

15
7 N 14,0067
15 P 30,9738
33 As 74,922
51 Sb 121,75
83 Bi 208,98

The Pnictogens

The chemistry of Group 15

Occurrence and isolation

15
7 N 14,0067
15 P 30,9738
33 As 74,922
51 Sb 121,75
83 Bi 208,98

Atmosphere (predominately as N₂, ~78%), as nitrate in minerals (NO₃⁻); fractional distillation of liquid air

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

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

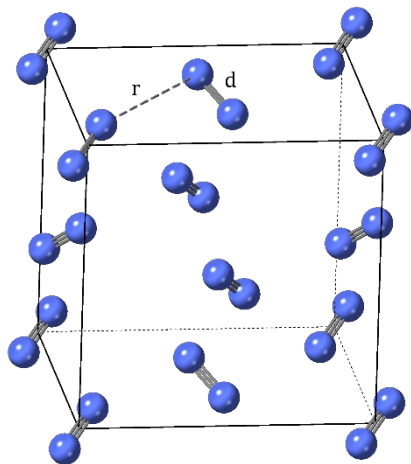
***Stibium** (lat.); antimonos (gr.) not alone; 0.2 ppm;; in sulfides and oxides*

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

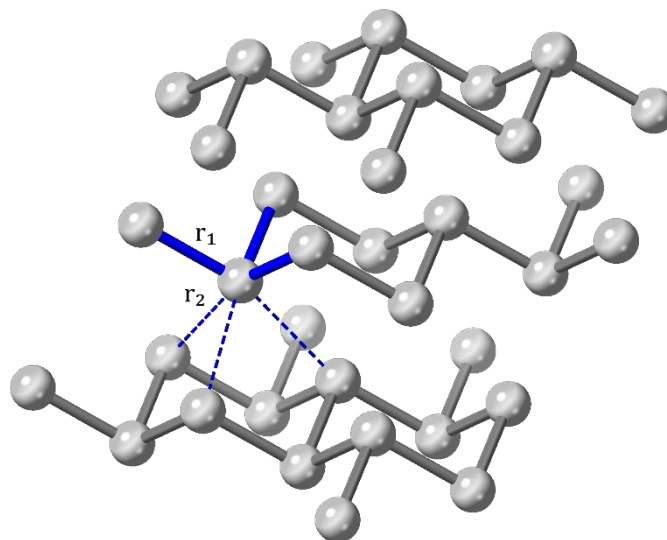
Data from J. Emsley 'The Elements' Oxford: Clarendon Press, 1989

Structural characteristics of elements

N_2 at 20 K (-253.15°C)



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

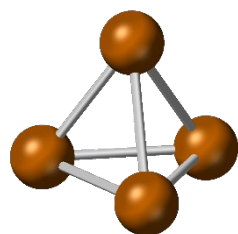


Arsenic, Sb and Bi
(most stable allotrope)

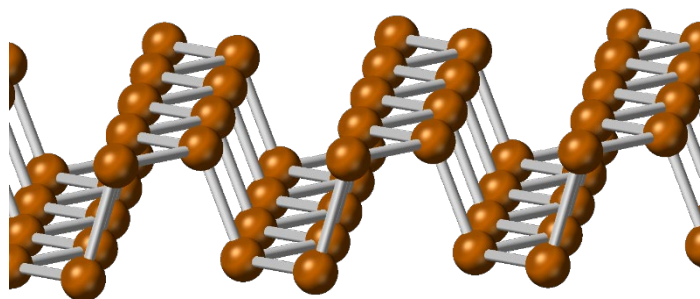
	r_1	r_2	r_2/r_1
As	251.7	312.0	1.240
Sb	290.8	335.5	1.153
Bi	307.2	352.9	1.149

(all distances in pm)

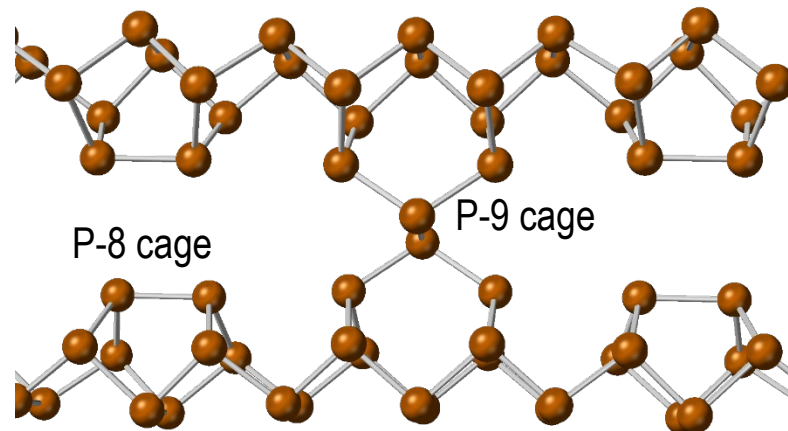
Phosphorus (most important allotropes)



P_4



Black phosphorus (P_∞)



Violet (Hittorf's) P (P_∞)

Structural characteristics of elements

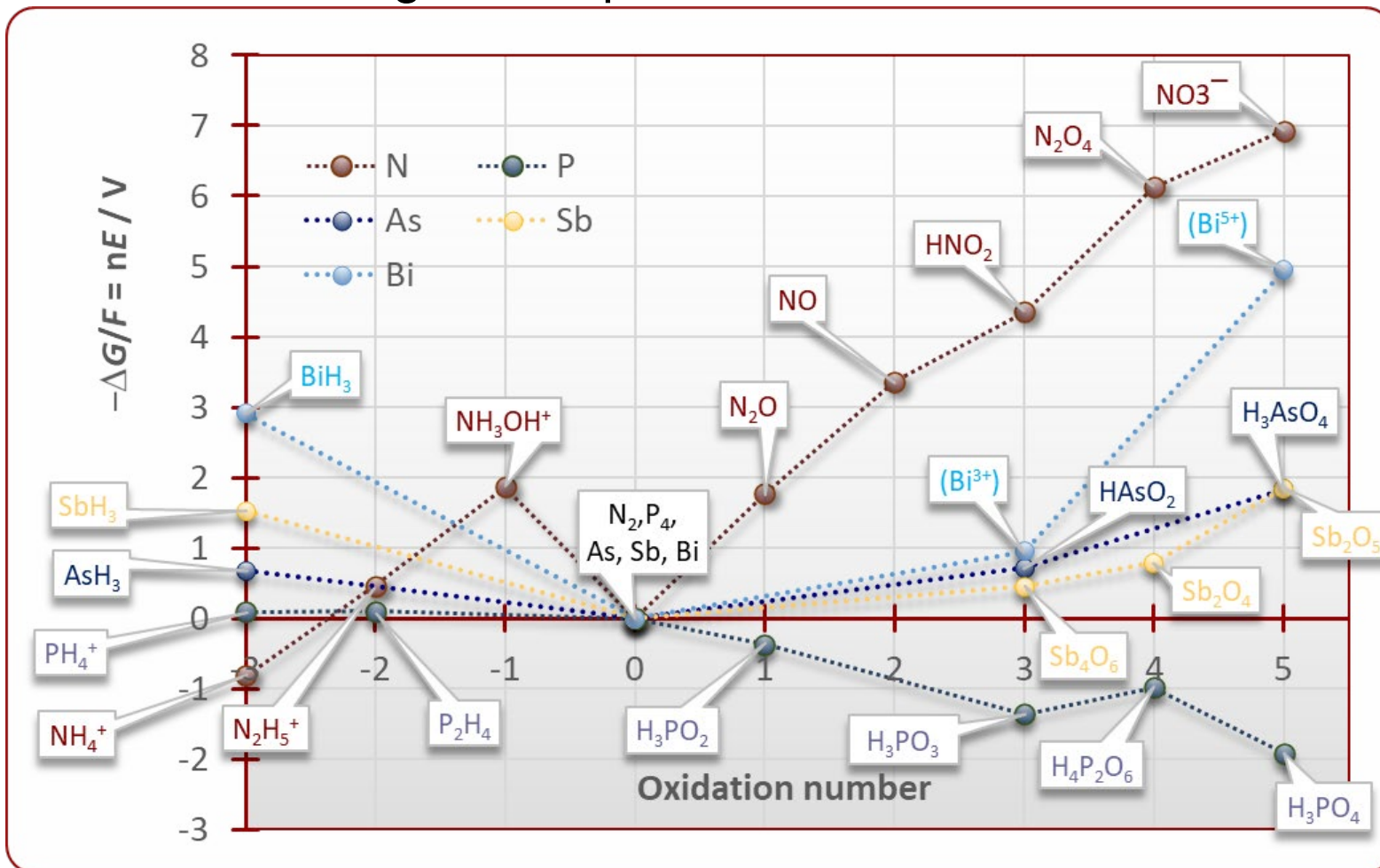
- Nitrogen comes as N_2 (dinitrogen), and retains this molecular structure even in solid state at -210°C (68K)
- Phosphorus:
 - Unlike N_2 , exists as gaseous P_2 only above 800°C ($\text{P-P} = 189 \text{ pm}$),
 - Most important allotropes are white (tetrahedral P_4 , very reactive), red (amorphous 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

- $\text{N}\equiv\text{N}$ triple bond makes dinitrogen molecule unreactive (kinetic effect, bond dissociation energy of N_2 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_3 and NH_4^+)
- 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	946	P≡P	490						
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	200	P–O	407	As–O	477	Sb–O	314	Bi–O	339
N=O	678	P=O	560						

Simple hydrides (EH₃)

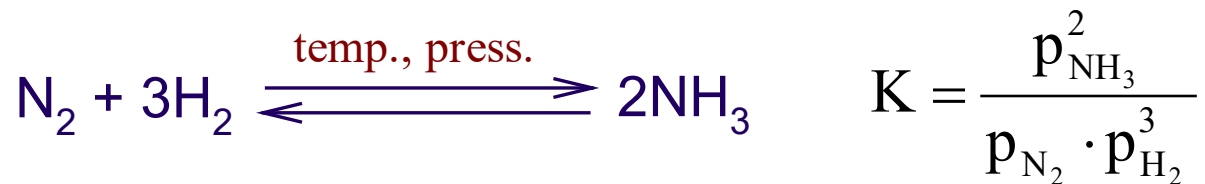
	NH ₃	PH ₃	AsH ₃	SbH ₃	BiH ₃
mp / °C	−77.8	−133.5	−116.3	−88	?
bp / °C	−34.5	−87.5	−62.4	−18.4	+16.8 (predicted)
ΔH _f / kJ mol ^{−1}	−46.1	5.4	66.4	145.1	277.8
d(E–H)/pm	101.7	141.9	151.9	170.7	?
∠(H–E–H)	107.8°	93.6°	91.8°	91.3°	?

- All except NH₃ can be obtained from ECl₃ and Li[AlH₄]:



- All are poisonous gasses.
- The most important hydride of Group 15 is NH₃ – 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 EH₃ are not suitable starting materials for respective element chemistry.

Synthesis of ammonia



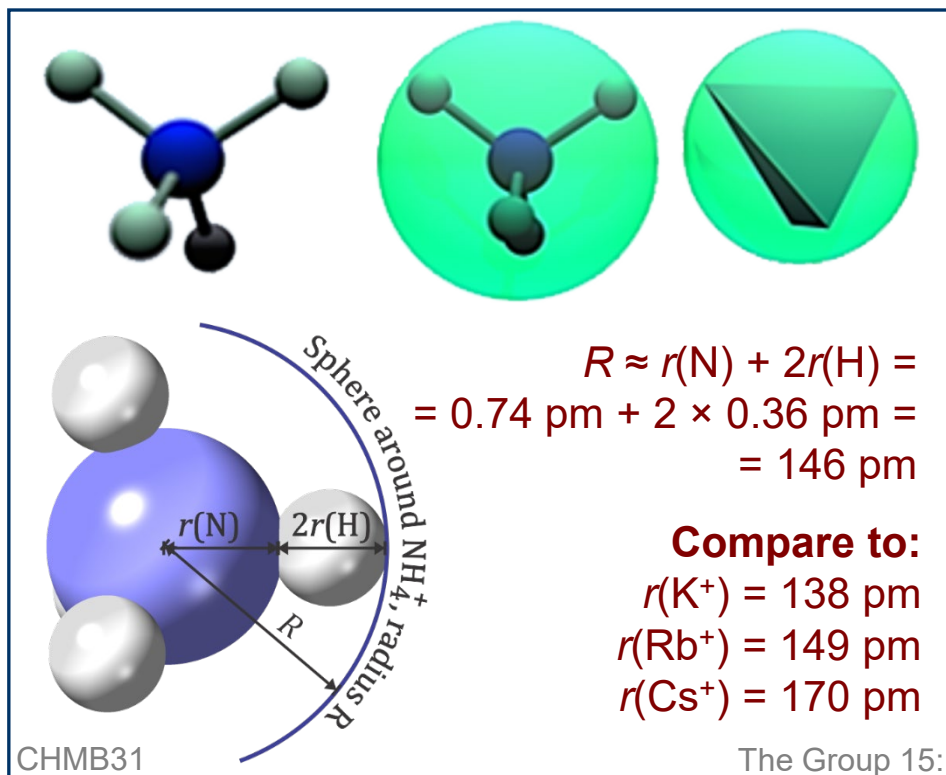
- Thermodynamics at room temperature (298 K) show a spontaneous reaction: $\Delta_r G = -16.4 \text{ kJ/mol}$, $\Delta_r H = -45.9 \text{ kJ/mol}$ with negative $\Delta_r S$: -99.0 J/(molK) .
- High E_a for this reaction is very problematic.
- Rate of reaction (reaction speed) can be increased and kinetic 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%.

'NH₄OH' and NH₄⁺ ion

- NH₃ dissolves in and reacts with water producing weakly basic solution but there is no molecule NH₄OH present:

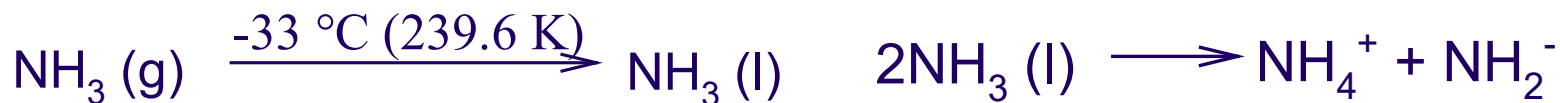


- Ammonium salts contain NH₄⁺ ion which is similar in size to Rb⁺ and ammonium salts are similar to those of K⁺, Rb⁺ and Cs⁺:



- Important salts are:
 - [NH₄]Cl (with CsCl structure),
 - [NH₄]₂SO₄ (fertilizer) &
 - [NH₄]NO₃ (fertilizer and explosive).

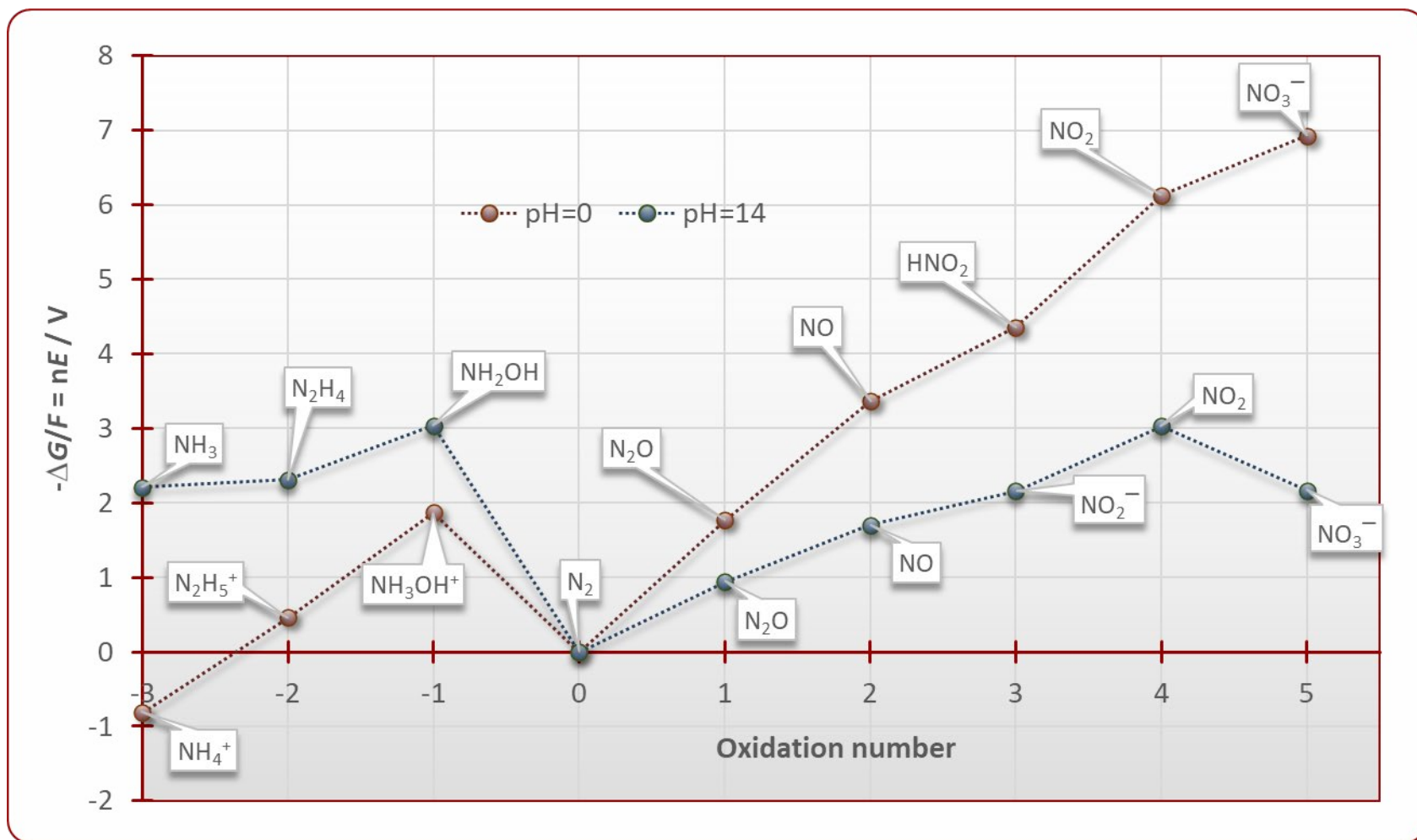
Liquid ammonia as solvent



Comparison of Properties:	NH ₃	H ₂ O
Molecular Weight	17.03	18.01
Melting Point, K/°C	196.3 / -77.65	273.0 / 0.00
Boiling Point, K/°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	5.1×10^{-27}	1.0×10^{-14}

- NH₃ is more basic than H₂O: weak acids in water become strong acids in NH₃
- NH₃ is less acidic than H₂O: strong bases can be handled without aminolysis (for example carbides C₂²⁻)

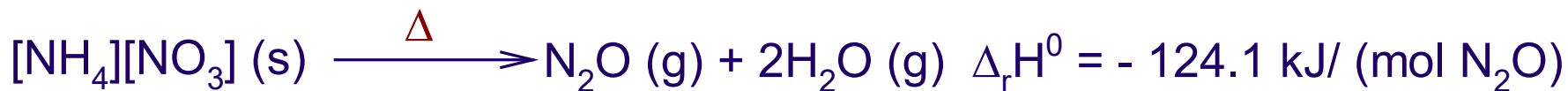
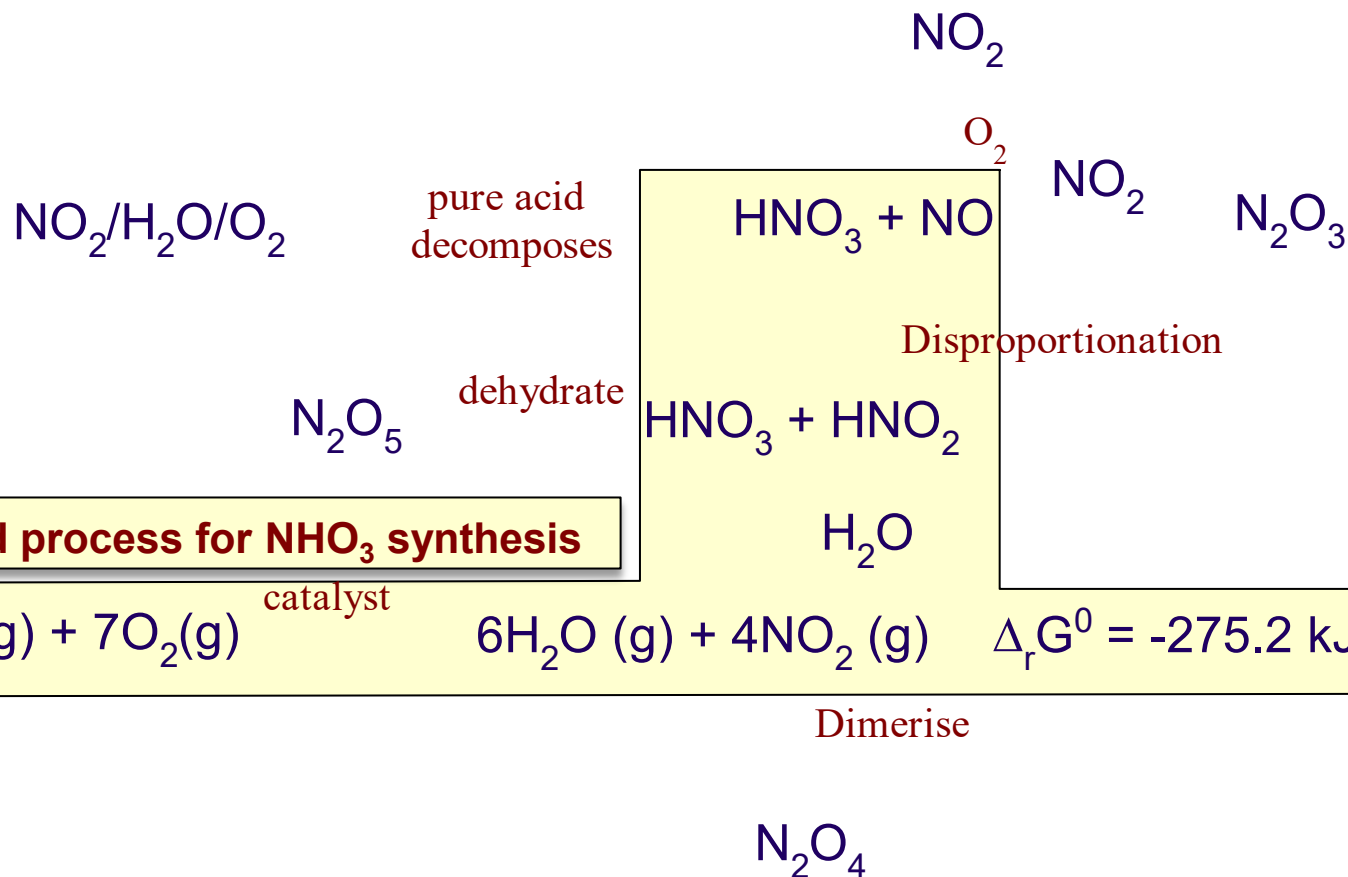
Frost diagrams for nitrogen



Nitrogen Oxides

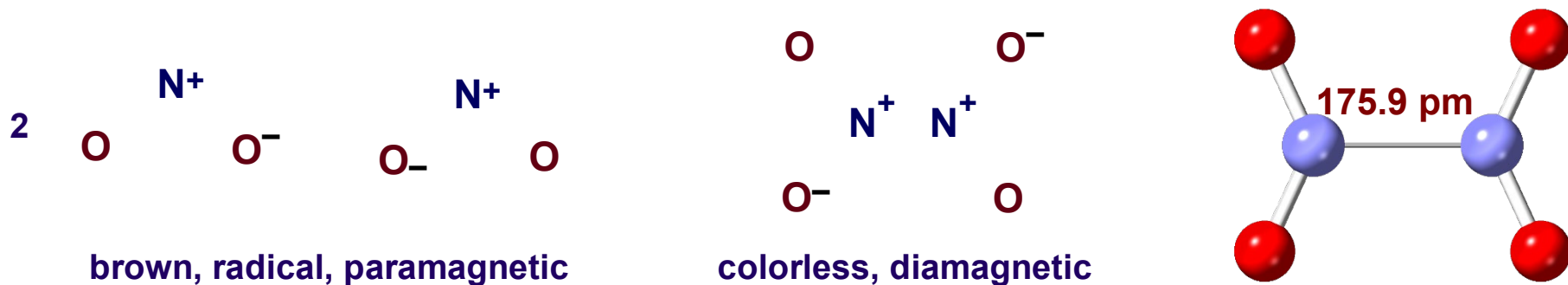
ON of nitrogen	Oxide thermodynamics			Name
+5	$\text{N}_2 (\text{g}) + 2\frac{1}{2} \text{O}_2 (\text{g})$	$\text{N}_2\text{O}_5 (\text{g})$	$\Delta_f G^0 = +117.1 \text{ kJ/mol}$	Nitrogen(V) oxide or Dinitrogen pentoxide
			$\Delta_f G^0 = -3.2 \text{ kJ/mol}$	
+4	$\text{N}_2 (\text{g}) + 2\frac{1}{2}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

Nitrogen Oxides and Their Oxoacids

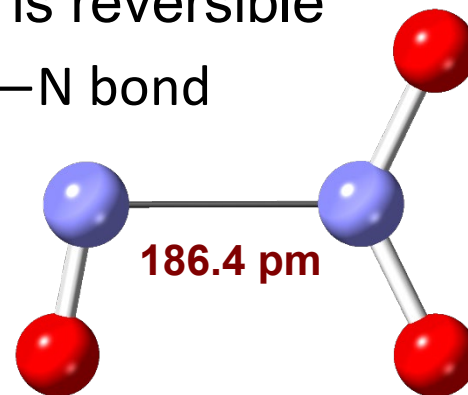


Structures and properties of oxides

- **Nitrogen(V) oxide** (dinitrogen pentoxide), N_2O_5 : a low melting point, ionic solid $[\text{NO}_2]^+[\text{NO}_3]^-$ (i.e. nitryl nitrate) but liquid and gas phase are molecular N_2O_5
- **Nitrogen(IV) oxide** (nitrogen dioxide and dinitrogen tetroxide)



- **Nitrogen(III) oxide** (Dinitrogen trioxide), N_2O_3 (dark blue liquid)
 - It easily dissociates into NO and NO_2 but it is reversible
 - It is planar molecule with unusually long $\text{N}-\text{N}$ bond
 - It is anhydride of nitrous acid (HNO_2)

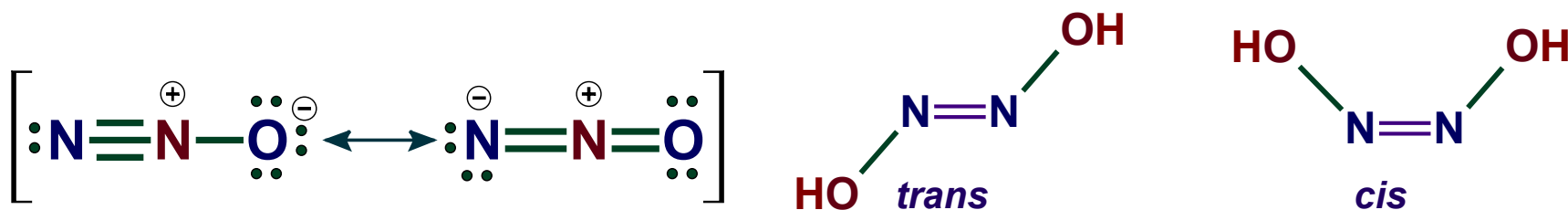


Structures and properties of oxides

- 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:

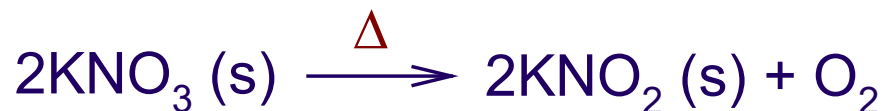


- Aqua regia* (royal or noble water):



- Nitrates**, salts of HNO_3 ,

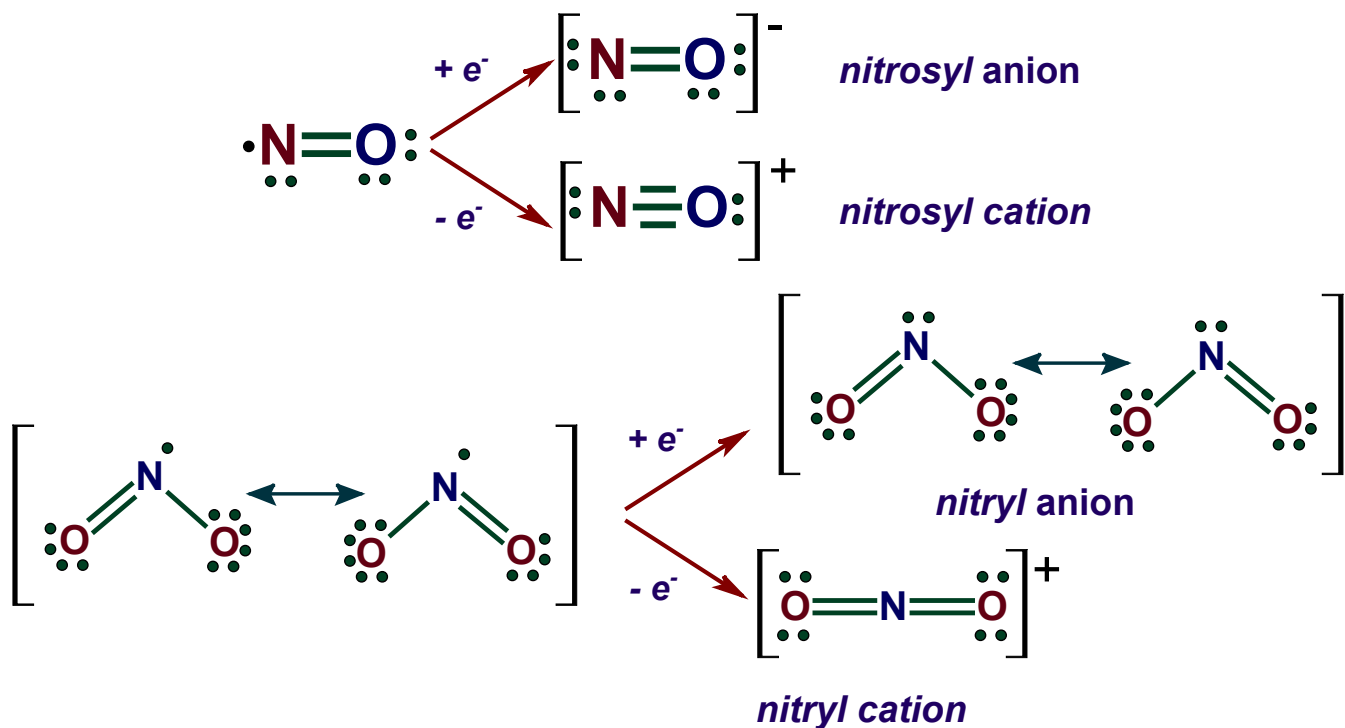
- Majority are soluble in water (even Ag^+ and Pb^{2+})
- Some are thermally unstable (particularly Group 1 and NH_4^+)



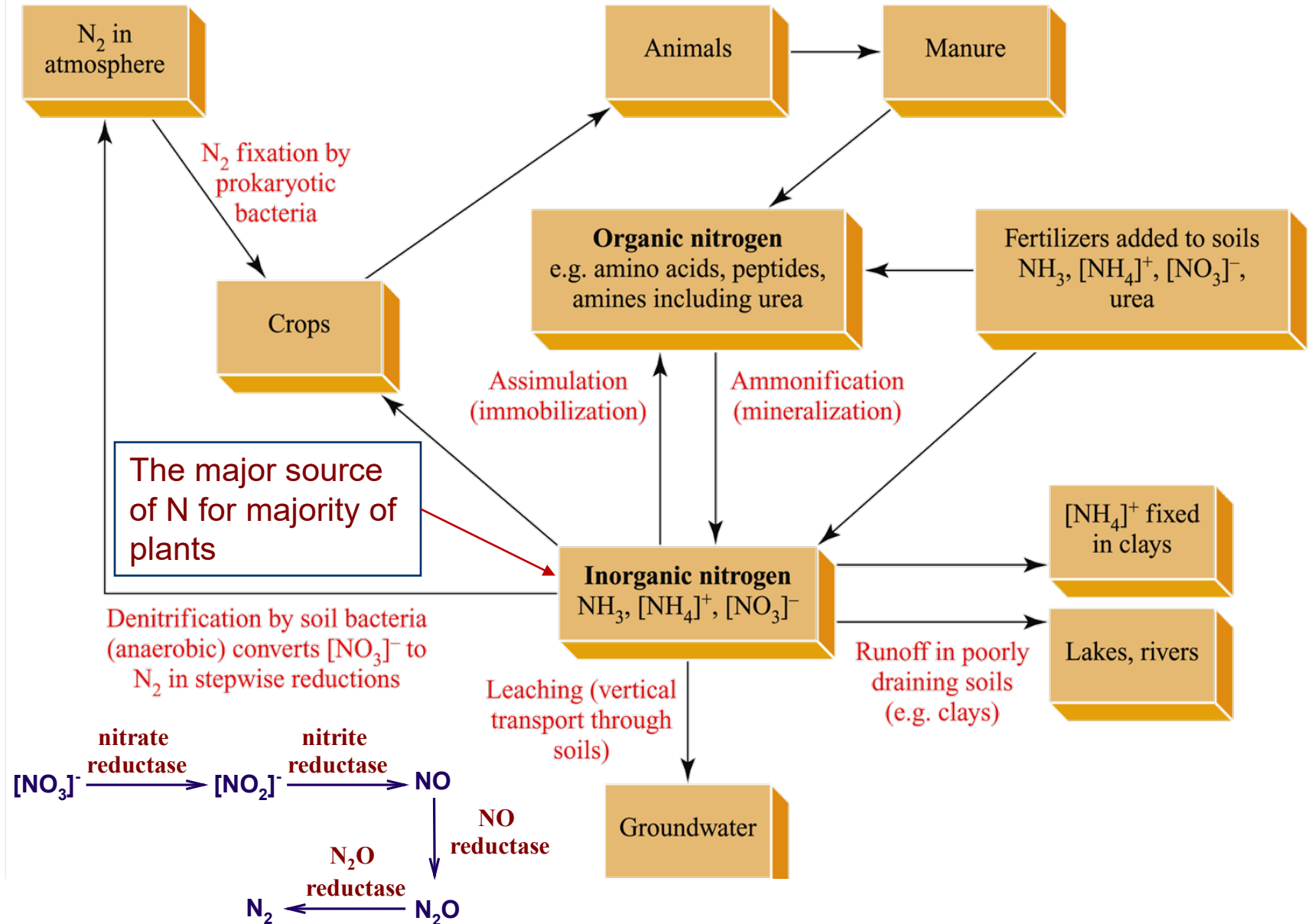
Nitrous acid

- Weak acid
- Unstable, cannot be isolated and easily disproportionates to NO and HNO₃

Other important oxo species

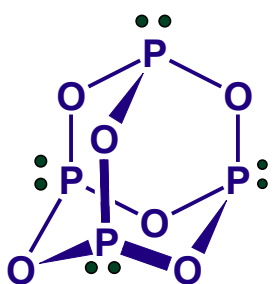
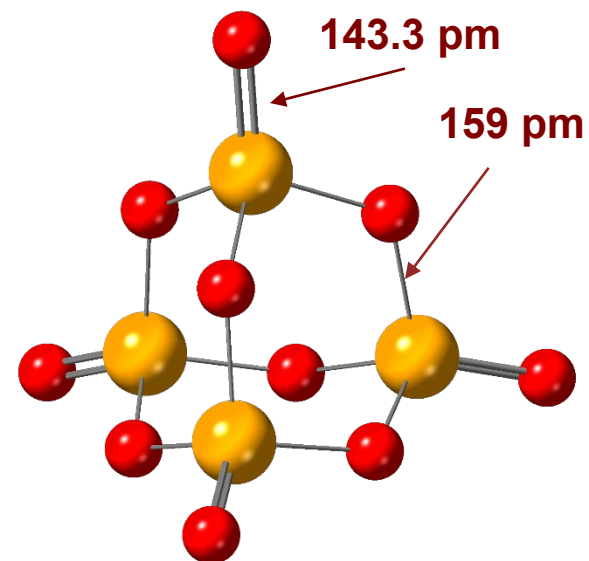


The nitrogen cycle

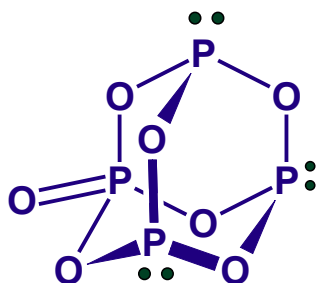


Phosphorus oxides

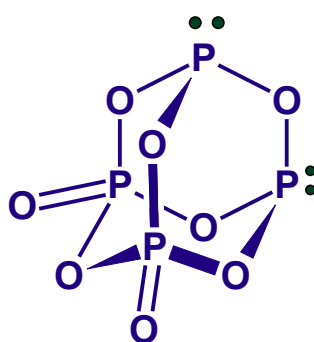
- Phosphorus(III) oxide (P_4O_6) obtained by oxidation of P_4 under restricted supply of O_2
- Phosphorus(V) oxide (P_4O_{10}) obtained from P_4O_6 or by burning P on air
- A series of mixed P(III)/P(V) oxides can be obtained:



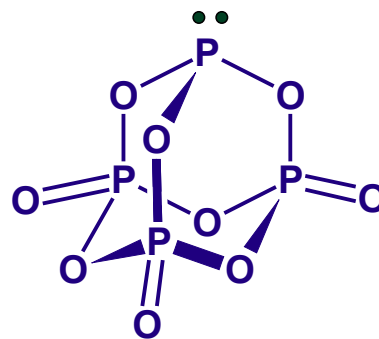
P_4O_6



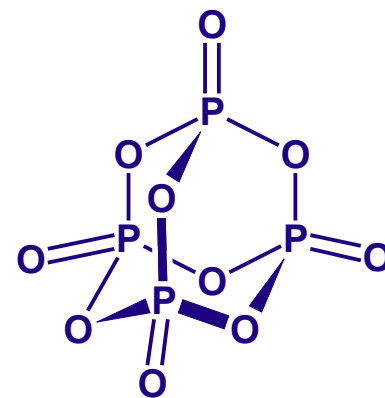
P_4O_7



P_4O_8



P_4O_9



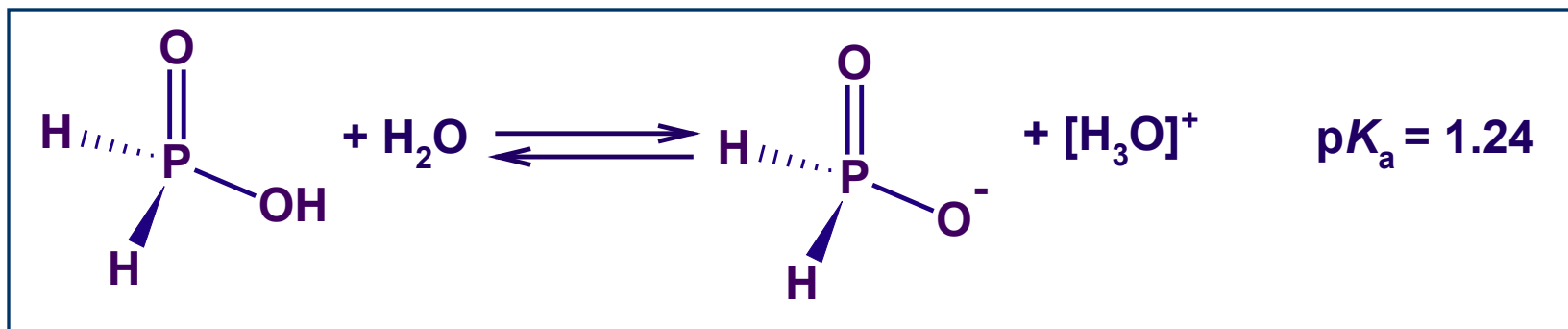
P_4O_{10}

Oxoacids of phosphorus: H_3PO_2

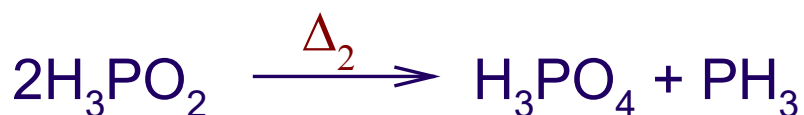
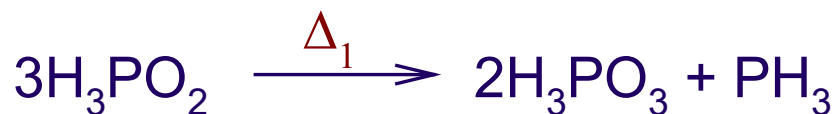
- **Phosphinic acid (H_3PO_2)** – obtained from P_4 and an aqueous base (hydroxide) as its salt:



- It is a fairly strong *monobasic* acid:



- Disproportionates easily on heating:

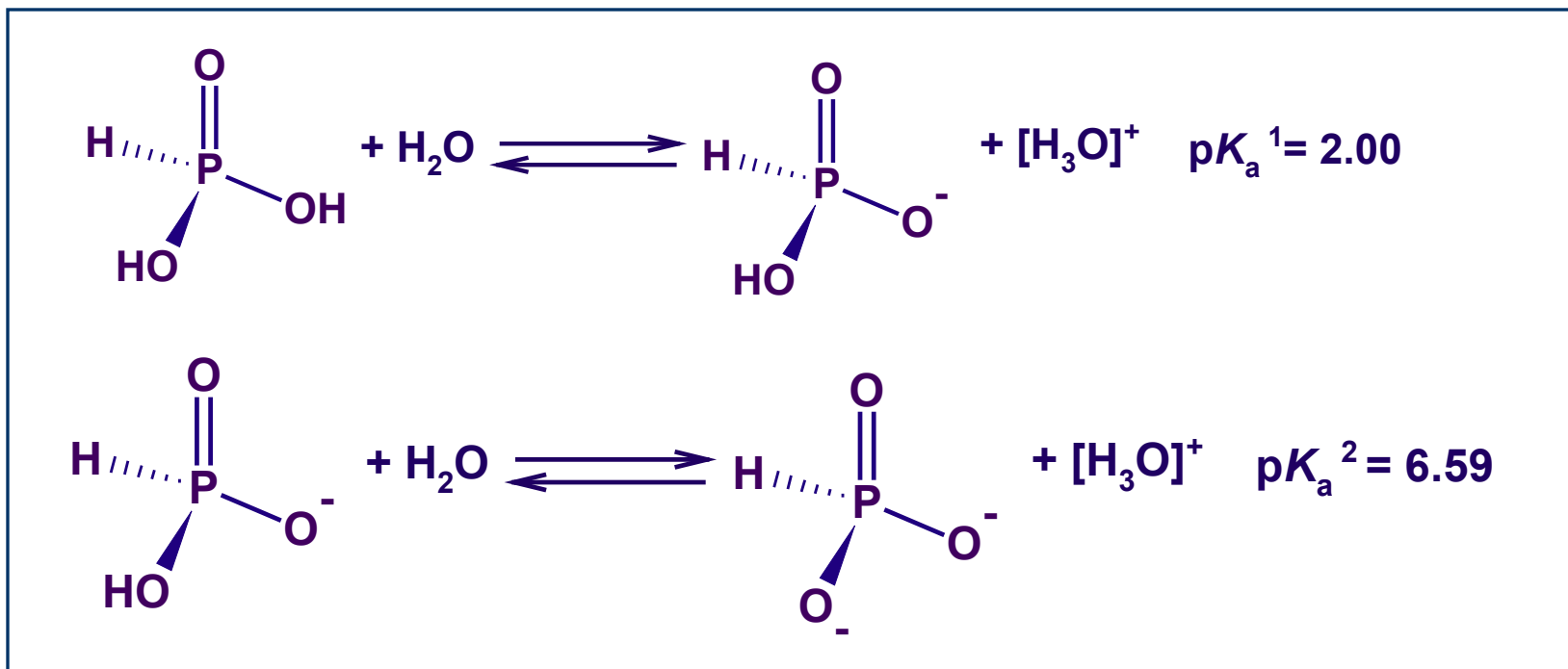


Oxoacids of phosphorus: H_3PO_3

- Phosphonic acid (H_3PO_3) is obtained from P_4O_6 and cold water:



- It is a *dibasic acid*:



Oxoacids of phosphorus: H_3PO_4

- **Phosphoric acid (H_3PO_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 P_4O_{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_3** (from ammonia), **N_2X_4** (from hydrazine), **N_2X_2** (from diazene, **N_2H_2**) and **N_3X** (from hydrogen azide, **HN_3**)
 - Partly halogenated derivatives of ammonia, i.e. **NH_2X** and **NHX_2** , are also known
 - Nitroaryl (**NOX**) and nitryl (**NO_2X**) halides



- All **N_yX_n** (except when **$\text{X}=\text{F}$**) are explosive

A look at phosphorus halides

- All phosphorus tri- and pentahalides are known
- Important are PCl_3 , PCl_5 and 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 AsF_5 and AsCl_5 are known; weak Lewis acidity,
- As_2O_3 is an anhydride of arsenous acid (H_3AsO_3): only salts are known, the acid has not been isolated
- As_2O_5 is an anhydride of arsenic acid (H_3AsO_4), well-known, good oxidizing agent

Overview of Sb and Bi chemistry

- Antimony's ON +3 is more stable than +5 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 BiF_5 is the only known one
- Oxides
- Sb_2O_3 and Sb_2O_5 – no oxoacids known (too much metallic character)
- Bi_2O_3 and Bi_2O_5 – no oxoacids, Bi(V) strong oxidant

Readings and problems

- **Readings (both 6th and 7th ed.):**

- Chapter 15 'The Group 15 Elements' (Sections 15.6, 15.8, 15.9, 15.17 and 15.18 are is not required)
- Boxes 15.1, 15.2, 15.5
- Go back to Chapter 4 (Chapter 5 in 7th ed.) 'Acids and Bases' and read 'Liquid Ammonia' and 'Dinitrogen tetroxide'

- **Problems**

6th 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

7th 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