

	15
7	N
	14,0067
15	P
	30,9738
23	As
	74,922
51	Sb
	121,75
53	Bi
	208,96

# The Pnictogens

The chemistry of Group 15

# Occurrence and isolation

15	N	14,0067
7	P	30,9738
33	As	74,922
51	Sb	121,75
55	Bi	208,96

*Atmosphere (predominately as N<sub>2</sub>, ~78%), as nitrate in minerals (NO<sub>3</sub><sup>-</sup>); fractional distillation of liquid air*

**Phosphorus** (*lat.*) – bringer of light, 1120 ppm, as phosphate mineral

**Arsenikon** (*gr.*) = mineral auripgment; *in sulfides, sulfosalts and arsenates*; 1.8 ppm

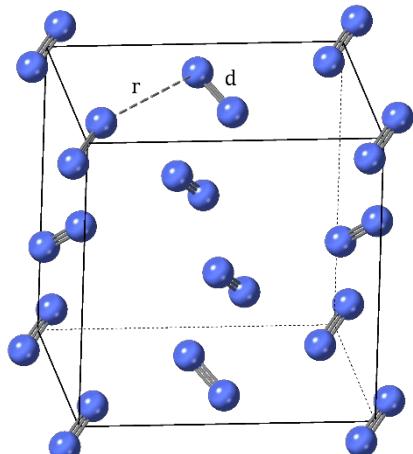
**Stibium** (*lat.*); *anit+monos* (*gr.*) not alone; 0.2 ppm;; *in sulfides and oxides*

**Bisemutum** (*ger. name*); 0.008 ppm; *in sulfides*

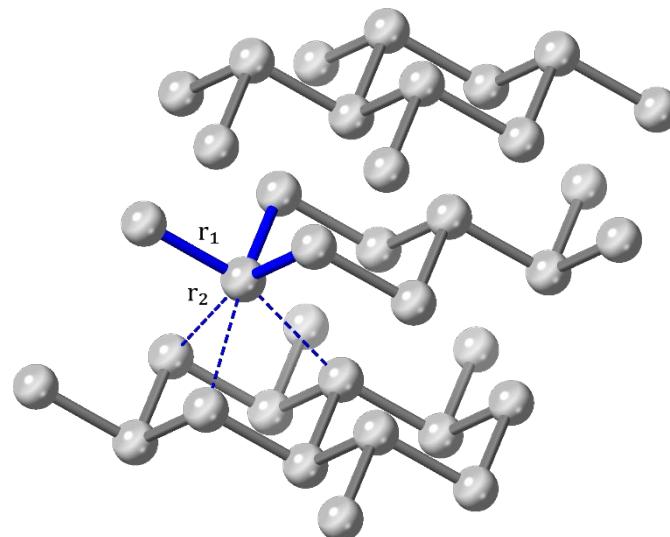
Data from J. Emsley 'The Elements' Oxford: Claredon Press, 1989

# Structural characteristics of elements

$\text{N}_2$  at 20 K ( $-253.15^\circ\text{C}$ )



$d = 109.8 \text{ pm} \& r = 306.4 \text{ pm}$

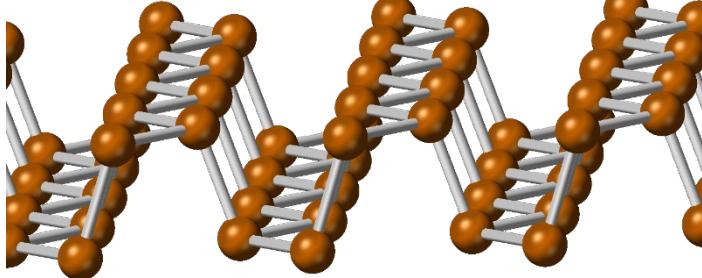
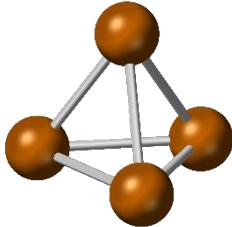


Arsenic, Sb and Bi  
(most stable allotrope)

	$r_1$	$r_2$	$r_2/r_1$
As	251.7	312.0	1.240
Sb	290.8	335.5	1.153
Bi	307.2	352.9	1.149

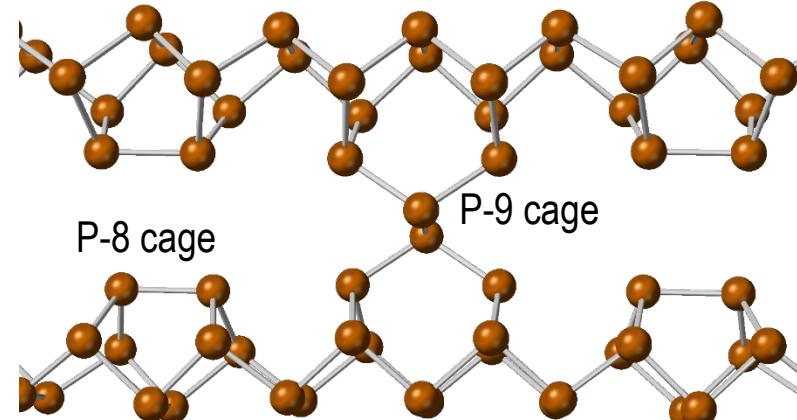
(all distances in pm)

Phosphorus (most important allotropes)



$\text{P}_4$

Black phosphorus ( $\text{P}_\infty$ )



Violet (Hittorf's) P ( $\text{P}_\infty$ )

# Structural characteristics of elements

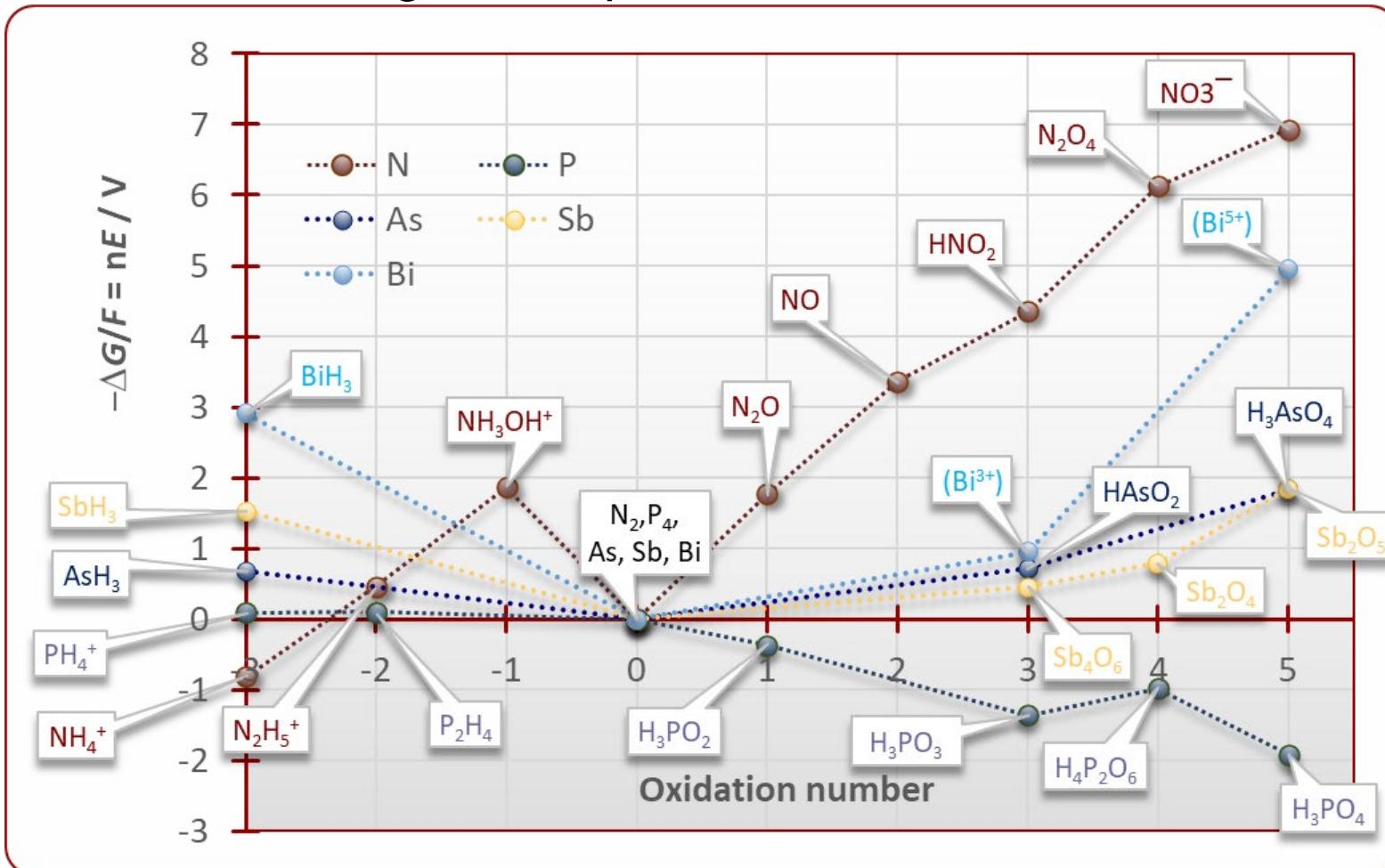
- Nitrogen comes as  $N_2$  (dinitrogen), and retains this molecular structure even in solid state at  $-210^{\circ}C$  (68K)
- Phosphorus:
  - Unlike  $N_2$ , exists as gaseous  $P_2$  only above  $800^{\circ}C$  ( $P-P = 189$  pm),
  - Most important allotropes are white (tetrahedral  $P_4$ , very reactive), red (amorphous solid, less reactive) and black (crystalline the least reactive allotrope) phosphorus.
  - There are other allotropes as well
- Arsenic, antimony and bismuth also have several allotropes, most stable is the layered structure (similar to black P)
  - Tetrahedral  $As_4$  has been detected at high temperatures; Sb and Bi do not form  $Sb_4/Bi_4$

# Nitrogen vs. other elements

- N≡N triple bond makes dinitrogen molecule unreactive (kinetic effect, bond dissociation energy of N<sub>2</sub> is a whopping 946 kJ/mol!)
- Nitrogen has a high electronegativity (3.0) and in many compounds N has a negative oxidation number (see the minimum in the Frost diagram at NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>)
- Its atom has small radius and thus cannot form bonds with more than 4 other atoms/ions (steric problems – there is no room around small N atom to fit more than 4 other atoms/ions)
  - But it can N–E multiple bonds easily exactly *because* of the small size.
  - A role plays the fact that N does not have easily accessible *d* orbitals from the same principal shell.
- Heavier elements are composed of bigger atoms and expanded octets are frequent.

# Chemical properties

- The Frost diagram for pH=0



- Going down the group the number of accessible oxidation numbers drops significantly
- Generally, odd oxidation numbers are more stable than even

# E-E and other bonds

- Selected bond dissociation energies (*BDE*) in kJ/mol:

Nitrogen		Phosphorus		Arsenic		Antimony		Bismuth	
N–N	160	P–P	209	As–As	348	Sb–Sb	299	Bi–Bi	200
N=N	415								
N≡N	<b>946</b>	<b>P≡P</b>	<b>490</b>						
N–H	390	P–H	328	As–H	245	Sb–H	257	Bi–H	194
N–Cl	193	P–Cl	319	As–Cl	293	Sb–Cl	313	Bi–Cl	285
N–O	<b>200</b>	<b>P–O</b>	<b>407</b>	As–O	477	Sb–O	314	Bi–O	339
N=O	678	P=O	560						

# Simple hydrides ( $\text{EH}_3$ )

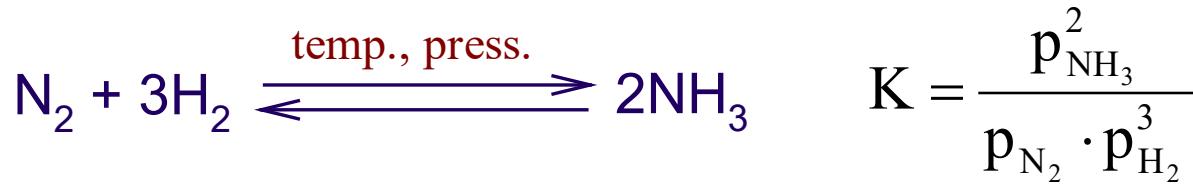
	$\text{NH}_3$	$\text{PH}_3$	$\text{AsH}_3$	$\text{SbH}_3$	$\text{BiH}_3$
mp / °C	-77.8	-133.5	-116.3	-88	?
bp / °C	-34.5	-87.5	-62.4	-18.4	+16.8 (predicted)
$\Delta H_f$ / kJ mol <sup>-1</sup>	-46.1	5.4	66.4	145.1	277.8
d(E–H)/pm	101.7	141.9	151.9	170.7	?
$\angle(\text{H}-\text{E}-\text{H})$	107.8°	93.6°	91.8°	91.3°	?

- All except  $\text{NH}_3$  can be obtained from  $\text{ECI}_3$  and  $\text{Li}[\text{AlH}_4]$ :



- All are poisonous gasses.
- The most important hydride of Group 15 is  $\text{NH}_3$  – it is the most important starting material for nitrogen compounds and probably *the most important* product of inorganic industrial chemistry (about 160 million tons are produced annually).
- Other  $\text{EH}_3$  are not suitable starting materials for respective element chemistry.

# Synthesis of ammonia



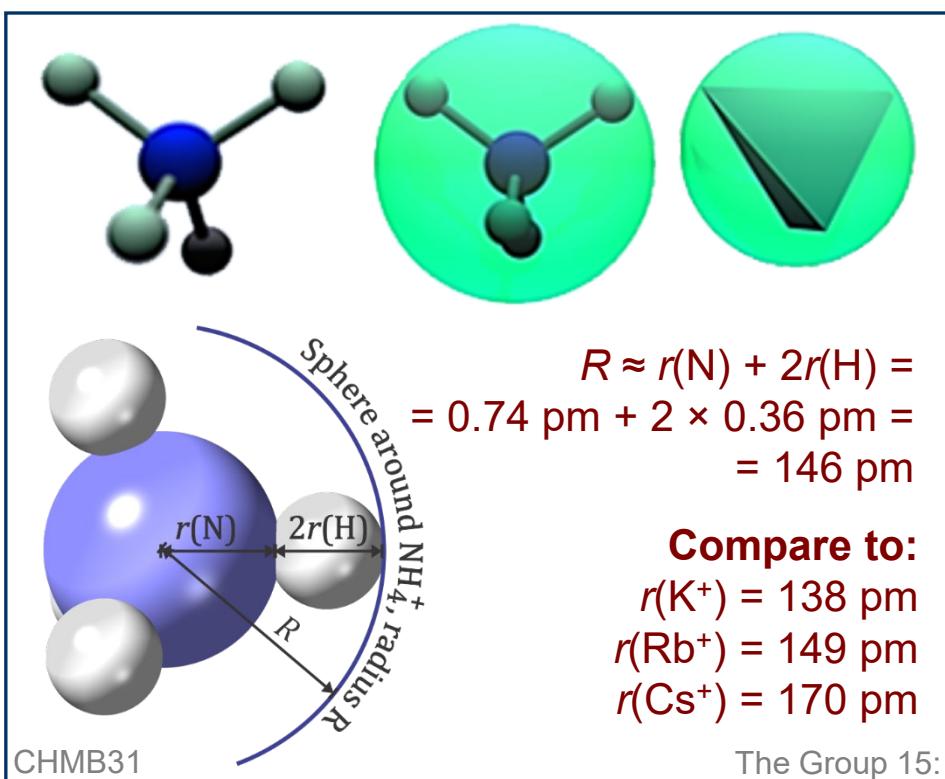
- Thermodynamics at room temperature (298 K) show a spontaneous reaction:  $\Delta_r G = -16.4 \text{ kJ/mol}$ ,  $\Delta_r H = -45.9 \text{ kJ/mol}$  with negative  $\Delta_r S: -99.0 \text{ J/(molK)}$ .
- High  $E_a$  for this reaction is very problematic.
- Rate of reaction (reaction speed) can be increased and kinetic barriers can overcome with high temperatures – BUT temperatures required for this task can result in  $\Delta_r G > 0!$
- However, an increase of pressure helps shift the equilibrium to right (Le Chatelier's principle!)
- In practice a compromise is found: temperature  $\sim 700\text{K}$ , pressure 20–260 kPa (!! with a catalyst (lowers the kinetic barrier) and yield is still only about 17%.

# 'NH<sub>4</sub>OH' and NH<sub>4</sub><sup>+</sup> ion

- NH<sub>3</sub> dissolves in and reacts with water producing weakly basic solution but there is no molecule NH<sub>4</sub>OH present:



- Ammonium salts contain NH<sub>4</sub><sup>+</sup> ion which is similar in size to Rb<sup>+</sup> and ammonium salts are similar to those of K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup>:



- Important salts are:
  - [NH<sub>4</sub>]Cl (with CsCl structure),
  - [NH<sub>4</sub>]<sub>2</sub>SO<sub>4</sub> (fertilizer) &
  - [NH<sub>4</sub>]NO<sub>3</sub> (fertilizer and explosive).

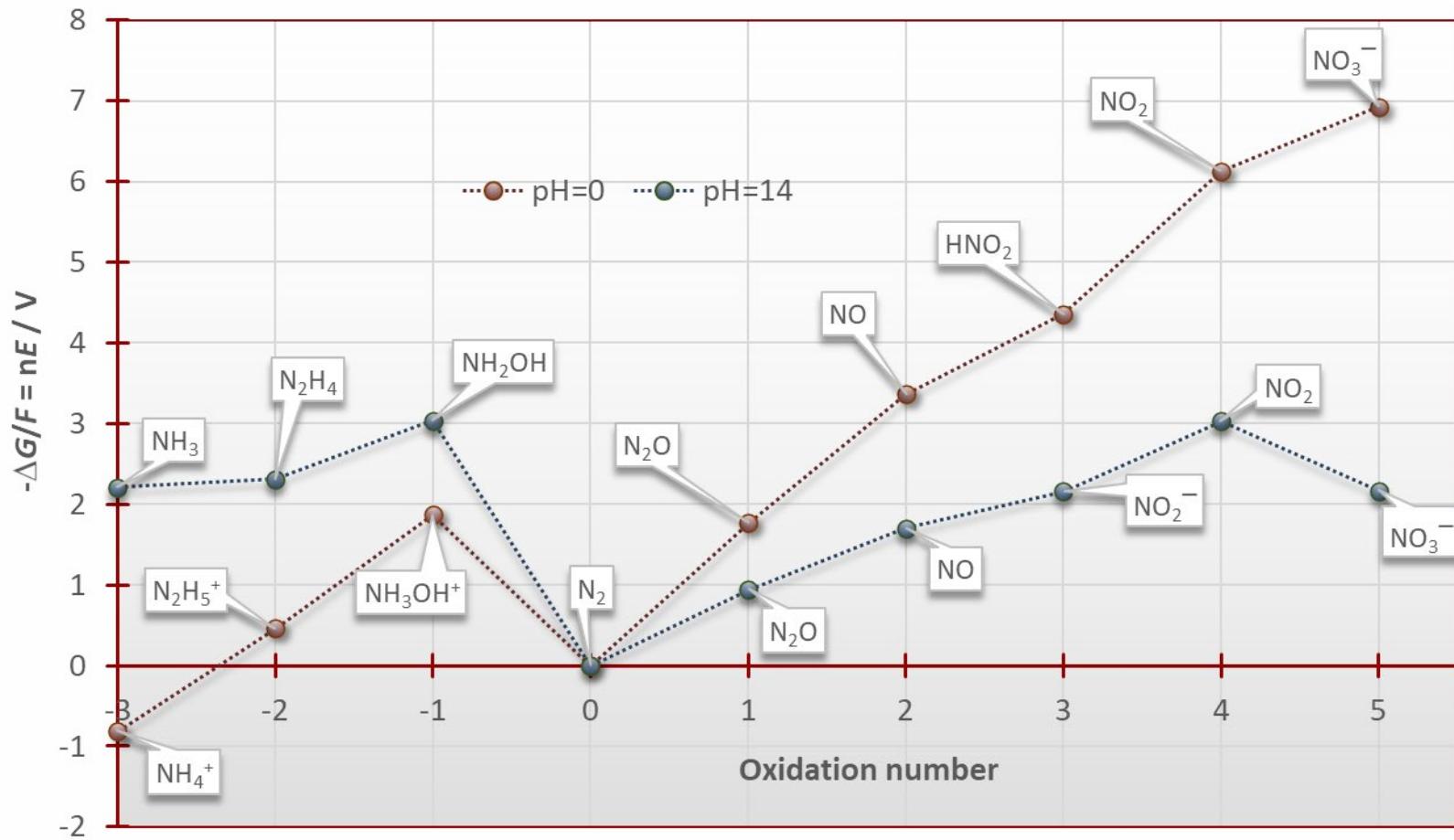
# Liquid ammonia as solvent



Comparison of Properties:	$\text{NH}_3$	$\text{H}_2\text{O}$
Molecular Weight	17.03	18.01
Melting Point, K/ $^\circ\text{C}$	196.3 / -77.65	273.0 / 0.00
Boiling Point, K/ $^\circ\text{C}$	239.6 / -33.33	373.0 / 100.00
Liquid state density, g cm $^{-1}$	0.73	1.00
Dipole moment, D	1.47	1.85
Self-ionization constant	$5.1 \times 10^{-27}$	$1.0 \times 10^{-14}$

- $\text{NH}_3$  is more basic than  $\text{H}_2\text{O}$ : weak acids in water become strong acids in  $\text{NH}_3$
- $\text{NH}_3$  is less acidic than  $\text{H}_2\text{O}$ : strong bases can be handled without amminolysis (for example carbides  $\text{C}_2^{2-}$ )

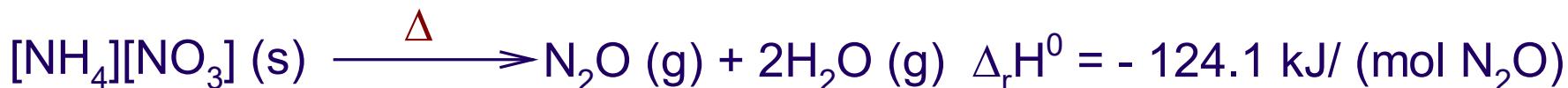
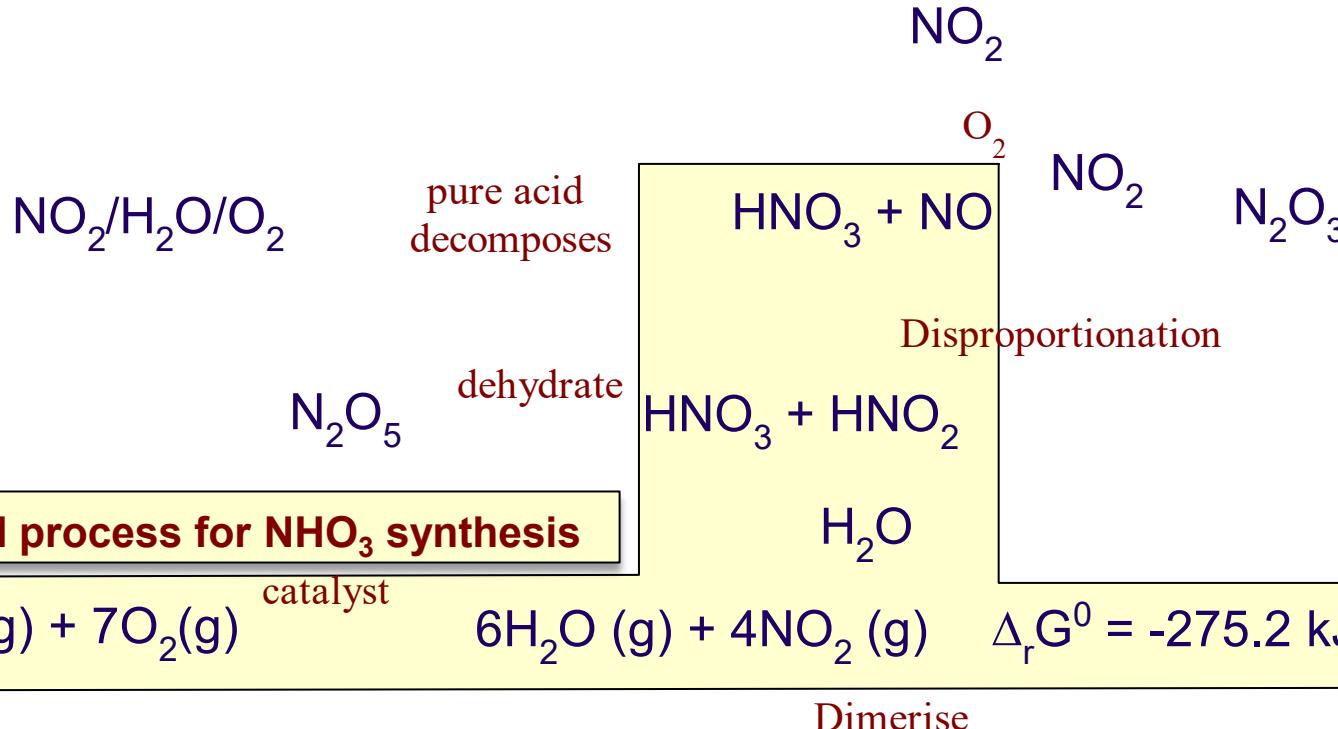
# Frost diagrams for nitrogen



# Nitrogen Oxides

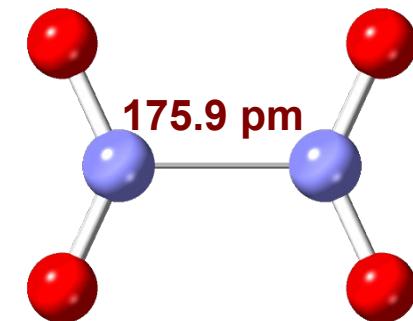
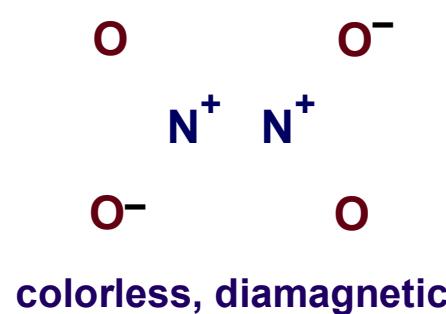
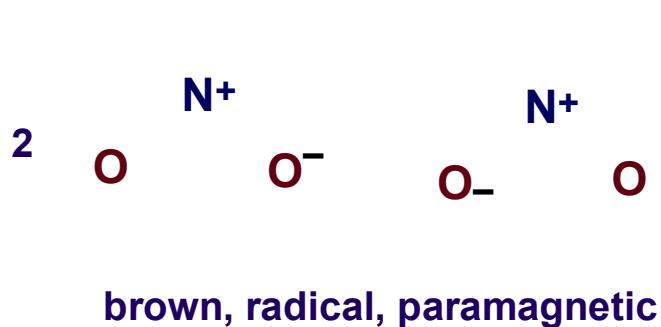
ON of nitrogen	Oxide thermodynamics	Name
+5	$\text{N}_2(\text{g}) + 2\frac{1}{2}\text{O}_2(\text{g}) \quad \text{N}_2\text{O}_5(\text{g}) \quad \Delta_f G^0 = +117.1 \text{ kJ/mol}$ $\Delta_f G^0 = -3.2 \text{ kJ/mol}$	Nitrogen(V) oxide or Dinitrogen pentoxide
	$\text{N}_2(\text{g}) + 2\frac{1}{2}\text{O}_2(\text{g}) \quad \text{N}_2\text{O}_5(\text{c}) \quad \Delta_f G^0 = +113.9 \text{ kJ/mol}$	
+4	$\frac{1}{2}\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \quad \text{NO}_2(\text{g}) \quad \Delta_f G^0 = +51.3 \text{ kJ/mol}$ $\Delta_f G^0 = -2.8 \text{ kJ/mol}$	Nitrogen(IV) oxide or nitrogen dioxide and Dinitrogen tetroxide
	$\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \quad \text{N}_2\text{O}_4(\text{g}) \quad \Delta_f G^0 = +99.8 \text{ kJ/mol}$	
+3	$\text{N}_2(\text{g}) + 1\frac{1}{2}\text{O}_2(\text{g}) \quad \text{N}_2\text{O}_3(\text{g}) \quad \Delta_f G^0 = +142.4 \text{ kJ/mol}$	Nitrogen(III) oxide or dinitrogen trioxide
+2	$\frac{1}{2}\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \text{NO}(\text{g}) \quad \Delta_f G^0 = +87.6 \text{ kJ/mol}$	Nitrogen(II) oxide or nitrogen monoxide
+1	$\text{N}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \text{N}_2\text{O}(\text{g}) \quad \Delta_f G^0 = +103.7 \text{ kJ/mol}$	Nitrogen(I) oxide or dinitrogen oxide

# Nitrogen Oxides and Their Oxoacids

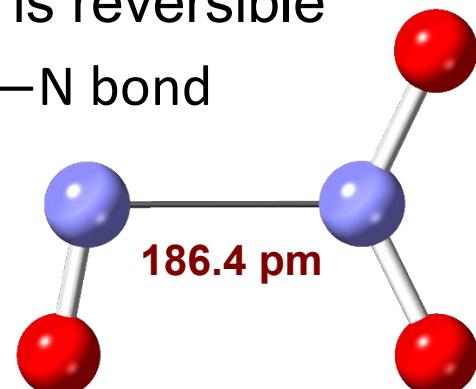


# Structures and properties of oxides

- **Nitrogen(V) oxide** (dinitrogen pentoxide),  $\text{N}_2\text{O}_5$ : a low melting point, ionic solid  $[\text{NO}_2]^+[\text{NO}_3]^-$  (i.e. nitryl nitrate) but liquid and gas phase are molecular  $\text{N}_2\text{O}_5$
- **Nitrogen(IV) oxide** (nitrogen dioxide and dinitrogen tetroxide)

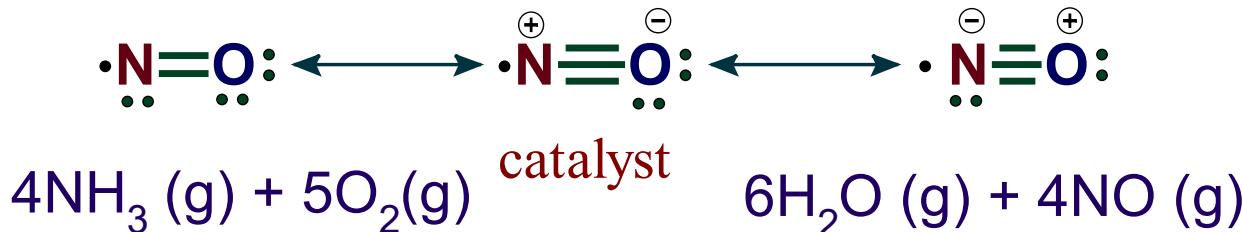


- **Nitrogen(III) oxide** (Dinitrogen trioxide),  $\text{N}_2\text{O}_3$  (dark blue liquid)
  - It easily dissociates into NO and  $\text{NO}_2$  but it is reversible
  - It is planar molecule with unusually long N—N bond
  - It is anhydride of nitrous acid ( $\text{HNO}_2$ )

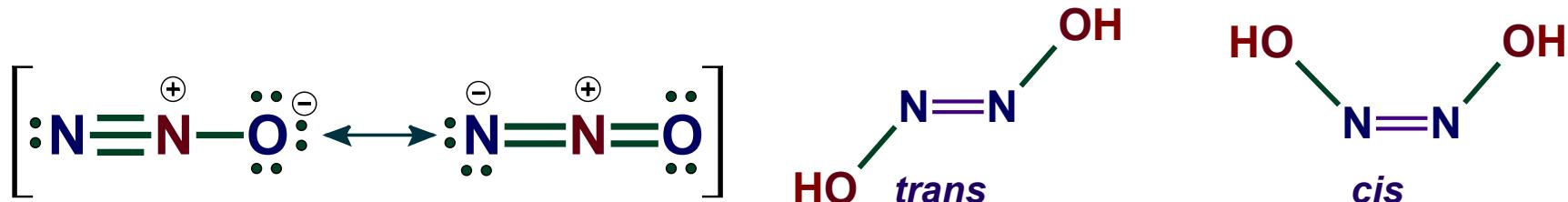


# Structures and properties of oxides

- **Nitrogen(II) oxide** (nitrogen oxide), the only oxide of nitrogen that does not form an acid with water (acid base neutral); colorless gas



- **Nitrogen(I) oxide** (dinitrogen oxide), also called a ‘laughing gas’; dissolves in water quite well and there is some evidence that it produces diazenediol (hyponitrous acid  $\text{H}_2\text{N}_2\text{O}_2$ )



- Interestingly, *cis* isomer of the acid is not known, but the salts with *cis* anion are

# Nitric acid

- The acid is good oxidizing agent, but the reduced nitrogen species obtained can vary greatly:



- Aqua regia* (royal or noble water):



- Nitrates**, salts of  $\text{HNO}_3$ ,

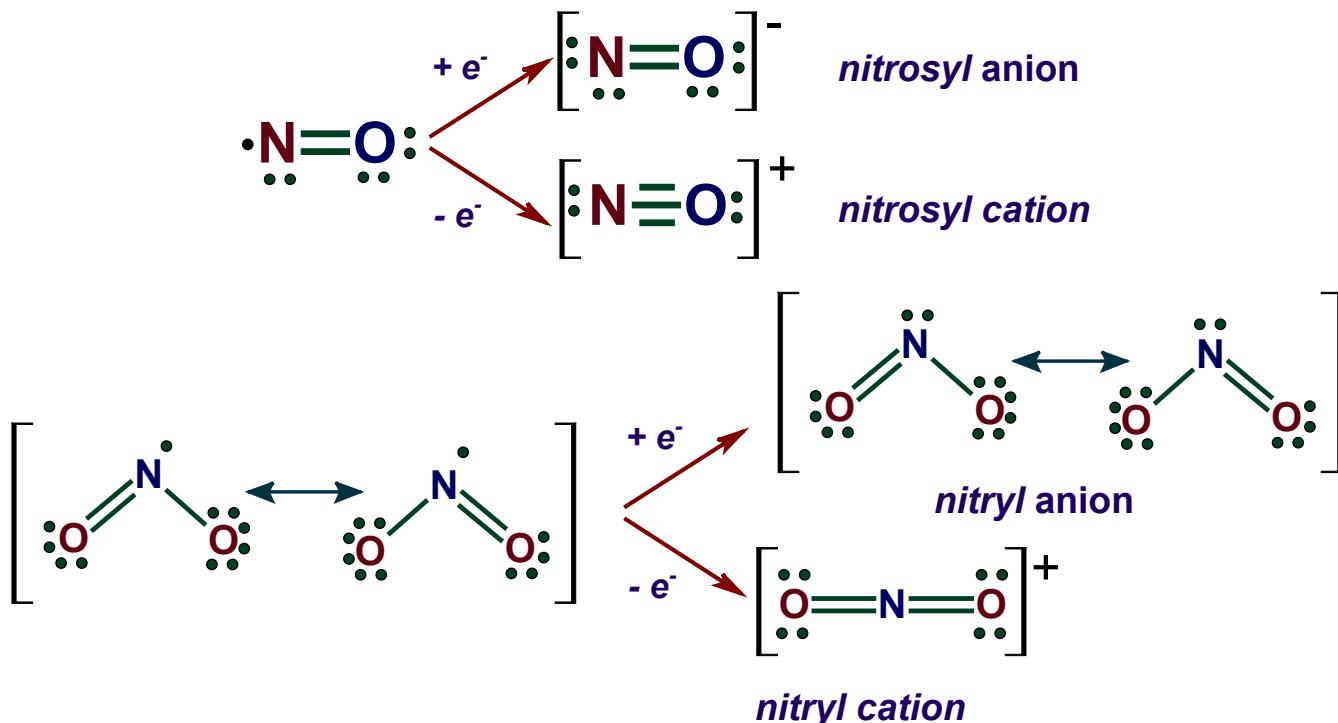
- Majority are soluble in water (even  $\text{Ag}^+$  and  $\text{Pb}^{2+}$ )
- Some are thermally unstable (particularly Group 1 and  $\text{NH}_4^+$ )



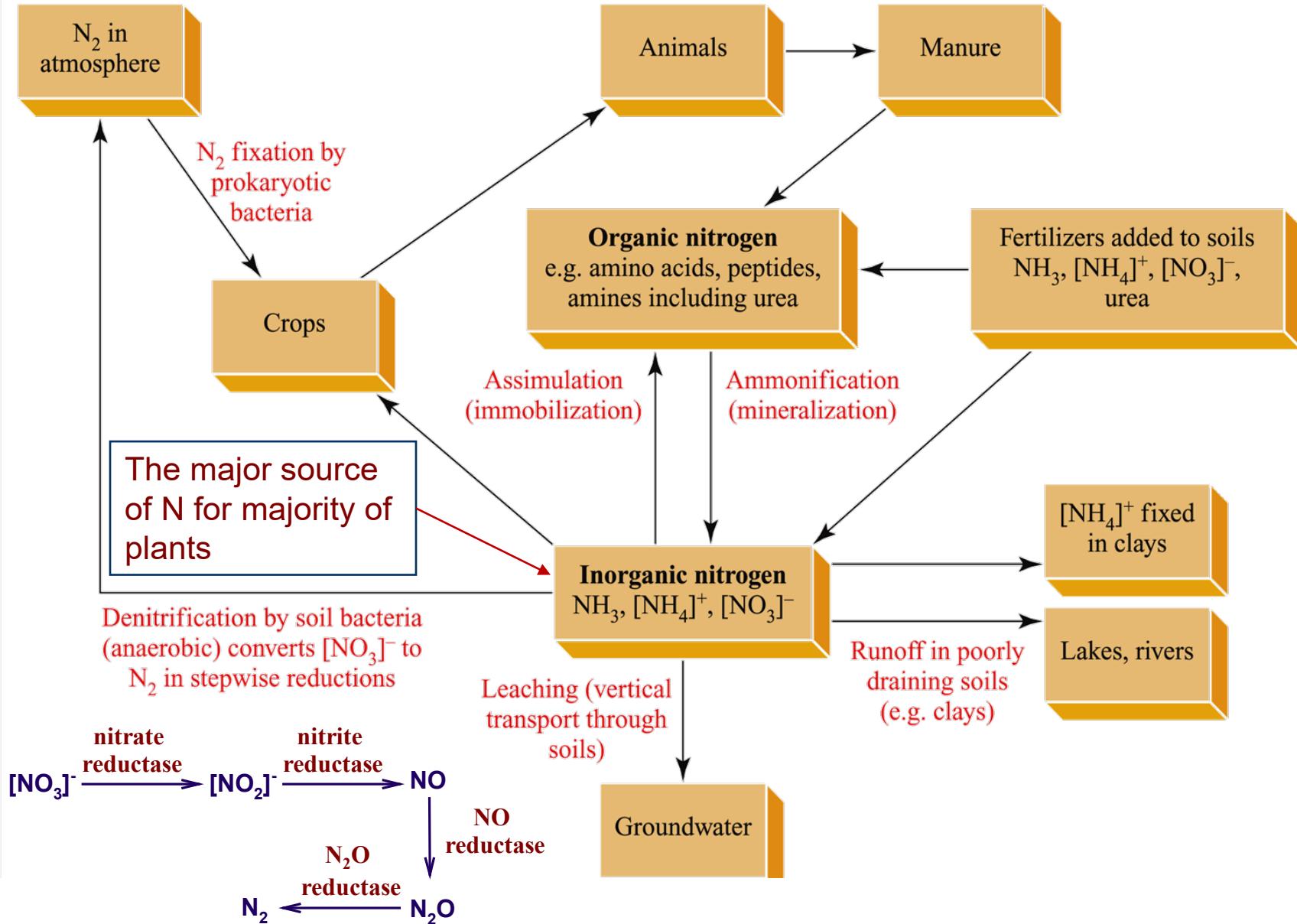
# Nitrous acid

- Weak acid
- Unstable, cannot be isolated and easily disproportionates to NO and  $\text{HNO}_3$

## Other important oxo species

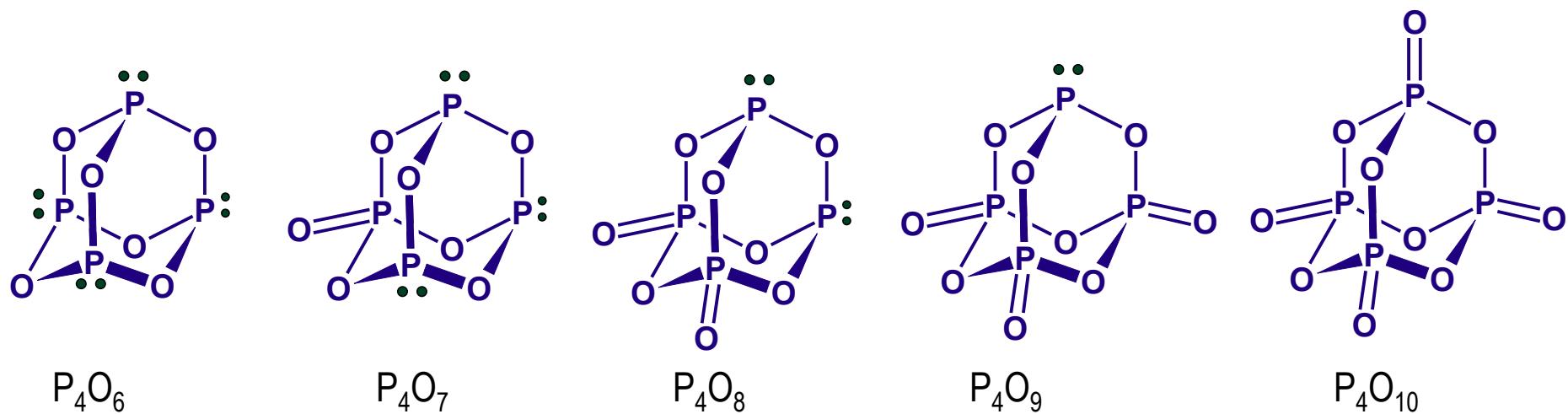
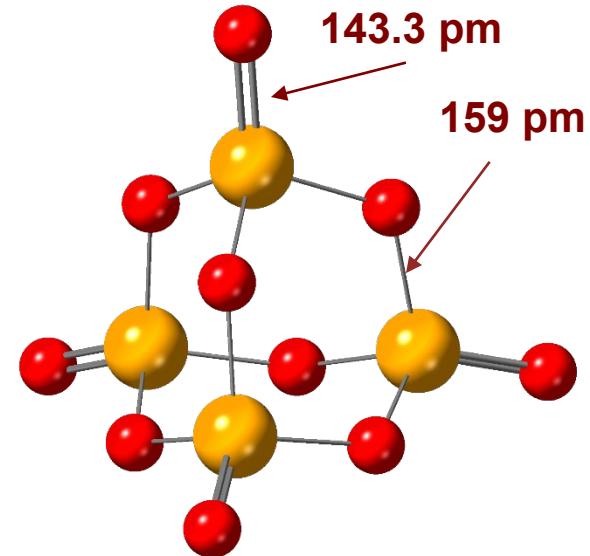


# The nitrogen cycle



# Phosphorus oxides

- Phosphorus(III) oxide ( $P_4O_6$ ) obtained by oxidation of  $P_4$  under restricted supply of  $O_2$
- Phosphorus(V) oxide ( $P_4O_{10}$ ) obtained from  $P_4O_6$  or by burning P on air
- A series of mixed P(III)/P(V) oxides can be obtained:

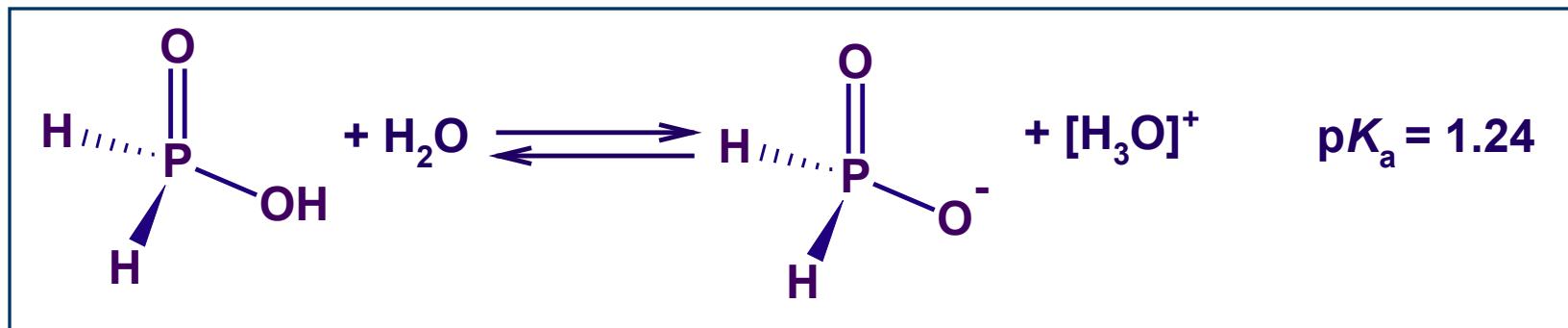


# Oxoacids of phosphorus: $\text{H}_3\text{PO}_2$

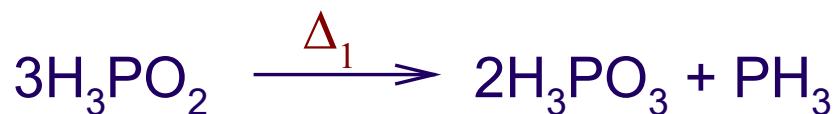
- **Phosphinic acid ( $\text{H}_3\text{PO}_2$ )** – obtained from  $\text{P}_4$  and an aqueous base (hydroxide) as its salt:



- It is a fairly strong *monobasic* acid:



- Disproportionates easily on heating:

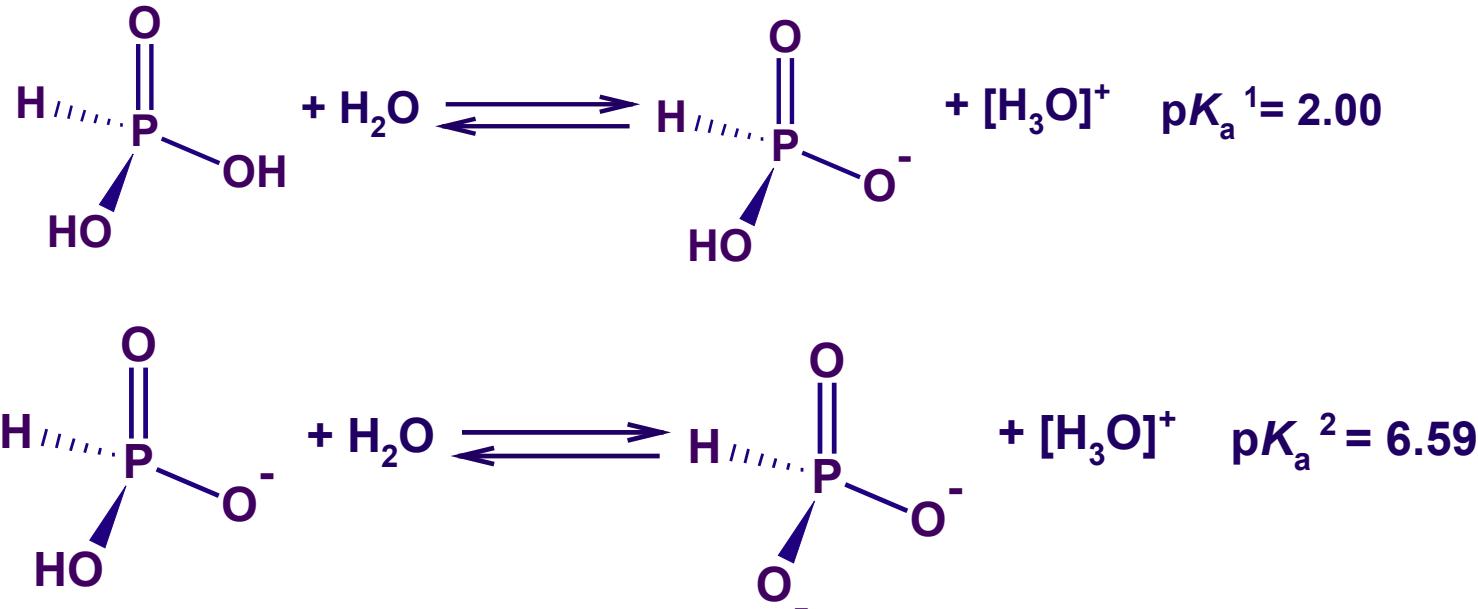


# Oxoacids of phosphorus: $\text{H}_3\text{PO}_3$

- **Phosphonic acid ( $\text{H}_3\text{PO}_3$ )** is obtained from  $\text{P}_4\text{O}_6$  and cold water:



- It is a *dibasic acid*:



# Oxoacids of phosphorus: $\text{H}_3\text{PO}_4$

- **Phosphoric acid ( $\text{H}_3\text{PO}_4$ )** the most important P acid, has huge environmental, industrial and biological impact
- Its salts are found in nature as phosphate minerals
- Obtained from apatite (industrially) or from  $\text{P}_4\text{O}_{10}$  and water (on small scale):



- First dissociation step is moderately strong ( $\text{p}K_{\text{a}1} = 2.21$ ), second and third are progressively weaker:  $\text{p}K_{\text{a}2} = 7.21$ ;  $\text{p}K_{\text{a}3} = 12.67$
- It can condense on heating (compare with Si!)



- For  $\text{H}_4\text{P}_2\text{O}_7$ :  $\text{p}K_{\text{a}1} = 0.85$ ;  $\text{p}K_{\text{a}2} = 1.49$ ;  $\text{p}K_{\text{a}3} = 5.77$  and  $\text{p}K_{\text{a}4} = 8.22$

# A look at nitrogen halides

- Many nitrogen halides exist (not as much as in the case of carbon):
  - A complete replacement of H in various nitrogen hydrides gives the following halides: **NX<sub>3</sub>** (from ammonia), **N<sub>2</sub>X<sub>4</sub>** (from hydrazine), **N<sub>2</sub>X<sub>2</sub>** (from diazene, **N<sub>2</sub>H<sub>2</sub>**) and **N<sub>3</sub>X** (from hydrogen azide, **HN<sub>3</sub>**)
  - Partly halogenated derivatives of ammonia, i.e. NH<sub>2</sub>X and NHX<sub>2</sub>, are also known
  - Nitrozyl (NOX) and nitryl (NO<sub>2</sub>X) halides



- All N<sub>y</sub>X<sub>n</sub> (except when X=F) are explosive

# A look at phosphorus halides

- All phosphorus tri- and pentahalides are known
- Important are  $\text{PCl}_3$ ,  $\text{PCl}_5$  and  $\text{POCl}_3$ : they are starting points for organophosphorus and good part of inorganic phosphorus chemistry
- These three easily participate in many reaction types
- Acid-base:
  - $\text{PCl}_3 + \text{BBr}_3 \rightleftharpoons \text{Br}_3\text{B}-\text{PCl}_3$
  - $\text{PCl}_5 + \text{BCl}_3 \rightleftharpoons [\text{PCl}_4][\text{BCl}_4]$
- Redox:
  - $\text{PCl}_3 + \text{S} \rightleftharpoons \text{PSCl}_3$
  - $2\text{PCl}_3 + \text{H}_2 \rightleftharpoons \text{P}_2\text{Cl}_4 + 2\text{HCl}$
- Substitution:
  - $\text{POCl}_3 + 3 \text{ROH} \rightleftharpoons \text{O}=\text{P}(\text{OR})_3 + 3\text{HCl}$
  - $\text{PCl}_3 + 3\text{NH}_3 \rightleftharpoons \text{P}(\text{NH}_2)_3 + 3\text{HCl}$
  - $\text{PCl}_5 + \text{H}_2\text{NNH}_2 \rightleftharpoons \text{Cl}_3\text{P}=\text{N}-\text{N}=\text{PCl}_3 + 4\text{HCl}$

# Overview of arsenic chemistry

- All arsenic compounds are strong poisons: soft metal binds strongly to S-residues in proteins
- Common in +3 and +5 ON
- All trihalides are known but of pentahalides only  $\text{AsF}_5$  and  $\text{AsCl}_5$  are known; weak Lewis acidity,
- $\text{As}_2\text{O}_3$  is an anhydride of arseenous acid ( $\text{H}_3\text{AsO}_3$ ): only salts are known, the acid has not been isolated
- $\text{As}_2\text{O}_5$  is an anhydride of arsenic acid ( $\text{H}_3\text{AsO}_4$ ), well-known, good oxidizing agent

# Overview of Sb and Bi chemistry

- Antimony's ON +3 is more stable than +3 ON for bismuth
- Halides:
  - **Sb** forms all trihalides but only pentafluoride and pentachloride; structures are complex structures, all are rather strong Lewis acids
  - **Bi** forms all trihalides but of pentahalides  $\text{BiF}_5$  is the only known one
- Oxides
- $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_5$  – no oxoacids known (too much metallic character)
- $\text{Bi}_2\text{O}_3$  and  $\text{Bi}_2\text{O}_5$  – no oxoacids, Bi(V) strong oxidant

# Readings and problems

- **Readings (both 6<sup>th</sup> and 7<sup>th</sup> ed.):**
  - Chapter 15 ‘The Group 15 Elements’ (Sections 15.6, 15.8, 15.9, 15.17 and 15.18 are not required)
  - Boxes 15.1, 15.2, 15.5
  - Go back to Chapter 4 (Chapter 5 in 7<sup>th</sup> ed.) ‘Acids and Bases’ and read ‘Liquid Ammonia’ and ‘Dinitrogen tetroxide’

## • Problems

### 6<sup>th</sup> edition

- *Examples and Self-tests:* 15.2, 15.3, 15.4
- *Exercises:* 15.3, 15.4, 15.6, 15.7, 15.8, 15.9 a) and b), 15.10, 15.14, 15.15, 15.17, 15.18, 15.19, 15.21, 15.22

### 7<sup>th</sup> edition

- *Examples and Self-tests:* 15.1, 15.2, 15.4, 15.5, 15.6, 15.7
- *Exercises:* 15.2, 15.5, 15.6, 15.7, 15.10, 15.11, 15.12, 15.13, 15.14 a) and b), 15.15, 15.19, 15.20, 15.22, 15.23, 15.24, 15.26, 15.27