
Topic 3

B, C, N groups

Group III (13)

B, Al, Ga, In, Tl

Melting/Boiling Points (Group III)

B: mostly nonmetallic behavior, semimetal

metals

Element	M.P. (°C)	B.P. (°C)
B	2180	3650
Al	660	2467
Ga	30	2403
In	157	2080
Tl	303	1457

M.P. - No simple pattern in m.p.:Why? Each element is organized a different way in the solid phase (crystal structure arrangements...fcc, etc).

B.p.- It is only when melted and crystal arrangements destroyed that we see (b.p.) that the metallic bond becomes weaker.

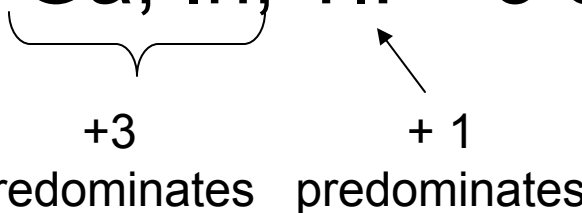
Charge Densities of Period 3 Metal Ions

Group	Ion	Charge Density (C/mm ³)
I	Na ⁺	24
II	Mg ²⁺	120
III (13)	Al ³⁺	364

A semimetal, B, favors covalent bond formation, BUT **covalency is common among the metallic members of the groups as well**. Why? Covalent behavior due to high charge and small radius of each metal ion. The high-charge density of Group III ions is sufficient to polarize almost any approaching anion enough to produce a covalent bond (see table).

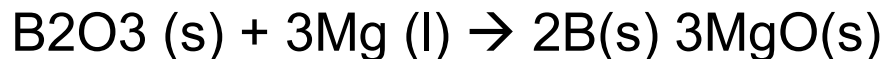
To stabilize the ionic state of Group III elements is to hydrate the metal ion. E.g. Al: enormous hydration enthalpy of Al³⁺ ion (-4665 kJ/mol) is almost enough on its own to balance the sum of the 3 ionization energies (+5137 kJ/mol). Hence, hydrated Al compounds regarded as ionic do not contain the aluminum ion, Al³⁺, as such, but the hexaaquaaluminum ion, [Al(OH₂)₆]³⁺.

Oxidation States of Group III (13)

- Al: +3 whether ionic or covalent
 - Ga, In, Tl: +3 or +1
- 
+3 predominates +1 predominates

B

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- Only element in group III not classified as a metal
 - Element can be obtained from its oxide by heating with a reactive metal (e.g. Mg)



- Rare element in earth's crust, but large deposits available near volcanic activity; salts $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (borax) and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ (kernite)
- Uses:
 - (1) 35% of B production \rightarrow borosilicate glass
 - (2) 20% of B production \rightarrow cleaning agents (NaBO_3 , sodium peroxoborate).
- Others:
 - (3) nuclear power plants; Boron-containing control rods are strong absorber of neutrons
 - (4) Borates in wood preservatives
 - (5) Borates as fire retardant in fabrics
 - (6) Borates as flux in soldering

Hydrides of Boron

- Diborane B_2H_6 is a gas (bp $-92.6^\circ C$) that is flammable in air and instantly hydrolyzed by H_2O :

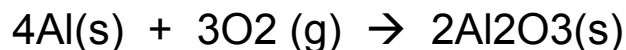
- Borane BH_3 is unstable and is formed via thermal decomposition of diborane:

- The oxidation of diborane B_2H_6 is extremely exothermic:

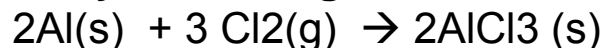
Al

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-
- High negative standard reduction potential (i.e. expected to be very reactive)
 - Al reacts with O₂ to form an oxide coating that acts as a barrier to further oxidation
 - Low density (2.7 g/cm³), construction material, (versus Mg, 1.7 g/cm³, Fe 7.9 g/cm³, Au 19.3 g/cm³)
 - Good conductor of heat (cookware) but Cu is better
 - Exceptional conductor of electricity (electrical power lines, home wiring is discouraged e.g. if Al is joined to a dissimilar metal, e.g. Cu, an electrochemical cell under damp conditions will develop causing oxidation (corrosion) of the Al → discouraged)
 - Chemical Properties:

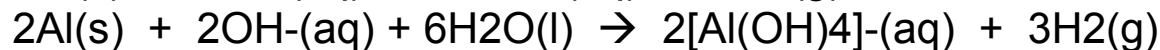
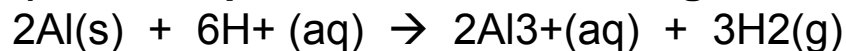
Al powder will burn in a flame



exothermically with halogens



Al (like Be) is an amphoteric metal, reacting with both acid and base



Group IV (14)

C, Si, Ge, Sn, Pb

Melting and Boiling Points (Group 14)

Very high m.p.
(Network
Covalent
Bonding)

Element	Melting Point (C)	Boiling Point (C)
C	Sublimes at 4100	
Si	1420	3280
Ge	945	2850
Sn	232	2623
Pb	327	1751

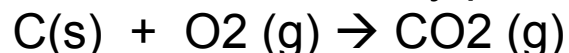
Low m. p., and
as common to metals, Sn and Pb
have long liquid ranges

Carbon

Historically, it was believed that carbon had only two allotropes, diamond, graphite)

- Diamond: network of single, tetrahedrally arranged covalent bonds, electrical insulator, excellent thermal conductor (ca. 5x copper); Diamond is a solid to 4000 C, due to enormous energy needed to break these strong covalent bonds, density=3.5 g/cm³

Humphry Davy – by borrowing one of his spouse's diamonds and setting fire to it – who showed that CO₂ was the only product when diamond burns:



- Graphite: layers of carbon atoms. Within the layers, covalent bonds hold the C atoms in 6-membered rings. The layered structure of graphite → conduct electricity in the plane of the sheets. Uses: electrode and lubricant – sliding of sheets and absorption of gas molecules (molecular ball bearings)
- Carbonaceous nanomaterials
(Fullerenes and nanotubes)

Graphite is thermodynamically more stable than diamond, but graphite is kinetically more reactive. Why? Separation of carbon sheets (e.g. graphite intercalation compounds are formed upon reaction with wide array of compounds from alkalis to halogens

Other forms of carbon

- Fullerenes:

- **Formation:** C (graphite) + laser beam \rightarrow C₆₀ (laser vaporization)
C (graphite) \rightarrow C₆₀ (electric-arc method)
- Sections of hexagonal graphite peel off and wrap into spherical structures.
- **Solubility:** Graphite, Diamonds \rightarrow insoluble due to strong network covalent structures
BUT Fullerenes ARE soluble (toluene, CS₂)

Color: Solid phase are black, Solution C₆₀ (magenta-purple), C₇₀ (wine red), C₈₄ (yellow-green)

Sublime: All fullerenes sublime when heated \rightarrow further evidence of weak intermolecular forces

Packing: fcc, face-centered cubic

Density: Low, 1.5 g/cm³

Conductors: Poor conductors of electricity

Reactivity: Rich array of organic chemistry and functionalization of the cage surface

External Doping: Doped with alkali metals, e.g. [Rb⁺]₃[C₆₀³⁻] superconductor at temp. below 28C

Internal Doping of Clusters:

(a) classical metallofullerenes (Gd@C₈₂, Sc₂@C₈₄, etc)

(b) metallic nitride fullerenes (Sc₃N@C₈₀, Gd₃N@C₈₀) discovered by Stevenson and Dorn in 1999

(c) metallic oxide fullerenes (Sc₄O₂@C₈₀) discovered by Stevenson in 2008

Cage Structures: C₃₆, C₅₀, C₇₂, C₇₄, C₈₀, I_h are very unstable, BUT C₆₀, C₇₀, C₇₆, C₇₈, C₈₂, C₈₄, C₈₆, C₈₈, C₉₀..... Are more stable)

Nanotubes

- Discovery (1991) by Iijima.
- Structure: tiny strips of graphite sheets rolled up and capped by $\frac{1}{2}$ fullerene at each end
- Synthesis: heating graphite, inert atmosphere at 1200 C.
- Strength: Due to strong covalent bonds, NT are extremely strong → 100 times that of a strand of steel
- Conductor: Excellent conductor of electricity if hexagons are aligned precisely down the long axis. Otherwise, if hexagons are aligned “with a twist” (spiral hexagonal arrangement), is a semiconductor.
- Hydrogen Storage: Open ended NT permit entry of H₂ inside the NT
- Two Classes: MWNT (concentric layers of tubes inside tubes) versus SWNT

Extensive Chemistry of Carbon

Carbon bonds	Bond Energy (kJ/mol)	Silicon Bonds	Bond Energy (kJ/mol)
C—C	346	Si—Si	222
C—O	358	Si—O	452

C—C and C—O energies are very similar

Si—Si and Si—O energies are very different. Hence, Si—O—Si—O—Si

Two properties that enable extensive array of chemistry

1. Catenation (Ability to form chains of atoms). Carbon shows greatest propensity for catenation of all elements. The ability to catenate decreases down Group 14.
2. Multiple Bonding (double, triple bonds)

Ability to Catenate

- (1) A bonding capacity (valence) greater than or equal to 2
- (2) An ability of the element to bond with itself; i.e. the self-bond must be about as strong as its bonds with other elements
- (3) A kinetic inertness of the catenated compound toward other molecules and ions

Group III (13)

N, P, As, Sb, Bi

Group V (15)

N, P, As, Sb, Bi

N, P → nonmetals, reactive P, unreactive N

As → really a semimetal: Why? It has both metallic-looking and nonmetallic allotropes and forms amphoteric oxides. Also, much of As' chemistry follows P → more behaviour of a nonmetal

Sb, Bi → weakly metallic behavior, Their resistivities are much higher than those of a "true" metal, such as Al ($2.8 \mu\Omega\cdot\text{cm}$), and even higher than a typical "weak" metal, such as lead ($22 \mu\Omega\cdot\text{cm}$).

Group 15 Properties

Element	Appearance at SATP	Electrical Resistivity ($\mu\Omega\cdot\text{cm}$)	Acid-Base Properties of Oxides
Nitrogen	Colorless gas	--	Acidic & neutral
Phosphorous	White, waxy solid	10^{17}	Acidic
Arsenic	Brittle, metallic solid	33	Amphoteric
Antimony	Brittle, metallic solid	42	Amphoteric
Bismuth	Brittle, metallic solid	120	Basic

Group 15 (m.p & b.p)

Element	Melting Point (oC)	Boiling Point (oC)
N ₂	-210	-196
P ₄	44	281
As	Sublimes at 615	
Sb	631	1387
Bi	271	1564

Note: If looking at M.P and B.P for metal versus nonmetal:

(1) m.p. of main group metals tend to decrease down a group (e.g. Alkalis)

(2) m.p. of nonmetals tend to increase down a group (e.g. Halogens)

Therefore, shift to metallic decreasing trend starts at Bi.

(3) Bi and Sb do have a characteristic long liquid range of metals.

Why N₂ unreactive, other Group 15 reactive

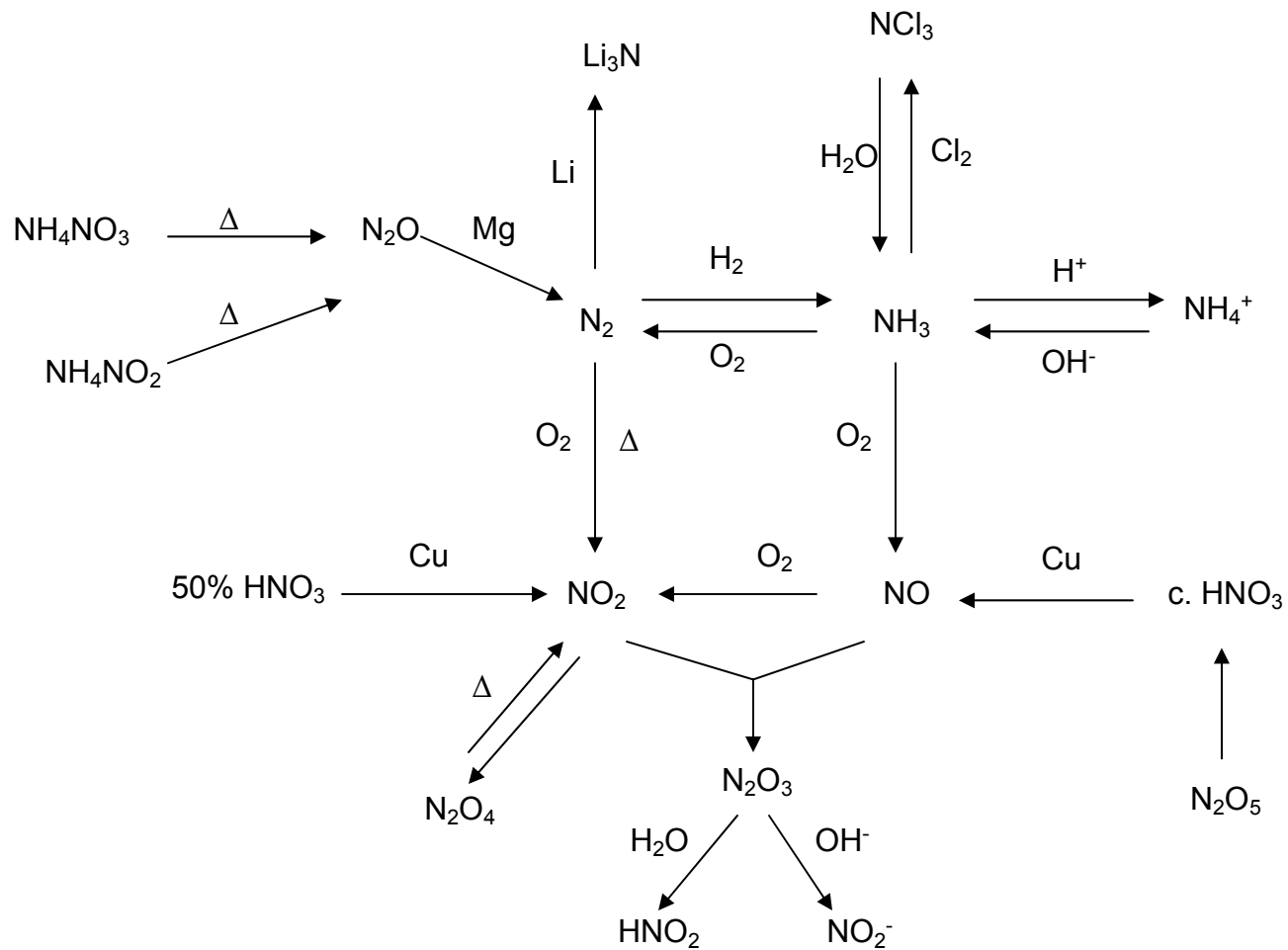
- Nitrogen chemistry is different than other Group 15 members. Why?
- N₂ is very stable, N₂ triple bond is 942 kJ/mol versus Phosphorous-Phosphorous triple bond (481 kJ/mol) and carbon- carbon triple bond (835 kJ/mol). Why? P orbitals involved in forming the two pi bonds overlap better.
- But nitrogen forms very weak single bonds (200 kJ/mol) versus C—C (346 kJ/mol). Why? Nitrogen atoms are further apart than C—C due to electronic repulsions of nonbonding electrons
- C vs N reactivity?
N₂H₄(g) hydrazine + O₂ (g) → N₂(g) + 2H₂O(g)
C₂H₄(g) ethene + O₂ (g) → 2CO₂(g) + 2H₂O(g)
- Catenation: Nitrogen doesn't → forms dinitrogen
but curiously phosphorus and sulfur are prone to catenation.
- Bonding Limitations?
Nitrogen forms only a trifluoride, NF₃ BUT phosphorous forms two common fluorides: PF₅ (hypervalent) and PF₃. Why? Some say N atom is too small.

Nitrogen

- 78% by moles of dry atmosphere
- One allotrope: N₂
- Inert diluent to O₂ in air
- Not very soluble in water
- N₂ prepared industrially by liquefying air, and then slowly warming the mixture – N₂ boils at -192 C, leaving behind O₂ (-183 C).
- Lab by gently warming solution of ammonium nitrite:



Chemistry of Nitrogen



Chemistry of Phosphorus

