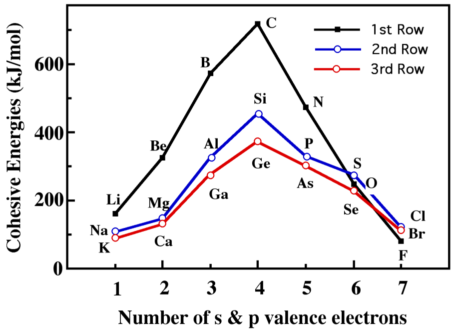
Groups 15-17 elements

CHEM 102
T. Hughbanks

Trends in atomization energies



Explanation?

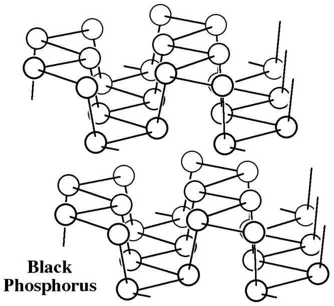
Group 15 Elements

- Range from electronegative nitrogen to somewhat electropositive Bi
- Atomic configurations ns^2np^3
- Bonding in the elements is strong and p orbital participation in bonding is dominant. sp^2 (N) and sp^3 hybridization is common in compounds. Bi in oxidation state III common ("inert pair" effect).

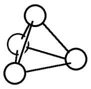
Elemental properties . . .

	melting pts. °C	boiling pts. °C	Density (g•cm^{3})	Form, properties
N	-210	-196	1.04(*l*)	colorless gas
P	44	660	1.82	Nonmetal, many forms
As	613(s)	sublimes	5.78	gray semimetal
Sb	631	1750	6.69	Blue-white, shiny semimetal
Bi	271	1650	8.90	metallic

Forms of phosphorus

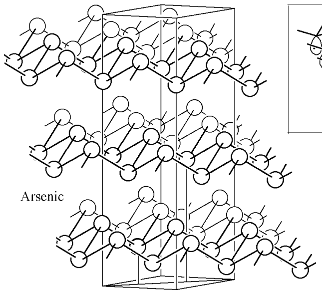


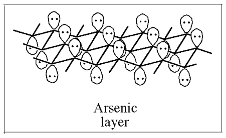
Black Phosphorus

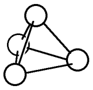


White Phosphorus

Arsenic

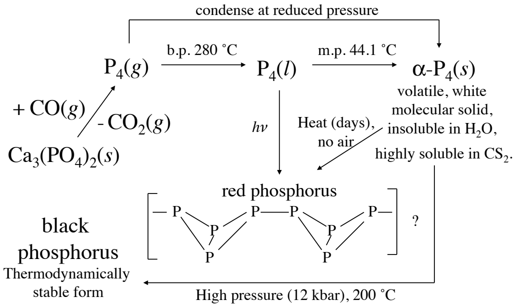






Gas phase

The story of phosphorus



Group 15 hydrogen compounds

NH_3	PH_3	AsH_3	SbH_3	BiH_3
391	322	247	255	A-H bond strength

decreasing basicity →

decreasing stability →

- Some laboratory ways to make ammonia:

$$6\,Li + N_2 \rightarrow 2\,Li_3N \xrightarrow{H_2O} 6\,Li(OH) + NH_3$$

$$6\,Al + N_2 \rightarrow 2\,AlN \xrightarrow{H_2O} Al(OH)_3 + NH_3$$

- Industrial method: Haber process (Fe/Fe_3O_4 catalyst). More moles of NH_3 produced than any other industrial chemical.
- NH_3 has some similarities to water, but is less polar and has a smaller self-ionization constant ($\sim 10^{-30}$ at -50 °C).

Haber process - reality check!

- All the following are important in the modern process:
  - $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3\,H_2(g)$ ~750°C, 40 atm
  - $ZnO(g) + H_2S(g) \rightarrow ZnS(s) + H_2O(g)$ remove H_2S from CH_4
  - $2\,CH_4(g) + {}^{1}/_{2}\,O_2(g) + 2\,N_2(g) \rightarrow CO(g) + 2\,H_2(g) + 2\,N_2(g)$

    Removes oxygen from added air ($\sim {}^{1}/_{2}\,O_2(g) + 2\,N_2(g)$)
  - $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$

    Converts CO to CO_2 (removable) and makes more H_2
  - $N_2(g) + 3\,H_2(g) \rightleftarrows 2\,NH_3(g)$

    $\Delta H^\circ = -92.2$ kJ/mol ; $K_{298} = 6.8 \times 10^5$

    Reactants are finally pure.

    Process conducted at 400-500 °C, 100 - 1000 atm

Nitrogen vs. Phosphorus, As, Sb

- N-X π bonding important
  - 3- and 2-coordination is common in multiple bonding to X = N, C, O
- P-X pπ-pπ bonding is weak
  - 3 single bonds + lone-pair or 4 single bonds (cation) both common.

  Eg., N_2 vs. P_4 or other forms of phosphorus, or As

  N_2O_5 vs. P_4O_{10}

Nitrogen vs. Phosphorus, As, Sb

- Nitrogen chemistry strongly influenced by stability of N_2, so 'fixing' of nitrogen a major chemical challenge
  - Many compounds have positive heats of formation
- for phosphorus, bonds to oxygen are important, P-P bonds tend to be reactive
  - no natural occurence of P-P bonds (not too difficult to synthesize, however)

Some important N/O compounds

- $NH_4NO_3(s) \rightarrow N_2O(g) + 3\,H_2O(g)$ ~250 °C

  N_2O: Useful anesthetic (laughing gas)
  - $4\,NH_3(g) + 5\,O_2(g) \rightarrow 4\,NO(g) + 6\,H_2O(g)$

    ~1000 °C, Pt catalyst (neurotransmitter)
- $2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$ rapid in air

  Significant pollutant, in eq. with $N_2O_4(g)$
- $3\,NO_2 + H_2O(l) \rightarrow NO(g) + 2\,HNO_3(aq)$

Steps shown are the Ostwald process for nitric acid.

P/O compounds

- $P_4(s) + 3\ O_2(g) \rightarrow P_4O_6(s)$ Limited oxidation
- $P_4(s) + 5\ O_2(g) \rightarrow P_4O_{10}(s)$ excess air

Both are subject to Hydrolysis to give acids

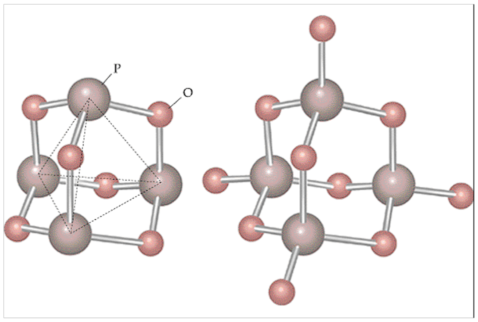
- Opening up of P-O-P bridges is highly exothermic in reactions with water.

Biologically very important:

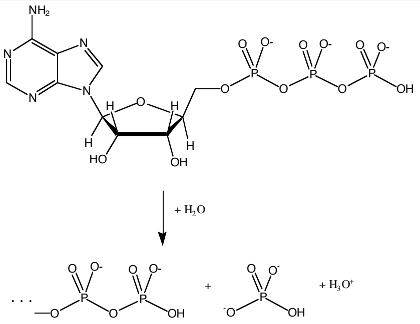
$ATP + H_2O \rightarrow ADP + HPO_4^{2-} + H_3O^+$

Adenosine triphosphate

P_4O_{10} (P_2O_5) and P_4O_6



Hydrolysis of ATP



Lewis basicity

- The electron-pair donating property of ammonia, amines, and phosphines is important in the chemistry of these compounds in reactions with metals.

Halogen compounds of Group 15

- NF_3 is stable, NCl_3 is reactive (bleach for flour), neither is very basic.
- Halides of P, As, and Sb are important laboratory chemicals: AX_3 and AX_5 forms are both important.
- PCl_3 and PBr_3 are reactive and useful as starting materials to other P-containing compounds. PF_3 more stable.
- PF_5, PCl_5, AsF_5, SbF_5, $SbCl_5$ are strong Lewis acids.

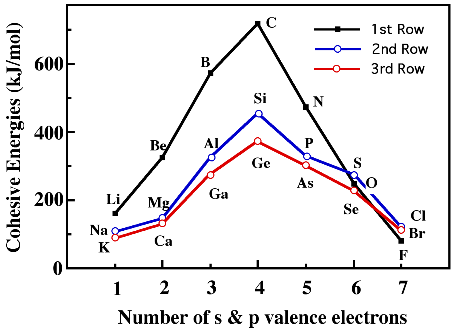
Group 16 - general characteristics

- Range from highly electronegative oxygen to metalloid Te
- Atomic configurations $ns^2\ np^4$
- pπ-pπ bonding is again most important for the first element, oxygen. With six valence electrons, in most molecules these atoms bear from 1 to 3 lone pairs and hence have fewer bonds.

Physical properties

	melting pts. °C	boiling pts. °C	Density (g•cm³)	Form, properties
O	-219	-182	1.27(*l*)	diatomic gas
S	119 (monoclin.)	440	2.06 (rhom.)	Yellow, S_8 rings, S_∞ chains
Se	220 (gray)	688	4.82	Gray, Se_8 rings, Se_∞ chains
Te	450	1390	6.25	Te_∞ chains
Po	radioactive			semimetallic, cubic

Trends in atomization energies



Explanation?

- Basic Oxides ("Ionic")

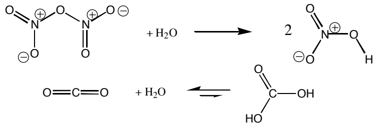
  Alkali, alkaline-earth, and other electropositive metal oxides, e.g.,

  $CaO + 2\ H_2O \rightarrow Ca^{2+}(aq) + 2\ OH^{-}(aq)$

  $[O^{2-} + H_2O \rightarrow 2\ OH^{-}(aq), \quad K > 10^{22}]$

- Acidic Oxides ("Covalent") - Acid anhydrides

  Element-oxygen bond not broken on dissolution in water. Either an E-O-E bridge is hydrolyzed or water is added across a double bond. e.g.,



Acidic Oxides - more

- Oxide → Acid

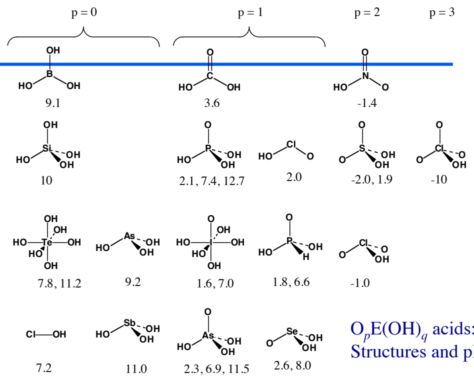
  $SO_3 \rightarrow H_2SO_4 = (O)_2S(OH)_2$

  $SO_2 \rightarrow$ "H_2SO_3" $= (O)S(OH)_2$ (not isolated)

  $P_4O_{10} \rightarrow H_3PO_4 = (O)P(OH)_3$

  $P_4O_6 \rightarrow H_3PO_3 = H(O)P(OH)_2$

  $N_2O_5 \rightarrow 2\ HNO_3 = (O)_2N(OH)$



$O_pE(OH)_q$ acids: Structures and pK_a's

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Properties

	m. p. ˚C	b. p. ˚C	Density (g•cm^3)	Description
F	-219	-182	1.513 (*l*, -188˚C)	pale yellow diatomic gas
Cl	-101	- 34	1.655 (*l*, -70˚C)	greenish-yellow diatomic gas
Br	-7.3	59.5	3.187	blood-red diatomic liquid
I	114	185	3.96	deep-purple diatomic solid
At	radioactive			

Halide Chemistry

- We have already discussed several compounds with halides in earlier lectures
- The elements are unremarkable: all have diatomic molecular structures, X_2, but intermolecular forces increase moving down the series.
- Halide compounds are important intermediates to other compounds.

Methods of preparing halides

- Direct reaction, useful for highest ox. state,

e.g., (M = Si, Ge, Sn, Ti, Zr) $\quad M(s) + X_2 \rightarrow MX_4$

or (M = Al, Ga, In, Sc, Y) $\quad M(s) + {}^3/_2 I_2 \rightarrow MI_3$

Higher ox. states favored by more electronegative X:

$Mo(s) + \text{excess } Cl_2 \rightarrow MoCl_5$

$Mo(s) + \text{excess } Br_2 \rightarrow MoBr_3$

$Fe(s) + \text{excess } X_2 \rightarrow FeX_3 \quad (X = Cl, Br)$

$Fe(s) + \text{excess } I_2 \rightarrow FeI_2$ (FeI_3 unknown)

More Methods of preparing halides

- Reaction with HX, useful for lower ox. state (why?),

e.g., $\quad Sn(s) + \text{conc. aq. HI} \rightarrow SnI_2$

$Cr(s) + 2HCl(g) \rightarrow CrCl_2$ - at red heat

compare: $Cr(s) + {}^3/_2 Cl_2 \rightarrow CrCl_3$ - 600 ˚C

- Dehydration, e.g.,

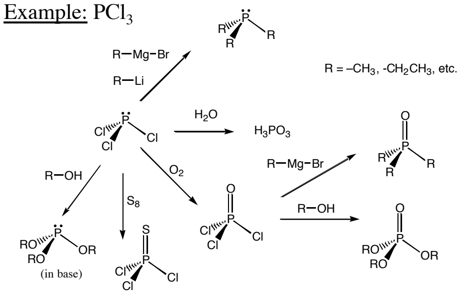
$MnCl_2 \bullet 4H_2O + \text{excess } SOCl_2(l) \rightarrow$

$MnCl_2(s) + SO_2(g) + HCl(g)$

[note: $SOCl_2(l) + H_2O(l) \rightarrow SO_2(g) + HCl(g)$]

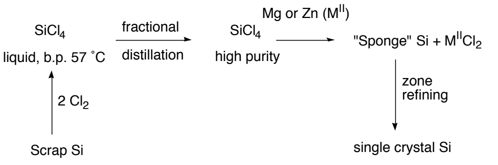
Halides often the route to other compounds

- Example: PCl_3



Halides often used as volatile intermediates

- Example: Silicon production



Scrap Si $\xrightarrow{2\ Cl_2}$ $SiCl_4$ liquid, b.p. 57 ˚C $\xrightarrow[\text{distillation}]{\text{fractional}}$ $SiCl_4$ high purity $\xrightarrow{\text{Mg or Zn } (M^{II})}$ "Sponge" Si + $M^{II}Cl_2$ $\xrightarrow{\text{zone refining}}$ single crystal Si

Fluorine vs. others; bond energy comparison

Typical average bond energies to halogens, kJ/mol

X	XX	HX	BX_3	AlX_3	CX_4
F	158	574	645	582	456
Cl	243	428	444	427	327
Br	193	363	368	360	272
I	151	294	272	285	239