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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Classes of Nitrides

Nitrogen forms binary compounds with many other elements. Many of them are important to daily life, they include NH₃ and Si₃N₄. Binary compounds of nitrogen with less electronegative elements, the nitrides, are classified into three main categories:

1. **Saline nitrides**, which may be considered to be largely ionic solids. These compounds are formed by the elements of Groups 1 and 2 and by zinc and cadmium.

2. **Metallic nitrides**, which have a metallic conductivity and lustre. These compounds are formed by d- and f-block elements.

3. **Covalent nitrides**, with a wide range of properties.

Lithium nitride, Li$_3$N, is the most stable binary alkali metal nitride and has a unique ‘layered’ structure. Lithium-nitrogen [Li$_2$N] layers are separated by layers of lithium atoms. Low concentrations of lithium vacancies in the [Li$_2$N] layers give rise to high Li$^+$ ion conductivity. The suitability of the material as a component in batteries is chiefly limited by its low decomposition voltage.
Lithium Nitride - Ionic Conductivity

Hexagonal bipyramids

View down a

Hexagonal bipyramids

View down a
Unit cells of some modern ceramic materials

zinc blende structure

A Silicon carbide

B Cubic BN (borazon)
# New Ceramics and Ceramic Materials

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC, Si₃N₄, TiB₂, Al₂O₃</td>
<td>Whiskers (fibers) to strengthen Al and other ceramics</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>Car engine parts; turbine rotors for “turbo” cars; electronic sensor units</td>
</tr>
<tr>
<td>Si₃N₄, BN, Al₂O₃</td>
<td>Supports or layering materials (as insulators) in electronic microchips</td>
</tr>
<tr>
<td>SiC, Si₃N₄, TiB₂, ZrO₂, Al₂O₃,</td>
<td>Cutting tools, edge sharpeners (as coatings and whole devices), scissors,</td>
</tr>
<tr>
<td>BN</td>
<td>surgical tools, industrial “diamond”</td>
</tr>
<tr>
<td>BN, SiC</td>
<td>Armor-plating reinforcement fibers (as in Kevlar composites)</td>
</tr>
<tr>
<td>ZrO₂, Al₂O₃</td>
<td>Surgical implants (hip and knee joints)</td>
</tr>
</tbody>
</table>
Metallic Nitrides

MN, M\(_2\)N, M\(_4\)N or non-stoichiometric

Properties: opaque, very hard, chemically inert, electrical conductors, metallic lustre

Radius ratio: \(~ 0.41 – 0.59\) (for \(r_N/r_M\))

On forming a nitride the metal structure changes from hcp to ccp and vice versa or from bcc to either hcp or ccp.

Examples: TiN, VN, CrN, LaN, NbN etc.
Cubic Metal Structures

bcc

fcc
Industrial Ammonia Production

Industrial Conditions:
- ~400°C
- 70-200 atm
- ~40% yield

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) + 91.8 \text{ kJ} \]
Industrial Ammonia Production

Catalyst: Fe$_3$O$_4$ (magnetite), Al$_2$O$_3$, K$_2$O

- Iron is reduced to the element under the reaction conditions
- Adsorption of gas molecules on the catalyst’s surface
- Formation of ‘surface nitride’ Fe$_4$N

Potential Energy Diagram (kJ/mol)
Two Component Mixtures: Alloys

A  Brass, a substitutional alloy

B  Carbon steel, an interstitial alloy
Two Component Mixtures: Alloys

Phase diagram for two metals that are completely miscible in the solid state and in the melt.
Two Component Mixtures: Alloys

Phase diagram for two metals that are completely miscible in the melt and immiscible in the solid state.
Tin and Lead Alloys

Tinman's solder - 60% Sn, 40% Pb; m.p. 180ºC
Type metal - 12% Sb, 5-12% Sn, remainder Pb; m.p. 240ºC
Wood's metal - 50% Bi, 27% Pb, 13% Sn, 10% Cd; m.p. 66ºC.
Pewter - 90-95% Sn, 1-8% Sb, 0.5-3% Cu.

The **Eutecticum** is the lowest melting point for such a phase mixture.
# Two Component Mixtures: Alloys

<table>
<thead>
<tr>
<th>Name</th>
<th>Composition (Mass %)</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>73–79 Fe, 14–18 Cr, 7–9 Ni</td>
<td>Cutlery, instruments</td>
</tr>
<tr>
<td>Nickel steel</td>
<td>96–98 Fe, 2–4 Ni</td>
<td>Cables, gears</td>
</tr>
<tr>
<td>High-speed steels</td>
<td>80–94 Fe, 14–20 W (or 6–12 Mo)</td>
<td>Cutting tools</td>
</tr>
<tr>
<td>Permalloy</td>
<td>78 Ni, 22 Fe</td>
<td>Ocean cables</td>
</tr>
<tr>
<td>Bronzes</td>
<td>70–95 Cu, 1–25 Zn, 1–18 Sn</td>
<td>Statues, castings</td>
</tr>
<tr>
<td>Brassess</td>
<td>50–80 Cu, 20–50 Zn</td>
<td>Plating, ornamental objects</td>
</tr>
<tr>
<td>Sterling silver</td>
<td>92.5 Ag, 7.5 Cu</td>
<td>Jewelry, tableware</td>
</tr>
<tr>
<td>14-Carat gold</td>
<td>58 Au, 4–28 Ag, 14–28 Cu</td>
<td>Jewelry</td>
</tr>
<tr>
<td>18-Carat white gold</td>
<td>75 Au, 12.5 Ag, 12.5 Cu</td>
<td>Jewelry</td>
</tr>
<tr>
<td>Typical tin solder</td>
<td>67 Pb, 33 Sn</td>
<td>Electrical connections</td>
</tr>
<tr>
<td>Dental amalgam</td>
<td>69 Ag, 18 Sn, 12 Cu, 1 Zn (dissolved in Hg)</td>
<td>Dental fillings</td>
</tr>
</tbody>
</table>
Lead Oxides

**Litharge**: red colour, $d = 9.355 \text{ g cm}^{-3}$, mp $897^\circ\text{C}$, layer structure, tetragonal; Pb-O distance $2.30 \text{ Å}$

**Massicott**: yellow colour, $d = 9.642 \text{ g cm}^{-3}$, stable above $488^\circ\text{C}$, distorted layer structure, orthorhombic;
(both can be prepared by heating of PbO$_2$ in air ($550^\circ\text{C}$ gives massicott; $650^\circ\text{C}$ gives litharge)).
Lead Oxides

\[
\text{PbO}_2 \text{ (rutile structure)}
\]


\[
\text{Red lead (Pb}_3\text{O}_4\text{)}
\]
Lead Oxides

**Plattnerite (PbO₂):** maroon colour, \( d = 9.643 \text{ g cm}^{-3} \), rutile structure, Pb-O distance 2.18 Å.

Formed by anodic oxidation of Pb\(^{2+}\) solutions or of Pb\(_3\)O\(_4\) with Cl\(_2\). Oxidation of strongly basic solution of lead(II) acetate with calcium hypochlorite. Strong oxidising agent.

**Red Lead (Pb\(_3\)O\(_4\), mixed oxide):** contains Pb(II) and Pb(IV) ions, \( d = 8.924 \text{ g cm}^{-3} \), tetragonal, Pb\(^{IV}\)-O distance 2.14 Å, Pb\(^{II}\)-O distance 2.18 Å (x2) and 2.13 Å (x1).

PbO or PbO\(_2\) + heat