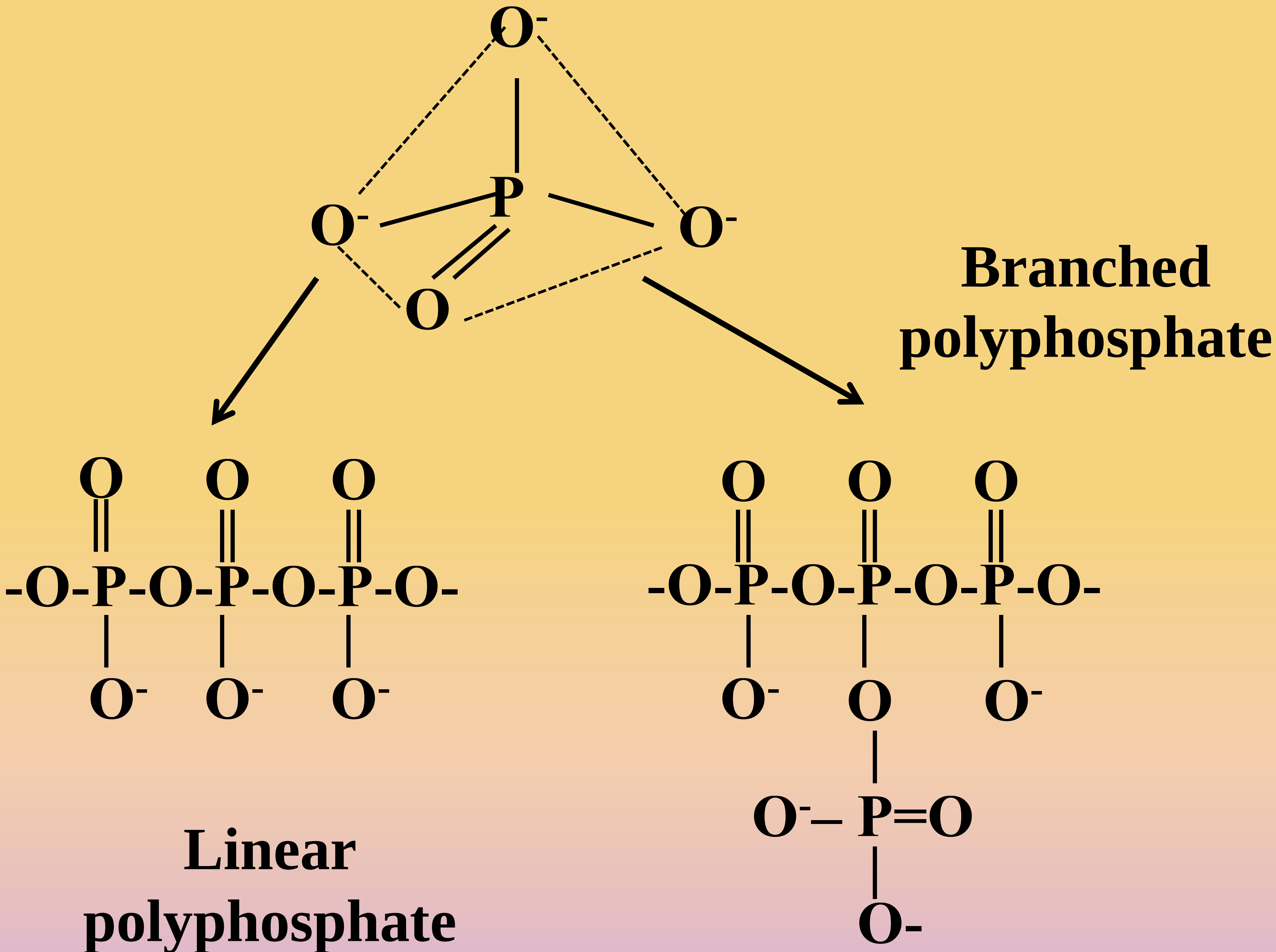
$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$

$pKa_1 = 2.148$; $pKa_2 = 7.198$; $pKa_3 = 12.319$

NaH_2PO_4 – sodium dihydrogenphosphate
Na_2HPO_4 – sodium hydrogenphosphate
Na_3PO_4 – sodium phosphate

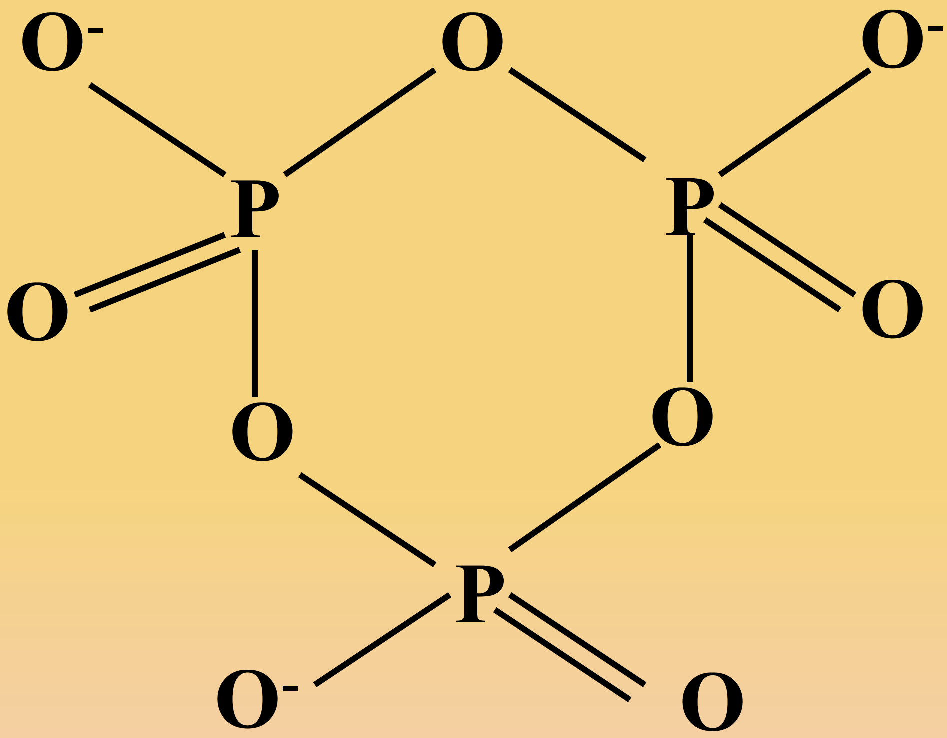
$Na_3PO_4 + H_2O \leftrightarrow NaOH + Na_2HPO_4$;
$PO_4^{3-} + H_2O \leftrightarrow OH^- + HPO_4^{2-}$
$Na_2HPO_4 + H_2O \leftrightarrow NaOH + NaH_2PO_4$;
$HPO_4^{2-} + H_2O \leftrightarrow OH^- + H_2PO_4^-$

$CaHPO_4 \downarrow$ и $Ca_3(PO_4)_2 \downarrow$



Branched polyphosphate

Linear polyphosphate



Cyclic metaphosphate

Polyphosphoric acids

Diphosphoric (or **pyrophosphoric) acid $H_4P_2O_7$**
$t_{melting}$ = 61°C. It is soluble in water.
This acid is stronger than **H_3PO_4**.
Its salts are called **diphosphates** or **pyrophosphates.**
$P_2O_7^{2-}$ ion is made from two tetraeders of **PO_4^{3-}** connected by the common oxygen atom.

Metaphosphoric acids have the common formula $H_nP_nO_{3n}$,
n varies from 3 to 8, **$(HPO_3)_n$**

These acids and their salts are poisonous.

Organic phosphates

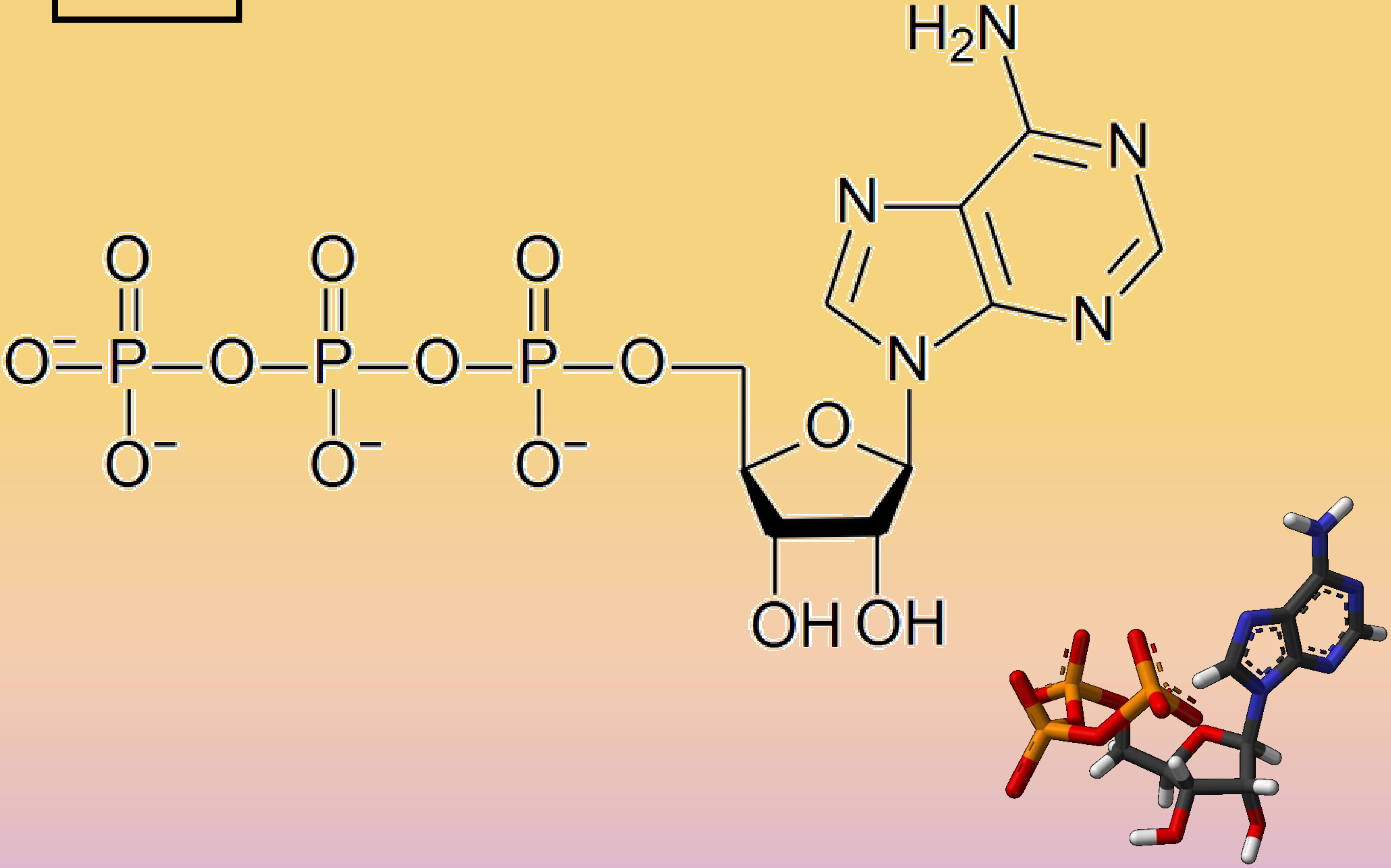
Esters of phosphoric acid have the same formula:

$\mathbf{(RO)_{n}P(O)(OH)_{3-n}}$,

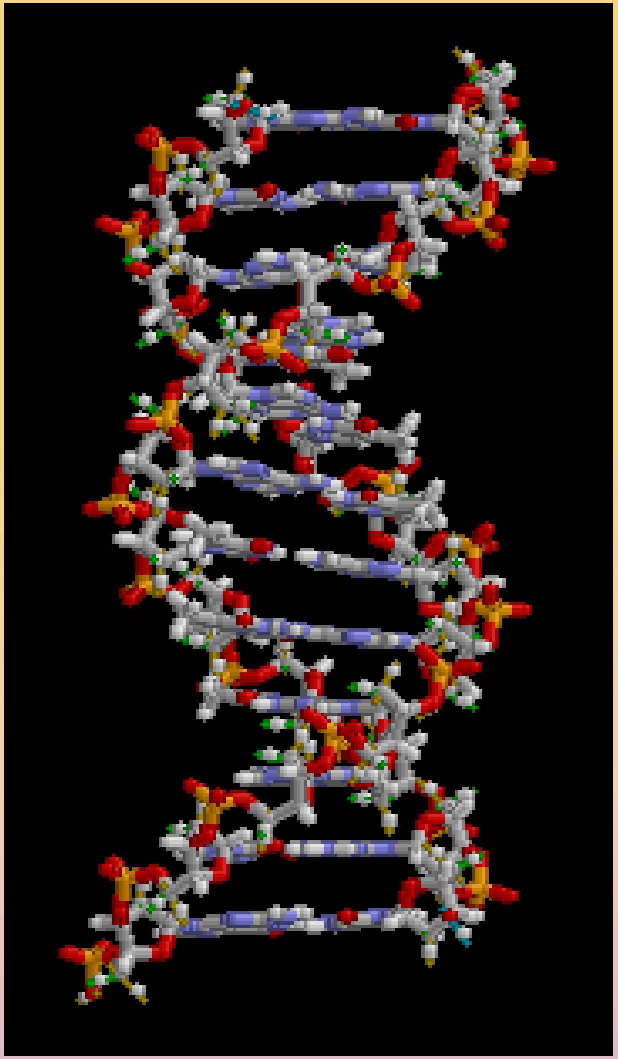
in which **R** is an organic radical, **n = 1-3.**

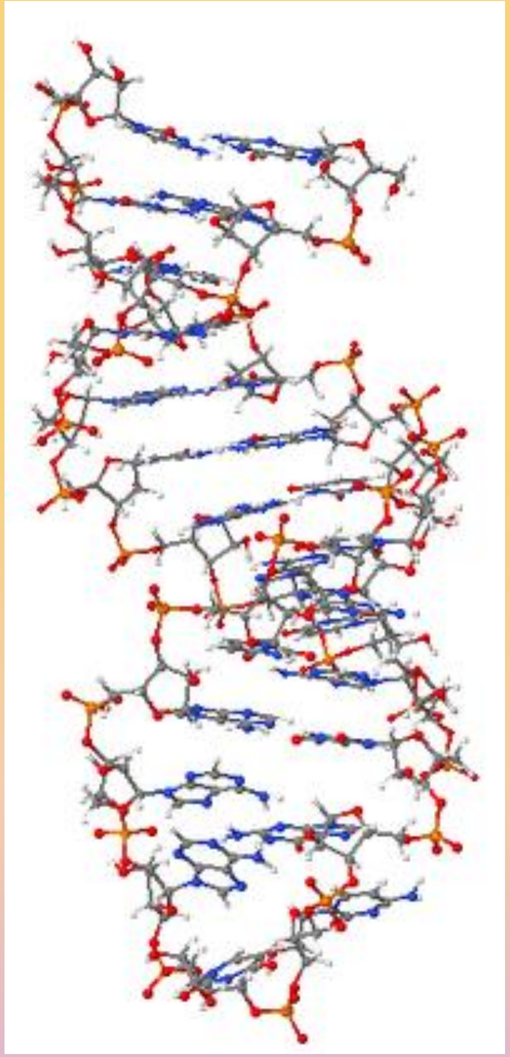
There are normal and acidic organic phosphates

ATP

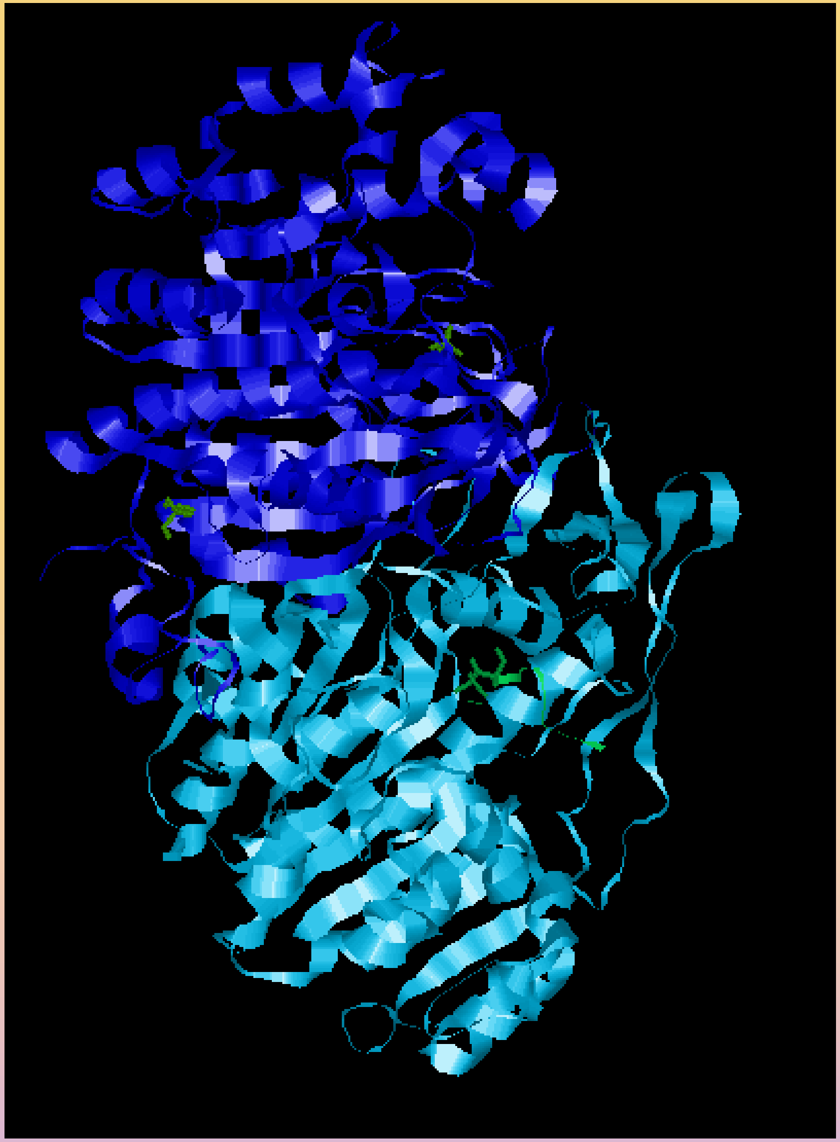


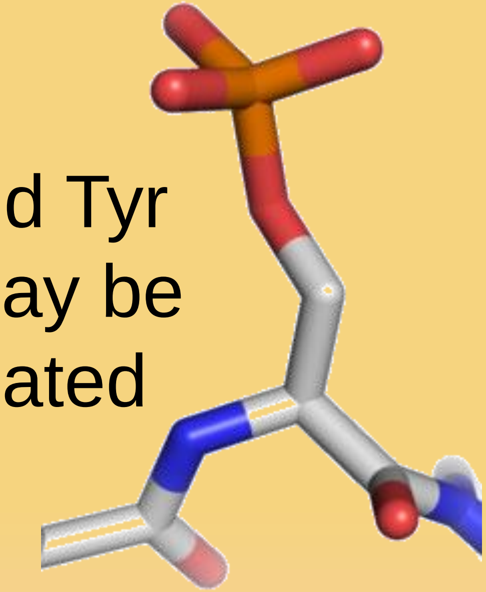
DNA and RNA





Phosphorylation of proteins





Ser, Thr and Tyr residues may be phosphorylated

Phosphate binding sites may include
His, Lys, Arg, Asp and Glu

Detection of phosphate anion

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 =$$

$$(NH_4)_3(H_3O)_4[P(Mo_2O_7)_6]\downarrow + 21NH_4NO_3 + 6H_2O$$

Phosphomolybdate of ammonium (yellow)

$$Na_3PO_4 + 3AgNO_3 \rightarrow Ag_3PO_4\downarrow + 3NaNO_3$$

Chemical properties of arsenic, antimony and bismuth containing compounds

- **As, Sb, and Bi** make the most stable bonds with oxygen and sulfur, unlike nitrogen that prefers carbon and hydrogen, and phosphorus that makes bonds mostly with oxygen.

- **As, Sb, and Bi** exist in form of sulfides in nature: **As_2S_3, Sb_2S_3, Bi_2S_3.**

Arsine AsH_3, Stibine SbH_3

These compounds are strong reducers:

$$AsH_3 + 6AgNO_3 + 3H_2O \rightarrow 6Ag\downarrow + As(OH)_3 + 6HNO_3$$

$2AsH_3 \rightarrow 2As + 3H_2$ arsine decomposes at room t°

$$2AsH_3 + 3O_2 \rightarrow As_2O_3 + 3H_2O \quad (t=200\ °C)$$

$$AsH_3 + 3Cl_2 \rightarrow AsCl_3 + 3HCl\ (t= -196\ °C)$$

With bromine and iodine arsine reacts in a similar way.

$$2AsH_3 + 3S \rightarrow 3H_2S + 2As$$

Marsh’s method for arsenic detection:

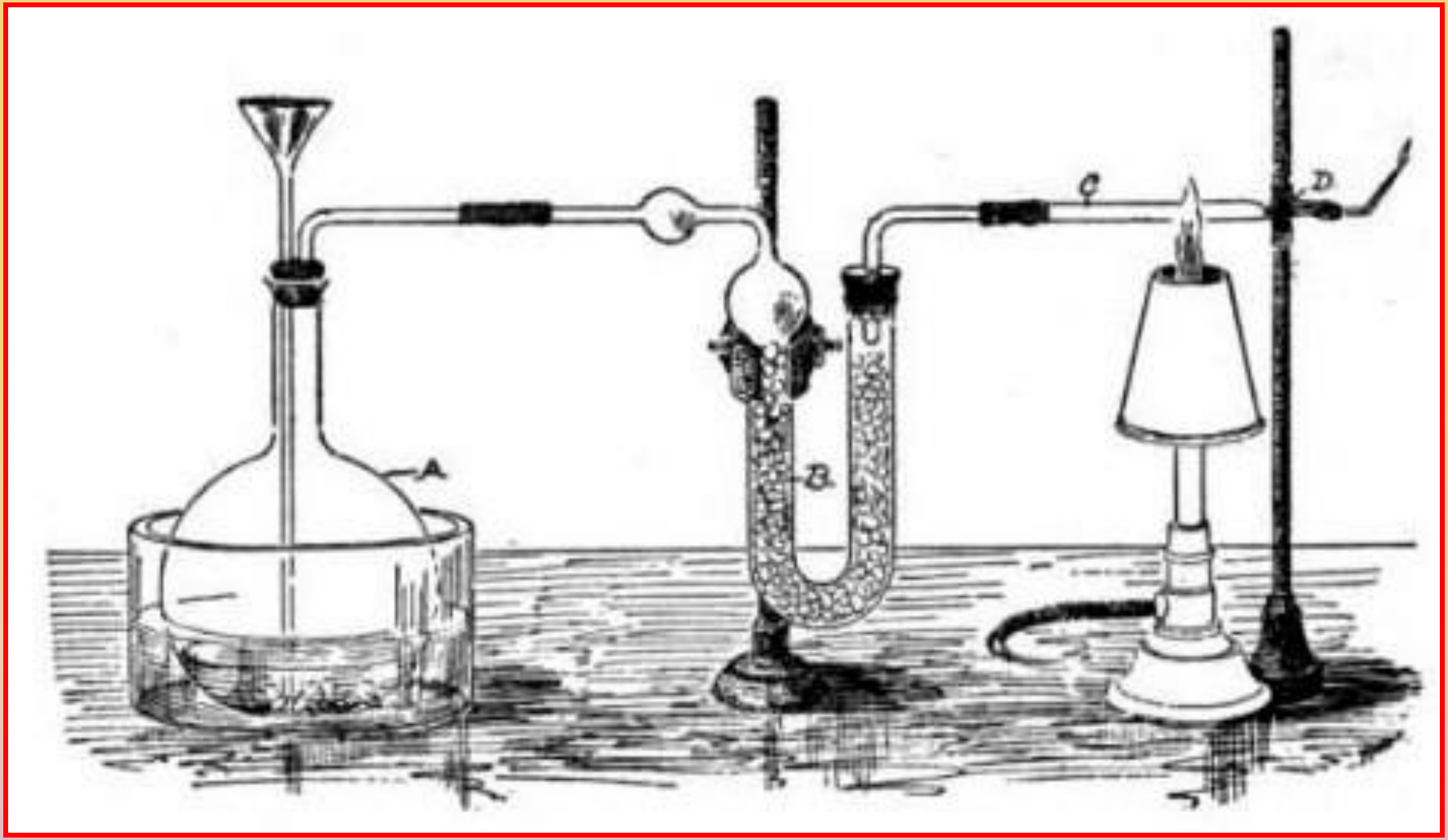
$$\overset{+3}{As}_2O_3 + 6Zn + 12HCl \rightarrow 2\overset{-3}{As}H_3 + 6ZnCl_2 + 3H_2O$$

The mixture of gases is passed through the hot quartz tube. Arsine decomposes and arsenic forms black shining “arsenic mirror” on the walls of that tube:

$$2AsH_3 = 2As^{\circ} + 3H_2$$

Using this method one can detect about **7^{-10}** mg of arsenic in a sample.

Marsh’s method for arsenic detection



Compounds of arsenic, antimony, and bithmuth in positive oxidation states .

Oxidation state of +3 : halides,
oxides,
sulfides and thiosulfides

Reactions of halides with water:

$$NCl_3 + 3H_2O \rightarrow \overset{-3}{N}H_3 + 3H\overset{+1}{Cl}O$$

$$PCl_3 + 3H_2O \rightarrow H_3\overset{+3}{P}O_3 + 3H\overset{-1}{Cl}$$

$$AsCl_3 + 2H_2O \leftrightarrow HAsO_2 + 3HCl$$

$$BiCl_3 + H_2O \leftrightarrow BiOCl + 2HCl$$

Sulfides, thiosulfides

As_2S_3 As_2S_5 Sb_2S_3 , Sb_2S_5 Bi_2S_3 Bi_2S_5.

Sulfides are produced by the way of melting:

$$2As + 3S \rightarrow As_2S_3$$

$$2As + 5S \rightarrow As_2S_5$$

Both sulfides can react with S^{-2} and form **thiosulfides.**

$As_2S_5 + 3\ Na_2S \rightarrow 2Na_3AsS_4$ sodium thioarsenate

$As_2S_3 + 3\ Na_2S \rightarrow 2Na_3AsS_3$ sodium thioarsenite

$Bi_2S_3 + 3\ Na_2S \rightarrow 2Na_3BiS_3$

Arsenic (III) oxide **As_2O_3** — has amphoteric properties, but it is mostly acidic.

$$\mathbf{As_2O_3\ (solid) + 3H_2O\ (liquid) \rightarrow 2H_3AsO_3\ (aq)\ or\ As(OH)_3}$$

Arsenic (III) hydroxide — is amphoteric, but, again, mostly acidic. **$As(OH)_3$** is known to exist in water solutions only where it is better described by **H_3AsO_3** formula (orthoarsenous acid). That acid is in the equilibrium with metaarsenous acid **$HAsO_2$**:

$$\mathbf{H_3AsO_3 \leftrightarrow HAsO_2 + H_2O}$$

Salts of those acids are known as orthoarsenites and metaarsenites.

$$\mathbf{As_2O_3 + 6KOH \rightarrow 2K_3AsO_3 + 3H_2O}$$

Arsenic (V) oxide:

$$\mathbf{As_2O_5 + 3H_2O \rightarrow 2H_3AsO_4}$$

(orthoarsenic acid is weaker than orthophosphoric).

Arsenates are produced in reactions between arsenic (V) oxide and alkalis

$$\mathbf{As_2O_5 + 6KOH \rightarrow 2K_3AsO_4 + 3H_2O}$$

Compounds of arsenic (V) and, especially, arsenic (III) are toxic. The mechanism of their toxicity is explained by the ability of arsenic to block -SH groups of ensymes and other biologically active molecules. Arsenic is also able to replace iodine, selenium and phosphorus.

Lethal dosage of arsenic is about **0.1 – 0.3 g.**

However, **As_2O_3** is used in the treatment of some dermatological diseases.

- In dentistry **As_2O_3** is used to necrotize soft tissues of a tooth.

- Arsenic-containing compounds (As_2O_3 and K_3AsO_3) were used to treat anemia and neurosis in XIX century (0.001 g in one dose).

- Human body can tolerate low doses of **As_2O_3**, and after the long time intake it can become resistant to higher doses of this compound.

Antimony (III) oxide **Sb_2O_3** is insoluble in water. It is amphoteric.

$$Sb_2O_3 + 3H_2SO_4 \rightarrow Sb_2(SO_4)_3 + 3H_2O$$
$$Sb_2O_3 + 2KOH + 3H_2O \rightarrow 2K[Sb(OH)_4]$$

Hydrolysis of antimony (III) compounds produces instable **$Sb(OH)_2^+$ cation,** that losed a water molecule and becomes stibyl (antimonyl) **SbO^+ cation**:

$$Sb^{3+} + 2H_2O \leftrightarrow Sb(OH)_2^+ + 2H^+$$
$$Sb(OH)_2^+ \rightarrow SbO^+ + H_2O$$

$$Sb_2O_3 \cdot nH_2O$$

Bismuth (III) oxide **Bi_2O_3** is insoluble in water. **Bi_2O_3** demonstrates mostly basic properties. **$Bi(OH)_3$** is a weak base.

Salts of bismuth (III) are hydrolyzed in water solutions and form bismuthyl cations **BiO^+:**

$$\mathbf{Bi^{3+} + H_2O \leftrightarrow BiO^+ + 2H^+}$$

Bi_2O_3 is a part of xeroform, that is an antiseptic for skin..

Bismuth nitrate and the products of its hydrolysis are used as one of the components for *Helicobacter pylori* eradication from stomach.

$Bi(NO_3)_3$: $Bi(OH)_2NO_3$, $BiONO_3$ and **BiOOH**.

Thank you for listening!