Group 15, 5A

- Valence-shell configuration: $ns^2\ np^3$
- Exhibits varied chemical properties.
  1. N and P are nonmetals;
  2. As and Sb are metalloids;
  3. Bi is a metal (the heaviest non-radioactive element)

Elements recognized as metalloids V·T·E

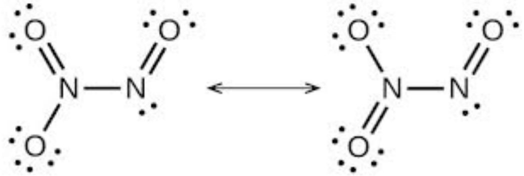
	13	14	15	16	17
2	B Boron	C Carbon	N Nitrogen	O Oxygen	F Fluorine
3	Al Aluminium	Si Silicon	P Phosphorus	S Sulfur	Cl Chlorine
4	Ga Gallium	Ge Germanium	As Arsenic	Se Selenium	Br Bromine
5	In Indium	Sn Tin	Sb Antimony	Te Tellurium	I Iodine
6	Tl Thallium	Pb Lead	Bi Bismuth	Po Polonium	At Astatine

Some Physical Properties, Sources, and Methods of Preparation

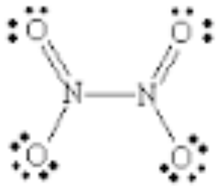
Table 20.13 ▶ Selected Physical Properties, Sources, and Methods of Preparation of the Group 5A Elements

Element	Electronegativity	Source	Method of Preparation
Nitrogen	3.0	Air	Liquefaction of air
Phosphorus	2.2	Phosphate rock $[Ca_3(PO_4)_2]$, fluorapatite $[Ca_5(PO_4)_3F]$	$2Ca_3(PO_4)_2 + 6SiO_2 \longrightarrow 6CaSiO_3 + P_4O_{10}$ $P_4O_{10} + 10C \longrightarrow 4P + 10CO$
Arsenic	2.2	Arsenopyrite (Fe_3As_2, FeS)	Heating arsenopyrite in the absence of air
Antimony	2.1	Stibnite (Sb_2S_3)	Roasting Sb_2S_3 in air to form Sb_2O_3 and then reduction with carbon
Bismuth	2.0	Bismite (Bi_2O_3), bismuth glance (Bi_2S_3)	Roasting Bi_2S_3 in air to form Bi_2O_3 and then reduction with carbon

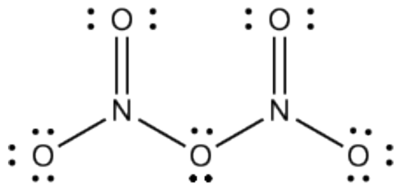
Oxides of Group 5A Elements

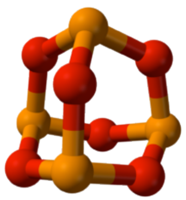


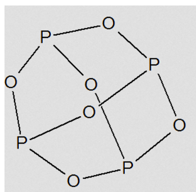
- Nitrogen: N_2O, NO, N_2O_3, NO_2, N_2O_4, N_2O_5;
- Phosphorus: P_4O_6 & P_4O_{10};
- Arsenic: As_2O_3 (As_4O_6) & As_2O_5;
- Antimony: Sb_2O_3 & Sb_2O_5
- Bismuth: Bi_2O_3 & Bi_2O_5

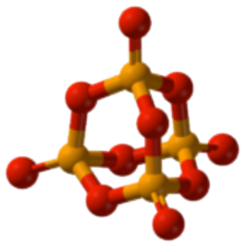


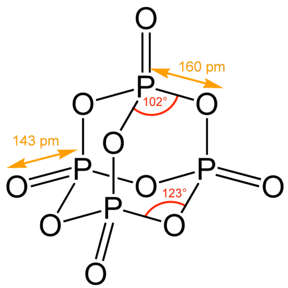
Dinitrogen tetroxide, N_2O_4











phosphorus in orange, oxygen in red

Chlorides of Group 5A Elements

- Nitrogen: only NCl_3;
- Phosphorus: PCl_3 and PCl_5;
- Arsenic: $AsCl_3$ and $AsCl_5$;
- Antimony: $SbCl_3$ and $SbCl_5$;
- Bismuth: $BiCl_3$
- All are molecular compounds.

Reactions of Oxides and Chlorides

- $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$;
- $N_2O_5(g) + H_2O(l) \rightarrow 2HNO_3(aq)$
- $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$;
- $As_2O_5(s) + 3H_2O(l) \rightarrow 2H_3AsO_4(aq)$;

- $PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$;
- $AsCl_5(s) + 4H_2O(l) \rightarrow H_3AsO_4(aq) + 5HCl(aq)$;
- $2SbCl_5(s) + 5H_2O(l) \rightarrow Sb_2O_5(s) + 10HCl(aq)$;

The Chemistry of Nitrogen

- The triple bonds (N≡N) in N_2 provide high stability to the molecule;
- Oxidation states from -3 to 5
- NH_2OH (-1), N_2H_4 (-2), and NH_3 (-3)
- Many reactions involving nitrogen gas are endothermic and compounds containing nitrogen decompose exothermically to the elements.

- $N_{2}(g) + O_{2}(g) \rightarrow 2NO(g)$ $\Delta H° = 180$ kJ
- $2NO_{2}(g) \rightarrow N_{2}(g) + O_{2}(g)$; $\Delta H° = -68$ kJ

$N_2H_4(g) \rightarrow N_2(g) + 2H_2(g)$; $\Delta H° = -95$ kJ

Nitrogen Fixation

- The process of transforming N_2 to other nitrogen–containing compounds.
- Atmospheric fixation (occurs naturally during thunderstorm):
- $N_{2}(g) + O_{2}(g) \rightarrow 2NO(g)$; $\Delta H^{o} = 180$ kJ
- $2NO(g) + O_{2}(g) \rightarrow 2NO_{2}(g)$; $\Delta H^{o} = -112$ kJ
- $3NO_{2}(g) + H_{2}O(l) \rightarrow 2HNO_{3}(aq) + NO(g)$;

  $\Delta H^{o} = -140$ kJ

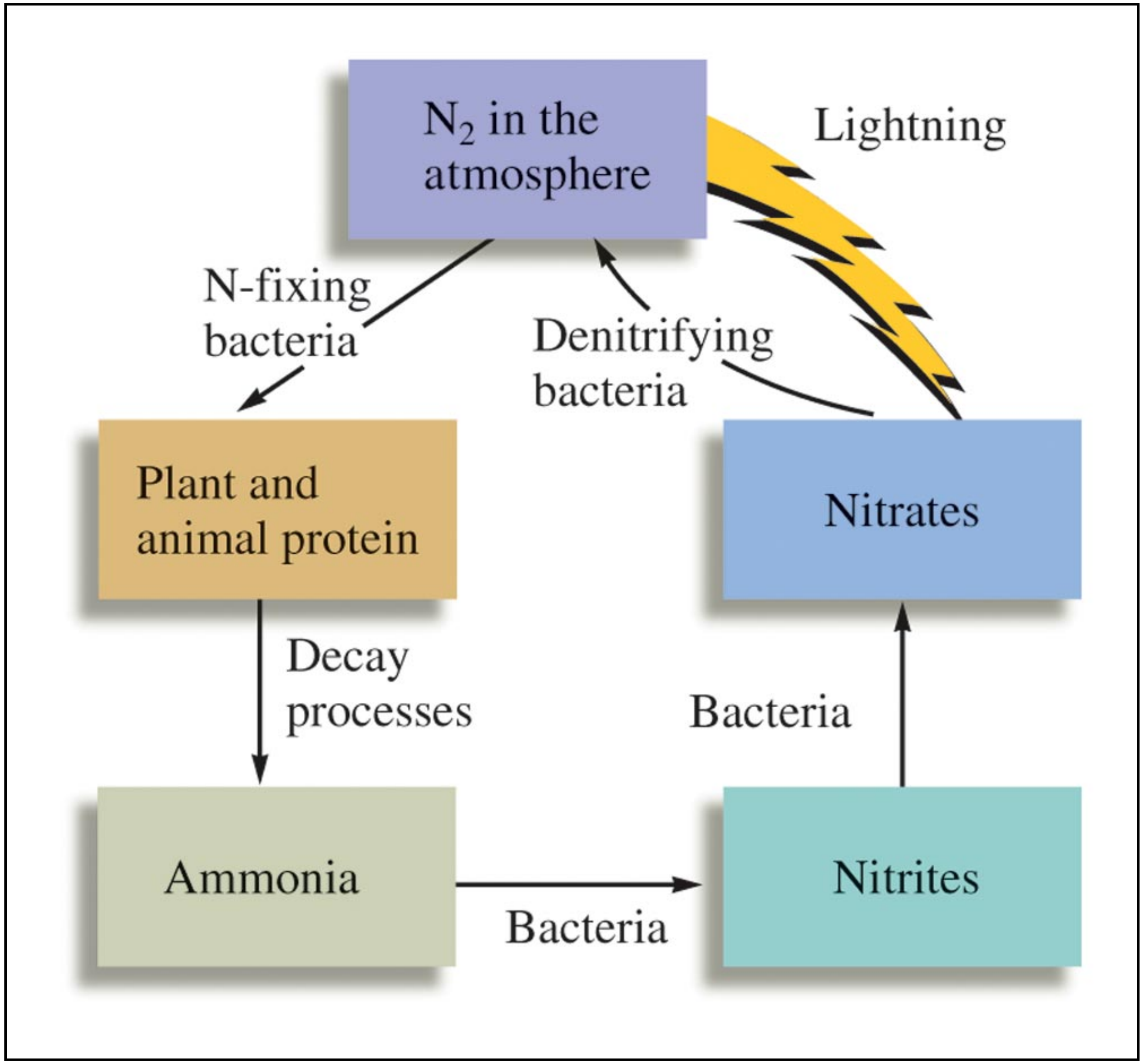
Biological Nitrogen Fixation

- Fixation of atmospheric N_2 by bacteria living in soils and water; some live in root nodules;
- Plants such as legumes and alfalfa have root nodules that contain nitrogen-fixing bacteria – they benefit directly from these bacteria;
- Other plants benefit when the bacteria die and release absorbable forms of nitrogen (NH_3, NH_4^+, and NO_3^-) to the soils;

Biological Nitrogen Fixation

- In nitrogen-fixing bacteria
  1. Atmospheric N_2 is first reduced to NH_3;
  2. In bacterial cells, NH_3 becomes NH_4^+, oxidized to NO_2^- and then to NO_3^-;
  3. NH_3, NH_4^+, and NO_3^- can be released into the surroundings (water or soils) and become available to plants;
- Denitrifying bacteria (in soils) change NO_3^- back to NO_2^-, NH_3, and finally to N_2 to complete the biological nitrogen cycle.

Biological Fixation and The Nitrogen Cycle



Industrial Nitrogen Fixation

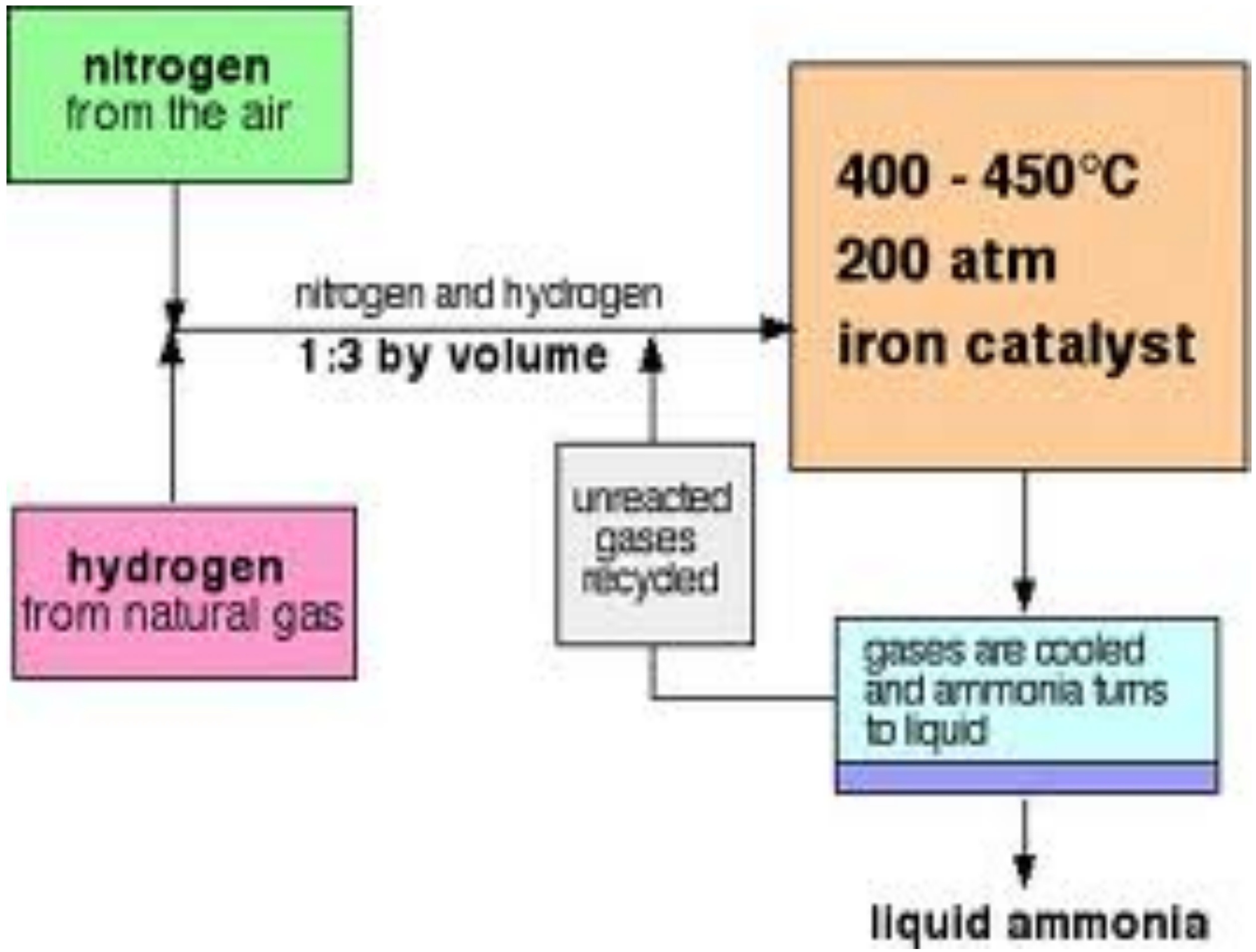
- Industrial Fixation (the Haber Process):

  $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$ $\Delta H^\circ = -92$ kJ

- Most NH_3 are converted to:

1. Fertilizers (~70%)
2. Nitric acid, HNO_3 (~20%)
3. Hydrazine, N_2H_4, and monomers for various plastics and nylons.

The Haber Process

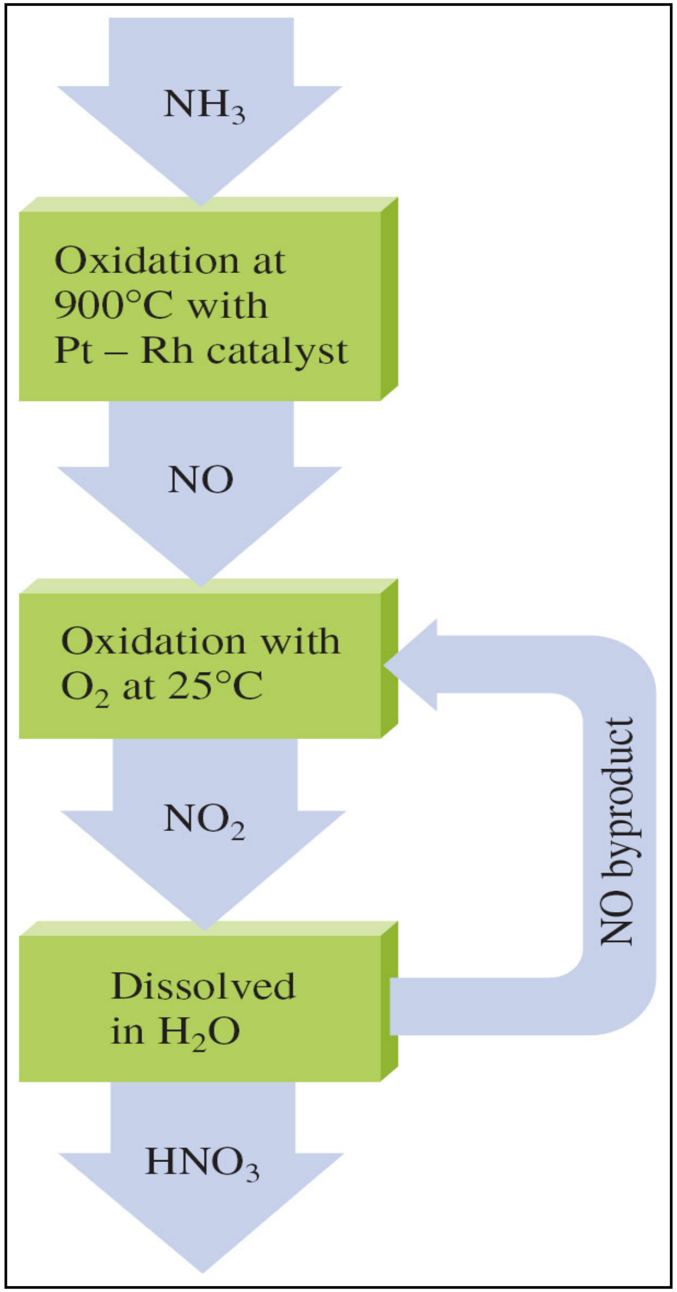


Important Hydrides of Nitrogen

- Ammonia, NH_3 (most important hydride)
  - Production of fertilizers (NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_3PO_4$, and $CO(NH_2)_2$), HNO_3, and N_2H_4
- Hydrazine, N_2H_4
  - Rocket propellant, manufacture of plastics, agricultural pesticides;
- Monomethylhydrazine, $CH_3N_2H_3$
  - Rocket fuels

Production of HNO_3 Oswald Process:

1. $NH_3(g) + O_2(g) \rightarrow NO(g) + H_2O(g)$
2. $2NO(g) + O_2(g) \rightarrow NO_2(g)$
3. $3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$



- HNO_3 - a strong acid and an oxidizing agent;
- Reactions with metals **does not produce H_2**

$Cu(s) + 4HNO_3(16\ M) \rightarrow$
$Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$

$3Cu(s) + 8HNO_3(aq, 6\ M) \rightarrow$
$3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$

$4Zn(s) + 10HNO_3(aq, 3\ M) \rightarrow$
$4Zn(NO_3)_2(aq) + N_2O(g) + 2H_2O(l)$

$$4HNO_3(l) \xrightarrow{hv} 4NO_2(g) + 2H_2O(l) + O_2(g)$$

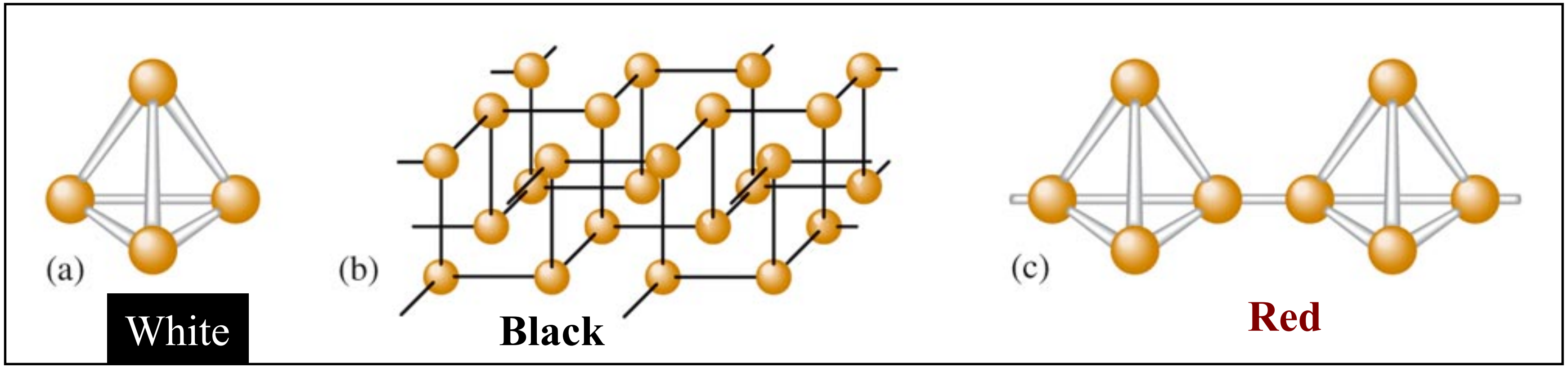
Allotropes of Phosphorus

- White Phosphorus: P_4 (tetrahedral) - very reactive
- Black Phosphorus: crystalline structure - much less reactive
- Red Phosphorus: amorphous with P_4 chains

$$P_{(white)} \xrightarrow{\text{heat, 1 atm, no air}} P_{(red)}$$

$$P_{(white)} \text{ or } P_{(red)} \xrightarrow{\text{high pressure}} P_{(black)}$$

Allotropes of Phosphorus



very reactive

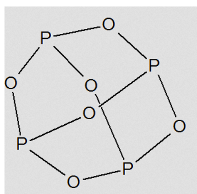
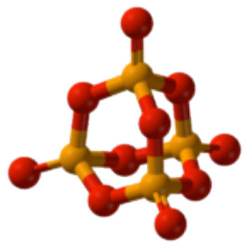
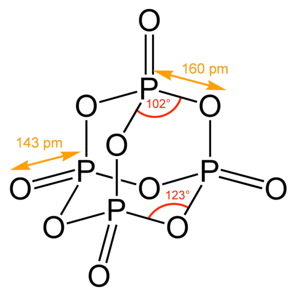
$$P_{(white)} \rightarrow (heat, 1 atm, no air) \rightarrow P_{(black)}$$

$$P_{(white)} \text{ or } P_{(red)} \rightarrow (high pressure) \rightarrow P_{(black)}$$

Oxides of Phosphorus

- Reaction of white phosphorus with oxygen:
  1. $P_4(s) + 3O_2(g) \rightarrow P_4O_6(l)$; (o.s. of P = +3)
  2. $P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$; (o.s. of P = +5)

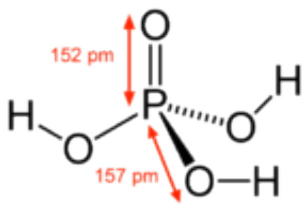
- Reactions of phosphorus oxides with water:
  1. $P_4O_6(l) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$;
  2. $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$;

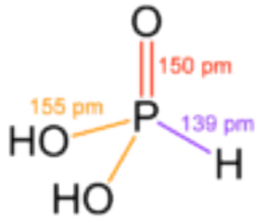





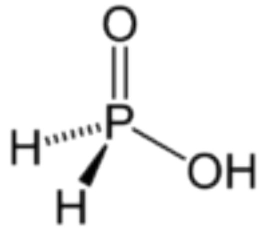
phosphorus in orange, oxygen in red

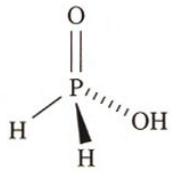
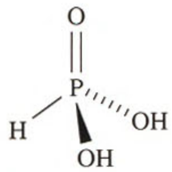
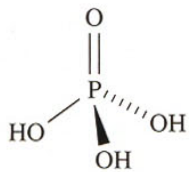
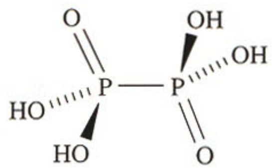
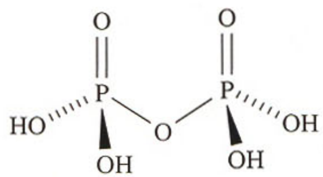
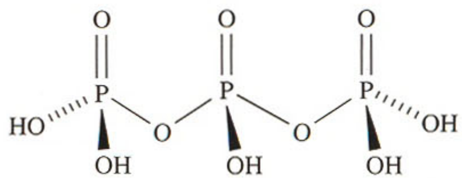
Oxyacids of Phosphorus

- Phosphoric acid, H_3PO_4 - triprotic
- Phosphorous acid, H_3PO_3 - diprotic
- Hypophosphorous acid, H_3PO_2 - monoprotic

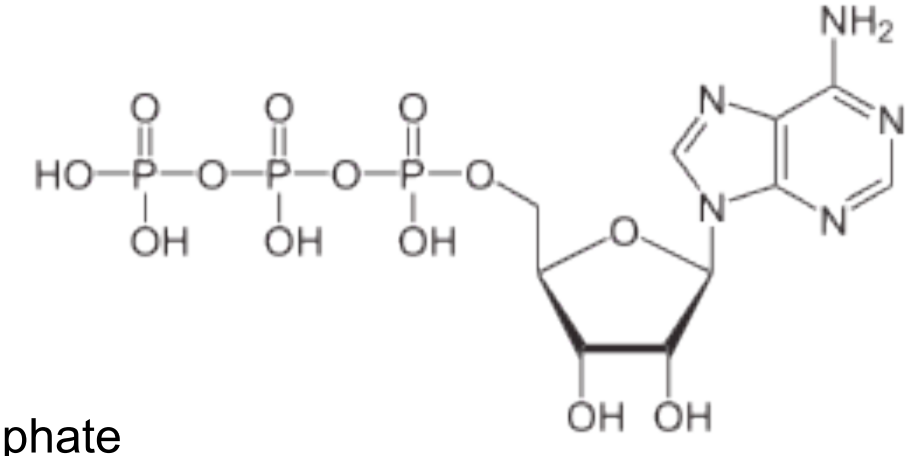






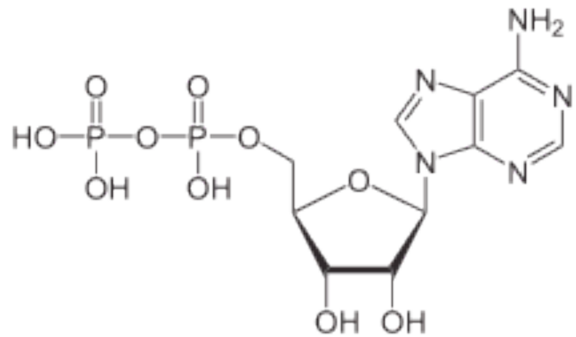
H_3PO_2	Phosphinic acid (hypophosphorous acid)		$pK_a = 1.24$
H_3PO_3	Phosphonic acid (phosphorous acid)		$pK_a(1) = 2.00$; $pK_a(2) = 6.59$
H_3PO_4	Phosphoric acid (orthophosphoric acid)		$pK_a(1) = 2.21$; $pK_a(2) = 7.21$; $pK_a(3) = 12.67$
$H_4P_2O_6$	Hypophosphoric acid		$pK_a(1) = 2.2$; $pK_a(2) = 2.8$; $pK_a(3) = 7.3$; $pK_a(4) = 10.0$
$H_4P_2O_7$	Diphosphoric acid (pyrophosphoric acid)		$pK_a(1) = 0.85$; $pK_a(2) = 1.49$; $pK_a(3) = 5.77$; $pK_a(4) = 8.22$
$H_5P_3O_{10}$	Triphosphoric acid		$pK_a(1) \leq 0$; $pK_a(2) = 0.89$; $pK_a(3) = 4.09$; $pK_a(4) = 6.98$; $pK_a(5) = 9.93$

ATP



Adenosine triphosphate

ADP Adenosine diphosphate



Phosphorus Halides

- Reactions of white phosphorus with halogens:

1. $P_{4(s)} + 6X_2 \rightarrow 4PX_{3(l)}$;
2. $P_{4(s)} + 10X_2 \rightarrow 4PX_{5(s)}$;

- Examples of reactions:

$$PCl_{3(l)} + Cl_{2(g)} \rightleftarrows PCl_{5(s)}$$

$$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$$

$$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$$

Important Compounds of Phosphorus

- $Ca_3(PO_4)_2$ & $Ca_5(PO_4)_3F$: source of phosphorus
- $Ca_5(PO_4)_3(OH)$: forms bones and teeth
- P_4O_{10} : formation of H_3PO_4
- H_3PO_4 : production of fertilizers & phosphates
- $H_2PO_4^-$ & HPO_4^{2-} : phosphate buffers
- Na_3PO_4 : scouring powder and paint remover
- $Na_5P_3O_{10}$: fabric softeners
- ADP & ATP : storage of metabolic energy
- PCl_5 : precursor for lithium hexafluorophosphate ($LiPF_6$), an electrolyte in lithium ion batteries;

Group 16, 6A

- Valence-shell configuration: $ns^2\ np^4$
- O, S, Se, Te, Po
- None of the Group 6A elements behaves as a typical metal.
- Elements form covalent bonds with other nonmetals.

Some Physical Properties

Table 15.1 Selected properties of the elements

	O	S	Se	Te	Po
Covalent radius/pm	74	104	117	137	140
Ionic radius/pm	140	184	198	221	
First ionization energy/(kJ mol^{-1})	1310	1000	941	870	812
Melting point/°C	−218	113 (α)	217	450	254
Boiling point/°C	−183	445	685	990	960
Pauling elecronegativity	3.5	2.5	2.4	2.1	2.0
Electron affinity*/(kJ mol^{-1})	141	200	195	190	183
	−844	−532			

* The first value is for $X(g) + e^-(g) \rightarrow X^-(g)$, the second value is for $X^-(g) + e^-(g) \rightarrow X^{2-}(g)$.

Table 15.3 Selected properties of the Group 16 hydrides

Property	H_2O	H_2S	H_2Se	H_2Te	H_2Po
Melting point/°C	0.0	−85.6	−65.7	−51	−36
Boiling point/°C	100.0	−60.3	−41.3	−4	37
$\Delta_f H^\circ/(\text{kJ mol}^{-1})$	−285.9	+20.1	+73.0	+99.6	
Bond length/pm	96	134	146	169	
Bond angle/°	104.5	92.1	91	90	
Acidity constants					
pK_{a1}	15.74	6.89	3.89	2.64	
pK_{a2}		14.15	~11	10.80	

$$H_2(g) + X(s) \xrightarrow{\Delta T} H_2X(g) \qquad X = S, Se$$

$$FeX(s) + 2\,HCl(aq) \rightarrow H_2X(g) + FeCl_2(aq)$$

For S, Se, Te - similar gases with characteristic odor, poisonous

Hydrogenchalkogenides $(HS)^{-I}$ **and chalkogenides** S^{-II}

Soluble in water alikali metals, alkaline earth and NH_4^+

$$H_2S\ (g) + NaOH\ (aq) \rightarrow NaHS\ (aq) + H_2O\ (l)$$

$$NaHS(aq) + NaOH\ (aq) \rightarrow Na_2S\ (aq) + H_2O\ (l)$$

Heavy metal sulfides – non-soluble – precipitation from aqueous solutions

$$2\ Bi^{3+}\ (aq) + 3\ S^{2-}\ (aq) \rightleftarrows Bi_2S_3\ (s)$$

- Sulfur used for removing small amounts of elemental mercury

$$Hg(l) + S(s) \rightarrow HgS(s)$$

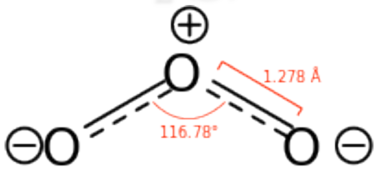
- Melting of sulfides with sulfur → **polysulfides**; e.g. Iron(II) disulfide FeS_2 (pyrite)

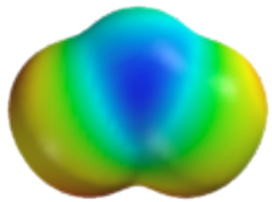
Oxygen

- O_2 makes up 21% of the Earth's atmosphere.
- O_3 (ozone) exists naturally in the upper atmosphere (the stratosphere) of the Earth.

Ozone – forming at electric discharges - pale blue gas

$$3O_2(g) \leftrightarrow 2O_3(g) \qquad K \cong 10^{-57}$$

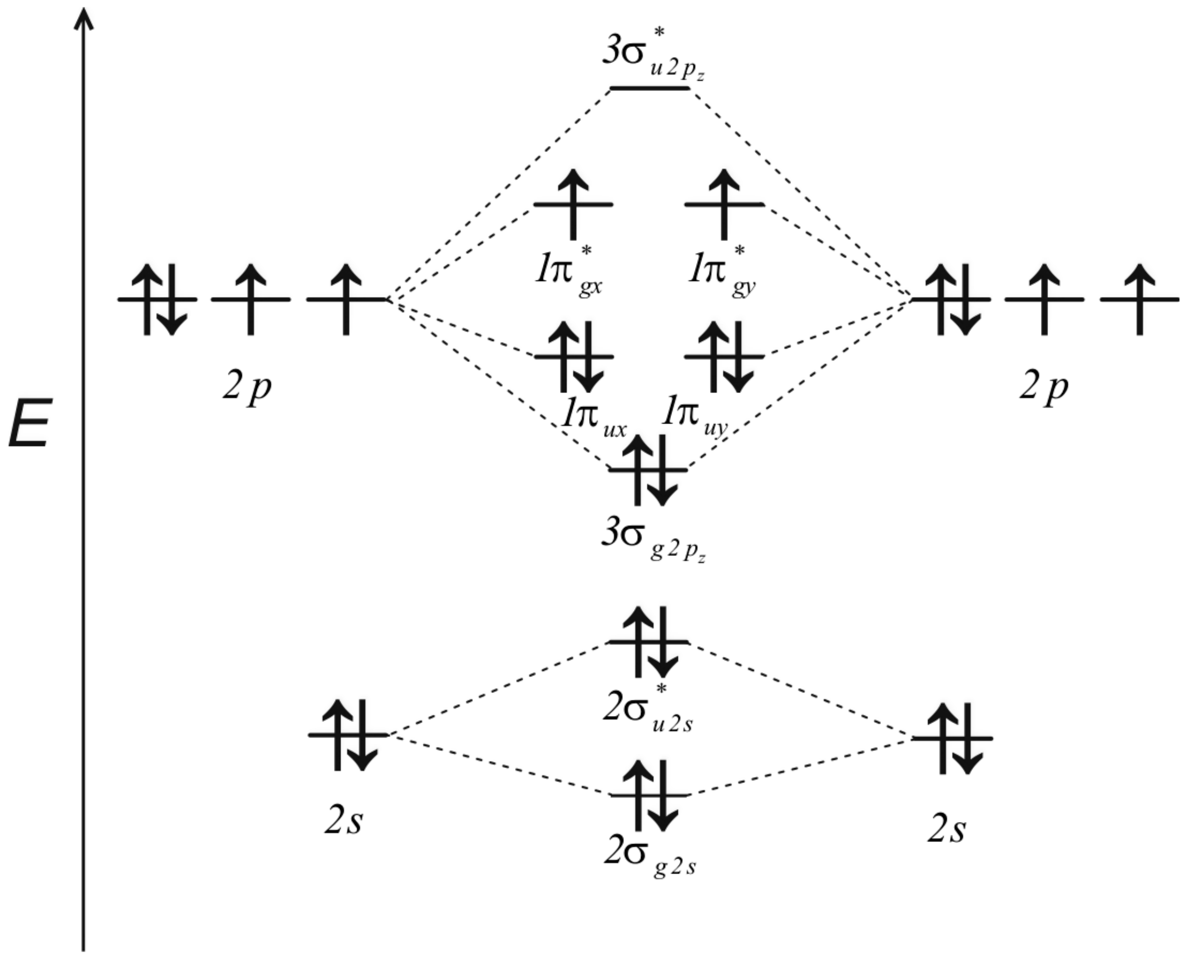




- Ozone layer absorbs UV light and acts as a screen to block most uv-radiation from reaching the Earth's surface.

$$2\,O_3\,(g) \xrightarrow{h\nu} 3\,O_2\,(g)$$

- We now know that Freons (CFCs = chloro-fluorocarbons) are promoting destruction of ozone layer.



Strong oxidizing agent

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l) \qquad E^o = 1{,}23\ \text{V}$$

$$O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(l) \qquad E^o = 0{,}40\ \text{V}$$

Various Forms of Oxides

- Metal oxides (ionic)
  1. Nonconductor – example: MgO
  2. Semiconductor – example: NiO
  3. Conductor – example: ReO_3
  4. Superconductor – example: $YBa_2Cu_3O_7$
- Nonmetal oxides (covalent):

  Molecular oxides – examples: CO_2, NO, NO_2, N_2O, SO_2, P_4O_{10}, etc.

  Covalent network oxide – SiO_2

Characteristics of Oxides

- Metallic oxides – basic or amphoteric

  Examples: Na_2O (basic); Al_2O_3 (amphoteric)
- Semi-metallic oxides – mild to weakly acidic

  Example: B_2O_3
- Nonmetallic oxides – weak to strong acids

  Examples:

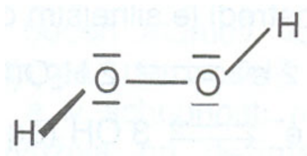
1. $SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3(aq)}$ (weak acid);
2. $SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$ (strong acid);

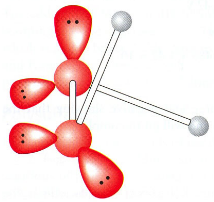
Redox properties of water

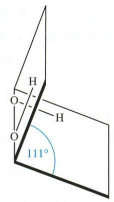
$$2\,Na(s) + 2\,H_2O(l) \rightarrow 2\,NaOH(aq) + H_2(g)$$

$$2\,F_2(g) + 2\,H_2O(l) \rightarrow 4\,HF(aq) + O_2(g)$$

Hydrogen peroxide







in solid

weak acid $$H_2O_2(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HO_2^-(aq)$$

$$pK_{a1} = 12$$

disproportionation

$$H_2O_2(aq) \rightarrow H_2O(l) + \tfrac{1}{2}O_2(g)$$

ΔHº of −98.2 kJ/mol; ΔS of 70.5 J/(mol·K)

Redox properties

$$2\,Ce^{3+}(aq) + H_2O_2(aq) + 2\,H^+(aq) \rightarrow 2\,Ce^{4+}(aq) + 2\,H_2O(l)$$ in acidic env.

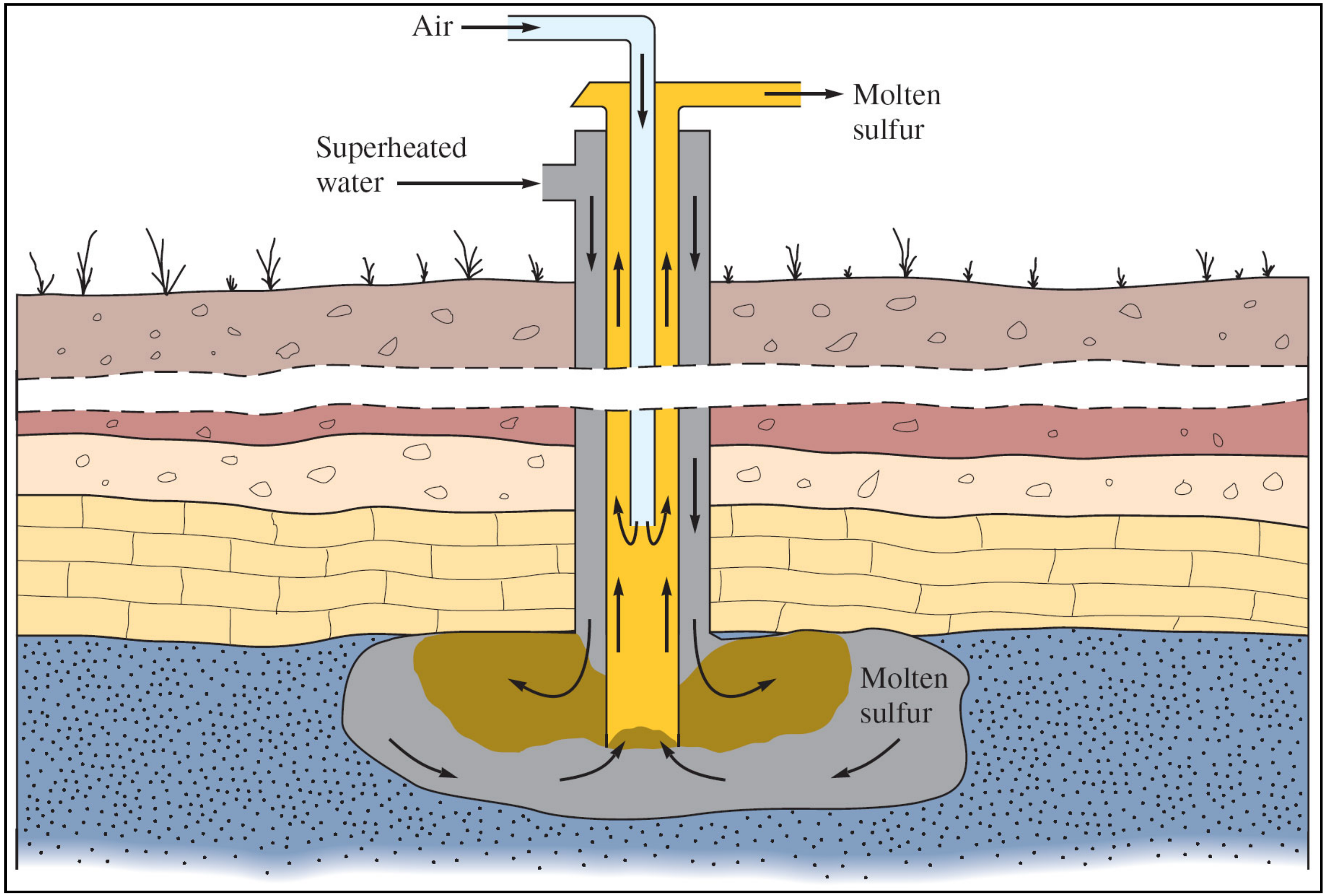
$$2\,Ce^{4+}(aq) + H_2O_2(aq) + 2\,OH^-(aq) \rightarrow 2\,Ce^{3+}(aq) + 2\,H_2O(l) + O_2(g)$$

in basic env.

Sulfur

- Sulfur is found in nature both in large deposits of the free element and in ores such as:
- Galena = PbS,
- Cinnabar = HgS,
- Pyrite = FeS_2,
- Gypsum = $CaSO_4 \cdot 2H_2O$,
- Epsomite = $MgSO_4.7H_2O$, and
- Glauberite = $Na_2Ca(SO_4)_2$

Sulfur Mining: Frasch Process



Aggregates of Sulfur

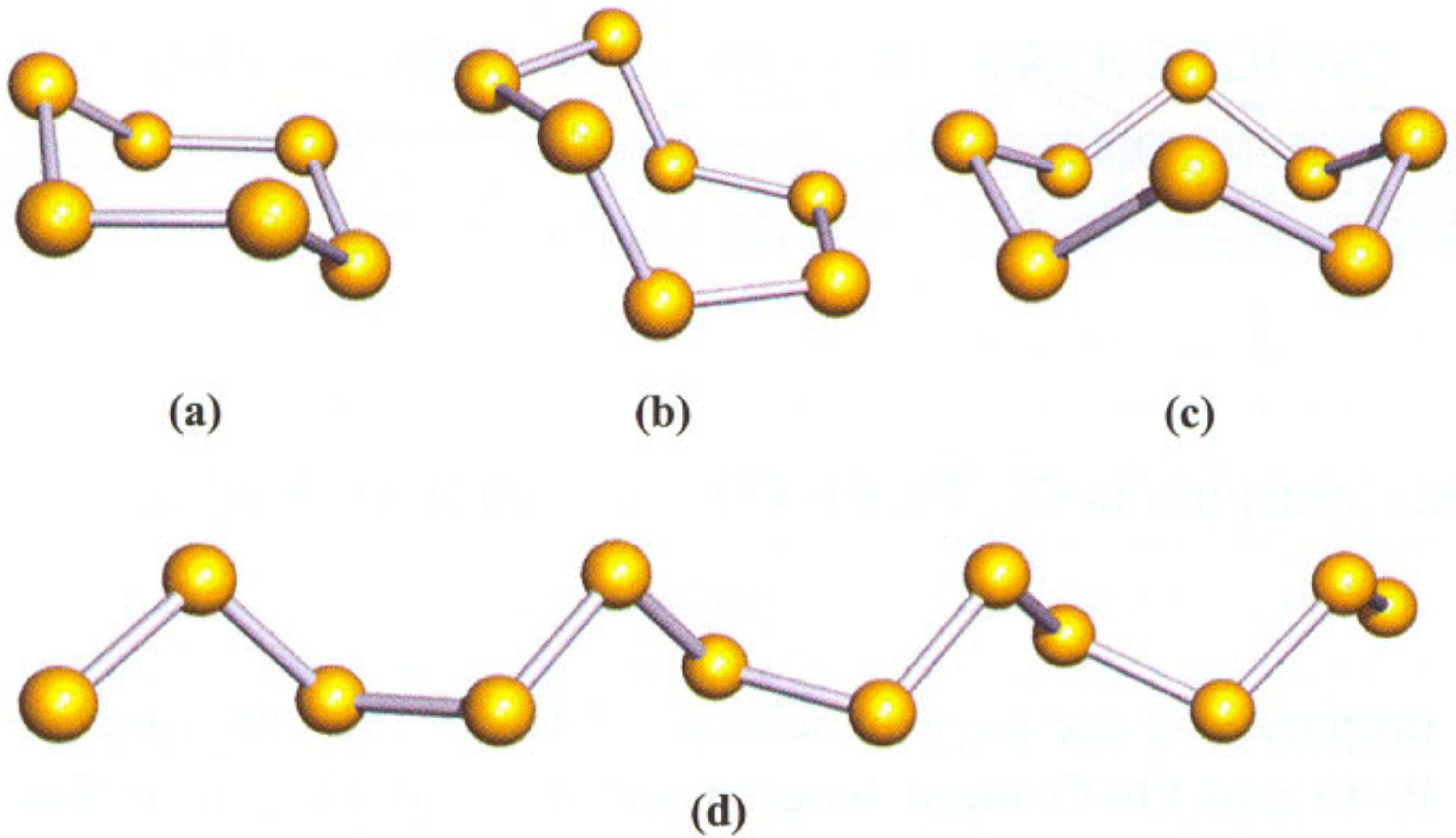


Fig. 15.6 Schematic representations of the structures of some allotropes of sulfur: (a) S_6, (b) S_7, (c) S_8 and (d) *catena*-S_∞ (the chain continues at each end).

Sulfur Oxides and Oxyacids

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$$

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

$$SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3(aq)}$$

$$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$$

- H_2SO_3 – diprotic; weak acid
- H_2SO_4 – diprotic; strong acid

Sulfuric Acid

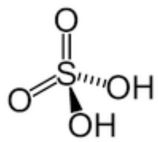
- Productions:

1. $S_{8(s)} + 8\ O_{2(g)} \rightarrow 8SO_{2(g)}$;
2. $2H_2S_{(g)} + 3\ O_{2(g)} \rightarrow 2SO_{2(g)} + 2H_2O_{(l)}$;
3. $FeS_{2(s)} + 11\ O_{2(g)} \rightarrow Fe_2O_{3(s)} + 8SO_{2(g)}$;

4. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$; ($V_2O_5/K_2O$ catalyst)
5. $2SO_{3(g)} + H_2SO_{4(l)} \rightarrow H_2S_2O_{7(l)}$;
6. $H_2S_2O_{7(l)} + H_2O_{(l)} \rightarrow 2H_2SO_{4(l)}$;

Oxyacids of sulfur

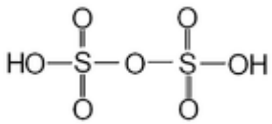
Sulfuric acid



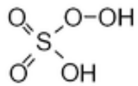
Polysulfuric acids

$H_2SO_4.nSO_3$

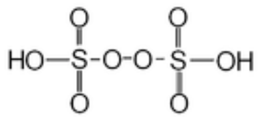
di-



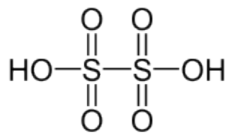
Peroxymonosulfuric acid



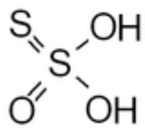
Peroxydisulfuric acid



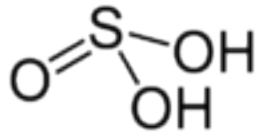
Dithionic acid



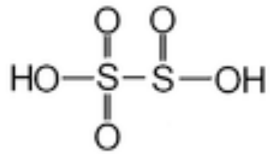
Thiosulfuric acid



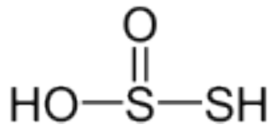
Sulfurous acid



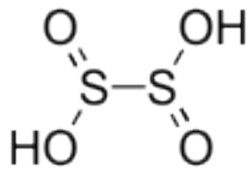
Disulfurous acid



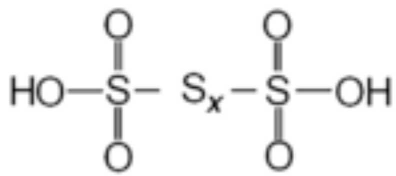
Thiosulfurous acid



Dithionous acid



Polythionic acids



Important Compounds of Sulfur

- H_2SO_4 – most important compound, for manufacture of fertilizer, soap, detergents, metal and textile processing, sugar refinery, and organic syntheses;
- SF_4 – for fluoridation
- SF_6 – as insulating and inert blanket
- $Na_2S_2O_3$ – as reducing agent and complexing agent for Ag^+ in photography (called "hypo");
- P_4S_3 – in "strike-anywhere" match heads

Exercise #8

- Draw Lewis structures for the following molecules:
  1. SO_2
  2. SF_2
  3. SF_4
  4. SF_6
  5. H_2SO_4
  6. H_2SO_3
  7. $H_2S_2O_7$