Bonding in Solid Materials

What types of bonds would you expect for…

**Salts:**

**Covalent Molecules:**

**Elements:**

- Noble gases
- Nonmetals: S, P, Se, C
- Diatomic gases
- Metals
- Metalloids (semi-metals)

Importance of INTERmolecular Forces
FYI: Phase Diagrams

Plot of pressure vs. temperature of the system showing the boundaries between the phases.

- coexistence curves
- triple point
- normal melting point
- normal boiling point
- pressure dependence of boiling point
- pressure dependence of melting point
- critical point
- supercritical fluid

- Predict what happens when the pressure and/or temperature of the system is changed

Structure of Solids

- **Amorphous**: no regular organization at a molecular level, eg. glass, coal
- **Crystalline**: regular 3-D array of atoms or molecules, eg. NaCl, ice, sugar
Structure of Crystalline Solids: Unit Cells

Crystal lattice: 3-D array of atoms

Unit cell: repeating unit of crystal lattice

Bonding in Ionic Solids

Examples of Ionic Solids:
• NaBr
• CaCO$_3$
• NH$_4$Cl
• FeCl$_2$
Bonding in ionic solids

Note that multiple types of bonding can be present in the same compound.

Bonding in Molecular Solids

Examples of Molecular/Atomic solids:

- Ar (atomic solid)
- water (ice)
- CO$_2$ (dry ice)
- hydrocarbons (gasoline)
- alcohols
- sugar
- methane
Bonding in Network Covalent Solids

Examples of Network Covalent Solids:
- SiC
- BN
- Metalloids
- B
- SiO₂ (quartz)
- C (diamond)
- C (graphite)

2-D silicate sheet, Si₂O₅²⁻

Allotropes of Carbon

• Structure
  • 1. Diamond
    - 4 σ bonds to each C
    - sp³ hybridization
    - tetrahedral, dense
  • 2. Graphite (crystalline)
    - 3 σ bonds to each C
    - planar sp² hybridization
    - delocalized π-bonds
    - planar, soft:
    - Carbon Black (amorphous)
    - Charcoal (amorphous)
    - Coke (amorphous)
  • 3. Fullerenes
    - 3 σ bonds to each C
    - sp² hybridization
    - delocalized π-bonds
    - MOLECULAR form
  • 4. Nanotubes
    - Sheets of graphite rolled up
    - capped by half of C₆₀ molecule
    - Multiwall or single walled
    - Armchair (metallic behavior)
    - Zigzag (diameter dictates semi-conductor or metallic behavior)

• Uses
  - hardest substance known (Gem)
  - abrasive, drill bits, cutting tools
  - conducts current, soft:
    - lubricant batteries (as electrode), pencils
    - van der waals forces between planes
    - tires, ink pigments, carbon paper
    - adsorb molecules in filters
    - reducing agent in metallurgical operation
  - No uses:
    - found in soot
    - C₆₀
  - nanoscale electronic circuits
  - stronger than steel on nanoscale
  - strong fibers with polymers
Ceramics

**Inorganic, nonmetallic solids**

- Typically hard and brittle
  - Less dense than metals, lighter
  - More elastic than metals
  - Resist corrosion and wear, don’t deform
- Stable at high temperatures
  - High melting
- Can be covalent network and/or ionic
  - Usually electrical insulators

### Crystalline:
- Oxides (Al₂O₃, ZrO₂, BeO)
- Carbides (SiC, Ca₂C)
- Nitrides (BN)
- Silicates (SiO₂ mixed with metal oxides)
- Aluminosilicates (Al₂O₃ + SiO₂ + metal oxides: Mica, Talc, Pottery, Clay)

### Amorphous (glasses)

Silicates;

*Si always found in nature in combination with O*

**Four types of structures:**

1) **Tetrahedral** orthosilicate ion (SiO₄⁴⁻ units); found in very few silicate minerals
   - Example: Zircon ZrSiO₄
   - One vertex linked: Disilicate ion Si₂O₇⁶⁻
     - Example: hardystonite Ca₂Zn(Si₂O₇)

Positive ions balance the charge; hold chains or sheets together
Most Silicate Minerals are *linked tetrahedra*

2) **Infinite Single Strand Chain**, 2 vertices linked: 
$(\text{SiO}_3)^{\times 2-}$ or $\text{Si}_2\text{O}_6^{4-}$

Examples: asbestos (fibrous silicate minerals), enstatite MgSiO$_3$

3) **Infinite 2-D Sheet**, 2 vertices linked: $(\text{Si}_2\text{O}_5)^{\times 2-}$

Example: talc Mg$_3$(Si$_2$O$_5$)$_2$(OH)$_2$

4) **3-D infinite Network**, all four vertices linked: SiO$_2$

Examples: quartz, sand, glass

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**Fused Silica Glass**

GLASS is made from SiO$_2$

Excellent materials properties:
- Transparent in visible and ultraviolet
- High index of refraction
- Low thermal conductivity
- Low thermal expansion coefficient

*But…* $T_g = 1600^\circ\text{C}$ for fused silica *(too high)*

**Additives lower processing temperature**

Usually oxides like Na$_2$O, CaO, B$_2$O$_3$, etc.

Break up covalent ring network with ionic bonds

Lower $T_g$ *(and therefore processing temp.)*

Example: soda-lime glass (window glass), contains Na$_2$O, CaO

Softens at 600°C
Changing the Properties of Glass

Soda-lime glass: SiO₂, Na₂O, CaO

Soda lime glass + CoO
deep blue (cobalt glass)

Use K₂O instead of Na₂O
harder glass, higher mp

Using PbO instead of CaO
denser “leaded” glass
greater refractive index
(bends light differently)

Pyrex Glass “borosilicate”
Contains B₂O₃ in addition to SiO₂, Na₂O
Has low thermal expansion coefficient
(doesn’t crack when rapidly heated or cooled)

Glass with AgCl or AgBr added
photochromic (dark when exposed to light, clear with little or no light)

Bonding in Metallic Solids

Examples of Metallic Solids:
• Mg
• Na
• W

Free Electron Model
Metals are positive ions in a “sea” of nearly free electrons.
Electrons bind metal ions together but are free to roam the crystal lattice.
Explains malleability, ductility and high electrical and thermal conductivity.
Classes of Solids

<table>
<thead>
<tr>
<th>Kind of Interaction</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td></td>
</tr>
<tr>
<td>Atomic</td>
<td></td>
</tr>
<tr>
<td>Molecular</td>
<td></td>
</tr>
<tr>
<td>Covalent Network</td>
<td></td>
</tr>
<tr>
<td>Metals</td>
<td></td>
</tr>
</tbody>
</table>

Bonding in the elements

What types of bonds would you expect for…

- Metals
- Metalloids (semi-metals)
- Nonmetals – noble gases
- Nonmetals – diatomic gases
- Nonmetals – S, P, Se
- Nonmetals – C
## Summary of Bonding in Solids

<table>
<thead>
<tr>
<th>Crystal Type</th>
<th>Unit</th>
<th>Forces</th>
<th>Example</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>atomic</td>
<td>atoms</td>
<td>dispersion</td>
<td>Ar, Kr</td>
<td>v. low M.P., soft</td>
</tr>
<tr>
<td>molecular</td>
<td>polar or nonpolar molecules</td>
<td>dispersion dipole-dipole</td>
<td>H-bonding</td>
<td>sugar CH₄, CO₂, H₂O</td>
</tr>
<tr>
<td>covalent (network)</td>
<td>atoms in covalent network</td>
<td>covalent bonds</td>
<td>diamond graphite</td>
<td>quartz</td>
</tr>
<tr>
<td>ionic</td>
<td>cations and anions</td>
<td>electrostatic</td>
<td>NaCl</td>
<td>high M.P., brittle</td>
</tr>
<tr>
<td>metallic</td>
<td>atoms</td>
<td>metallic bonds</td>
<td>metals Cu, Fe, Al, Ni</td>
<td>wide range of M.P., softer, malleable, ductile</td>
</tr>
</tbody>
</table>
Example Problems

1. Which type of crystal will form when $C_6H_6$ (benzene) solidifies?
   1. ionic
   2. molecular
   3. metallic
   4. covalent-network
   5. amorphous

2. Indicate the type of crystal (molecular, metallic, covalent-network, or ionic) each of the following would form upon solidification:
   1. Zr
   2. $N_2O_4$
   3. $SiO_2$
   4. Ne
   5. $Ni(ClO_3)_2$
Example Problems

3. For each of the following pairs of substances, predict which will have the higher melting point.

   KBr   Br$_2$

   SiO$_2$  CO$_2$

   Ar   Xe