

Greenwood & Earnshaw

2nd Edition

Chapter 13

Arsenic, Antimony & Bismuth

Arsenic, Antimony & Bismuth

¹⁴N 99.634% ³¹P 100% ⁷⁵As 100% ¹²¹Sb 57.25% ²⁰⁹Bi 100%
¹⁵N 0.366% ¹²³Sb 42.75%

➤ As, Sb & Bi have been known since antiquity. Sulfides are the most common minerals. Bismuth has been used from 1440 to the present as “type metal”.

➤ As & Sb have both nonmetallic (M₄) and α-metallic forms. Sb₄ is unstable above -90°C.

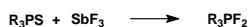
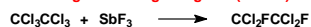
➤ α-As, α-Sb, α-Bi have a puckered sheet structure based on pyramidal coordination. α-As has no ductility, high resistivity, is volatile and amphoteric. As resists oxidation to As(V), are strong oxidizing agents. Arsenates mimic the phosphates in structure.

Group 15 Trihalides

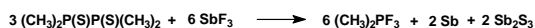
AsF₃ ≡ PF₃ as a ligand, but more oxidizing and more readily hydrolysed.

AsCl₃/SbCl₃ Low viscosity solvents for Cl⁻ ion exchange/transfer reactions.

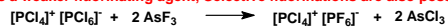
AsF₃/SbF₃ Good halogen exchange reagents (Cl to F) for nonmetal halides.



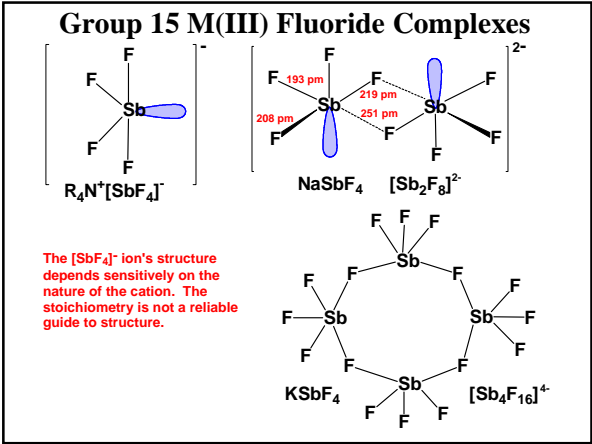
Oxidation sometimes occurs simultaneously:

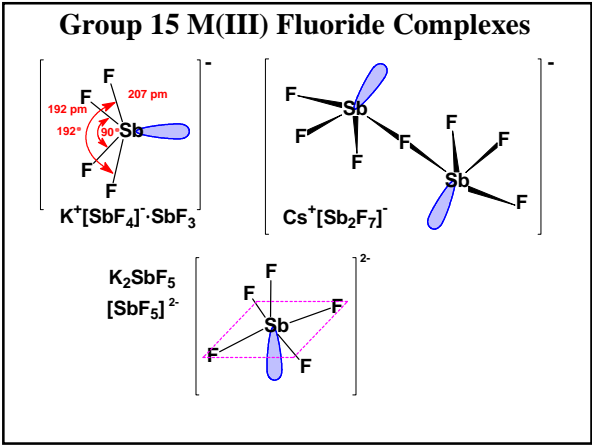


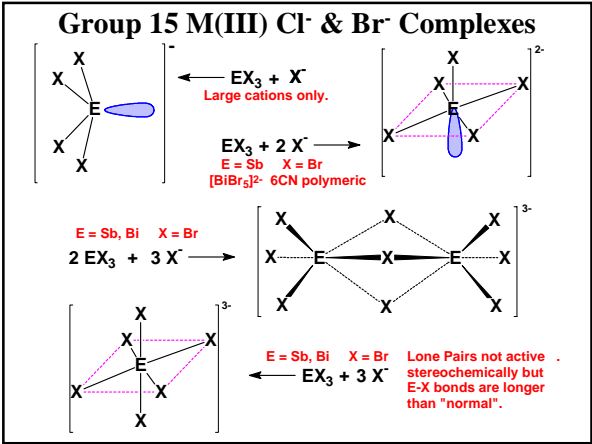
AsF₃ is a weaker fluorinating agent, Selective fluorinations are also possible. .



AsCl₃ (bp 130°C) can be distilled off more easily than SbCl₃ (bp 223°C).







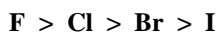
Group 15 M(III) Cl⁻ & Br⁻ Complexes

Trends in Electron Lone-Pair Stereochemical Activity

As one goes down the Group: As > Sb > Bi

With increase in coordination number of the central atom: 4 > 5 > 6

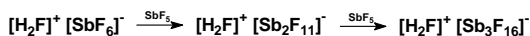
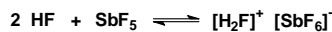
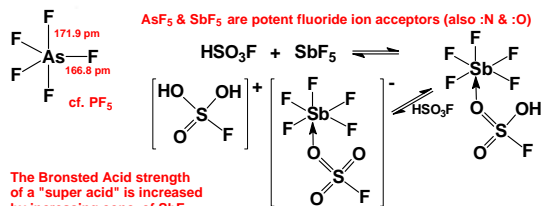
As the halogen atom becomes heavier:



Pentahalides of Group 15

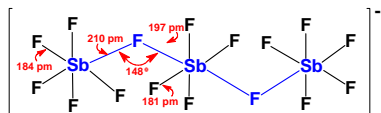
Table 13.9 Some properties of the known pentahalides

Property	AsF ₅	SbF ₅	BiF ₅	AsCl ₅	SbCl ₅
mp/°C	-79.8	9.3	154.4	~ -58 (6)	4
bp/°C	-51.8	141	230	—	140 (6)
Density (MCl ₅) g cm ⁻³	2.33 (1-33°)	3.11 (25°)	5.40 (25°)	—	2.35 (27°)



Oligomeric & Mixed Antimony(V) Halides

The trans-bridged ion: [Sb₃F₁₆]⁻



Mixed Halides:

SbF₅ is a very syrupy, viscous liquid. Addition of small amounts of SbCl₅ dramatically lowers the viscosity, and raises conductivity. Fluorine bridges are broken, cyclic, tetrameric and ionic species are formed.

