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 Carbides

Carbon forms binary compounds with most other elements. Many of them are important to daily life, they include CO$_2$ and Fe$_3$C, the latter a major constituent of steel. Binary compounds of carbon with metals and metalloids, the carbides, are classified into three main categories:

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

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

3. **Metalloid carbides**, which are hard covalent solids formed by boron and silicon.

Classes of Carbides

The figure above summarises the distribution of the different types in the periodic table. This classification is very useful for the purpose of correlating chemical and physical properties, however, borderlines are sometimes indistinct.

Figure 11.28, p. 489 - Shriver, Atkins and Langford
**Saline Carbides**

**SALINE CARBIDES**
These may be divided into three categories:

Graphite intercalation compounds, *e.g.* KC$_8$.
Dicarbides or acetylides, which contain the C$_2^{2-}$ anion.
Methides, which contain formally the C$_4^{4-}$ anion.

*Graphite intercalation* compounds are formed by the Group 1 metals by a redox process by the reaction of graphite with alkali metal vapour or with metal-ammonia solution. For example contact between graphite and potassium vapour in a sealed tube at 300°C produces KC$_8$. 
Graphite Intercalation Compounds

Figure 11.20, p. 481 - Shriver, Atkins and Langford
Graphite & KC$_8$
**Saline Carbides**

**Dicarbides** are formed from Groups 1 and 2 and the lanthanides. The $\text{C}_2^{2-}$ ion has a very short CC distance in some dicarbides (1.19 Å in CaC$_2$) which is consistent with it being a triply bonded $[\text{C}=\text{C}]^{2-}$ ion isoelectronic with $[\text{C}=\text{N}]^{2-}$ and $[\text{N}=\text{N}]$.

Figure 8.12, p. 320 – Greenwood & Earnshaw
Synthesis of Carbides

**Synthetic routes:**

1. Direct reaction of the elements at high temperatures

   \[ \text{Ca}(l) + 2\text{C}(s) \xrightarrow{2000^\circ C} \text{CaC}_2(s) \]

2. Reaction of a metal oxide and carbon at high temperature

   \[ \text{CaO}(s) + 3\text{C}(s) \xrightarrow{2200^\circ C} \text{CaC}_2(l) + \text{CO}(g) \]

3. Reaction of acetylene with a metal-ammonia solution

   \[ 2\text{Na}(am) + \text{C}_2\text{H}_2(g) \rightarrow \text{Na}_2\text{C}_2(s) + \text{H}_2(g) \]
Reactions of Carbides

The saline carbides have high electron density on carbon, so they are readily oxidised and protonated e.g.

\[
\text{CaC}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca(OH)}_2(\text{s}) + \text{HCCH(}g) 
\]

Carbides such as Be\textsubscript{2}C and Al\textsubscript{4}C\textsubscript{3} are borderline between saline and metalloid.
Covalent Carbides

The two elements that approach carbon closely in size and electronegativity, silicon and boron, give completely covalent compounds.

**Silicon carbide** (SiC), known as carborundum, is an extremely hard, infusible, and chemically stable material - made by reducing SiO$_2$ with carbon in an electric furnace.

**Silicon carbide** has three structural modifications - in each there are infinite three-dimensional arrays of Si and C atoms, each tetrahedrally surrounded by four of the other kind.

**Boron carbide** (B$_4$C or more correctly B$_{13}$C$_2$) is also an extremely hard, infusible and inert substance, made by reduction of B$_2$O$_3$ with carbon in an electric furnace.
‘$\text{B}_4\text{C}$’ has a very unusual structure - the C atoms occur in linear chains of 3, and the boron atoms in icosahedral groups of 12 (as in crystalline boron). These two units are then packed together in a NaCl-like array. There are, of course, covalent bonds between C and B atoms as well as between B atoms in different icosahedra.

Figure 6.8, p. 167 - Greenwood and Earnshaw.
Covalent Carbides

Figure 6.9, p. 168 - Greenwood and Earnshaw.
Unit cells of some modern ceramic materials

A Silicon carbide

SiC

B Cubic BN (borazon)

BN
cubic boron nitride (borazon)
Metallic Carbides

Most metallic carbides are formed by the $d$ metals. They are sometimes referred to as interstitial carbides because their structures are often related to those of metals by the insertion of C atoms in octahedral holes.

The metallic carbides of composition $MC$ have an fcc or hcp arrangement of metal atoms with the C atoms in the octahedral holes. The fcc arrangement results in a rock-salt structure.

The C atoms in carbides of composition $M_2C$ occupy only half the octahedral holes between the close-packed metal atoms.
Metallic Carbides

These carbides characteristically have very high melting points, great hardness and metallic conductivity.

The hardness and other properties of metallic carbides are due to strong metal-carbon bonding.

Tungsten carbide WC - is used for cutting tools and high pressure equipment (such as that used to produce diamond). Cementite (Fe$_3$C) is a major constituent of steel and cast iron.
Crystal structures of metals

cubic closest packing

hexagonal closest packing
Cubic Metal Structures

bcc

fcc
Iron – Carbon Alloys

**PART OF THE IRON-CARBON PHASE DIAGRAM**

- **906°C**: 906°C Low-carbon steel
- **723°C**: 723°C Medium-carbon steel
- 20% perlite
- 70% perlite
- **Austenite**
- **Ferrite + perite**
- **Ferrite + cementite**

**Graph**

- **Austenite (γ)**
- **Austenite + Liquid**
- **Liquid**
- **Ferrite (α)**
- **Ferrite + cementite**
- **Weight per cent C**
- **Temperature °C**
Examples for Martensite
Phasetransition from bcc to fcc
## 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, BN</td>
<td>Cutting tools, edge sharpeners(as coatings and whole devices), scissors, surgical tools, industrial “diamond”</td>
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<tr>
<td>BN, SiC</td>
<td>Armor-plating reinforcement fibers(as in Kevlar composites)</td>
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<tr>
<td>ZrO₂, Al₂O₃</td>
<td>Surgical implants(hip and knee joints)</td>
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