Chem3I2F – Sem 1, 2004

- Week 8: Group 13
- **Week 9:** Group 15
- Week 10: Group 16 – 17
- Week 11: Carbides
- Week 12: Nitrides/Alloys
- Week 13: Summary/Tutorial

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Group 15: Properties

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic No.</th>
<th>Atomic Mass</th>
<th>Valence e- configuration</th>
<th>Common oxidation states</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>33</td>
<td>74.92</td>
<td>4s^24p^3</td>
<td>(-3, +5, +3)</td>
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<tr>
<td>Sb</td>
<td>51</td>
<td>121.8</td>
<td>5s^25p^3</td>
<td>(-3, +5, +3)</td>
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<tr>
<td>Bi</td>
<td>83</td>
<td>209.0</td>
<td>6s^26p^3</td>
<td>(+3)</td>
</tr>
</tbody>
</table>

**KEY**
- Atomic No.
- Symbol
- Atomic mass
- Valence e- configuration
- Common oxidation states
Group 15: Properties

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic radius (pm)</th>
<th>Ionic radius (pm)</th>
<th>First ionization energy (kJ/mol)</th>
<th>Electronegativity</th>
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</thead>
<tbody>
<tr>
<td>N</td>
<td>75</td>
<td>N³⁻ 146</td>
<td>1402</td>
<td>3.0</td>
</tr>
<tr>
<td>P</td>
<td>110</td>
<td>P³⁻ 212</td>
<td>1012</td>
<td>2.1</td>
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<tr>
<td>As</td>
<td>120</td>
<td></td>
<td>947</td>
<td>2.0</td>
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<tr>
<td>Sb</td>
<td>140</td>
<td></td>
<td>834</td>
<td>1.9</td>
</tr>
<tr>
<td>Bi</td>
<td>150</td>
<td>Bi³⁺ 103</td>
<td>703</td>
<td>1.9</td>
</tr>
</tbody>
</table>

- **Temperature (°C)**: N (BP -210, MP -196), P (BP -210, MP 44.1), As (BP 615 (subl), MP 815 (at 39 atm)), Sb (BP 631, MP 1587), Bi (BP 271, MP 1564)

- **Density of solid (g/mL)**: N 0.879, P 1.82, As 5.78, Sb 6.70, Bi 9.81
**Group 15: Important Compounds**

**Important Compounds**

1. Ammonia, \( \text{NH}_3 \). First substance formed when atmospheric \( \text{N}_2 \) is used to make N-containing compounds. Annual multimillion-ton production for use in fertilizers, explosives, rayon, and polymers such as nylon, urea-formaldehyde resins, and acrylates.

2. Hydrazine, \( \text{N}_2\text{H}_4 \) (see margin note, p. 576).

3. Nitric oxide (NO), nitrogen dioxide (\( \text{NO}_2 \)), and nitric acid (\( \text{HNO}_3 \)). Oxides are intermediates in \( \text{HNO}_3 \) production. This acid is used in fertilizer manufacture, nylon production, metal etching, and the explosives industry (see *Highlights of Nitrogen Chemistry*).

4. Amino acids, \( \text{H}_2\text{N}^+ \text{—CH(R) — COO}^- \) (\( R \) = one of 20 different organic groups). Occur in every organism, both free and linked together into proteins. Essential to the growth and function of all cells. Synthetic amino acids are used as dietary supplements.

5. Phosphorus trichloride, \( \text{PCl}_3 \). Used to form many organic phosphorus compounds, including oil and fuel additives, plasticizers, flame retardants, and insecticides. Also used to make \( \text{PCl}_5 \), \( \text{POCl}_3 \), and other important P-containing compounds.

6. Tetraphosphorus decaoxide (\( \text{P}_4\text{O}_{10} \)) and phosphoric acid (\( \text{H}_3\text{PO}_4 \)) (see *Highlights of Phosphorus Chemistry*).

7. Sodium tripolyphosphate, \( \text{Na}_3\text{P}_3\text{O}_{10} \). As a water-softening agent (Calgon), it combines with hard-water \( \text{Mg}^{2+} \) and \( \text{Ca}^{2+} \) ions, preventing them from reacting with soap anions, and thus improves cleaning action. Its use has been curtailed in the United States because it pollutes lakes and streams by causing excessive algal growth (see photo).

8. Adenosine triphosphate (ATP) and other biophosphates. ATP acts to transfer chemical energy in the cell; necessary for all biological processes requiring energy. Phosphate groups occur in sugars, fats, proteins, and nucleic acids.

9. Bismuth subsalicylate, \( \text{BiO(C}_2\text{H}_3\text{O}_2) \). The active ingredient in Pepto-Bismol (see photo), a widely used remedy for diarrhea and nausea. (The pink color is not due to this white compound.)
Group 15: Important Reactions

**Important Reactions**

General group behavior is shown in reactions 1 to 3, whereas phosphorus chemistry is the theme in reactions 4 and 5.

1. Nitrogen is “fixed” industrially in the Haber process:
   \[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]
   Further reactions convert \( \text{NH}_3 \) to \( \text{NO} \), \( \text{NO}_2 \), and \( \text{HNO}_3 \) (see Highlights of Nitrogen Chemistry). Hydrides of some other group members are formed from reaction in water (or \( \text{H}_2\text{O}^- \)) of a metal phosphide, arsenide, and so forth:
   \[ \text{Ca}_3\text{P}_2(s) + 6\text{H}_2\text{O}(l) \rightarrow 2\text{PH}_3(g) + 3\text{Ca(OH)}_2(aq) \]

2. Halides are formed by direct combination of the elements:
   \[ 2E(s) + 3X_2 \rightarrow 2EX_3 \quad (E = \text{all except N}) \]
   \[ \text{EX}_3 + X_2 \rightarrow \text{EX}_5 \quad (E = \text{all except N and Bi} \text{ with } X = \text{F and Cl}; \ E = \text{P for } X = \text{Br}) \]

3. Oxoacids are formed from the halides in a reaction with water that is common to many nonmetal halides:
   \[ \text{EX}_3 + 3\text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{EO}_3(aq) + 3\text{HX}(aq) \]
   \( (E = \text{all except N}) \)
   \[ \text{EX}_5 + 4\text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{EO}_4(aq) + 5\text{HX}(aq) \]
   \( (E = \text{all except N and Bi}) \)
   Note that the oxidation number of \( E \) does *not* change.

4. Phosphate ions are dehydrated to form polyphosphates:
   \[ 3\text{NaH}_2\text{PO}_4(s) \rightarrow \text{Na}_3\text{P}_3\text{O}_9(s) + 3\text{H}_2\text{O}(g) \]

5. When \( \text{P}_4 \) reacts in basic solution, its oxidation state both decreases *and* increases (disproportionation):
   \[ \text{P}_4(s) + 3\text{OH}^-(aq) + 3\text{H}_2\text{O}(l) \rightarrow \text{PH}_3(g) + 3\text{H}_2\text{PO}_2^-(aq) \]

Analogous reactions are typical of many nonmetals, such as \( S_8 \) and \( X_2 \) (halogens).
The Nitrogen Cycle

Bacterial nodule on pea root
Haber, 1909 - Bosch, 1913

Fritz Haber

Haber synthesised 100g in 1909
Bosch scaled up for industry, 1913.
Now 110 million tonnes per year produced

Haber’s original experimental apparatus.

Haber, Nobel Prize, 1918
Bosch, Nobel Prize, 1931
Industrial Conditions:
- ~400°C
- 70-200 atm
- ~40% yield

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) + 91.8 \text{kJ} \]
Uses of ammonia

- Nitric acid: 79%
- Fertilizer: 5.9%
- Nylon: 5%
- Chemicals: 2%
- Miscellaneous: 7.9%
The structures of nitric and nitrous acids and their oxyanions

[Diagram showing the structures of nitric acid (HNO₃) and nitrous acid (HNO₂), and their oxyanions: nitrate ion (NO₃⁻) and nitrite ion (NO₂⁻).]
# Structure and Properties of the Nitrogen Oxides

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>Space-filling Model</th>
<th>Lewis Structure</th>
<th>Oxidation State of N</th>
<th>$\Delta H^\circ_r$ (kJ/mol) at 298 K</th>
<th>Comment</th>
</tr>
</thead>
</table>
| $\text{N}_2\text{O}$ | Dinitrogen monoxide (dinitrogen oxide; nitrous oxide) | ![Space-filling Model](image) | $\overset{\cdot}{\text{N}}=\overset{\cdot}{\text{O}}$     | +1  
(0, +2)                          | 82.0  | Colorless gas; used as dental anesthetic ("laughing gas") and aerosol propellant |
| $\text{NO}$       | Nitrogen monoxide (nitrogen oxide; nitric oxide)     | ![Space-filling Model](image) | $\overset{\cdot}{\text{N}}=\overset{\cdot}{\text{O}}$     | +2 | 90.3  | Colorless, paramagnetic gas; biochemical messenger; air pollutant       |
| $\text{N}_2\text{O}_3$ | Dinitrogen trioxide                               | ![Space-filling Model](image) | $\overset{\cdot}{\text{N}}=\overset{\cdot}{\text{O}}$     | +3  
(+2, +4) | 83.7  | Reddish brown gas (reversibly dissociates to NO and NO$_2$)             |
| $\text{NO}_2$      | Nitrogen dioxide                                   | ![Space-filling Model](image) | $\overset{\cdot}{\text{N}}=\overset{\cdot}{\text{O}}$     | +4 | 33.2  | Orange-brown, paramagnetic gas formed during HNO$_3$ manufacture; poisonous air pollutant |
| $\text{N}_2\text{O}_4$ | Dinitrogen tetraoxide                              | ![Space-filling Model](image) | $\overset{\cdot}{\text{N}}=\overset{\cdot}{\text{O}}$     | +4 | 9.16  | Colorless to yellow liquid (reversibly dissociates to NO$_2$)             |
| $\text{N}_2\text{O}_5$ | Dinitrogen pentaoxide                              | ![Space-filling Model](image) | $\overset{\cdot}{\text{N}}=\overset{\cdot}{\text{O}}$     | +5 | 11.3  | Colorless, volatile solid consisting of NO$_2^+$ and NO$_3^-$; gas consists of N$_2$O$_5$ molecules |
The Formation of Photochemical Smog

![Graph showing the formation of photochemical smog over time.]
Ammoniumnitrate Explosions

Oppau (Germany), 1921

Ryongchon (North Korea), 2004
Two allotropes of phosphorus

White phosphorus ($P_4$)

Strained bonds in $P_4$

Red phosphorus
Interconversion of phosphorus allotropes


Reactions of phosphorus allotropes


FIG. 11-1. Some typical and important reactions of red and white phosphorus.
Important oxides of phosphorus

$\text{P}_4\text{O}_6$

$\text{P}_4\text{O}_{10}$
Phosphoric acid

$$3 \text{H}_2\text{SO}_4(\ell) + \text{Ca}_3(\text{PO}_4)_2(s) + 6 \text{H}_2\text{O}(\ell) \rightleftharpoons 2 \text{H}_3\text{PO}_4(s) + 3 \text{CaSO}_4\cdot2\text{H}_2\text{O}(s)$$

Uses of phosphoric acid

Fertilizers: 80%
Detergents: 10%
Miscellaneous: 10%
The diphosphate ion and polyphosphates
The Phosphorus Cycle
Industrial Uses of Phosphorus

PHOSPHATE ROCK (100%)

- Elemental phosphorus (10%)
- Phosphorus sulfides
- Phosphorus chlorides
- Organic phosphorus compounds (2%)
- Phosphoric acid (pure) (12.5%)
- Metal treatment (e.g., pickling, cleaning, rust-proofing, polishing) (2.5%)
- Pharmaceuticals
  - Detergent phosphate
  - Industrial phosphate
  - Food phosphate (10%)
- Fertilizer (85.5%)
- Phosphoric acid (impure) (90%)
Arsenic Minerals

- \( \text{As}_4\text{S}_4 \) Realgar
- \( \text{As}_2\text{S}_3 \) Orpiment
- \( \text{As}_2\text{O}_3 \) Arsenolite
- \( \text{FeAs}_2 \) Loellingite
- \( \text{FeAsS} \) Arsenopyrite

\[
\text{FeAsS} \quad \xrightarrow{700^\circ\text{C}} \quad \text{FeS} + \text{As(g)} \rightarrow \text{As(s)}
\]

Uses:
- Bronzes and alloys - found in early bronze age implements
- Insecticides and herbicides (now phased out)
- Gallium arsenide - semiconducting material
Uses of Arsenic Compounds
Antimony/Bismuth

The most important ore of antimony is stibnite $\text{Sb}_2\text{S}_3$ other oxides are common.

Ores containing 40-60% Sb are liquated at 550-600ºC under reducing conditions to give $\text{Sb}_2\text{S}_3$ and then treated with scrap iron to remove the sulfide:

$$\text{Sb}_2\text{S}_3 + 3\text{Fe} \rightarrow 2\text{Sb} + 3\text{FeS}$$

Further purification by electrolysis - > 99.9% purity - then by zone refining.

Bismuth occurs mainly as bismite ($\alpha$-$\text{BiO}_2$), bismuthinite ($\text{Bi}_2\text{S}_3$) and bismutite \{$\text{(BiO)}_2\text{CO}_3$\} and occasionally as the element in association with Pb, Ag, or Co ores.

The main commercial source of the element is as a by product from Pb/Zn and Cu refining.

Sulfide ores are roasted to the oxide and then reduced by iron or charcoal. Because of its low mp, very low solubility in Fe, and fairly high oxidative stability in air, Bi can be melted and cast (like lead) in iron and steel vessels.