Group 13 (3A) - The Elements - Boron

- Boron is a hard, crystalline, black, semimetal found in borate ores such as borax, $Na_2B_4O_5(OH)_4 \cdot 8H_2O$, found in vast deposits in Death Valley, Nevada & California.

- The element boron has powerful abilities to strengthen, toughen and make fire-resistant glasses, metals, wood, and fibers. It is used in approximately three hundred high-tech products. A few of its uses are as soldering flux, in welding rods, as preservatives for wood and fabric, as fire retardant, in insecticides, in pottery glaze, as antiseptics, in hybrid fuels, and in experimental fuel cells.[1]

- Impure boron is obtained by reduction of the oxide with Mg, followed by washing with alkali, HCl(*aq*), and HF(*aq*).

$$B_2O_3 + 3Mg \xrightarrow[\Delta]{} 3MgO + 2B \text{ (~95\% pure)}$$

- High purity boron is obtained with difficulty by pyrolysis or reduction of a halide over a hot Ta, W, or BN surface.

$$2BI_3(g) + 3H_2(g) \xrightarrow[800\text{-}1000^\circ C]{Ta} 2B(s) + 6HI(g)$$

---

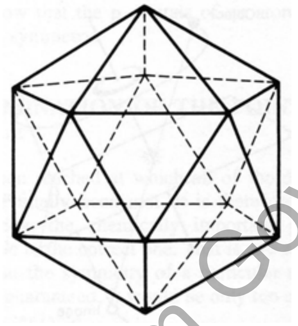
[1] Death Valley National Park website: http://www.nps.gov/deva/faqs.htm

Boron Physical and Chemical Properties

- Boron is very non-reactive and high melting (m.p. = 2300 °C), making it useful for fire resistant and high-temperature applications.

- Naturally occurring boron consists of two stable isotopes, ^{10}B (19.6%) and ^{11}B (80.4%).

- Boron has several crystal forms, all containing B_{12} icosahedra (I_h).



  - Individual icosahedra are linked by $3c$-$2e$ bonds.

- Boron, boron nitride (BN), and carborundum (BC), have hardness approaching diamond.

  Mohs scale: diamond = 10, BC = 9.3

- BN has forms isomorphous with diamond and graphite, but it resists oxidation up to 800 °C.

Group 13 (3A) - The Elements - Aluminum

- Aluminum is the third most abundant element and the most abundant metal.
  - Samples of it were rare before the Hall process.

- Charles M. Hall in 1886 developed a technique for electrolyzing poorly conductive fused bauxite (Al_2O_3) by adding cryolite (K_3AlF_6).

$$Al_2O_3 \xrightarrow[K_3AlF_6/\text{elect.}]{1000^{o}C} 4Al + 3O_2$$

  - Canada is the principal source of bauxite for American use.

- Al is an active metal.

$$\begin{array}{lll} 2(Al & \rightarrow Al^{3+} + 3e^{-}) & -E^{o} = 1.66\ V \\ 3(2H_2O + 2e^{-} & \rightarrow H_2 + 2OH^{-}) & E^{o} = -0.83\ V \\ \hline 6H_2O + 2Al & \rightarrow 3H_2 + 6OH^{-} + 2Al^{3+} & E^{o}_{cell} = 0.83\ V \end{array}$$

- Aluminum in contact with air immediately forms an amphoteric oxide coating that passivates the metal.
  - In acid or base the coating dissolves and the metal becomes reactive.

$$Al_2O_3 + 2OH^{-} + 3H_2O \rightarrow 2Al(OH)_4^{-}$$

$$Al_2O_3 + 6H^{+}(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O$$

  - With the oxide coating removed, Al shows typical active-metal reactivity with acid.

$$2Al(s) + 6H^{+}(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$$

- The very exothermic heat of formation of Al_2O_3 ($\Delta H^{o}_{f} = -1670$ kJ/mol) is the driving force of the Goldschmidt or thermite reaction.

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe \qquad \Delta H^{o} = -849\ \text{kJ/mol}$$

Group 13 (3A) - The Elements - Gallium, Indium, Thallium

- Ga, In, and Tl are rare elements.

- All are soft, white, lustrous, and reactive metals with long liquid ranges.
  - Ga has longest known liquid range: m.p. = 30 °C, b.p. = 2071 °C.
  - Ga(*l*) wets glass, like H_2O, and expands below its m.p.

- Obtained by electrolysis of aqueous solutions of their salts.

Ion	Ga^{3+}	In^{3+}	Tl^{3+}	Tl^{+}
E^o (V) $M^{n+} \rightarrow M$	–0.549	–0.3382	0.741	–0.3363

$E(H_2O) = -0.42$ V @ pH 7

  - Ga^{3+} can be reduced from aqueous solution, despite an unfavorable E^o, because of a high hydrogen over-voltage on Ga.

Group 13 Bonding

Ionic Radii of Group 13 Elements

	B	Al	Ga	In	Tl
r^+ (pm)	—	—	113	132	140
r^{3+} (pm)	20	50	62	81	95

- The group-characteristic oxidation state is +3, but +1 becomes more important down the group.
  - The stable state of thallium is +1.

$$Tl^{3+} \xrightarrow{+1.247\text{ V}} Tl^{+} \xrightarrow{-0.336\text{ V}} Tl^{o}$$

  - Tl^+ has an ionic radius intermediate between K^+ (133 pm) and Rb^+ (148 pm), resulting in very similar ionic chemistry.

- In the +3 state, all have high charge density, so compounds have significant covalent character.

- All boron compounds are covalent, although some (e.g., BF_3) have very polar bonds.
  - The B–F bond is the strongest known single bond (D = 757 kJ/mol).
  - There is no ionic boron chemistry.

- Only Al_2O_3 and AlF_3 are considered ionic among Al compounds.

Oxidation State and the "Inert Pair Effect"

- Increasing stability of the lower state for heavier group elements in group 13 and succeeding groups is sometimes called the "inert pair effect" for the reluctance to lose the *ns*^{2} pair.
  $\mathrm{Tl}\ [\mathrm{Hg}]6s^26p^1 \rightarrow \mathrm{Tl}^+\ [\mathrm{Hg}]6s^2 \rightarrow \mathrm{Tl}^{3+}\ [\mathrm{Hg}]$

- Increasing stability of the lower state is the result of rapidly declining bond strength and less rapidly declining ionization energy going down the group.
  - Poor shielding by filled $(n\text{-}1)d^{10}$ subshell makes ionization energies of Ga, In, Tl comparable to Al.
  - Very poor shielding of $4f^{14}$ subshell makes ionization energies of Tl greater than In, despite larger size.

Ionization Enthalpies (kJ/mol)

	B	Al	Ga	In	Tl
$M \rightarrow M^+$	800.6	577.5	578.8	558.3	589.4
$M \rightarrow M^{3+}$	6885	5139	5521	5083	5439

Mean Bond Enthalpies (kJ/mol)[2]

	H	F	Cl	Br	I
B	334	757	536	423	220
Al	284	664	511	444	370
Ga	274	577	481	444	339
In	243	506	439	414	331
Tl	188	445	372	334	272

---

[2] Data from P. Atkins, T. Overton, J. Rourke, M. Weller, and F. Armstrong, *Inorganic Chemistry*, 4th ed., Freeman, NY, 2006, p. 289.

Ions in Solution

- In aqueous solution, all M^{3+} ions are acidic, although $B^{3+}(aq)$ does not exist.

Ion	K_a
$[B(H_2O)_3^{3+}]$	$>>10^{+3}$ (?)
$Al(H_2O)_6^{3+}$	1.12×10^{-5}
$Ga(H_2O)_6^{3+}$	2.5×10^{-3}
$In(H_2O)_6^{3+}$	2.0×10^{-4}
$Tl(H_2O)_6^{3+}$	$\sim 1 \times 10^{-1}$

- Greater acidity of heavier ions is due to poor shielding by underlying *d* subshells (Ga^{3+}, In^{3+}, Tl^{3+}) and 4*f* subshell (Tl^{3+}).

- If $B(H_2O)_3^{3+}$ existed it would immediately hydrolyze to form boric acid, $B(OH)_3$.

$$B(H_2O)_3^{3+} + 3H_2O \rightarrow B(OH)_3 + 3H_3O^+$$

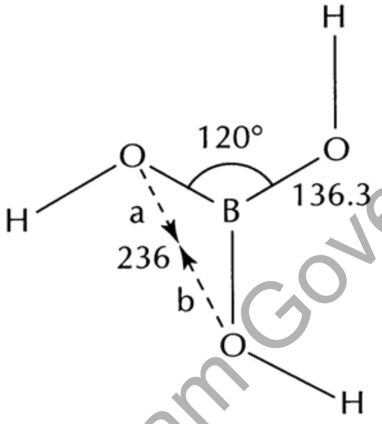
Boric Acid

- Orthoboric acid (boric acid) is unique in its acid hydrolysis, acting as a hydroxide acceptor, rather than a proton donor.

$$B(OH)_3 + 2H_2O \rightleftharpoons B(OH)_4^- + H_3O^+ \qquad pK_a = 9.3$$

- Made in vast quantities commercially by acidification of borax.

- Individual $B(OH)_3$ molecules are planar, C_{3h}.



- In the solid, molecules are linked together in sheets by asymmetric hydrogen bonds, with large separation between sheets (318 pm), similar to graphite.

- $B(OH)_3$ is the expected hydrolysis product of many boron compounds, rather than the hydrated ion as with the other group 13 elements.

$BCl_3 + 3H_2O \rightarrow B(OH)_3 + 3HCl$

$Al_2Cl_6 + 12H_2O \rightarrow 2Al(H_2O)_6^{3+} + 6Cl^-$

Group 13 Hydroxides

- As charge density declines, the hydroxides go from acidic to amphoteric and then to basic.

$B(OH)_3$	$Al(OH)_3$	$Ga(OH)_3$	$In(OH)_3$	$Tl(OH)_3$	$TlOH$
acidic	amphoteric	amphoteric	basic	basic	basic

- Hydrated $Al(OH)_3$ is precipitated as a gelatinous solid whenever Al^{3+}(*aq*) is treated with a base:

$$Al(H_2O)_6^{3+} + 3OH^- \rightarrow Al(H_2O)_3(OH)_3 + 3H_2O$$
$$Al(H_2O)_6^{3+} + 3NH_3 \rightarrow Al(H_2O)_3(OH)_3 + 3NH_4^+$$
$$Al(H_2O)_6^{3+} + 3HCO_3^- \rightarrow Al(H_2O)_3(OH)_3 + 3CO_2 + 3H_2O$$

- A strong base is required to make $Al(OH)_3$ behave as an acid:

$$Al(H_2O)_3(OH)_3 + OH^- \rightarrow Al(H_2O)_2(OH)_4^- + H_2O$$
$$Al(H_2O)_3(OH)_3 + NH_3 \rightarrow \text{no rxn}$$
$$Al(H_2O)_3(OH)_3 + HCO_3^- \rightarrow \text{no rxn}$$

- Treating solutions of In^{3+}(aq) or Tl^{3+}(*aq*) with base only gives the hydroxide:

$$In(H_2O)_6^{3+} + 3OH^- \rightarrow In(H_2O)_3(OH)_3 + 3H_2O$$
$$In(H_2O)_3(OH)_3 + OH^- \rightarrow \text{no rxn}$$

- $Tl(H_2O)_6^{3+}$ (D_{4h}) is so acidic that the hydrous oxide precipitates even at pH 1 – 2.5.

Boron Oxygen Compounds

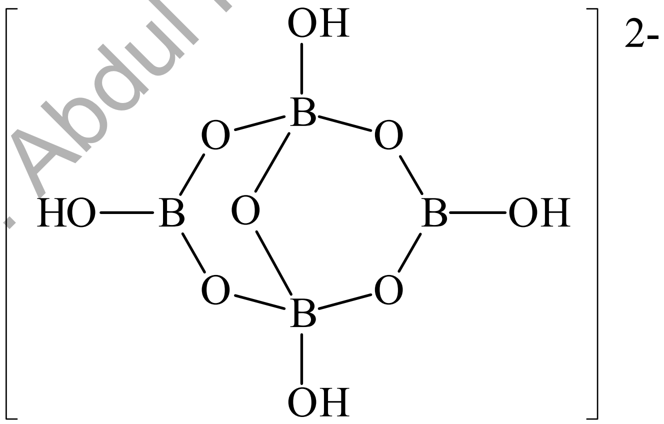
- Boron has a large and complex chemistry, including boron-oxygen compounds.

- The oxide is formed by fusing boric acid:

$$2B(OH)_3 \xrightarrow[\Delta]{} B_2O_3 + 3H_2O$$

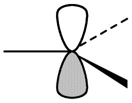
  - B_2O_3 is a glass-like substance with random B_3O_3 rings connected by bridging oxygen atoms.
  - Similarity to SiO_2 structure makes it possible to mix B_2O_3 in glass to make borosilicate glass (Pyrex®).

- Oxoanions contain BO_4 and BO_3 units.
  - The simplest oxoanion is $B(OH)_4^-$, the conjugate base of $B(OH)_3$.
  - In concentrated solutions $B(OH)_4^-$ polymerizes to form a variety of ions, predominated by $B_3O_3(OH)_4^-$.
  - The anion in borax, $Na_2B_4O_5(OH)_4 \cdot 8H_2O$, is $B_4O_5(OH)_4^{2-}$:

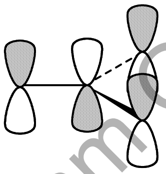


Boron Trihalides

- All trihalides, BX_3 (X = F, Cl, Br, I), have a trigonal planar structure (D_{3h}).
  - The VB model has B with sp^2 hybrids with an "empty" p_z orbital that serves as a site of nucleophilic attack by a Lewis base when BX_3 functions as a Lewis acid.



  - In the MO model, the LUMO is $\pi^*(a_2'')$, which involves overlap of B $2p_z$ with the A_2'' SALC formed from np_z orbitals on the three X atoms.



- Lewis acid strength increases in the order $BF_3 \ll BCl_3 < BBr_3 < BI_3$.
  - With small amounts of water BF_3 forms Lewis acid-base adducts $BF_3{\cdot}H_2O$ and $BF_3{\cdot}2H_2O$, but it does not readily hydrolyze.
  - When small amounts of $BF_3(g)$ are passed through water, a solution of fluoroboric acid results:

$$4BF_3 + 6H_2O \rightarrow 3H_3O^+ + 3BF_4^- + B(OH)_3$$

  - The others hydrolyze completely and vigorously (BI_3 explodes!).

$$BX_3 + 3H_2O \rightarrow B(OH)_3 + 3HX \qquad X = Cl, Br, I$$

Lewis Acid Strength of BX_3 Compounds

- The order of the BX_3 Lewis acid strengths, $BF_3 << BCl_3 < BBr_3 < BI_3$, is contrary to expectations based on steric or electronegativity arguments.

- The "classic" explanation for the order of Lewis acid strengths is the effectiveness of pi bonding as an inhibition to forming CN4 coordination about the boron atom.
  - Calculations suggest that the order of pi-bond strength is $BF_3 > BCl_3 > BBr_3 > BI_3$.
  - Adduct formation of the type $BX_3 + :Y \rightarrow BX_3Y$ results in tetrahedral coordination about B, which precludes effective pi bonding.

- Size alone is not the principal factor, because BF_4^- is quite stable, but BCl_4^- and BBr_4^- can only be stabilized with large cations such as Cs^+ and $N(CH_3)_4^+$.

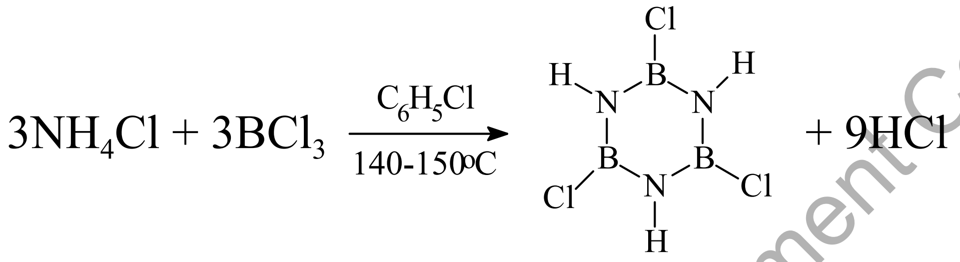
- Low BF_3 acid strength may have more to do with the strength of the B–F bond and the unfavorable thermodynamics to lengthen it in forming tetrahedrally coordinated B in adducts.

- There is no single explanation that is completely satisfying!

Borazines

- Borazines are B–N analogues of benzene.

- B-trichloroborazine, $B_3N_3H_3Cl_3$, can be synthesized by refluxing NH_4Cl and BCl_3 in chlorobenzene:



- Borazine, $B_3N_3H_6$ (b.p. 55°), is formed by reaction of $B_3N_3H_3Cl_3$ with $NaBH_4$.

$$4B_3N_3H_3Cl_3 + 3NaBH_4 \rightarrow 4B_3N_3H_6 + 3NaBCl_4$$

- B-trimethylborazine, $B_3N_3H_3(CH_3)_3$, is formed from $B_3N_3H_3Cl_3$ by reaction with methyl magnesium bromide.

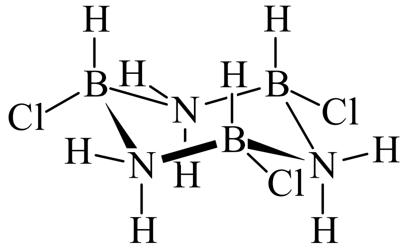
$$B_3N_3H_3Cl_3 + 3CH_3MgBr \rightarrow B_3N_3H_3(CH_3)_3 + 3MgBrCl$$

- Aminoboranes are ethane analogues:

$$CH_3NH_2 + BCl_3 \xrightarrow[\text{boil}]{C_6H_5Cl} Cl_3B\text{–}NH_2CH_3 \qquad \text{m.p. } 126\text{-}128\ ^{\circ}C$$

- Polarity of the B–N bond favors addition over substitution:

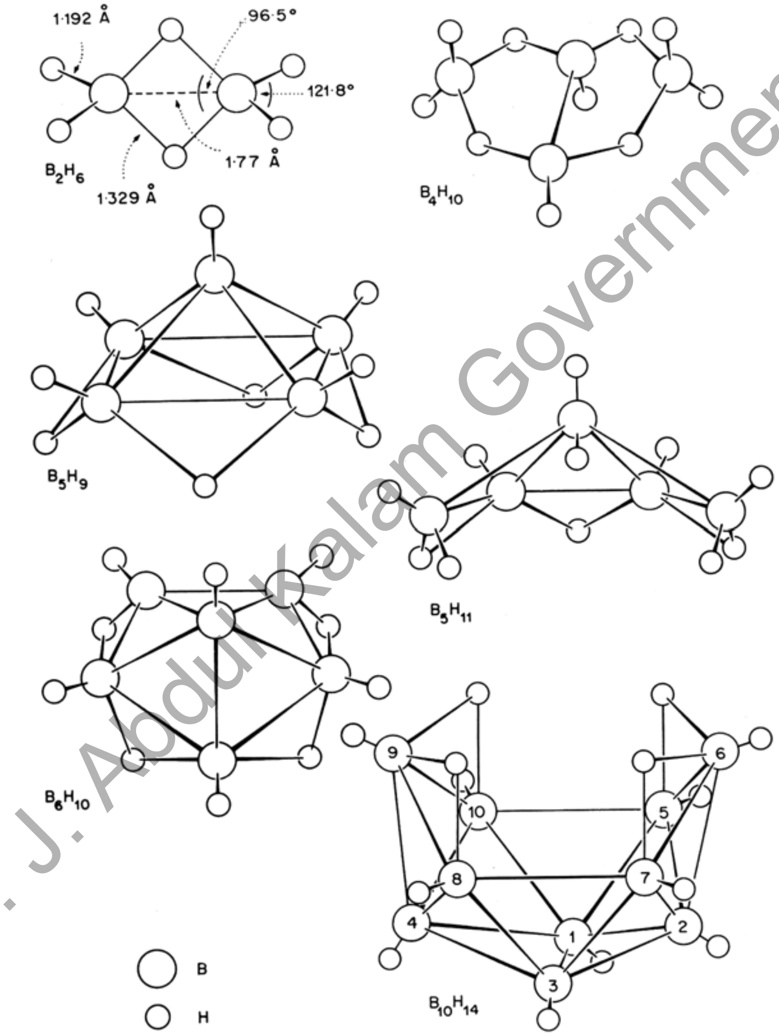
$$B_3N_3H_6 + 3HCl \rightarrow B_3N_3H_9Cl_3$$



B-trichlorocycloborazine

Boranes

- Boranes are boron hydrides, which were first prepared by Alfred Stock in the period 1912-1936, using acidification of MgB_2 to yield a mixture of boranes.
  - Most boranes are flammable, so Stock developed glass vacuum-line apparatus and techniques to do the work.



  - Air flammability decreases with molecular weight, becoming stable at B_6H_{10}, and $B_{10}H_{14}$ is very stable.

  - Most are liquids, but B_2H_6 is a flammable gas, and $B_{10}H_{14}$ is a white solid (m.p 99.7 ^{o}) stable in air.

Synthesis of Boranes

- The simplest isolable borane is diborane(6), B_2H_6, which can be made in quantitative yield in ether at room temperature in a vacuum line:

$$3NaBH_4 + 4BF_3 \xrightarrow{\text{ether}} 2B_2H_6 + 3NaBF_4$$

  - A convenient laboratory synthesis is

$$2NaBH_4 + I_2 \xrightarrow{\text{diglyme}} B_2H_6 + 2NaI + H_2$$

  - Industrial quantities are prepared by the following reaction:

$$2BF_3 + 6NaH \rightarrow B_2H_6 + 6NaF$$

- Thermal decomposition of B_2H_6, resulting in transient BH_3, leads to higher boranes.

$$2B_2H_6 \xrightarrow[\Delta]{} [BH_3] + B_3H_9 \rightarrow \text{higher boranes}$$

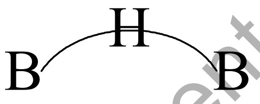
Bonding in Boranes

- Bonding in boranes defies simple VB modeling.

- The following bond types are used to describe borane structures:

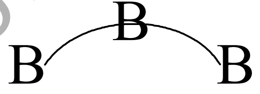
Terminal 2*c*-2*e* boron-hydrogen bond B–H

3*c*-2*e* Hydrogen bridge bond

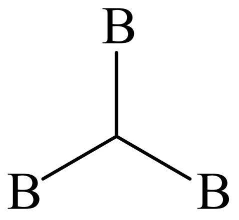


2*c*-2*e* boron-boron bond B–B

Open 3*c*-2*e* boron bridge bond



Closed 3*c*-2*e* boron bond

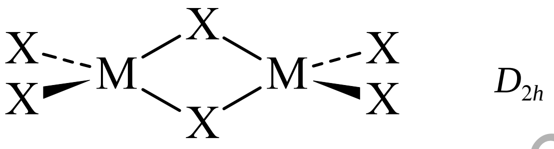


- Complete description requires an MO approach for each compound.

Compounds of Al, Ga, In, Tl

- All trihalides are known, but TlI_3 is $[Tl^+][I_3^-]$.

- Trihalides of Al, Ga, and In are more stable than those of Tl.
  - Fluorides are ionic $[M^{3+}][X^-]_3$.
  - Other trihalides are dimeric with normal 2*c*-2*e* bridge bonds.

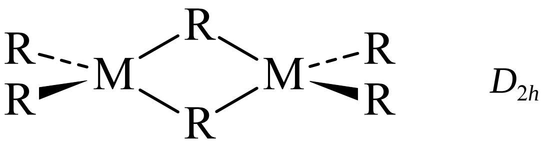


M = Al, Ga, In; X= Cl, Br, I

- Hydrides are limited to simple tetrahedral species; e.g., AlH_4^-, GaH_4^-, $R_3N{:}AlH_3$.

- Allane, AlH_3 may exist in the gas phase, but the solid is polymerized $(AlH_3)_n$.
  - Failure to form analogues to the boranes results from weaker M–M bonds and greater size, which precludes M–H–M bridge bonds.

- Only important organometallic compounds are those of aluminum.
  - With simple R groups, these are dimeric Al_2R_6, with a C of the R group making 3*c*-2*e* bridge bonds.

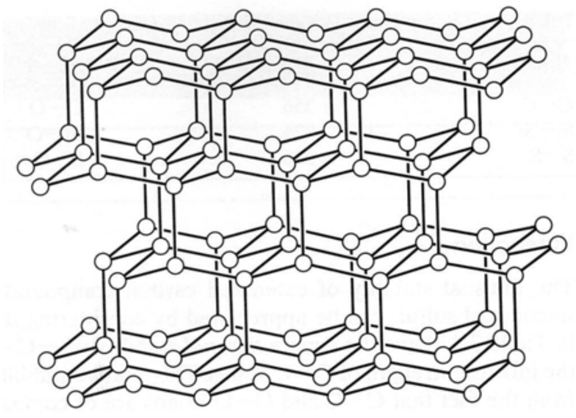


R = CH_3, C_6H_5, cyclo-C_3H_5, $H_2C{=}CH_2$

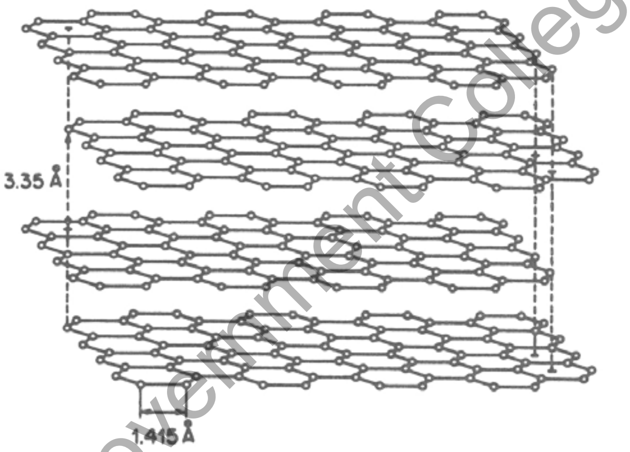
  - Bonding in Al_2R_6 is similar to polymeric $Be(CH_3)_2$.

Group 14 - The Elements
Carbon

- Carbon's two naturally occurring allotropes are graphite and diamond, with graphite the more stable form.



Diamond



Graphite

allotrope	bond order	$d_{\text{C-C}}$ (pm)	ΔH°_{f} kJ/mol	ΔG°_{f} kJ/mol	S° J/mol·K
diamond	1	154	1.88	2.84	2.43
graphite	1⅓	141.5	0	0	5.69

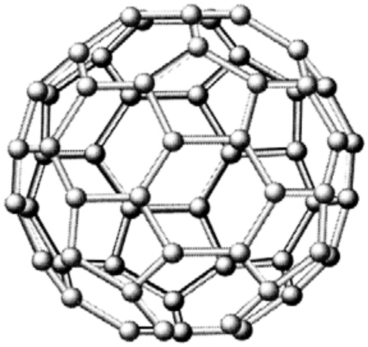
- Graphite is the stable form because it has shorter and stronger bonds, owing to π-delocalization in the hexagonal rings that comprise the sheets.

- Diamond, being a more ordered structure, has lower absolute entropy.

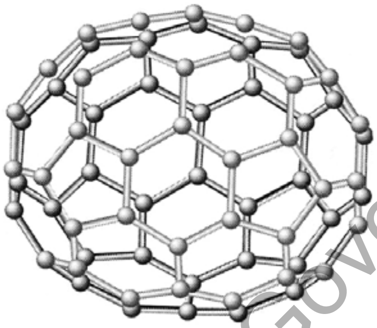
- Although conversion of diamond to graphite is thermodynamically favored, it is kinetically inhibited.

Fullerenes

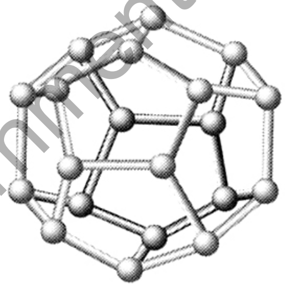
- Fullerenes are a family of allotropes with the formula C_{2n} ($2n = 20, 60, 70, 76, 78, 82, 84, 96$) made by passing a large electrical current through graphite rods in a helium atmosphere, thereby evaporating the rods and producing "fullerene soot."



C_{60} (I_h)



C_{70} (D_{5h})



C_{20} (I_h)

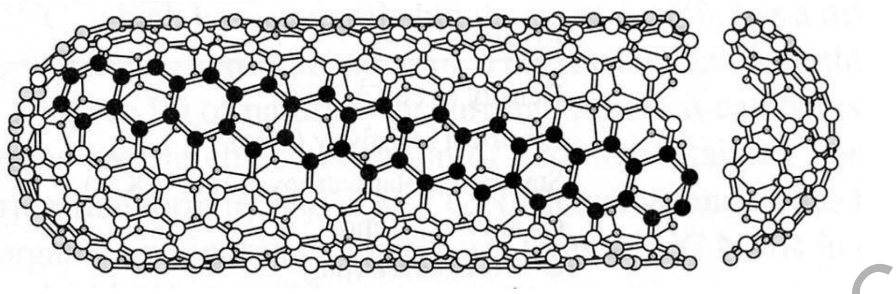
  - The soot is soluble in benzene and other organic solvents, allowing chromatographic isolation of gram quantities of C_{60} and C_{70}, and smaller quantities of other fullerenes.

- All C atoms of C_{60} are equivalent, but there are both single and double bonds with C–C distances of 145.3 pm and 138.3 pm.
  - C_{60} has 20 hexagons and 12 pentagons, like a soccer ball.
  - C_{60} is one of the most strained molecules known, but is kinetically stable.
  - C_{60} decomposes at ~750 °C.

- Fullerenes are less stable than graphite or diamond.

  C_{60} $\Delta H^{o}_{f} \approx 42.5$ kJ/mol $\qquad$ C_{70} $\Delta H^{o}_{f} \approx 40.4$ kJ/mol

Nanotubes



- Carbon nanotubes are prepared by arc-evaporating graphite.
- They are needle-like cylindrical tubes with graphite-structured walls, capped by fullerene-like hemispheres.
- Nanotubes are metallic, semiconducting, or insulating, depending on their preparation.
- Tube ends can be opened by nitric acid and then filled with various metal oxides.

Silicon and Germanium

- Si and Ge are hard and brittle solids with the diamond structure ($d_{\text{Si-Si}}$ = 235 pm).

- Si is the second most abundant element by weight (after oxygen) on earth.
    - Si is found in many minerals and silica (SiO_2 - quartz, sand, etc.).

- Ge is recovered from flue dusts and coal ash.

- Both Si and Ge are important semiconductors.

Tin and Lead

- Tin is found as the mineral cassiterite, SnO_2, in Indonesia, Bolivia, Zaire, Nigeria, Thailand, and China (largest producer).

- Tin has two well characterized allotropes, nonmetallic grey tin (α-Sn) and metallic white tin (β-Sn).

$$\alpha\text{-Sn} \overset{18\ ^{o}C}{\rightleftharpoons} \beta\text{-Sn} \overset{232\ ^{o}C}{\rightleftharpoons} \text{Sn}(l)$$

  - Grey tin ("tin pest") has a diamond structure and is brittle, hard, and fragile.
  - White (metallic) tin has a distorted close-packed structure.

- Sn(*l*) is used in making plate glass.

- Lead only has a *ccp* metallic form.

- Lead is found as its ore galena, PbS, from which the metal can be won by roasting.

$$PbS + O_2 \xrightarrow[\Delta]{} Pb + SO_2$$

Obtaining Si, Ge, Sn, Pb

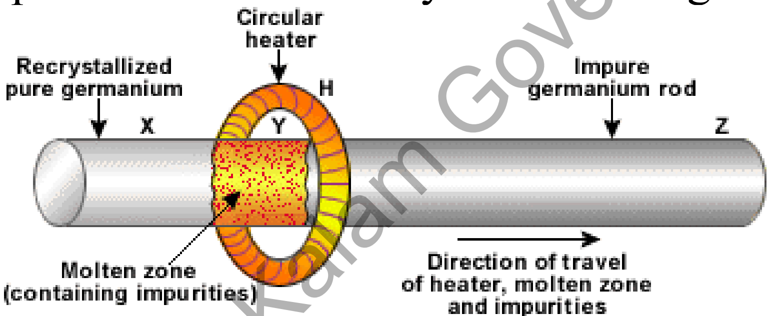
- All can be obtained by reduction of their oxides with carbon.

$$MO_2 + C \xrightarrow[\Delta]{} M + CO_2 \qquad M = Si, Ge, Sn, Pb$$

- Si and Ge can be obtained in high purity for semiconductor use by reduction of the chloride or thermal decomposition of the iodide over a hot Ta wire.

$$SiCl_4 + 2H_2 \xrightarrow{\text{hot Ta wire}} Si + 4HCl$$
$$SiI_4 \xrightarrow{\text{hot Ta wire}} Si + 2I_2$$

- Further purification is done by zone refining.[1]



Zone refining of germanium metal.

---

[1] Image source: http://home.att.net/~cat6a/metals-XI.htm

Catenation

- Carbon uniquely can form chains of M–M bonds (catenation) without limit, owing to the following factors.
  - Strength of M–M bond decreases with size.

M–M Bond Energy (kJ/mol)

C–C	Si–Si	Ge–Ge	Sn–Sn
356	210-250	190-210	105-145

  - Disparity between M–M and M–X bond strengths increases with size.

M–X Bond Energies (kJ/mol)

C–O	Si–O		
336	368		
C–H	Si–H	Ge–H	Sn–H
416	323	290	252
C–Cl	Si–Cl	Ge–Cl	Sn–Cl
327	391	356	344

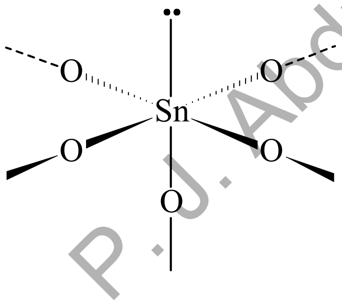
  - As size increases, $p\pi$-$p\pi$ bonding rapidly becomes less effective, being significant only for carbon.

Group Oxidation States

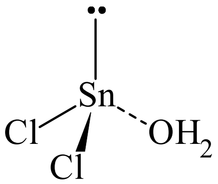
- Although +4 is the group characteristic oxidation state, the +2 state becomes more stable down the group.
- Stable carbon and silicon compounds have +4 state.
- At Ge and Sn, both +2 and +4 states are stable.
- At Pb, the bond strength is too low to compensate for the slightly higher ionization energy requirement of the Pb(IV) state in many cases. Hence, the +2 state is favored.

☛ The increasing stability of the +2 state is another example of the so-called "inert-pair effect."

- With Sn^{2+} the unused pair appears to be stereochemically important in cases like SnO(*s*) and $SnCl_2{\cdot}2H_2O$(*s*).



SnO coordination in solid



$SnCl_2{\cdot}2H_2O$
(Other H_2O in crystal lattice, lost at 80 °C)

- Similarly, $GeCl_3^-$ has trigonal pyramidal (C_{3v}) geometry.

Carbon Chemistry - The Oxides

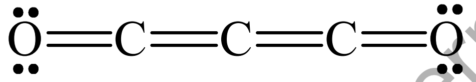
- There are three oxides:

C_3O_2	CO	CO_2
carbon suboxide	carbon monoxide	carbon dioxide

- C_3O_2 is an evil smelling gas formed by dehydration of malonic acid.

$$3CH_2(CO_2H)_2 + P_4O_{10} \rightarrow 3C_3O_2 + 4H_3PO_4$$

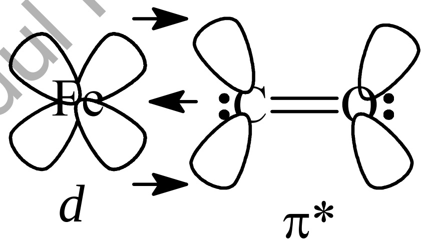
  - C_3O_2 is linear ($D_{\infty h}$).



- CO can be prepared by a similar dehydration with formic acid, using conc. H_2SO_4.

$$HCO_2H \xrightarrow{\text{conc } H_2SO_4} CO + H_2O$$

  - Toxicity is related to its ability to bind to Fe^{2+} in hemoglobin through a back-bonding mechanism.



  - Donation of *d* electron density into the π* MO of CO weakens the bond, shifting the i.r. frequency lower.

Carbon Chemistry - The Oxides

- CO_2 dissolves in water to function as carbonic acid, but the principal species in solution is $CO_2(aq)$, which is only loosely hydrated.
  - On this basis, acid hydrolysis equilibria should be written as

$$CO_2 + 2H_2O \rightleftharpoons HCO_3^- + H_3O^+ \qquad K_1 = 4.3 \text{ x } 10^{-7}$$
$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+ \qquad K_2 = 5.6 \text{ x } 10^{-11}$$

  - H_2CO_3 does exist, and using the "true" activity of H_2CO_3 has a $K_1 \approx 2 \text{ x } 10^{-4}$, in keeping with its structure as $(HO)_2CO$ (C_{2v}).[2]

- The rate of equilibrium between CO_2 and H_2CO_3 is measurably slow, which is physiologically, analytically, and industrially important.

- Neutralization at pH < 8 involves a two-step mechanism beginning with direct hydration of CO_2:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad \text{slow}$$
$$H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O \qquad \text{fast}$$
$$Rate = -d[CO_2]/dt = k_1[CO_2]$$

- Neutralization at pH > 10 involves direct attack on CO_2:

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad \text{slow}$$
$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O \qquad \text{fast}$$
$$Rate = -d[CO_2]/dt = k_2[CO_2][OH^-]$$

---

[2] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, NY, 1999, p. 227.

Carbides

- Carbon forms binary carbides with active metals, most important of which are methanides and acetylides.

- Methanides, which behave as if they contain C^{4-} ions, are formed with high charge-density cations.
  - Methanides hydrolyze to give methane.

    $Al_4C_3 + 12H_2O \rightarrow 3CH_4 + 4Al(OH)_3$

    $Be_2C + 4H_2O \rightarrow CH_4 + Be(OH)_2$

- Acetylides, which contain C_2^{2-} ions, are known with a number of metal cations:

    M_2C_2 M^{I} = group 1, Cu, Ag, Au

    MC_2 M^{II} = group 2

    $M_2(C_2)_3$ M^{III} = Al, La, Pr, Tb
  - C_2^{2-} is isoelectronic with N_2 and has a short bond length (119-124 pm), consistent with a triple bond.
  - Acetylides hydrolyze to give acetylene.

    $CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$

- A sesquicarbide, containing linear C_3^{4-} ions, can be prepared by reacting Mg dust with *n*-pentane at ~680 ^{o}.[3]
  - In acid this hydrolyzes to give allene.

    $Mg_2C_3 + 4HCl \rightarrow C_3H_4 + 2MgCl_2$

---

[3] Cotton *et al.*, *ibid.*, p. 220.

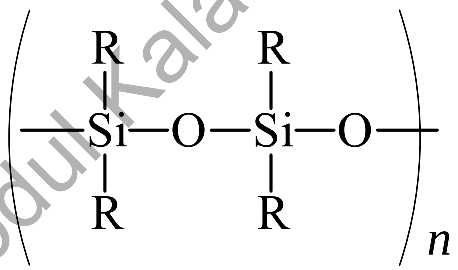
Silicon and Germanium

- SiO_2 (silica) is the most important silicon compound.
  - SiO_2 melts at ~1700 ^{o} to give quartz glass.
  - Other glasses contain silicates (SiO_3^-, $Si_2O_7^{6-}$, etc.), which are built up of linked SiO_3 and SiO_4 units, similar to borates. (n.b., diagonal relationship)

- A number of hydrides, called silanes, are known and are alkane analogues.

$$SiH_4,\ Si_2H_6,\ ...,\ Si_6H_{14} \quad ☛ \quad Si_nH_{2n+2},\ n = 1\text{–}6$$

- Greater strength of the Si–O bond over the Si–Si bond favors formation of silicate structures.
  - Silicates include the well known silicone polymers.



$$\left(-\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O-\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O- \right)_n$$

- Ge chemistry is similar to Si chemistry, but less extensive.
  - The +2 state becomes more important, and the +4 state can sometime easily convert to the +2 state; e.g.,

$$GeCl_4 + Ge \rightarrow 2GeCl_2$$

Tin and Lead Chemistry

- Tin(II) solutions readily hydrolyze in all but the most acidic media, producing trimeric $[Sn_3(OH)_4]^{2+}$.
  $3Sn^{2+}(aq) + 8H_2O \rightleftharpoons [Sn_3(OH)_4]^{2+} + 4H_3O^+ \qquad K = 1.7 \times 10^{-7}$
  - Hypothetical $[Sn(H_2O)_6]^{2+}$ is estimated to have $K_a \approx 10^{-2}$.

- Both SnO and SnO_2 are amphoteric.
  - In base SnO_2 hydrolyzes to give the stannate ion.
    $SnO_2 + 2OH^- + 2H_2O \rightleftharpoons Sn(OH)_6^{2-}$

- Lead(IV) is known only in covalent compounds, not as a free Pb^{4+} ion.

- PbO_2 is a powerful oxidizing agent used in the lead storage battery.

Cathode:	$PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$	$\rightleftharpoons$	$PbSO_4 + 2H_2O$	$E^o = 1.46$ V
Anode:	$SO_4^{2-} + Pb$	$\rightleftharpoons$	$PbSO_4 + 2e^-$	$-E^o = 0.36$ V
Cell:	$PbO_2 + 4H^+ + 2SO_4^{2-} + Pb$	$\rightleftharpoons$	$2PbSO_4 + 2H_2O$	$E^o_{cell} = 1.82$ V

- Lead forms $Pb(CH_3)_4$ and $Pb(C_2H_5)_4$, which were used as anti-knock ingredients in gasoline.
  - Their commercial synthesis involves a complicated reaction sequence that is not fully understood, but the overall reaction is
    $4NaPb + 4RCl \xrightarrow{80\text{-}100\ ^oC} R_4Pb + 3Pb + 4NaCl$
  - $Pb(CH_3)_4$ and $Pb(C_2H_5)_4$ are nonpolar, highly toxic liquids.
  - $Pb(CH_3)_4$ decomposes at ~200 ° and $Pb(C_2H_5)_4$ decomposes at ~110 ° via a free radical mechanism.

Group 15 - 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.)

- Nitrogen shows little tendency to form stable catenated species beyond N_2.

  - Recently characterized unstable species include $N_5^+[AsF_6]$ and SrN_2

  - N_2^{2-} ion is isoelectronic with O_2 with the same MO scheme (B.O. = 2)

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).

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

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

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

- 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 °C.

- Red phosphorous, an inert and nontoxic form, is obtained from white by heating in an inert atmosphere at 250 °C.
  - 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
pπ-pπ	strong	unstable
pπ-dπ	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.

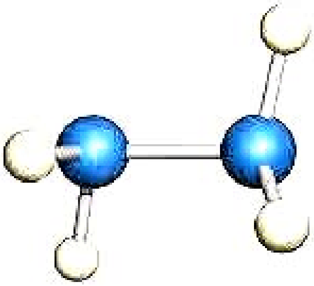
Nitrogen Chemistry - Hydrides - Hydrazine

- 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.

  $N_2H_4 + 4OH^- \rightleftharpoons N_2 + 4H_2O + 4e^-$ $-E^\circ = +1.16$ 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:

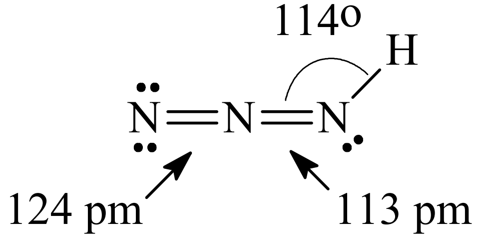
    $NH_3 + NaOCl \rightarrow NaOH + NH_2Cl$ (fast)

    $NH_2Cl + NH_3 + NaOH \rightarrow N_2H_4 + NaCl + H_2O$
  - 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 ($\Delta H^\circ_f = +50$ 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:

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

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

- 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:

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

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

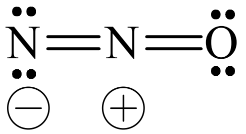
Nitrogen Chemistry - Oxides

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

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

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

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



  - $\Delta G^o_f = +103.6$ 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:

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

- 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

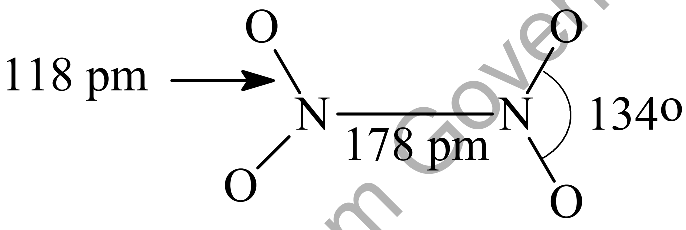
$$3KNO_2 + KNO_3 + Cr_2O_3 \xrightarrow[\Delta]{\text{melt}} 2K_2CrO_4 + 4NO$$

Nitrogen Chemistry - Oxides (cont.)

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

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

  - $K = [N_2O_4]/[NO_2]^2 = 0.67$ @25 ºC.
  - 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 °C.

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

- N_2O_5 can be made by dehydrating HNO_3 with P_4O_{10}.

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

Nitrogen Oxoacids - HNO_2

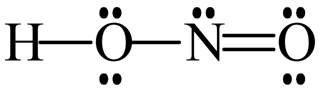
- Nitrous acid, HNO_2, can be obtained in solution by acidifying solutions of nitrites:

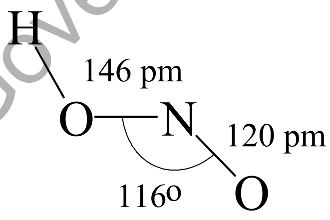
$$Ba(NO_2)_2(aq) + H_2SO_4(aq) \rightarrow 2HNO_2(aq) + BaSO_4(s)$$

- 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:

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

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

- 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.

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

- The classic synthesis is the Ostwald process:

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

$$2NO + O_2 \rightarrow 2NO_2$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

  - 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.

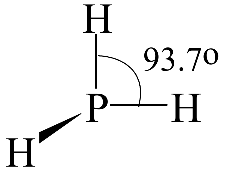
$$4Zn(s) + 8H^+(aq) + H_3AsO_4(aq) \rightarrow AsH_3(g) + 4Zn^{2+}(aq) + 4H_2O(l)$$

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

  - As(*s*) forms as a silver mirror on the walls of the test tube above the solution.

- 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.

    $PX_5 + H_2O \rightarrow POX_3 + 2HX$

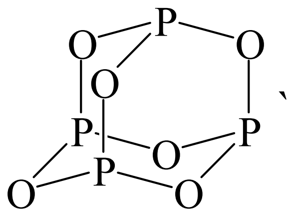
  - Organic derivatives of phosphoryl halides can be formed:

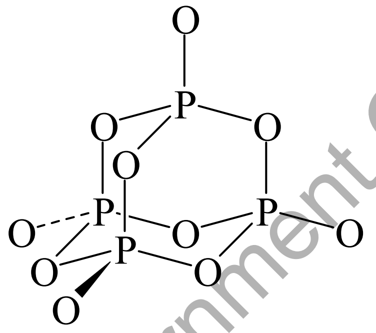
    $POX_3 + 3ROH \rightarrow (RO)_3PO + 3HX$

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

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.





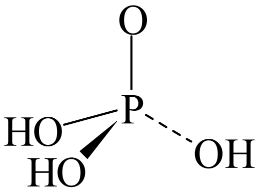
- Adding P_4O_{10} to water gives several oxoacids, most importantly *orthophosphoric* acid, H_3PO_4 (usually called *phosphoric* acid).

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

  - 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:

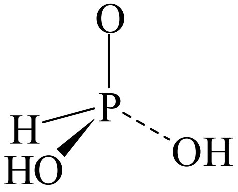
$$K_1 = 7.5 \times 10^{-3}, K_2 = 6.2 \times 10^{-8}, K_3 = 4.2 \times 10^{-13}$$

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).



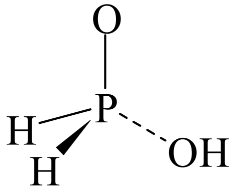
  - H_3PO_3 is a diprotic acid:

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

- *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:

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

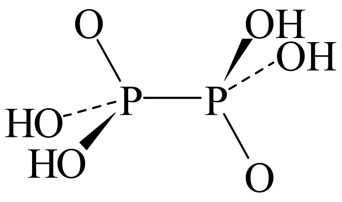
  - It has a tetrahedral structure (C_s) with two non-acidic P–H bonds.

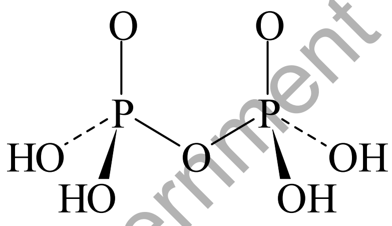


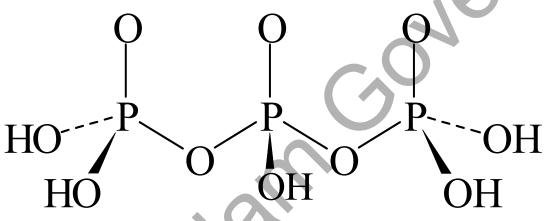
  - H_3PO_2 is a monoprotic acid with $K \approx 10^{-2}$.

Higher Phosphoric Acids and Anions

Formula	Name	$\mathrm{p}K_1$	$\mathrm{p}K_2$	$\mathrm{p}K_3$	$\mathrm{p}K_4$	$\mathrm{p}K_5$
$H_4P_2O_6$	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.

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

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

  $$H_3AsO_4 + 2H^+ + 2e^- \rightleftharpoons H_3AsO_3 + H_2O \qquad E^o = +0.559\ V$$

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

Group 16 Elements - Oxygen

- Stable allotropes of oxygen are $O_2(g)$ and $O_3(g)$.

- Standard laboratory preparations for $O_2(g)$ include the following:

$$2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$$

$$2HgO \xrightarrow[\Delta]{} 2Hg + O_2$$

$$2H_2O \xrightarrow{\text{electrolysis}} 2H_2 + O_2$$

- $O_2(g)$ is paramagnetic due to two unpaired electrons in separate π* MOs: $(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$
  - Bond order is 2, and the bond length is 120.75 pm.

- Ozone is produced by passing an electric discharge through $O_2(g)$.
  - It is produced naturally by u.v. (240-300 nm).

$$O_2 \xrightarrow{h\nu} 2O$$

$$O + O_2 \rightarrow O_3$$

- Ozone is a bent molecule ($\angle$O–O–O = 116.8°).
  - Bond order is 1½ for each O–O bond, and the bond length is 127.8 pm.

- Both O_2 and O_3 are powerful oxidizing agents.

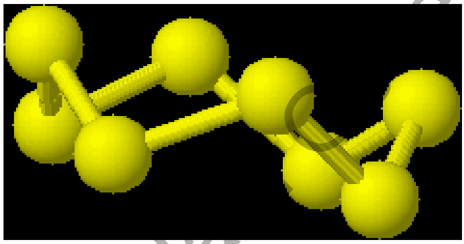
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad E^o = +1.23\text{ V}$$

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \qquad E^o = +2.07\text{ V}$$

Group 16 Elements - Sulfur

- Sulfur is found free in nature in vast underground deposits.
  - It is recovered by the Frash process, which uses superheated steam to melt and expel the fluid.

- Three principal allotropes:
  rhombic, S_8 (<96 ºC, mp = 112.8 ºC)
  monoclinic, S_8 (>96 ºC, mp = 119. ºC)
  amorphous, S_n (metastable "plastic" sulfur)
  - Rhombic and monoclinic forms contain crown-shaped S_8 rings (D_{4d}).



  - Amorphous sulfur, containing long S_n chains, is formed when molten sulfur is rapidly quenched; conversion to rhombic S_8 can take years.

Group 16 Elements - Se, Te, Po

- Se is recovered as an impurity in sulfur deposits.

- Se has several solid allotropes: rhombic (red), monoclinic (red), black, hexagonal (gray).
  - Red forms contain Se_8 units.
  - Black form has large polymeric rings.
  - Gray form (thermodynamically most stable) contains infinite helical chains (Se–Se distance = 237 pm).

- Se is a poorly conducting semimetal in the dark, but its conductance increases >20 times in light.

- Te has one form, isostructural with gray Se.

- Polonium, Po, is usually obtained as ${}^{210}_{84}Po$ ($t_{1/2}$ = 138 days).
  - Dangerous α emitter.

- Most common group oxidation states are -2, +4, +6.

Oxygen Chemistry - Ozone

- Ozone is one of the most powerful oxidants known.
  - Relative to O_2, its oxidations are generally faster and more vigorous.

- O_3 is photochemically produced in smog:

$$NO_2 \xrightarrow{h\nu} NO + O$$

$$O + O_2 \rightarrow O_3$$

$$O_3 + NO \rightarrow O_2 + NO_2$$

  - O_3 reacts with hydrocarbons to produced oxygenated species, which are irritants and potentially carcinogens.
  - Inhibits germination of plants, probably by destroying pollen.

- O_3 absorbs u.v strongly and is essential in the upper atmosphere.
  - O_3 is depleted by trace amounts of NO_2 or $Cl\cdot$ by a complicated series of reactions, including the following.

$$\begin{array}{rcl} NO_2 + O_3 & \rightarrow & NO_3 + O_2 \\ NO_3 & \rightarrow & NO + O_2 \\ NO + O_3 & \rightarrow & NO_2 + O_2 \\ \hline 2O_3 & \rightarrow & 3O_2 \end{array}$$

$$\begin{array}{rcl} Cl\cdot + O_3 & \rightarrow & ClO\cdot + O_2 \\ ClO\cdot + O & \rightarrow & Cl\cdot + O_2 \\ \hline O_3 + O & \rightarrow & 2O_2 \end{array}$$

Oxygen Chemistry - Peroxide

- Hydrogen peroxide is a good oxidant and reductant, which leads to its tendency to decompose by autoredox.

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E^o = 1.77\ V$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \qquad -E^o = -0.68 V$$

$$2H_2O_2 \rightarrow O_2 + 2H_2O \qquad E^o_{cell} = 1.05\ V$$

  - The reaction is catalyzed by light, Ag^+, MnO_2, HBr, base, and saliva.

- H_2O_2 can be made by acidification of BaO_2 with H_2SO_4:

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4\downarrow + H_2O_2$$

- Today most is made by cold electrolysis of ammonium hydrogen sulfate to make peroxidsulfate, $S_2O_8^{2-}$, followed by heating to induce hydrolysis.

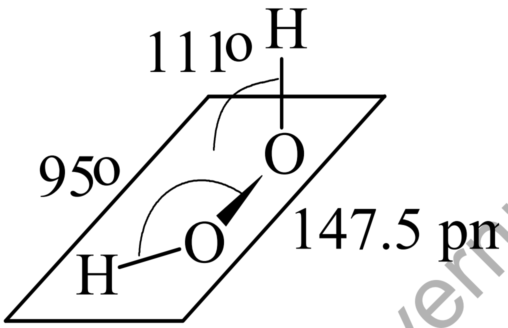
$$2NH_4HSO_4(aq) \xrightarrow[\sim 0\,^oC]{\text{electrolysis}} (NH_4)_2S_2O_8(aq) + H_2(g)$$

$$(NH_4)_2S_2O_8(aq) + 2H_2O \rightarrow 2NH_4HSO_4(aq) + H_2O_2(l)$$

  - Reduced pressure fractional distillation gives a 98% pure product.

Oxygen Chemistry - Peroxide (cont.)

- In the gas phase H_2O_2 has the following C_2 structure, but the internal dihedral angle is very variable due to a low barrier to rotation.



- H_2O_2 is appreciably dissociated when pure.

$$2H_2O_2 \rightleftharpoons H_3O_2^+ + O_2H^- \qquad K = 1.5 \times 10^{-12}$$

  - It has a higher dielectric constant ($\varepsilon = 93$) than water ($\varepsilon = 78$), and a 65% solution has an even higher dielectric constant ($\varepsilon = 120$).
  - H_2O_2 would be a good ionizing solvent if it were not for its redox activity and tendency to decompose.

Hydrides of S, Se, Te

- All three dihydrides are poisonous and have obnoxious smells.
  - Toxicity of H_2S is far greater than HCN.

- H_2S dissolves in water at 1 atm to give a solution that is ~0.1M.

- All are weak acids.

H_2A	K_1	K_2
H_2S	1.02×10^{-7}	1×10^{-19}
H_2Se	2×10^{-4}	—
H_2Te	2.3×10^{-3}	—

- Sulfide salts of transition metals and other heavy metals are among the most insoluble binary ionic compounds.
  - Their K_{sp} values[1] are so small that they precipitate even though the concentration of S^{2-} ion in a saturated solution of H_2S is only ~10^{-19} M.

Compound	CdS	CuS	PbS	NiS	Ag_2S	SnS
K_{sp}	8×10^{-28}	6×10^{-37}	3×10^{-28}	3×10^{-20}	6×10^{-51}	1×10^{-26}

---

[1] For a solubility equilibrium of the type $MS(s) + H_2O \rightleftharpoons M^{2+}(aq) + HS^{-}(aq) + OH^{-}(aq)$

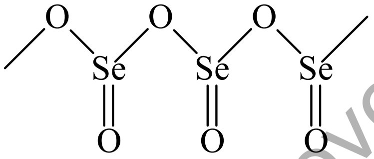
Oxides

- Both +4 and +6 oxides, oxoanions, and oxoacids exist.

- Burning the element in air yields the dioxide; e.g.,

$$S + O_2 \rightarrow SO_2$$

  - SO_2 is a gas, structurally similar to ozone, but its liquid (bp –10 °C) is a useful nonaqueous solvent despite its low dielectric constant ($\varepsilon \approx 15$).
  - SeO_2 is a volatile solid with a chain structure.



  - TeO_2 is a nonvolatile solid with a three dimensional structure having four-coordinated Te.
  - PoO is a nonvolatile solid with the fluorite (CaF_2) structure.

- Only important trioxide is SO_3, formed by oxidizing SO_2 in the *contact process*.

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

  - SO_3 is planar (D_{3h}) with π delocalization (bond order 1⅓).
  - SeO_3 is made by dehydrating H_2SeO_4 with P_4O_{10} at 160 °C.
  - TeO_3, an orange solid, is made by dehydrating $Te(OH)_6$.

Sulfur Oxoacids - H_2SO_3

- SO_2 dissolves in water to give an acidic solution generally called "sulfurous acid," but H_2SO_3 either does not exist or is present in only vanishingly small concentration.

- The equilibria in aqueous solution should be written as follows:

$$SO_2 + xH_2O \rightleftharpoons SO_2{\cdot}xH_2O \qquad \text{(hydrated } SO_2\text{)}$$
$$SO_2{\cdot}xH_2O \rightleftharpoons HSO_3^- + H_3O^+ + (x-2)H_2O$$
$$SO_2{\cdot}xH_2O \rightleftharpoons H_2SO_3 \qquad K << 1$$

  - The first acid hydrolysis constant, K_1, is

$$K_1 = \frac{[HSO_3^-][H_3O^+]}{[SO_2]} = 1.3 \times 10^{-2}$$

where $[SO_2] = C_{SO_2} - [HSO_3^-] - [SO_3^{2-}]$.

  - K_2 is the acid hydrolysis constant of the hydrogen sulfite ion:

$$K_2 = \frac{[SO_3^{2-}][H_3O^+]}{[HSO_3^-]} = 5.6 \times 10^{-8}$$

Sulfur Oxoacids - H_2SO_4

- Sulfuric acid is formed when SO_3 is dissolved in water:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

  - Reaction is too exothermic to serve as a commercial process for making sulfuric acid.

- $K_1 >> 1$, $K_2 = 1.2 \times 10^{-2}$

- Most sulfuric acid is made by the *contact process*:

(1) Oxidation of SO_2

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

(2) Bubbling through concentrated H_2SO_4 to make "oleum", $H_2S_2O_7$ (*pyrosulfuric acid*).

$$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$$

(3) Dilution to make sulfuric acid of the desired concentration.

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

Selenium and Tellurium Oxoacids

- SeO_2 dissolves in water to give $H_2SeO_3 = (OH)_2SeO$ ($K_1 = 2.3 \times 10^{-3}$, $K_2 = 5.3 \times 10^{-9}$).

  $$SeO_2 + H_2O \rightarrow H_2SeO_3$$

  - It is a moderately strong oxidizing agent:

    $$H_2SeO_3 + 4H^+ + 4e^- \rightleftharpoons Se + 3H_2O \qquad E^o = 0.74\ V$$

- H_2TeO_3 (uncertain structure) is best made by hydrolysis of a tetrahalide, because TeO_2 is not soluble in water; e.g.,

  $$TeCl_4 + 3H_2O \rightarrow H_2TeO_3 + 4HCl$$

- SeO_3 is difficult to obtain, but H_2SeO_4 can be synthesized by oxidizing H_2SeO_3 with H_2O_2.

  $$H_2SeO_3 + H_2O_2 \rightarrow H_2SeO_4 + H_2O$$

  - Dehydration with P_4O_{10} gives SeO_3.
  - Pure H_2SeO_4 is a clear solid (mp 57 °C).
  - H_2SeO_4 is somewhat less strong than H_2SO_4 ($K_1 >> 1$; $K_2 = 1.2 \times 10^{-2}$).

- $Te(OH)_6$ is the tellurium +6 oxoacid, made by oxidizing TeO_2:

  $$TeO_2 + H_2O_2 + 2H_2O \rightarrow Te(OH)_6$$

  - It is a very weak diprotic acid ($K_1 \approx 10^{-7}$) with an octahedral structure.

Sulfur Oxo- and Thio- Ions

- Sulfur forms a number of acids and oxoanions with –O–, O–O, and S–S bonds.

Name	Formula	Bond type
thiosulfuric	$H_2S_2O_3$	S–S
dithionous	$H_2S_2O_4$	S–S
disulfurous	$H_2S_2O_5$	S–S
dithionic	$H_2S_2O_6$	S–S
disulfuric	$H_2S_2O_7$	S–O–S
polythionic	$H_2S_{n+2}O_6$	$S–S_n–S$
peroxomonosulfuric	H_2SO_5	S–O–OH
peroxidisulfuric	$H_2S_2O_8$	S–O–O–S

- Peroxydisulfate is formed by cold electrolysis of H_2SO_4.
  - It is a very strong oxidant.

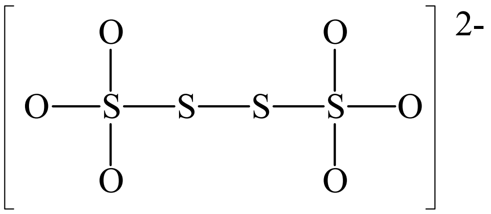
$$S_2O_8^{2-} + 4H^+ + 2e^- \rightarrow 2H_2SO_4 \qquad E^o = +2.01\ V$$

- Solutions of SO_3^{2-} in contact with solid sulfur form thiosulfate, $S_2O_3^{2-}$, a tetrahedral ion with C_{3v} symmetry.

$$SO_3^{2-}(aq) + S(s) \rightarrow S_2O_3^{2-}(aq)$$

  - It acts as a mild reducing agent, producing tetrathionate ion:

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \qquad -E^o = -0.08\ V$$



Sulfur Catenation

- Sulfur shows limited ability to catenate, as seen in the dithionate ion.
- The S–S bond (D = 429 kJ) is competitive with the S-O bond (D = 522 kJ).
  - This allows some chain species to form, as in sulfur's allotropes.
- When sulfide solutions are heated with sulfur, solutions containing mostly S_3^{2-} and S_4^{2-} are formed.

$$S^{2-} + xS(s) \rightarrow S_{x+1}^{2-} \qquad x = 2,3,..$$

  - Only S_3^{2-} and S_4^{2-} are stable in solution, but a number of crystalline compounds with S_n^{2-} ions with n = 3–6 can be prepared, especially with large cations (e.g., Cs^+, NH_4^+, $en H_2^{2+}$).

Halides and Oxohalides

- A large number of halides are known.
- The only hexahalides are SF_6, SeF_6 and TeF_6.
- The MX_4 halides exist for X = F, Cl, Br
  - The only +4 iodide is TeI_4.
- A number of dihalides and dimeric monohalides are known; e.g., OF_2, O_2F_2, S_2Cl_2, SCl_2, Se_2Cl_2, $SeCl_2$, S_2F_2, S_2Cl_2, ...
- Sulfur has two important oxohalides, SO_2Cl_2 (sulfuryl chloride) and $SOCl_2$ (thionyl chloride).
  - Thionyl chloride is an effective dehydrating agent for hydrated metal chlorides that would decompose with heating:

$$SOCl_2 + H_2O \rightarrow SO_2 + 2HCl$$

$$M_mCl_n{\cdot}xH_2O + xSOCl_2 \rightarrow M_mCl_n + xSO_2 + 2xHCl$$

Group 17 - Halogens - The Elements

- All are diatomic molecules in all their phases.
  - Standard states and phase transition temperatures are consistent with van der Waals intermolecular forces.

Element	Standard State	mp (K)	bp (K)	E^o (V) $X_2 + 2e^- \rightleftharpoons 2X^-$
F_2	yellow gas	40	85	2.85
Cl_2	green gas	172	239	1.36
Br_2	red-brown liquid	266	332	1.06
I_2	violet solid	387	458	0.62

cf. $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \quad E^o = +1.23$ V

- All are too reactive to exist free in nature.

- Astatine is a short-lived species in the natural decay series of uranium.
  - Named from the Greek αστατος (astatos), meaning "unstable."
  - Longest-lived isotope is $^{210}_{85}At$, $t_{½} = 8.3$ hr.
  - No macroscopic samples have ever been obtained.

The Elements - Fluorine

- Fluorine is prepared by electrolysis of fused KHF_2, made as a mixture of KF(s) and HF(*g*):

$$2KHF_2 \xrightarrow[70\text{-}100^o]{\text{electrolysis}} H_2 + F_2 + 2KF$$

  - Fluorine is so reactive that care must be taken to separate the H_2 produced at the cathode from the F_2 produced at the anode.

- F_2 reacts at room temperature with all elements (sometimes violently) except O, N, He, Ne.

- F_2 reacts with silica, SiO_2, but only if some HF is present, which initiates a chain reaction.

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$
$$2H_2O + 2F_2 \rightarrow 4HF + O_2$$

$$SiO_2 + 2F_2 \rightarrow SiF_4 + O_2$$

The Elements - Chlorine, Bromine, Iodine

- Chlorine is prepared by electrolysis of fused NaCl or (more commonly) brine, NaCl(*aq*).
  - Aqueous electrolysis is possible because $O_2(g)$ has a high overvoltage at a Pt electrode.

- Bromine and iodine can be obtained by electrolysis from aqueous solution, but chemical means are more frequently used.

$$2X^-(aq) + Cl_2(g) \rightarrow X_2(g/l) + 2Cl^-(aq) \qquad X = Br, I$$

- Other reactions that produce Cl_2, Br_2, or I_2 include the following:

$$2IO_3^- + 5HSO_3^- \rightarrow I_2 + 5SO_4^{2-} + 3H^+ + H_2O$$
$$MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O(l)$$
$$2MnO_4^- + 16H^+ + 10Br^- \rightarrow 2Mn^{2+} + 5Br_2 + 8H_2O$$
$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

- Reactivity decreases down the group along with electron affinity.

X(*g*)	F	Cl	Br	I	At
A (kJ/mol)	328.0	349.0	324.6	295.18	270.1

  - Fluorine's electron affinity is anomalously low probably owing to small size and electron repulsions.

- Principal group oxidation states are ±1, +3, +5, +7.
  - Fluorine only has –1.

Group 17 Chemistry - Hydrides - HF

- HF in dilute solution behaves as a typical weak acid.

  $HF + H_2O \rightleftharpoons H_3O^+ + F^- \qquad K_a = 7.2 \times 10^{-4}$

  - At 5-15M, the following equilibrium occurs:

    $F^- + HF \rightleftharpoons [F\text{–}H\text{–}F]^- \qquad K = 5.1$

  - Concentrated HF is therefore a stronger acid:

    $2HF + H_2O \rightleftharpoons H_3O^+ + HF_2^- \qquad K_a \times K = 3.7 \times 10^{-3}$

☛ Hydrofluoric acid must be handled with extreme caution, as indicated by the following excerpt from its MSDS:[1]

POISON! DANGER! CORROSIVE. EXTREMELY HAZARDOUS LIQUID AND VAPOR. CAUSES SEVERE BURNS WHICH MAY NOT BE IMMEDIATELY PAINFUL OR VISIBLE. MAY BE FATAL IF SWALLOWED OR INHALED. LIQUID AND VAPOR CAN BURN SKIN, EYES AND RESPIRATORY TRACT. CAUSES BONE DAMAGE. REACTION WITH CERTAIN METALS GENERATES FLAMMABLE AND POTENTIALLY EXPLOSIVE HYDROGEN GAS.

J.T. Baker SAF-T-DATA(tm) Ratings

Health Rating: 4 - Extreme (Poison)
Flammability Rating: 0 - None
Reactivity Rating: 2 - Moderate
Contact Rating: 4 - Extreme (Corrosive)
Lab Protective Equip: GOGGLES & SHIELD; LAB COAT & APRON; VENT HOOD; PROPER GLOVES

- Glass or quartz vessels cannot be used with HF because it etches these materials by fluorination.

  $SiO_2(s) + 6HF(aq) \rightarrow SiF_6^{2-}(aq) + 2H^+(aq) + 2H_2O(l)$

- HF is made industrially by the following reaction:

$$CaF_2 + H_2SO_4 \xrightarrow[\Delta]{} 2HF(g) + CaSO_4(s)$$

---

[1] Source: http://www.bu.edu/es/labsafety/ESMSDSs/MSHydFluoricAcid.html

Group 17 Chemistry - Hydrides - HCl, HBr, HI

- HCl, HBr, and HI are all strong acids, principally due to weaker bonds than HF.

- HCl is made industrially by acidification of NaCl.

  $$NaCl(s) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + HCl(g)$$

  - HSO_4^- is formed instead of SO_4^{2-} because HCl is a strong acid.

- Br^- and I^- are too strong as reducing agents to form HBr and HI by H_2SO_4 acidification of bromide or iodide salts.
  - Redox occurs instead.

    $2NaBr + 3H_2SO_4 \rightarrow Br_2 + SO_2 + 2NaHSO_4 + 2H_2O$

    $8NaI + 9H_2SO_4 \rightarrow 4I_2 + H_2S + 8NaHSO_4 + 4H_2O$

- Both HBr and HI can be prepared with H_3PO_4 and heat:

  $$NaX(s) + H_3PO_4(aq) \xrightarrow[\Delta]{} NaH_2PO_4(aq) + HX(g) \quad X = Br, I$$

- Direct combination on Pt is a preferred industrial synthesis for HBr and HI.

  $$H_2(g) + X_2(g) \xrightarrow[Pt]{} 2HX(g) \qquad X = Br, I$$

Halogen Oxides[2] and Oxoacids

Fluorine	bp (°C)	mp (°C)	Chlorine	bp (°C)	mp (°C)	Bromine	bp (°C)	Iodine
F_2O	–145	–224	Cl_2O	~4	–116	Br_2O	–18	I_2O_4
F_2O_2	–57	–163	Cl_2O_3			Br_2O_3		I_4O_9
			ClO_2	~10	–5.9	Br_2O_5		I_2O_5
			Cl_2O_4	44.5	–117			
			Cl_2O_6		3.5			
			Cl_2O_7	82	–91.5			

- Most are unstable, but OF_2 is a stable compound formed when $F_2(g)$ is bubbled through $NaOH(aq)$:

$$2F_2(g) + 2OH^-(aq) \rightarrow 2F^-(aq) + OF_2(g) + H_2O(l)$$

- ClO_2 is made on a commercial scale for use in bleaching by the exothermic reaction of $NaClO_3$ in 4-4.5 M H_2SO_4 containing 0.5-0.25 M Cl^- with SO_2:

$$2NaClO_3 + SO_2 + H_2SO_4 \rightarrow 2ClO_2 + 2NaHSO_4$$

---

[2] Data source: Cotton, *et al.*, *Advanced Inorganic Chemistry*, 6th ed., p. 560

Halogen Oxoacids

Name	Fluorine	Chlorine	Bromine	Iodine
hypohalous	HOF	HOCl*	HOBr	HOI*
halous		HOClO*	HOBrO*	—
halic		$HOClO_2$*	$HOBrO_2$*	$HOIO_2$
perhalic		$HOClO_3$	$HOBrO_3$*	$HOIO_3$ (meta)
				$(HO)_5IO$ (para)
				$H_4I_2O_9$ (meso)

* Stable only in solution.

- As indicated, most are unstable and exist only in solution (i.e., cannot be obtained pure).

- The related anions are

hypohalous	XO^-
halous	XO_2^-
halic	XO_3^-
perhalic	XO_4^-

Hypohalous Acids and Hypohalites

- HOX acids are formed in varying amounts when halogens react with water:

  $$X_2 + 2H_2O \rightleftharpoons H_3O^+ + X^- + HOX$$

  - HOF is formed only with ice.
  - Equilibria lie to the left.

    $K(Cl_2) = 4.2 \times 10^{-4}$ $K(Br_2) = 7.2 \times 10^{-9}$ $K(I_2) = 2.0 \times 10^{-13}$
  - At saturation of Cl_2, [HOCl] = 0.03 M.

- HOX acids are more conveniently made by the following:

  $$2X_2 + 2HgO + H_2O \rightarrow HgO\cdot HgX_2 + 2HOX \qquad X \neq F$$

- Adding halogens to basic solutions yields hypohalite ions, OX^-.

  $$X_2 + 2OH^- \rightleftharpoons X^- + OX^- + H_2O \qquad X \neq F$$

  - Equilibria are favorable.

    $K(Cl_2) = 7.5 \times 10^{15}$ $K(Br_2) = 2 \times 10^{8}$ $K(I_2) = 30$

- Stability of OCl^- (e.g., chlorine bleach) is due to kinetics.
  - At ~75 °C, OCl^- disproportionates essentially completely.

    $$3OCl^- \rightleftharpoons 2Cl^- + ClO_3^-$$
  - Bleaching function is a result of strong oxidizing ability.

    $OCl^-(aq) + H_2O(l) + 2e^- \rightleftharpoons Cl^-(aq) + 2OH^-(aq) \qquad E^o = +0.89\ V$

    $ClO_3^-(aq) + 3H_2O(l) + 6e^- \rightleftharpoons Cl^-(aq) + 6OH^-(aq) \qquad E^o = +0.62\ V$

Chlorous Acid and Chlorite

- Chlorous acid is the only halous acid definitely known to exist, although it cannot be obtained pure.
  - Solutions of HOClO (= $HClO_2$) are prepared by acidifying a suspension of barium chlorite with sulfuric acid and filtering the precipitate:

    $$Ba(ClO_2)_2(s) + H_2SO_4(aq) \rightarrow HClO_2(aq) + BaSO_4(s)$$
  - Chlorous acid is weak ($K_a \approx 10^{-2}$).

- Chlorites are made by the ton by reacting ClO_2 with bases:

  $$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^-$$
  - Chlorites are used as industrial bleaching powders,

    $$ClO_2^- + 4H^+ + 3e^- \rightleftharpoons \tfrac{1}{2}Cl_2 + 2H_2O \qquad E^o = +1.64\ V$$
  - Chlorite salts can also be made by the following reaction:

    $$Na_2O_2 + 2ClO_2 \rightarrow 2NaClO_2 + O_2$$

Halic Acids and Halites

- All three halic acids are known, but only HIO_3 can be obtained pure (as a solid).
  - The acids and their anions are strong oxidizing agents.
  - Solutions are prepared by acidifying the barium salt:

$$Ba(XO_3)_2\,(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2HXO_3(aq) \quad X \neq F$$

- Iodic acid is prepared by direct oxidation of iodine with hydrogen peroxide.

$$I_2 + 5H_2O_2 \rightarrow 2HIO_3 + 4H_2O$$

- Simple halite salts include some useful compounds:

$NaClO_3$	weed killer
$KClO_3$	fireworks oxidant
$KBrO_3$, KIO_3	titrimetric redox reagents

Perhalic Acids

- All three perhalic acids can be prepared by electrolysis of the corresponding halate salt, followed by acidification.

$$XO_3^- + H_2O \rightarrow XO_4^- + 2H^+ + 2e^-$$

- Perchloric acid, $HClO_4$, is the most important.
  - $HClO_4$ is the strongest of all simple acids ($K_a \approx 10^{+11}$).
  - $HClO_4$ is a strong but sluggish oxidant.
    $ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O \qquad E^o = +1.23\ V$
  - When hot or concentrated it oxidizes materials rapidly and often explosively.
  - Commercial product is supplied as 72% $HClO_4$ for safety.
  - Perchloric acid is particularly dangerous when dehydrated to $HClO_4 \cdot 2H_2O$.
  - Contact of concentrated perchloric acid with organic material such as wood or paper causes an immediate fire.
  - $HClO_4$ is used less as an acid and more as an oxidizing agent.

☛ Avoid using perchlorate as an ion for isolating crystalline solids of cations that are organic or contain organic ligands because they can detonate dangerously.

- Nearly half of commercially produced perchlorate is used to make ammonium perchlorate, used with aluminum in solid booster rockets.

$$6NH_4ClO_4 + 8Al \rightarrow 4Al_2O_3 + 3N_2 + 3Cl_2 + 12H_2O$$

Perbromic Acid and Perbromate

- $HBrO_4$ and BrO_4^- were long thought not to exist and elaborate theoretical arguments were made to explain their absence.

- Solutions of perbromate were first prepared by Appleman in 1969.[3]
  - BrO_4^- solutions can be prepared by electrolysis of BrO_3^- solutions or by one of the following syntheses:

$$BrO_3^- + F_2 + OH^- \rightarrow BrO_4^- + 2F^- + H_2O$$
$$BrO_3^- + XeF_2 + H_2O \rightarrow BrO_4^- + Xe + 2HF$$

- Like $HClO_4$, $HBrO_4$ is a strong but sluggish oxidizing agent.
  - Solutions of $HBrO_4$ are stable up to ~6 M.

---

[3] Applemen, *Inorg. Chem.*, **1969**, *8*, 223.

Periodic Acid and Periodates

- Periodic acid exists in several forms.

- The *para* form, H_5IO_6 [$(OH)_5IO$], exists in strong acid solutions.
  - H_5IO_6 is essentially a weak diprotic acid: $K_1 = 5.1 \times 10^{-4}$, $K_2 = 2 \times 10^{-7}$.

- In less acidic solutions, the *para* form is in equilibrium with the *meta* form, HIO_4.

$$H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O \qquad K = 40$$

- Vacuum dehydration gives *meso*-periodic acid, $H_4I_2O_9$.

$$2H_5IO_6 \xrightarrow{80^oC/vac.} H_4I_2O_9 + 3H_2O$$

Interhalogen Compounds and Ions

- There is a wide variety of interhalogens and interhalogen ions, both cations and anions.
  - Most have structures predictable by VSEPR considerations.
  - In all, the less or least electronegative element is central.

- Among the anions, those of iodine are most significant.
  - In the presence of I_2, I^- readily forms the linear triiodide ion, I_3^-.

$$I^- + I_2 \rightleftharpoons I_3^-$$

  - $I_3^-(aq)$ is colorless, in contrast to brown $I_2(aq)$ and the purple starch-iodine complex.
    - The color differences are used as an indicator in iodometric titrations.
  - Other polyiodide ions include I_5^-, I_7^-, I_9^-, and I_8^{2-}.

Pseudo-Halogens and -Halides

- Several polyatomic molecules and their related ions mimic halogen and halide behavior.

pseudohalogen	$(CN)_2$	$(SCN)_2$	—
pseudohalide	CN^-	SCN^-	N_3^-

- The following reactions illustrate pseduohalogen behavior:

$4HSCN + MnO_2 \rightarrow (SCN)_2 + Mn(SCN)_2 + 2H_2O$

$(CN)_2 + 2OH^- \rightarrow OCN^- + CN^- + H_2O$

$H_2C{=}CH_2 + (SCN)_2 \rightarrow NCS\text{-}CH_2\text{—}CH_2\text{-}SCN$

$Ag^+(aq) + CN^-(aq) \rightarrow AgCN(s)$

$AgCN(s) + CN^-(aq) \rightarrow Ag(CN)_2^-(aq)$