Lecture 7

Crystal structure and bonding thermodynamics

Reminder: Journal Club next Monday
Quiz 1: Worth 3 extra points on homework #1.

1. Write Your Name
2. Based on this correlation diagram, indicate which shape (linear or bent) BeH$_2$ is expected to adopt.

[Diagram of bond energy vs bond angle with labels 1b$_1$, 1b$_2$, 2a$_1$, 1$\sigma_u$, 1$\sigma_g$, 1$\pi_u$, with a metal crystal of Be and a hint: $Z_{Be}=4$.]
# Bonding in solids

Bonds are distinguished based on the electron distribution functions in the molecules.

<table>
<thead>
<tr>
<th>Bonding Type</th>
<th>e⁻ distribution</th>
<th>Characteristics</th>
<th>Examples</th>
<th>Strength (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent</td>
<td>Highest between pairs of nearest neighbors</td>
<td>Hard solids with low electrical conductivity</td>
<td>C, Si, Ge, H</td>
<td>4-8</td>
</tr>
<tr>
<td>Metallic</td>
<td>Spread more uniformly (sea of e⁻s)</td>
<td>Close-packed crystals with high conductivity</td>
<td>Na, Li, Fe</td>
<td>1-9</td>
</tr>
<tr>
<td>Van der Waals</td>
<td>Dipole interactions</td>
<td>Low melting point</td>
<td>Ar, polymers</td>
<td>0.02-0.3</td>
</tr>
<tr>
<td>Ionic</td>
<td>Transfer of valence electrons between atoms</td>
<td>Low electrical conductivity, high ionic conductivity</td>
<td>NaCl, MgO, Ag₂S</td>
<td>5-10</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H⁺ interacting with lone pair of e⁻s</td>
<td>Molecular crystals</td>
<td>H₂O, DNA</td>
<td>0.1-0.4</td>
</tr>
</tbody>
</table>
Ketelaar Triangle

Ionic Bond

Metallic Bond

Covalent Bond

Electronegativity Difference

Avg. Electronegativity
Arrangement of atoms in a solid

- 1611 – Kepler suggests hexagonal symmetry of snowflakes is due to “regular packing of the constituent particles”

- 1665 – Hooke suggests that crystals are composed of packed spheres

- 1913 – W.H. and W.L. Bragg prove with X-ray diffraction that salt is composed of Na\(^+\) and Cl\(^-\) ions in a periodic lattice (Nobel prize in 1915)
Crystal structure basics

Lattice + Basis = Crystal

3D crystal systems:

- Cubic
- Tetragonal
- Orthorhombic
- Monoclinic
- Triclinic
- Rhombohedral (trigonal)
- Hexagonal
Close packing of spheres

- Atoms/ions treated as hard spheres

ABAB…
hexagonal close-packed (hcp)

ABCABC…
cubic close-packed (ccp)
face-centered cubic (fcc)
**Interstitials**

Unoccupied spaces between spheres can be occupied by other smaller atoms

- Octahedral hole

- Tetrahedral hole
Predicting structures of ionic compounds

- The radius ratio indicates the likely coordination numbers of the ions in a compound

\[
\text{Radius Ratio} = \frac{r_{\text{small}}}{r_{\text{large}}} \quad (\text{usually}) = \frac{r_{\text{cation}}}{r_{\text{anion}}}
\]

\[
\frac{r_{\text{cation}}}{r_{\text{anion}}} > \text{ideal} \quad \text{Stable}
\]

\[
\frac{r_{\text{cation}}}{r_{\text{anion}}} = \text{ideal} \quad \text{Stable}
\]

\[
\frac{r_{\text{cation}}}{r_{\text{anion}}} < \text{ideal} \quad \text{Unstable}
\]
Radius ratio rules for ionic crystals

<table>
<thead>
<tr>
<th>Radius Ratio</th>
<th>Triangular</th>
<th>Tetrahedral</th>
<th>Octahedral</th>
<th>Cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.155</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>0.225</td>
<td></td>
<td></td>
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<tr>
<td>0.414</td>
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<td></td>
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</tr>
<tr>
<td>0.732</td>
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<td></td>
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<tr>
<td>1</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Coordination #: 3 4 6 8

Example: Table salt, NaCl

Na\(^+\): 102 pm
Cl\(^-\): 181 pm

\[
\frac{r_{Na^+}}{r_{Cl^-}} = 0.56
\]
Thermo 101

- First law: energy can neither be created nor destroyed
- Second law: entropy increases during spontaneous processes
- Third Law: entropy of a perfect crystal is 0 at T=0K

For this class:
- A compound tends to adopt the crystal structure that corresponds to the lowest Gibbs free energy

\[ G = H - TS = U + PV - TS \]

G = Gibbs free energy; H = enthalpy; S = entropy; U = internal energy
Reaction thermodynamics

• It is primarily changes in H, S, and G that are important in calculations of thermodynamic or chemical equilibria
  \[ \Delta H = \text{heat absorbed or released by a process} \]
  \[ \Delta S = \text{change in the degree of disorder of the system} \]

• For any isothermal, isobaric process:
  \[ \Delta G = \Delta H - T\Delta S \]

• And for a reaction:
  \[ \Delta G_{\text{rxn}} = \sum G(\text{products}) - \sum G(\text{reactants}) \]
  \[ \Delta H_{\text{rxn}} = \sum H(\text{products}) - \sum H(\text{reactants}) \]
  \[ \Delta S_{\text{rxn}} = \sum S(\text{products}) - \sum S(\text{reactants}) \]
Spontaneity

A process or reaction only proceeds spontaneously when $\Delta G$ is negative.

$$\Delta G = \Delta H - T\Delta S$$

The thermodynamic driving force can be a decrease in enthalpy or an increase in entropy, or both.

When $\Delta G = 0$ the system is in equilibrium.
Standard states

- It is often more convenient to express free energy changes in terms of transformations of reactants and products from their standard states.
- Standard state = equilibrium state at atmospheric pressure and the temperature in question.
- Example: the standard Gibbs free energy of formation of a material $\Delta G_f^o(T)$ is the free energy change corresponding to the formation of a material from the elemental reactants in their standard states.

$$\text{Si (s) + O}_2 \text{(g)} \rightarrow \text{SiO}_2 \text{(s)}$$

$$\Delta G_f^o(\text{Si(s), 300K}) = 0$$
$$\Delta G_f^o(\text{O}_2(\text{g}, 300K)) = 0$$
$$\Delta G_f^o(\text{SiO}_2(\text{s}, 300K)) = -853.3 \text{ kJ/mol}$$

$$\Delta G_{\text{rxn}}^o(300K) = \Delta G_f^o(\text{SiO}_2(\text{s}, 300K)) - \Delta G_f^o(\text{Si(s), 300K}) - \Delta G_f^o(\text{O}_2(\text{g}, 300K))$$
$$= -853.3 \text{ kJ/mol}$$
Energetics of ionic bonding

• Solid formation from a gas of ions:

\[ \text{M}^+ (g) + \text{X}^- (g) \rightarrow \text{MX} (s) \]

\[ \Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T \Delta S_{\text{rxn}} \approx \Delta H_{\text{rxn}} \]

This reaction is usually so exothermic (\(\Delta H << 0\)) that at and near room temperature the contribution of the entropy change to the change in Gibbs free energy can be neglected.

• Lattice enthalpy: standard molar enthalpy change accompanying the formation of a gas of ions from the solid

\[ \text{MX} (s) \rightarrow \text{M}^+ (g) + \text{X}^- (g) \]

\[ \Delta H_{L}^o > 0 \]

The most stable crystal structure of the compound is that with the greatest lattice enthalpy.
Born-Haber cycle

- Hess’s law:
  \[ \Delta H_x = \Delta H_1 + \Delta H_2 \]

- Born-Haber cycle: a closed loop of reactions that includes lattice formation as one step

Enthalpy is a state property, so the sum of the enthalpy changes around a complete cycle is zero
Born-Haber cycle of KCl

\[ \text{KCl}(s) \rightarrow \text{K}(s)+\frac{1}{2}\text{Cl}_2(g) \quad -\Delta H^\circ_f = 438 \]

\[ \text{K}(s) \rightarrow \text{K}(g) \quad \Delta H^\circ_{\text{sub}} = 89 \]

\[ \text{K}(g) \rightarrow \text{K}^+(g)+e^- (g) \quad \Delta H^\circ_{\text{ion}} = 425 \]

\[ \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{Cl}(g) \quad \Delta H^\circ_{\text{dis}} = 122 \]

\[ \text{Cl}(g)+e^- (g) \rightarrow \text{Cl}^-(g) \quad \Delta H^\circ_{\text{eg}} = -355 \]

\[ \text{K}^+(g)+\text{Cl}^-(g) \rightarrow \text{KCl} (s) \quad \Delta H^\circ_L = 719 \]
Born-Mayer equation

- Used to calculate lattice enthalpies from first principles
- Example: 1-D line of alternating singly-charged cations and anions

For a given ion, the potential due to Coulombic interactions is:

\[ V = \sum \frac{q_i q_i}{4\pi \varepsilon_0} \frac{1}{r_i - r_i} = \frac{e^2}{4\pi \varepsilon_0} \left( -\frac{2}{d_0} + \frac{2}{2d_0} + \cdots \right) = -\frac{2e^2}{4\pi \varepsilon_0 d_0} \ln(2) \]

For the whole line (multiply by \( N_A \), divide by 2):

\[ V = -\frac{N_A e^2}{4\pi \varepsilon_0 d_0} A \]

A=\( \ln(2) \) is the Madelung constant for this particular geometry
Born-Mayer equation

- The attractive electrostatic force will be balanced by a repulsive force due to quantum interactions of the valence electrons of neighboring ions

\[
V = -\frac{N_A e^2}{4\pi\varepsilon_0 d_0} A + B \exp \left( -\frac{d}{d_0} \right)
\]

\(d = \text{range of repulsive interaction}\)
\(B = \text{magnitude of this interaction}\)

- Using the fact that \(dV/dd_0=0\) at the minimum, we find:

\[
V = -\frac{N_A e^2}{4\pi\varepsilon_0 d_0} \left( 1 - \frac{d}{d_0} \right) A
\]

Lattice enthalpy for arbitrarily charged ions:

\[
\Delta H_L = -V = \frac{N_A |z_A z_B| e^2}{4\pi\varepsilon_0 d_0} \left( 1 - \frac{d}{d_0} \right) A
\]
Consequences of lattice enthalpy

- Lattice enthalpies can explain trends in
  - Thermal stability
  - Oxidation state stability
  - Solubility

- First, the electrostatic parameter:

\[ \Delta H_L \propto \frac{|z_A z_B|}{d_0} = \xi \]

Highly charged, closely spaced ions form more stable lattices
Thermal stabilities of ionic solids

Decomposition reaction (i.e., trends in carbonate decomposition):

$$\text{MCO}_3(s) \rightarrow \text{MO}(s) + \text{CO}_2(g)$$

Decomposition becomes favorable when

$$\Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T \Delta S_{\text{rxn}} \leq 0 \quad \text{with} \quad T \geq \Delta H_{\text{rxn}} / \Delta S_{\text{rxn}}$$

In discussing trends, $\Delta S_{\text{rxn}}$ is essentially constant (dominated by $\text{CO}_2$ production)

$$\Delta H_{\text{rxn}} \approx \Delta H_{\text{decomp}} + \Delta H_L(\text{MCO}_3,s) - \Delta H_L(\text{MO},s)$$

large, constant

$$\text{CO}_3^{2-}(s) \rightarrow \text{O}^2-(g) + \text{CO}_2(g)$$
Thermal stabilities of ionic solids

- Which carbonate will be more stable, MgCO$_3$ or BaCO$_3$?

$\xi = \frac{|z_A z_B|}{d_0}$

T$_{\text{decomp}}$ = 573K

T$_{\text{decomp}}$ = 1573K
Stabilities of oxidation states

- The same argument is used to account for the fact that high oxidation states are stabilized by small anions

\[
+1 \quad +2
MX(s) + \frac{1}{2}X_2(g) \rightarrow MX_2(s) \quad X=\text{halogen}
\]

CuF$_2$ exists, CuI$_2$ does not:

F is smaller, thus the difference in lattice enthalpies is larger, and F is able to stabilize the higher oxidation state
Solubilities

\[ MX(s) \rightarrow M^+(aq) + X^-(aq) \]

- Dissolution is a complicated process, but lattice enthalpies and hydration enthalpies play important roles (don’t forget about entropy!)

- Generally, the larger the difference in radii, the more soluble in water