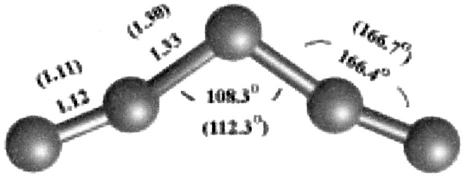
Group 15 (Pnicogens) - The Elements
Nitrogen

- N_2 comprises 78% by volume of air.
  - $N_2(g)$ is obtained by fractional distillation of air (b.p. 77K).
  - The very stable N≡N bond (D = 941 kJ/mol) accounts for the inertness of $N_2(g)$ and its utility as a means of achieving a chemically inert atmosphere. (Only Li reacts with it at room temperature.)

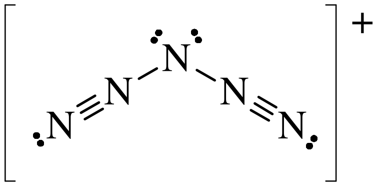
- The only molecular species containing just nitrogen were N_2 and the azide ion, N_3^{-}, but in 1999 Christe et al.[1] synthesized N_5^+ by the following reaction

$$[N_2F]^+[AsF_6]^- + HN_3 \xrightarrow[-78\ ^oC]{HF} N_5^+[AsF_6]^- + HF$$

  - Ab initio calculations predict the following C_{2v} structure:[2]



  - Structure confirmed from low-temperature i.r. and Raman.
  - Idealized Lewis structure:



  - $N_5^+[AsF_6]^-$ is a strongly oxidizing material that can detonate violently.

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[1] K. O. Christe, W. W. Wilson, J. A. Sheehy, and J. A. Boatz, *Angew. Chem., Int. Ed.*, **1999**, *38*, 2004.

[2] Calculated at B3LYP and CCSD(T)/6-311G(2d) levels of theory.

Group 15 - The Elements - Nitrogen (cont.)

- In 2001 Auffermann et al.[3] synthesized SrN_2, containing the N_2^{2-} ion, from Sr_2N under nitrogen pressure at 5500 bar at a temperature of 920 K.

$$2Sr_2N + 3N_2 \xrightarrow{\text{5500 bar/920 K}} 4SrN_2$$

  - N_2^{2-} is isoelectronic with O_2 and on the basis of MO considerations has a bond order of 2.

$$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$$

  - x-ray and neutron diffraction studies from microcrystalline powder samples show an N–N distance of 122.4 pm, comparable to 120.7 for O_2.

  - SrN_2 is air- and moisture-sensitive.

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[3] G. Auffermann, Y. Prots, and R. Kniep, *Angew. Chem. Int. Ed.,* **2001**, *40*, 547.

Group 15 - The Elements - Phosphorous

- Phosphorous occurs in minerals, such as collophanite, $Ca_3(PO_4)_2{\cdot}2H_2O$.
  - High temperature fusion with coke and silica yields the element:

$$2Ca_3(PO_4)_2{\cdot}2H_2O + 6SiO_2 + 10C \xrightarrow[\Delta]{} 6CaSiO_3 + P_4 + 10CO + 4H_2O$$

  - There are three basic allotropes and many intermediate forms.

- White phosphorous is the most reactive.
  - Contains strained P_4 tetrahedral units held together by van der Waals forces.
  - Exists in two forms α (cubic) and β (hexagonal).

$$\alpha\text{-}P_4 \xrightleftharpoons{> -76.9\ ^{o}C} \beta\text{-}P_4$$

  - Can be stored under water, but oxidizes with a yellow-green glow in air and combusts spontaneously above 50 ºC or when finely divided:

$$P_4 + 5O_2 \rightarrow P_4O_{10} \qquad \Delta H^o = -2940 \text{ kJ/mol}$$

- Black phosphorous is least reactive form, obtained by heat and pressure from white form.
  - Composed of trigonally coordinated atoms in a puckered sheet structure, similar to graphite.
  - Inert in air up to ~400 ºC.

- Red phosphorous, an inert and nontoxic form, is obtained from white by heating in an inert atmosphere at 250 ºC.
  - Sheet structure with a random network.

Group 15 - The Elements - As, Sb, Bi

- Occur in sulfide minerals of Cu, Ag, and Pb.
- All have metallic forms, but As and Sb have unstable nonmetallic yellow forms, obtained by rapid condensation of vapors, that probably contain M_4 units.
- Stable form of all is α-rhombahedral form, similar to black phosphorous.
- Bi is the heaviest element to have a stable, nonradioactive nucleus.

Oxidation States and Bonding

- Principal oxidation states of the group are +5, +3, –3.
  - Nitrogen also has +1, +2, and +4 states, and phosphorous +4 compounds are known, too.
  - Bi does not form compounds with a –3 state.

- Bonding in nitrogen and phosphorous compounds is very different, owing to the different modes of effective bonding available to each.

Mode	N	P
$p\pi$-$p\pi$	strong	unstable
$p\pi$-$d\pi$	rare	weak-moderate
hypervalence	no	yes

Nitrogen Chemistry - Hydrides - Ammonia

- Ammonia, the most important hydride of nitrogen, is made by the Haber process.

$$3H_2 + N_2 \xrightleftharpoons{500\ ^{o}C/250\ atm/Fe} 2NH_3$$

$$\Delta H^o = -92\ kJ,\ \Delta G^o = -33\ kJ$$

  - Liquid NH_3 b.p. = –33.35 °C and $\Delta H_{vap} = 23.677$ kJ/mol.
  - $NH_3(l)$ is a moderately good ionizing solvent.

$$2NH_3 = NH_4^+ + NH_2^- \qquad K = 1.9 \times 10^{-33} \text{ at } -50^oC$$

- In water, NH_3 hydrolyzes to give small amounts of NH_4^+ and OH^-, but there is no evidence for the existence of “ammonium hydroxide, NH_4OH.”

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = 1.78 \times 10^{-5}$$

- Ammonia burns in air to give N_2.

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

  - With Pt catalyst, NO is produced instead.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

  This is the basis of the Ostwald process for making HNO_3.

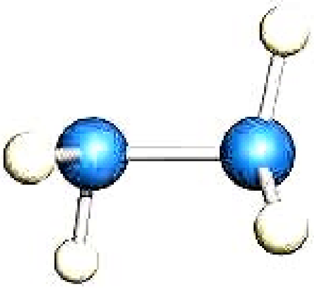
Nitrogen Chemistry - Hydrides - Hydrazine

- N_2H_4 is a fuming liquid that functions as a diacidic base:

  $N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$ $K_1 = 8.5 \times 10^{-7}$

  $N_2H_5^+ + H_2O \rightleftharpoons N_2H_6^{2+} + OH^-$ $K_2 = 8.9 \times 10^{-10}$

- At 25 °C it appears to have a gauche configuration (C_2).



- It is a powerful reducing agent.

  $N_2H_4 + 4OH^- \rightleftharpoons N_2 + 4H_2O + 4e^-$ $-E^o = +1.16$ V

- Hydrazine is made by the Raschig synthesis:

  $2NH_3 + OCl^- \xrightarrow{\text{glue}} N_2H_4 + Cl^- + H_2O$

  - Reaction proceeds quantitatively at 0 °C with a 3:1 ratio of NH_3 and OCl^- by a two-step process:

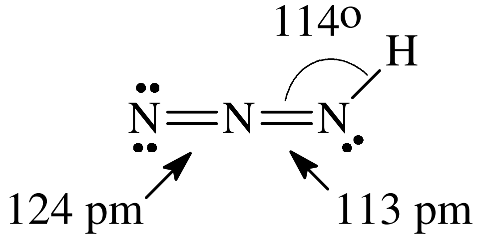
    $NH_3 + NaOCl \rightarrow NaOH + NH_2Cl$ (fast)

    $NH_2Cl + NH_3 + NaOH \rightarrow N_2H_4 + NaCl + H_2O$
  - Chloramine, NH_2Cl, is explosive as a solid or liquid.
  - Without glue (or gelatin) a parasitic reaction predominates:

    $2NH_2Cl + N_2H_4 \rightarrow 2NH_4Cl + N_2$

- Hydrazine is metastable ($\Delta H^o_f = +50$ kJ/mol) and burns in air, sometimes explosively.
  - It is used as rocket fuel.

Nitrogen Chemistry - Hydrides - Hydrazoic Acid



- Hydrazoic acid, HN_3, is a weak acid ($K_a = 1.8 \times 10^{-5}$)

- HN_3 is obtained by ion exchange of solutions of NaN_3, prepared by either of the following syntheses:

$$3NaNH_2 + NaNO_3 \xrightarrow{175\ ^oC} NaN_3 + 3NaOH + NH_3$$

$$2NaNH_2 + N_2O \xrightarrow{190\ ^oC} NaN_3 + NaOH + NH_3$$

- Pure HN_3 (b.p. 37 °C) is explosive, as are heavy-metal or organic azides (e.g., AgN_3, $Pb(N_3)_2$).

- Alkali metal azides decompose smoothly when heated:

$$2NaN_3 \xrightarrow[\Delta]{} 2Na + 3N_2$$

$$3LiN_3 \xrightarrow[\Delta]{} Li_3N + 4N_2 \quad (Li_3N = \text{lithium nitride})$$

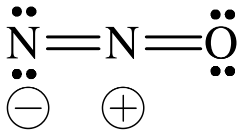
Nitrogen Chemistry - Oxides

- Nitrogen forms at least six oxides, all with $\Delta G^\circ_f > 0$.

- Nitrous oxide, N_2O, is "laughing gas", made by heating ammonium nitrate.

$$NH_4NO_3 \xrightarrow[\Delta]{} N_2O + 2H_2O \qquad \Delta H^\circ = -26\text{ kJ}$$

  - Isoelectronic with CO_2 and also linear ($C_{\infty v}$).



  - $\Delta G^\circ_f = +103.6$ kJ/mol, but it is kinetically quite inert (i.e., metastable).

  - Propellant for whipped cream (pH neutral, moderately soluble in cream; FDA approved)

☞ Thermal decomposition of NH_4NO_3 at moderate temperature yields N_2O, but at high temperature it decomposes explosively by the following reaction:

$$NH_4NO_3 \xrightarrow[\Delta]{} N_2 + \tfrac{1}{2}O_2 + 2H_2O \qquad \Delta H^\circ = -206\text{ kJ}$$

- Nitric oxide, NO, is a colorless paramagnetic gas produced in a number of oxidations with NO_2^- and NO_3^-.
  - Bond order is 2.5: $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2(\pi^*_{2p})^1$
  - A lab preparation is

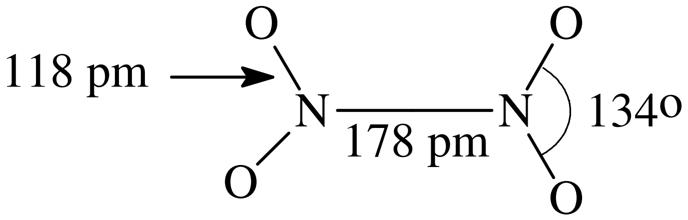
$$3KNO_2 + KNO_3 + Cr_2O_3 \xrightarrow[\Delta]{\text{melt}} 2K_2CrO_4 + 4NO$$

Nitrogen Chemistry - Oxides (cont.)

- NO readily oxidizes in air to nitrogen dioxide, NO_2, which exists in equilibrium with its dimer.

$$\underset{\text{colorless}}{N_2O_4} \rightleftharpoons \underset{\text{brown}}{2NO_2} \qquad \Delta H^\circ = 57 \text{ kJ/mol}$$

  - $K = [N_2O_4]/[NO_2]^2 = 0.67$ @25 °C.
  - NO_2 is a free radical
  - Both forms are toxic components of smog.
  - The dimer has a long N–N bond.



  - MO calculations indicate a σ pair delocalized over the entire molecule.

Nitrogen Chemistry - Oxides (cont.)

- N_2O_3 and N_2O_5 are formal anhydrides of HNO_2 and HNO_3, respectively.

- N_2O_3 is an intense blue liquid, formed by oxidation of NO, which is not stable above –30 ºC.

$$4NO + O_2 \xrightarrow{< -30\ ^{o}C} 2N_2O_3$$

- N_2O_5 (m. 30 ºC, d. 47 ºC) can be made by dehydrating HNO_3 with P_4O_{10}.

$$12HNO_3 + P_4O_{10} \rightarrow 6N_2O_5 + 4H_3PO_4$$

It is unstable (sometimes exploding) and is obtained by distillation in a stream of ozonized oxygen.

Nitrogen Oxoacids - HNO_2

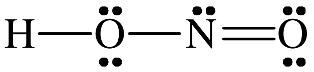
- Nitrous acid, HNO_2, can be obtained in solution by acidifying solutions of nitrites:

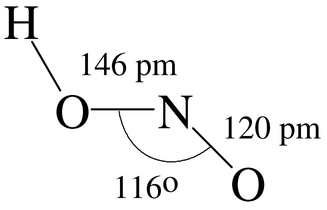
$$Ba(NO_2)_2(aq) + H_2SO_4(aq) \rightarrow 2HNO_2(aq) + BaSO_4(s)$$

- HNO_2 is unstable and has not been obtained pure:

$$3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$$

- Structurally it is HONO, a bent molecule (C_s) having structural parameters consistent with its Lewis structure and VSEPR predictions.





- It is a weak acid with $K_a = 6.03 \times 10^{-6}$.

- Nitrites can function as oxidants or reductants:

$$HNO_2 + H^+ + e^- \rightarrow NO + H_2O \qquad E^\circ = 1.0\ V$$

$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^- \qquad -E^\circ = -0.94\ V$$

- Nitrite salts are obtained by reducing nitrates:

(Chile saltpeter) $2NaNO_3 \xrightarrow[\Delta]{} 2NaNO_2 + O_2$

(saltpeter) $KNO_3 + Pb \xrightarrow[\Delta]{} KNO_2 + PbO$

Nitrogen Oxoacids - HNO_3

- Nitric acid is made by a variety of processes.
- Today, most HNO_3 is made by acidifying saltpeter in concentrated sulfuric acid, followed by distillation.

$$2KNO_3 + \text{conc-}H_2SO_4 \xrightarrow{0\ ^oC} 2HNO_3 + K_2SO_4$$

- The classic synthesis is the Ostwald process:

$$4NH_3 + 5O_2 \xrightarrow[Pt]{750\text{-}850\ ^oC} 4NO + 6H_2O \qquad \Delta H = -1170\text{kJ}$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

  - NO produced in the third step is recycled for use in the second.
  - Product is concentrated to 70% (16 M) by distillation.

- HNO_3 photo-decomposes, causing the reagent to turn brown after prolonged exposure to light.

$$4HNO_3 \xrightarrow{h\nu} 4NO_2 + 2H_2O + O_2$$

- HNO_3 is not only a strong acid but also a strong oxidant.

$$4H^+ + NO_3^- + 3e^- \rightarrow NO + 2H_2O \qquad E^o = +0.96\ \text{V}$$

  - Below 2M there is little oxidizing ability, and it behaves like any other strong acid.

Nitrogen Halides

- The following pure halides are known: NF_3, NCl_3, N_2F_4, NF_2Cl, $NFCl_2$, XN_3 (X = F, Cl, Br, I).
  - All except NF_3 are metastable.

- Unlike NH_3, NF_3 is a poor Lewis base due to the polarity of the N–F bonds.

- NBr_3 and NI_3 exist as ammonia complexes, which are shock sensitive explosives.

$$5NH_3(aq) + 3I_2 \xrightarrow{NH_3(aq)} NI_3\cdot NH_3 + 3NH_4I$$

Compounds of P, As, Sb, Bi - Hydrides

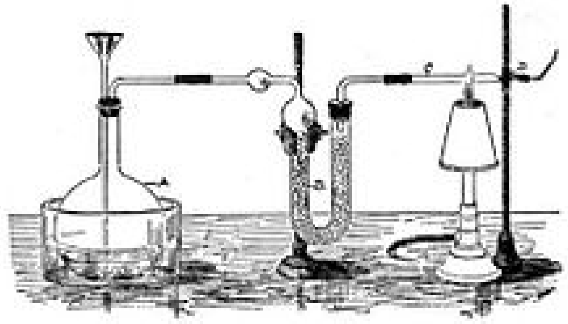
- All MH_3 hydrides are known.
  - Stability falls off rapidly through the series, and SbH_3 and BiH_3 exist in only trace amounts.

- The Marsh test, a classic qualitative test for the presence of arsenic, is based on the thermal instability of arsine.

$$4Zn(s) + 8H^+(aq) + H_3AsO_4(aq) \rightarrow AsH_3(g) + 4Zn^{2+}(aq) + 4H_2O(l)$$

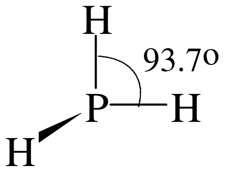
$$2AsH_3(g) \xrightarrow[\Delta]{} 2As(s) + 3H_2(g)$$

  - As(*s*) forms as a silver mirror on the walls of a heated tube through which the gas is passed.



- Unlike NH_3, these other hydrides are neither acid nor base in water.

- Although pyramidal (C_{3v}) they have small bond angles consistent with LCP considerations and a *p*-only bonding model.



  - Less accessible 3*s* lone pair on P makes PH_3 a poorer Lewis base than NH_3.

Compounds of P, As, Sb, Bi - Halides

- Both MX_3 and MX_5 halides can be formed by direct combination.

- Except PF_3, all MX_3 halides hydrolyze in water.
  - PX_3 and AsX_3 hydrolyze to the +3 oxoacids:

    $PX_3 + 3H_2O \rightarrow 3HX + H_3PO_3$ (not PF_3)

    $AsX_3 + 3H_2O \rightarrow 3HX + H_3AsO_3$
  - SbX_3 and BiX_3 hydrolyze to give solutions containing the antimonyl and bismuthyl cations, respectively.

    $SbX_3 + H_2O \rightarrow 2HX + SbO^+ + X^-$

    $BiX_3 + H_2O \rightarrow 2HX + BiO^+ + X^-$

- The MX_5 halides include MF_5, PCl_5, PBr_5, and $SbCl_5$.
  - PX_5 halides hydrolyze to H_3PO_4, the +5 oxoacid.

    $PX_5 + 4H_2O \rightarrow H_3PO_4 + 5HX$
  - In limited water, phosphoryl halides are formed as molecular species.

    $PX_5 + H_2O \rightarrow POX_3 + 2HX$

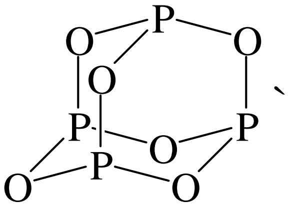
  - Organic derivatives of phosphoryl halides can be formed:

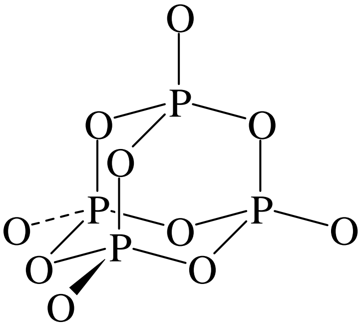
    $POX_3 + 3ROH \rightarrow (RO)_3PO + 3HX$

    $POX_3 + 3RMgX \rightarrow R_3PO + 3MgX_2$

Phosphorous Oxides and Oxoacids

- When P_4 is burned, either P_4O_6 or P_4O_{10} is formed, depending on the oxygen supply.
  - Both structures have T_d symmetry.





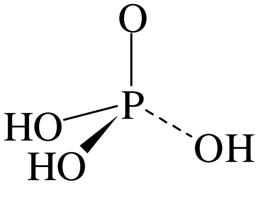
- Adding P_4O_{10} to water gives several oxoacids, most importantly *orthophosphoric* acid, H_3PO_4 (usually called *phosphoric* acid).

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4 \text{ (+ others)}$$

  - In addition to P_4O_{10} hydrolysis, H_3PO_4 is commercially prepared as follows:

$$Ca_3(PO_4)_3 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4$$

  - Phosphoric acid is supplied as an 85% solution with a syrupy consistency.
  - The structure is C_{3v}.



  - H_3PO_4 is triprotic:

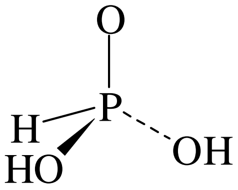
$$K_1 = 7.5 \times 10^{-3},\ K_2 = 6.2 \times 10^{-8},\ K_3 = 4.2 \times 10^{-13}$$

Phosphorous Oxides and Oxoacids (cont.)

- Adding P_4O_6 to water gives *orthophosphorous* acid (also called *phosphorus* acid or *phosphonic* acid).

  $$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$$

  - H_3PO_3 is a deliquescent, clear solid.
  - It has a tetrahedral structure with a non-acidic P–H bond (C_s).



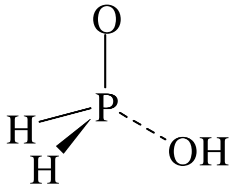
  - H_3PO_3 is a diprotic acid:

  $$K_1 = 1.6 \text{ x} 10^{-2}, K_2 = 7 \text{ x } 10^{-7}$$

- *Hypophosphorous* acid (also called *phosphinic* acid), H_3PO_2, is obtained as a white solid following oxidation of PH_3 with I_2 in water:

  $$PH_3 + 2I_2 + 2H_2O \rightarrow H_3PO_2 + 4HI$$

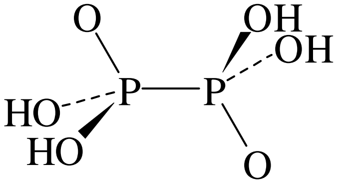
  - It has a tetrahedral structure (C_s) with two non-acidic P–H bonds.

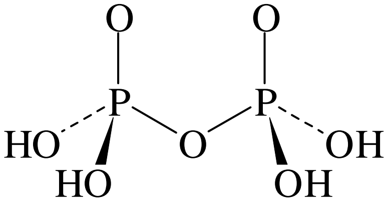


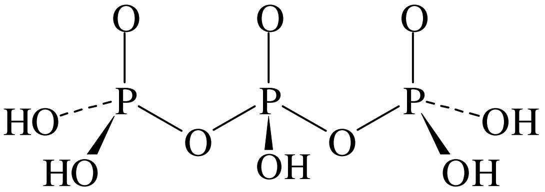
  - H_3PO_2 is a monoprotic acid with $K \approx 10^{-2}$.

Higher Phosphoric Acids and Anions

Formula	Name	pK_1	pK_2	pK_3	pK_4	pK_5
$H_4P_2O_6$	hypophosphoric	2.2	2.8	7.3	10.0	—
$H_4P_2O_7$	pyrophosphoric	0.85	1.49	5.77	8.22	—
$H_5P_3O_{10}$	triphosphoric	<0	0.89	4.09	6.98	9.93







Oxides and Oxoacids of As, Sb, Bi

- As, Sb, and Bi form the +3 oxides when burned in air (n.b., greater stability of lower state for heavier group 15 elements).
  - As_4O_6 and Sb_4O_6 are molecular and isostructural with P_4O_6.
  - Bi_2O_3 is ionic

- As and Sb +5 oxides are *not* isostructural with P_4O_{10}, and their formulas are usually written As_2O_5 and Sb_2O_5.

- Arsenic acid, H_3AsO_4, is analogous to H_3PO_4 but somewhat weaker.

  $$K_1 = 5.6 \text{ x } 10^{-3}, K_2 = 1.0 \text{ x } 10^{-7}, K_3 = 3.0 \text{ x } 10^{-12}$$

  - As the Marsh test suggests, it is a moderately strong oxidizing agent.

  $$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons H_3AsO_3 + H_2O \qquad E^\circ = +0.559 \text{ V}$$

- Arsenous acid, H_3AsO_3, functions as a monoprotic acid with $K_a = 5.1 \text{ x } 10^{-10}$.
  - Raman spectra show that in acidic solutions of As_4O_6 the only detectable species is pyramidal $As(OH)_3$ (C_{3v}).