Chapter 13: Chemistry of Solids

•Crystal Lattices and Unit Cells
•Ionic Solids
•Lattice Energy
•Phase Changes
12.9 Types of Solids

**Crystalline Solids** – have ordered atomic & molecular structure

**Amorphous Solids** – have randomly arranged atomic & molecular structure
Types of Crystalline Solids

Molecular Solid - held together by intermolecular forces (ice)

Ionic Solid - cations & anions held together by Coulombic forces (salt)

Atomic Solids (2 Types)

-Metallic Solid - Positive “core nuclei” held together by “sea of delocalized electrons” (copper)

-Covalent Network Solid - held together by covalent bonds (diamond, quartz-SiO₂)
Structure & Bonding in Metals

- very strong
- non directional

Consider structure to result from closest packing of identical atoms
Structure & Bonding in Metals

Electron Sea Model – nuclei and core electrons occupy closest pack positions while valence electrons are delocalized and not attached to any specific nuclei

Band Theory – Extension of MO theory to account for mixing of energy levels resulting in a continuum of energy levels
Crystal Lattices

3 Dimensional geometric arrangement of atoms or cations & anions which result in a crystal

Unit Cell - smallest 3D structure which when repeated, produces the crystal lattice
Unit Cell

7 Basic Shapes

1. Cubic  \( a=b=c \)  \( \alpha=\beta=\gamma=90^\circ \)
2. Tetragonal  \( a=b\neq c \)  \( \alpha=\beta=\gamma=90^\circ \)
3. Orthorhombic  \( a\neq b\neq c \)  \( \alpha=\beta=\gamma=90^\circ \)
4. Monoclinic  \( a\neq b\neq c \)  \( \alpha=\beta=90^\circ \gamma\neq 90^\circ \)
5. Hexagonal  \( a=b=c \)  \( \alpha=\beta=90^\circ \gamma=120^\circ \)
6. Rhombohedral  \( a=b\neq c \)  \( \alpha=\beta=\gamma\neq 90^\circ \)
7. Triclinic  \( a\neq b\neq c \)  \( \alpha\neq\beta\neq\gamma\neq 90^\circ \)
Cubic Unit Cells

3 Types

1. Simple or Primitive
2. Body Centered
3. Face Centered
Primitive Unit Cell

(simple)

- Least Efficient Packing
  (53% Efficient)

- 1 atom/unit Cell

- Coordination # = 6
Body Centered Cubic

- all Alkali Metals & Many other Metals
- 68% Efficient
- 2 Particles/Unit Cell
- Coordination # = 8
Face Centered Cubic

(Cubic Closest Packed)

- Most Efficient (74% Efficient)

- 4 atoms/unit cell

- Coordination # = 12
FCC Problem

Calcium forms a face centered cubic cell. The density of calcium is 1.54g/ml. What is the radius of the calcium ion in Angstrums?
Write Down What is Given:

1.54g = 1cm³
40.08g = 1mol
1mol = 6.022 \times 10^{23} \text{ atom}
1 \text{ FCC unit cell} = 4 \text{ atoms}

Vol of cube = a³ where a = length of side

\[ a^2 + a^2 = c^2 \]

4r = c (the diagonal has 4 radii (2 in the diameter of the face centered cell and one in each corner))
FCC Problem

1. Calculate the Volume of the Unit Cell

\[
\frac{4 \text{atoms Ca}}{\text{FCC cell}} \left( \frac{\text{mol Ca}}{6.02 \times 10^{23} \text{ atoms}} \right) \left( \frac{40.078 \text{ gCa}}{\text{mol}} \right) \left( \frac{\text{cm}^3}{1.54 \text{gCa}} \right) = 1.729 \times 10^{-22} \text{cm}^3/\text{cell}
\]

2. Calculate the Length of the Unit Cell

\[
V = l^3 \Rightarrow l = 3\sqrt{V} = 3\sqrt{1.729 \times 10^{-22} \text{cm}^3} = 5.57 \times 10^{-8} \text{cm}
\]

3. Calculate the Length of the Diagonal

\[
\alpha^2 + \alpha^2 = c^2, \text{ c is the diagonal, } c = \sqrt{2\alpha^2} = \sqrt{2\left(5.57 \times 10^{-8} \text{cm}\right)^2} = 7.877 \times 10^{-8} \text{cm}
\]

4. Calculate the radii noting FCC has 4 radii/diagonal

\[
r = \frac{7.877 \times 10^{-8} \text{cm}}{4} \left( \frac{10^{10} \text{A}}{10^2 \text{cm}} \right) = 1.969 \text{ Angstroms}
\]
 Ionic Solids

(a) Sodium chloride (NaCl) crystal structure

(b) Perspective view of the sodium chloride (NaCl) crystal structure
Ionic Solids
13.3 Formation of Ionic Crystals

Let's look at the Formation of Lithium Fluoride from Li’s Ionization Potential and Chlorines Electron Affinity

\[
\text{Li} \rightarrow \text{Li}^+ + e^- \quad I_p = 520 \text{ kJ/mol}
\]

\[
\text{F} + e^- \rightarrow \text{F}^- \quad E_{ea} = -328 \text{ kJ/mol}
\]

\[
\text{Li} + \text{F} \rightarrow \text{LiF} \quad E = 192 \text{ kJ/mol}
\]

This says LiF is not stable, yet it is.

Why?
Crystal Lattice Energies

The extra stabilization due to the crystal lattice

How Do We Measure Lattice Energies?
Born-Haber Cycle

The Internal Energy is a **State Function**

- The energy difference between two states is independent of the path

**The lattice energy is the energy required to form the lattice from the isolated (gas phase) ions**

\[ \text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{NaCl}(s) \]

*Note: Many texts define Lattice Energy as the energy released when the lattice is destroyed, giving it a positive value (you had to add energy to break the lattice apart), our text defines it as the energy of formation of the lattice (which is negative). The video does the opposite.*
Born-Haber Cycle

$\text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{NaCl}(s)$

\[ \Delta H_f (\text{NaCl}(s)) = \Delta H_f (\text{Cl}(g)) + \Delta H_{\text{sub}} (\text{Na}) + I_P (\text{Na}(g)) + E_A (\text{Cl}(g)) + \Delta H_{\text{Lattice}} (\text{NaCl}(s)) \]

1. \( \Delta H_f (\text{Cl}(g)) = 121.3 \text{ kJ/mol} \)
2. \( \Delta H_{\text{sub}} (\text{Na}(s)) = 107.3 \text{ kJ/mol} \)
3. \( I_P (\text{Na}(g)) = 496 \text{ kJ/mol} \)
4. \( E_A (\text{Cl}(g)) = -349 \text{ kJ/mol} \)
5. \( \Delta H_{\text{Lattice}} (\text{NaCl}(s)) \) written as a formation constant
Crystal Defects

Can give crystals unique properties

1. **Substitutional**: another ion can substitute one in the lattice. Ruby is Al$_2$O$_3$ with a few Cr$^{+3}$ replacing Al$^{+3}$

2. **Interstitial**: Impurities can squeeze in between the ions, can be nonstoichiometric
Alloys

Mixture of two or more types of metal atoms in lattice

2 Types of Alloys

- **substitutional** both metals fixed in crystal lattice
  - **interstitial** one metal fits in pockets of lattice
Solid Phase Solutions

A Brass, a substitutional alloy

B Carbon steel, an interstitial alloy
Similar materials are being researched as a method of storing hydrogen as a fuel.
Network Atomic Solids

-often called Network Covalent

-Diamond
-Graphite
-Silicates

Allotropes of Carbon
(pure carbon but in different forms)
Diamond

- Hardest Structure Known
- Tetrahedral atomic arrangement

What hybrid state do you think the carbon has?
Graphite

- Form planar sheets
- actually more stable than diamond

What hybrid state do you think the carbon has?
<table>
<thead>
<tr>
<th>Type of Solid</th>
<th>Intermolecular Forces</th>
<th>Properties</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>Ion–ion forces</td>
<td>Brittle, hard, high-melting</td>
<td>NaCl, KBr, MgCl₂</td>
</tr>
<tr>
<td>Molecular</td>
<td>Dispersion forces, dipole–dipole forces, hydrogen bonds</td>
<td>Soft, low-melting, nonconducting</td>
<td>H₂O, Br₂, CO₂, CH₄</td>
</tr>
<tr>
<td>Covalent network</td>
<td>Covalent bonds</td>
<td>Hard, high-melting</td>
<td>C (diamond, graphite), SiO₂</td>
</tr>
<tr>
<td>Metallic</td>
<td>Metallic bonds</td>
<td>Variable hardness and melting point, conducting</td>
<td>Na, Zn, Cu, Fe</td>
</tr>
</tbody>
</table>
13.5 Phase Diagrams

Know:
- Triple Pt
- Critical Pt
- Phase Changes

1 atm Isobar
Critical Temperature & Pressure

At High Temperature & Pressure the Vapor/Fluid Boundary Disappears

- High T means high KE, which overcomes intermolecular forces (like gas)
- High P means molecules are forced next to each other (like liquid)

Critical Point - the highest pt where both phases can coexist
What Would the Phase Diagram of Water Look Like?

Why is the Solid/Liquid Slope Negative?
Assignment:

Draw Phase Diagram for Carbon Dioxide Labeling All Phases, the Triple Pt., The Critical Pt. And Include a 1 Isobar Line
CO$_2$ Phase Diagram

- **Solid**
- **Liquid**
- **Gas**
- **Supercritical fluid**

Pressure (atm) vs. Temperature (°C):
- Pressure levels: 1, 5.11, 73.0 atm
- Temperature levels: -78.5, -56.4, 31.1 °C