Skills to Develop

- To understand the trends in properties and reactivity of the group 14 elements: the pnictogens.

Antimony (Sb) was probably the first of the pnictogens to be obtained in elemental form and recognized as an element. Its atomic symbol comes from its Roman name: stibium. It is found in stibnite (Sb$_2$S$_3$), a black mineral that has been used as a cosmetic (an early form of mascara) since biblical times, and it is easily reduced to the metal in a charcoal fire (Figure 1). The Egyptians used antimony to coat copper objects as early as the third millennium BC, and antimony is still used in alloys to improve the tonal quality of bells.

In the form of its yellow sulfide ore, orpiment (As$_2$S$_3$), arsenic (As) has been known to physicians and professional assassins since ancient Greece, although elemental arsenic was not isolated until centuries later. The history of bismuth (Bi), in contrast, is more difficult to follow because early alchemists often confused it with other metals, such as lead, tin, antimony, and even silver (due to its slightly pinkish-white luster). Its name comes from the old German wismut, meaning “white metal.” Bismuth was finally isolated in the 15th century, and it was used to make movable type for printing shortly after the invention of the Gutenberg printing process in 1440. Bismuth is used in printing because it is one of the few substances known whose solid state is less dense than the liquid. Consequently, its alloys expand as they cool, filling a mold completely and producing crisp, clear letters for typesetting.

Phosphorus was discovered in 1669 by the German alchemist Hennig Brandt, who was looking for the “philosophers’ stone,” a mythical substance capable of converting base metals to silver or gold. Believing that human urine was the source of the key ingredient, Brandt obtained several dozen buckets of urine, which he allowed to putrefy. The urine was distilled to dryness at high temperature and then condensed; the last fumes were collected under water, giving a waxy white solid that had unusual properties. For example, it glowed in the dark and burst into flames when removed from the water. (Unfortunately for Brandt, however, it did not turn lead into gold.) The element was given its current name (from the Greek phos, meaning “light,” and phoros, meaning “bringing”) in the 17th century. For more than a century, the only way to obtain phosphorus was the distillation of urine, but in 1769 it was discovered that phosphorus could be obtained more easily from bones. During the 19th century, the demand for phosphorus for matches was so great that battlefields and paupers’ graveyards were systematically scavenged for bones. Early matches were pieces of wood coated with elemental phosphorus that were stored in an evacuated glass tube and ignited when the tube was broken (which could...
cause unfortunate accidents if the matches were kept in a pocket!).

Unfortunately, elemental phosphorus is volatile and highly toxic. It is absorbed by the teeth and destroys bone in the jaw, leading to a painful and fatal condition called “phossy jaw,” which for many years was accepted as an occupational hazard of working in the match industry.

Preparation and General Properties of the Group 15 Elements

The three non-nitrogen pnictogens are much less abundant than nitrogen: arsenic is found in Earth’s crust at a concentration of about 2 ppm, antimony is an order of magnitude less abundant, and bismuth is almost as rare as gold. All three elements have a high affinity for the chalcogens and are usually found as the sulfide ores (M₂S₃), often in combination with sulfides of other heavy elements, such as copper, silver, and lead. Hence a major source of antimony and bismuth is flue dust obtained by smelting the sulfide ores of the more abundant metals.

In group 15, as elsewhere in the p block, we see large differences between the lightest element (N) and its congeners in size, ionization energy, electron affinity, and electronegativity (Table 1). The chemical behavior of the elements can be summarized rather simply: nitrogen and phosphorus behave chemically like nonmetals, arsenic and antimony behave like semimetals, and bismuth behaves like a metal. With their ns²np³ valence electron configurations, all form compounds by losing either the three np valence electrons to form the +3 oxidation state or the three np and the two ns valence electrons to give the +5 oxidation state, whose stability decreases smoothly from phosphorus to bismuth. In addition, the relatively large magnitude of the electron affinity of the lighter pnictogens enables them to form compounds in the −3 oxidation state (such as NH₃ and PH₃), in which three electrons are formally added to the neutral atom to give a filled np subshell. Nitrogen has the unusual ability to form compounds in nine different oxidation states, including −3, +3, and +5. Because neutral covalent compounds of the trivalent pnictogens contain a lone pair of electrons on the central atom, they tend to behave as Lewis bases.

<table>
<thead>
<tr>
<th>Property</th>
<th>Nitrogen</th>
<th>Phosphorus</th>
<th>Arsenic</th>
<th>Antimony</th>
<th>Bismuth</th>
</tr>
</thead>
<tbody>
<tr>
<td>atomic symbol</td>
<td>N</td>
<td>P</td>
<td>As</td>
<td>Sb</td>
<td>Bi</td>
</tr>
</tbody>
</table>

*The configuration shown does not include filled d and f subshells.

†For white phosphorus.

‡For gray arsenic.

§The values cited are for six-coordinate ions in the indicated oxidation states. The N⁵⁺, P⁵⁺, and As⁵⁺ ions are not known species.

‖The chemical form of the elements in these oxidation states varies considerably. For N, the reaction is NO₃⁻ + 3H⁺ + 2e⁻ → HNO₂ + H₂O; for P and As, it is H₃EO₄ + 2H⁺ + 2e⁻ → H₃EO₃ + H₂O; and for Sb it is Sb₂O₅ + 4e⁻ + 10H⁺ → 2Sb³⁺ + 5H₂O.
<table>
<thead>
<tr>
<th>Property</th>
<th>Nitrogen</th>
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<th>Arsenic</th>
<th>Antimony</th>
<th>Bismuth</th>
</tr>
</thead>
<tbody>
<tr>
<td>atomic number</td>
<td>7</td>
<td>15</td>
<td>33</td>
<td>51</td>
<td>83</td>
</tr>
<tr>
<td>atomic mass (amu)</td>
<td>14.01</td>
<td>30.97</td>
<td>74.92</td>
<td>121.76</td>
<td>209.98</td>
</tr>
<tr>
<td>valence electron configuration*</td>
<td>$2s^22p^3$</td>
<td>$3s^23p^3$</td>
<td>$4s^24p^3$</td>
<td>$5s^25p^3$</td>
<td>$6s^26p^3$</td>
</tr>
<tr>
<td>melting point/boiling point (°C)</td>
<td>$-210/-196$</td>
<td>$44.15/281^c$</td>
<td>817 (at 3.70 MPa)/603 (sublimes)$^\dagger$</td>
<td>631/1587</td>
<td>271/1564</td>
</tr>
<tr>
<td>density (g/cm$^3$) at 25°C</td>
<td>1.15 (g/L)</td>
<td>1.82$^\dagger$</td>
<td>5.75$^\ddagger$</td>
<td>6.68</td>
<td>9.79</td>
</tr>
<tr>
<td>atomic radius (pm)</td>
<td>56</td>
<td>98</td>
<td>114</td>
<td>133</td>
<td>143</td>
</tr>
<tr>
<td>first ionization energy (kJ/mol)</td>
<td>1402</td>
<td>1012</td>
<td>945</td>
<td>831</td>
<td>703</td>
</tr>
<tr>
<td>common oxidation state(s)</td>
<td>$-3$ to $+5$</td>
<td>$+5$, $+3$, $-3$</td>
<td>$+5$, $+3$</td>
<td>$+5$, $+3$</td>
<td>$+3$</td>
</tr>
<tr>
<td>ionic radius (pm)$^\S$</td>
<td>146 ($-3$), 16 ($+3$)</td>
<td>212 ($-3$), 44 ($+3$)</td>
<td>58 ($+3$)</td>
<td>76 ($+3$), 60 ($+5$)</td>
<td>103 ($+3$)</td>
</tr>
<tr>
<td>electron affinity (kJ/mol)</td>
<td>0</td>
<td>$-72$</td>
<td>$-78$</td>
<td>$-101$</td>
<td>$-91$</td>
</tr>
<tr>
<td>electronegativity</td>
<td>3.0</td>
<td>2.2</td>
<td>2.2</td>
<td>2.1</td>
<td>1.9</td>
</tr>
</tbody>
</table>

*The configuration shown does not include filled d and f subshells.

$^\dagger$For white phosphorus.

$^\ddagger$For gray arsenic.

$^\S$The values cited are for six-coordinate ions in the indicated oxidation states. The $N^{5+}$, $P^{5+}$, and $As^{5+}$ ions are not known species.

$^\|The chemical form of the elements in these oxidation states varies considerably. For N, the reaction is $NO_3^-$ + $3H^+$ + $2e^-$ → $HNO_2$ + $H_2O$; for P and As, it is $H_3EO_4$ + $2H^+$ + $2e^-$ → $H_3EO_3$ + $H_2O$; and for Sb it is $Sb_2O_5$ + $4e^-$ + $10H^+$ → 2$Sb^{3+}$ + 5$H_2O$. 

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<tr>
<th>Property</th>
<th>Nitrogen</th>
<th>Phosphorus</th>
<th>Arsenic</th>
<th>Antimony</th>
<th>Bismuth</th>
</tr>
</thead>
<tbody>
<tr>
<td>standard reduction potential ((E^\circ, V)) ((E^V \rightarrow E^{III} \text{ in acidic solution}))</td>
<td>+0.93</td>
<td>−0.28</td>
<td>+0.56</td>
<td>+0.65</td>
<td>—</td>
</tr>
<tr>
<td>product of reaction with (O_2)</td>
<td>NO₂, NO</td>
<td>(P_4O_6, P_4O_{10})</td>
<td>(As_4O_6)</td>
<td>(Sb_2O_5)</td>
<td>(Bi_2O_3)</td>
</tr>
<tr>
<td>type of oxide</td>
<td>acidic (NO₂), neutral (NO, (N_2O))</td>
<td>acidic</td>
<td>acidic</td>
<td>amphoteric</td>
<td>basic</td>
</tr>
<tr>
<td>product of reaction with (N_2)</td>
<td>—</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>product of reaction with (X_2)</td>
<td>none</td>
<td>(PX_3, PX_5)</td>
<td>(AsF_5, AsX_3)</td>
<td>(SbF_5, SbCl_5, SbBr_3, SbI_3)</td>
<td>(BiF_5, BiX_3)</td>
</tr>
<tr>
<td>product of reaction with (H_2)</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
</tbody>
</table>

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In group 15, the stability of the +5 oxidation state decreases from \(P\) to \(Bi\).

Because neutral covalent compounds of the trivalent group 15 elements have a lone pair of electrons on the central atom, they tend to be Lewis bases.

### Reactions and Compounds of the Heavier Pnicogens

Like the heavier elements of group 14, the heavier pnicogens form catenated compounds that contain only single bonds, whose stability decreases rapidly as we go down the group. For example, phosphorus exists as multiple allotropes, the
most common of which is white phosphorus, which consists of P\textsubscript{4} tetrahedra and behaves like a typical nonmetal. As is typical of a molecular solid, white phosphorus is volatile, has a low melting point (44.1°C), and is soluble in nonpolar solvents. It is highly strained, with bond angles of only 60°, which partially explains why it is so reactive and so easily converted to more stable allotropes. Heating white phosphorus for several days converts it to red phosphorus, a polymer that is air stable, virtually insoluble, denser than white phosphorus, and higher melting, properties that make it much safer to handle. A third allotrope of phosphorus, black phosphorus, is prepared by heating the other allotropes under high pressure; it is even less reactive, denser, and higher melting than red phosphorus. As expected from their structures, white phosphorus is an electrical insulator, and red and black phosphorus are semiconductors. The three heaviest pnicogens—arsenic, antimony, and bismuth—all have a metallic luster, but they are brittle (not ductile) and relatively poor electrical conductors.

As in group 14, the heavier group 15 elements form catenated compounds that contain only single bonds, whose stability decreases as we go down the group.

The reactivity of the heavier pnicogens decreases as we go down the column. Phosphorus is by far the most reactive of the pnicogens, forming binary compounds with every element in the periodic table except antimony, bismuth, and the noble gases. Phosphorus reacts rapidly with O\textsubscript{2}, whereas arsenic burns in pure O\textsubscript{2} if ignited, and antimony and bismuth react with O\textsubscript{2} only when heated. None of the pnicogens reacts with nonoxidizing acids such as aqueous HCl, but all dissolve in oxidizing acids such as HNO\textsubscript{3}. Only bismuth behaves like a metal, dissolving in HNO\textsubscript{3} to give the hydrated Bi\textsuperscript{3+} cation.

The reactivity of the heavier group 15 elements decreases as we go down the column.

The heavier pnicogens can use energetically accessible 3d, 4d, or 5d orbitals to form dsp\textsuperscript{3} or d\textsuperscript{2}sp\textsuperscript{3} hybrid orbitals for bonding. Consequently, these elements often have coordination numbers of 5 or higher. Phosphorus and arsenic form halides (e.g., AsCl\textsubscript{5}) that are generally covalent molecular species and behave like typical nonmetal halides, reacting with water to form the corresponding oxoacids (in this case, H\textsubscript{3}AsO\textsubscript{4}). All the pentahalides are potent Lewis acids that can expand their coordination to accommodate the lone pair of a Lewis base:

\[
\text{AsF}_5(\text{soln}) + F^-_{(\text{soln})} \rightarrow \text{AsF}_6^{2-}(\text{soln}) \tag{Eq4}\]

In contrast, bismuth halides have extended lattice structures and dissolve in water to produce hydrated ions, consistent with the stronger metallic character of bismuth.

Except for BiF\textsubscript{3}, which is essentially an ionic compound, the trihalides are volatile covalent molecules with a lone pair of electrons on the central atom. Like the pentahalides, the trihalides react rapidly with water. In the cases of phosphorus and arsenic, the products are the corresponding acids, H\textsubscript{3}PO\textsubscript{3} and H\textsubscript{3}AsO\textsubscript{3}, where E is P or As:

\[
\text{EX}_3(l) + 3\text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{EO}_3(aq) + 3\text{HX}(aq) \tag{Eq5}\]

Phosphorus halides are also used to produce insecticides, flame retardants, and plasticizers.
Phosphorus has the greatest ability to form π bonds with elements such as O, N, and C.

With energetically accessible d orbitals, phosphorus and, to a lesser extent, arsenic are able to form π bonds with second-period atoms such as N and O. This effect is even more important for phosphorus than for silicon, resulting in very strong P–O bonds and even stronger P=O bonds. The first four elements in group 15 also react with oxygen to produce the corresponding oxide in the +3 oxidation state. Of these oxides, P₄O₆ and As₄O₆ have cage structures formed by inserting an oxygen atom into each edge of the P₄ or As₄ tetrahedron (part (a) in Figure \(\PageIndex{2}\)), and they behave like typical nonmetal oxides. For example, P₄O₆ reacts with water to form phosphorous acid (H₃PO₃). Consistent with its position between the nonmetal and metallic oxides, Sb₄O₆ is amphoteric, dissolving in either acid or base. In contrast, Bi₂O₃ behaves like a basic metallic oxide, dissolving in acid to give solutions that contain the hydrated Bi³⁺ ion. The two least metallic elements of the heavier pnicogens, phosphorus and arsenic, form very stable oxides with the formula E₄O₁₀ in the +5 oxidation state (part (b) in Figure \(\PageIndex{2}\)). In contrast, Bi₂O₅ is so unstable that there is no absolute proof it exists.

![Figure \(\PageIndex{2}\): The Structures of Some Cage Compounds of Phosphorus. (a, b) The structures of P₄O₆ and P₄O₁₀ are both derived from the structure of white phosphorus (P₄) by inserting an oxygen atom into each of the six edges of the P₄ tetrahedron; P₄O₁₀ contains an additional terminal oxygen atom bonded to each phosphorus atom. (c) The structure of P₄S₃ is also derived from the structure of P₄ by inserting three sulfur atoms into three adjacent edges of the tetrahedron.](image)

The heavier pnicogens form sulfides that range from molecular species with three-dimensional cage structures, such as P₄S₃ (part (c) in Figure \(\PageIndex{2}\)), to layered or ribbon structures, such as Sb₂S₃ and Bi₂S₃, which are semiconductors. Reacting the heavier pnicogens with metals produces substances whose properties vary with the metal content. Metal-rich phosphides (such as M₄P) are hard, high-melting, electrically conductive solids with a metallic luster, whereas phosphorus-rich phosphides (such as MP₁₅) are lower melting and less thermally stable because they contain catenated Pₙ units. Many organic or organometallic compounds of the heavier pnicogens containing one to five alkyl or aryl groups are also known. Because of the decreasing strength of the pnicogen–carbon bond, their thermal stability decreases from phosphorus to bismuth.

The thermal stability of organic or organometallic compounds of group 15 decreases down the group due to the decreasing strength of the pnicogen–carbon bond.

Example \(\PageIndex{1}\)
For each reaction, explain why the given products form.

a. \( \text{Bi(s)} + \frac{3}{2} \text{Br(l)} \rightarrow \text{BiBr}_3(s) \)
b. \( 2(\text{CH}_3)_3\text{As(l)} + \text{O}_2(g) \rightarrow 2(\text{CH}_3)_3\text{As}=\text{O(s)} \)
c. \( \text{PBr}_3(l) + 3\text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{PO}_3(aq) + 3\text{HBr(aq)} \)
d. \( \text{As(s)} + \text{Ga(s)} \xrightarrow{\Delta} \text{GaAs(s)} \)

**Given:** balanced chemical equations

**Asked for:** why the given products form

**Strategy:**

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the reaction products form.

**Solution:**

a. Bromine is an oxidant, and bismuth is a metal that can be oxidized. Hence a redox reaction is likely to occur. To identify the product, recall that bismuth can form compounds in either the +3 or +5 oxidation state. The heaviest pnicogen, bismuth is rather difficult to oxidize to the +5 oxidation state because of the inert-pair effect. Hence the product will probably be bismuth(III) bromide.

b. Trimethylarsine, with a lone pair of electrons on the arsenic atom, can act as either a Lewis base or a reductant. If arsenic is oxidized by two electrons, then oxygen must be reduced, most probably by two electrons to the −2 oxidation state. Because As(V) forms strong bonds to oxygen due to π bonding, the expected product is \((\text{CH}_3)_3\text{As}=\text{O}\).

c. Phosphorus tribromide is a typical nonmetal halide. We expect it to react with water to produce an oxoacid of P(III) and the corresponding hydrohalic acid. Because of the strength of the P=O bond, phosphorous acid \((\text{H}_3\text{PO}_3)\) is actually \(\text{HP(O)(OH)}_2\), which contains a P=O bond and a P–H bond.

d. Gallium is a metal with a strong tendency to act as a reductant and form compounds in the +3 oxidation state. In contrast, arsenic is a semimetal. It can act as a reductant to form compounds in the +3 or +5 oxidation state, or it can act as an oxidant, accepting electrons to form compounds in the −3 oxidation state. If a reaction occurs, then a binary compound will probably form with a 1:1 ratio of the elements. GaAs is an example of a III-V compound, many of which are used in the electronics industry.

**Exercise**

Predict the products of each reaction and write a balanced chemical equation for each reaction.

a. \( \text{PCl}_5(s) + \text{H}_2\text{O(l)} \rightarrow \)
b. \( \text{Bi}_2\text{O}_5(s) \xrightarrow{\Delta} \)
c. \( \text{Ca}_3\text{P}_2(s) + \text{H}^+(aq) \rightarrow \)
d. \( \text{NaNH}_2(s) + \text{PH}_3(\text{soln}) \rightarrow \)

**Answer:**

a. \( \text{PCl}_5(s) + 4\text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{PO}_4(aq) + 5\text{HCl(aq)} \)
b. $\text{Bi}_2\text{O}_5(s) \xrightarrow{\Delta} \text{Bi}_2\text{O}_3(s) + \text{O}_2(g)$

c. $\text{Ca}_3\text{P}_2(s) + 6\text{H}^+(aq) \rightarrow 2\text{PH}_3(g) + 3\text{Ca}^{2+}(aq)$

d. $\text{NaNH}_2(s) \rightarrow \text{NaPH}_2(s) + \text{NH}_3(\text{soln})$

**Summary**

The reactivity of the heavier group 15 elements decreases down the group, as does the stability of their catenated compounds. In group 15, nitrogen and phosphorus behave chemically like nonmetals, arsenic and antimony behave like semimetals, and bismuth behaves like a metal. The stability of the +5 oxidation state decreases from phosphorus to bismuth because of the inert-pair effect. Due to their higher electronegativity, the lighter pnicogens form compounds in the −3 oxidation state. Because of the presence of a lone pair of electrons on the pnicogen, neutral covalent compounds of the trivalent pnicogens are Lewis bases. The reactivity of the pnicogens decreases with increasing atomic number. Compounds of the heavier pnicogens often have coordination numbers of 5 or higher and use $d^{sp^3}$ or $d^2sp^3$ hybrid orbitals for bonding. Because phosphorus and arsenic have energetically accessible d orbitals, these elements form $\pi$ bonds with second-period atoms such as O and N. Phosphorus reacts with metals to produce phosphides. Metal-rich phosphides are hard, high-melting, electrically conductive solids with metallic luster, whereas phosphorus-rich phosphides, which contain catenated phosphorus units, are lower melting and less thermally stable.