BONDING, Part 4

Energetics of Bond Formation

\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) \]
\[ \Delta H = -850.3 \text{kJ mol}^{-1} \]

Energetics of Covalent Bond Formation

\[ \frac{3}{2}\text{H}_2(g) + \frac{1}{2}\text{I}_2(g) \rightarrow \text{HI}(g) \]
\[ \Delta H = +26.5 \text{kJ mol}^{-1} \]
Trends in Bond Energies

• the more electrons two atoms share, the stronger the covalent bond
  ✓ C≡C (837 kJ) > C=C (611 kJ) > C−C (347 kJ)
  ✓ C≡N (891 kJ) > C=N (615 kJ) > C−N (305 kJ)

• the shorter the covalent bond, the stronger the bond
  ✓ Br−F (237 kJ) > Br−Cl (218 kJ) > Br−Br (193 kJ)
  ✓ bonds get weaker down the column
Using Bond Energies to Estimate $\Delta H^\circ_{\text{rxn}}$

- the actual bond energy depends on the surrounding atoms and other factors
- we often use **average bond energies** to estimate the $\Delta H_{\text{rxn}}$
  - works best when all reactants and products in gas state
- bond breaking is endothermic, $\Delta H(\text{breaking}) = +$
- bond making is exothermic, $\Delta H(\text{making}) = -$  
  $$\Delta H_{\text{rxn}} = \sum (\Delta H(\text{bonds broken})) + \sum (\Delta H(\text{bonds formed}))$$
Estimate the Enthalpy of the Following Reaction

\[ \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{g}) \]

reaction involves breaking 1 mol H-H and 1 mol O=O and making 2 mol H-O and 1 mol O-O

bonds broken (energy cost)

\[ (+436 \text{ kJ}) + (+498 \text{ kJ}) = +934 \text{ kJ} \]

bonds made (energy release)

\[ 2(464 \text{ kJ}) + (142 \text{ kJ}) = -1070 \]

\[ \Delta H_{\text{rxn}} = (+934 \text{ kJ}) + (-1070 \text{ kJ}) = -136 \text{ kJ} \]
Example: acetylene reacts with bromine according to the following equation:

\[
\begin{align*}
C_2H_2 + 2 \text{Br}_2 & \rightarrow C_2H_2\text{Br}_4 \\
\text{H-C≡C-H} + \text{Br-Br} & \rightarrow \text{H-C-Br-Br}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Bonds Broken</th>
<th>Bonds Formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 C≡C 812 kJ</td>
<td>4 C-Br 4(-285 kJ)</td>
</tr>
<tr>
<td>2 Br-Br 2(193 kJ)</td>
<td>1 C-C -346 kJ</td>
</tr>
<tr>
<td>1198 kJ</td>
<td>-1468 kJ</td>
</tr>
</tbody>
</table>

\[\Delta H_{rxn} = 1198 \text{ kJ (broken)} - 1468 \text{ kJ (formed)} = -288 \text{ kJ}\]

Trends in Bond Lengths

- the more electrons two atoms share, the shorter the covalent bond
  - C≡C (120 pm) < C=C (134 pm) < C−C (154 pm)
  - C≡N (116 pm) < C=N (128 pm) < C−N (147 pm)
- decreases from left to right across period
  - C−C (154 pm) > C−N (147 pm) > C−O (143 pm)
- increases down the group
  - F−F (144 pm) > Cl−Cl (198 pm) > Br−Br (228 pm)
- in general, as bonds get longer, they also get weaker
Energetics of Ionic Bond Formation

- the ionization energy of the metal is endothermic
  - $\text{Na}(s) \rightarrow \text{Na}^+(g) + 1 \text{ e}^- \quad \Delta H^\circ = +603 \text{ kJ/mol}$
- the electron affinity of the nonmetal is exothermic
  - $\frac{1}{2}\text{Cl}_2(g) + 1 \text{ e}^- \rightarrow \text{Cl}^-(g) \quad \Delta H^\circ = -227 \text{ kJ/mol}$
- generally, the ionization energy of the metal is larger than the electron affinity of the nonmetal, therefore the formation of the ionic compound should be endothermic
- but the heat of formation of most ionic compounds is exothermic and generally large; Why?
  - $\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{NaCl}(s) \quad \Delta H_f^\circ = -410 \text{ kJ/mol}$
Ionic Bonds

• electrostatic attraction is nondirectional!!
  ✓ no direct anion-cation pair

• **no ionic molecule**
  ✓ chemical formula is an empirical formula, simply giving the ratio of ions based on charge balance

• ions arranged in a pattern called a **crystal lattice**
  ✓ every cation surrounded by anions; and every anion surrounded by cations
  ✓ maximizes attractions between + and - ions

Lattice Energy

• the **lattice energy** is the energy released when the solid crystal forms from separate ions in the gas state
  ✓ always exothermic
  ✓ hard to measure directly, but can be calculated from knowledge of other processes

• lattice energy depends directly on size of charges and inversely on distance between ions
Born-Haber Cycle

- method for determining the lattice energy of an ionic substance by using other reactions
  - use Hess’s Law to add up heats of other processes
    - metal atoms (g) → cations (g), $\Delta H^\circ_f = \text{ionization energy}$
      - don’t forget to add together all the ionization energies to get to the desired cation
        - $M^{2+} = 1^{\text{st}} \text{IE} + 2^{\text{nd}} \text{IE}$
    - nonmetal atoms (g) → anions (g), $\Delta H^\circ_f = \text{electron affinity}$

\[ \Delta H^\circ_f(\text{salt}) = \Delta H^\circ_f(\text{metal atoms, g}) + \Delta H^\circ_f(\text{nonmetal atoms, g}) + \Delta H^\circ_f(\text{cations, g}) + \Delta H^\circ_f(\text{anions, g}) + \Delta H^\circ_f(\text{crystal lattice}) \]

where
\[ \Delta H^\circ_f(\text{crystal lattice}) = \text{Lattice Energy} \]
Born-Haber Cycle

metal atoms (g) → cations (g), $\Delta H^\circ_f = \text{ionization energy}$

sum all the ionization energies to get to the desired cation

e.g., $M^{2+} = 1^{\text{st}} \text{IE} + 2^{\text{nd}} \text{IE}$

nonmetal atoms (g) → anions (g), $\Delta H^\circ_f = \text{electron affinity}$

Figure 9.6

The Born-Haber cycle for lithium fluoride
Practice - Given the Information Below, Determine the Lattice Energy of MgCl₂

\[ \begin{align*}
\text{Mg}(s) &\rightarrow \text{Mg}(g) \quad \Delta H_1^\circ_f = +147.1 \text{ kJ/mol} \\
\frac{1}{2} \text{Cl}_2(g) &\rightarrow \text{Cl}(g) \quad \Delta H_2^\circ_f = +121.3 \text{ kJ/mol} \\
\text{Mg}(g) &\rightarrow \text{Mg}^{+1}(g) \quad \Delta H_3^\circ_f = +738 \text{ kJ/mol} \\
\text{Mg}^{+1}(g) &\rightarrow \text{Mg}^{+2}(g) \quad \Delta H_4^\circ_f = +1450 \text{ kJ/mol} \\
\text{Cl}(g) &\rightarrow \text{Cl}^{-1}(g) \quad \Delta H_5^\circ_f = -349 \text{ kJ/mol} \\
\text{Mg}(s) + \text{Cl}_2(g) &\rightarrow \text{MgCl}_2(s) \quad \Delta H_6^\circ_f = -641.3 \text{ kJ/mol}
\end{align*} \]
**Periodic Trends in Lattice Energy**

**Coulomb's Law**

- Electrostatic force: \( \propto \frac{\text{charge A} \times \text{charge B}}{\text{distance}^2} \)
- Energy = force \( \times \) distance
- Therefore:
  - Electrostatic energy: \( \propto \frac{\text{charge A} \times \text{charge B}}{\text{distance}} \)
  - Electrostatic energy: \( \propto \frac{\text{cation charge} \times \text{anion charge}}{\text{cation radius} + \text{anion radius}} \)
  - \( \Delta H^0_{\text{lattice}} \)

**Lattice Energy vs. Ion Size**

<table>
<thead>
<tr>
<th>Metal Chloride</th>
<th>Lattice Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>-834</td>
</tr>
<tr>
<td>NaCl</td>
<td>-787</td>
</tr>
<tr>
<td>KCl</td>
<td>-701</td>
</tr>
<tr>
<td>CsCl</td>
<td>-657</td>
</tr>
</tbody>
</table>
Trends in Lattice Energy

Ion Charge

• the force of attraction between oppositely charged particles is directly proportional to the product of the charges
• larger charge means the ions are more strongly attracted
  ✓ larger charge = stronger attraction = larger lattice energy
• of the two factors, ion charge generally more important

Lattice Energy = -910 kJ/mol

Lattice Energy = -3414 kJ/mol
Metallic Bonds

- low ionization energy of metals allows them to lose electrons easily
- the simplest theory of metallic bonding involves the metals atoms releasing their valence electrons to be shared by all to atoms/ions in the metal
  - an organization of metal cation islands in a sea of electrons
  - electrons delocalized throughout the metal structure
- bonding results from attraction of cation for the delocalized electrons
Metallic Bonding
Model vs. Reality

• metallic solids conduct electricity
• because the free electrons are mobile, it allows the electrons to move through the metallic crystal and conduct electricity
• as temperature increases, electrical conductivity decreases
• heating causes the metal ions to vibrate faster, making it harder for electrons to make their way through the crystal

Metallic Bonding
Model vs. Reality

• metallic solids conduct heat
• the movement of the small, light electrons through the solid can transfer kinetic energy quicker than larger particles
• metallic solids reflect light
• the mobile electrons on the surface absorb the outside light and then emit it at the same frequency
Metallic Bonding
Model vs. Reality

- metallic solids are malleable and ductile
- because the free electrons are mobile, the direction of the attractive force between the metal cation and free electrons is adjustable
- this allows the position of the metal cation islands to move around in the sea of electrons without breaking the attractions and the crystal structure

Metallic Bonding
Model vs. Reality

- metals generally have high melting points and boiling points
  ✓ all but Hg are solids at room temperature
- the attractions of the metal cations for the free electrons is strong and hard to overcome
- melting points generally increase to right across period
- the charge on the metal cation increases across the period, causing stronger attractions
- melting points generally decrease down column
- the cations get larger down the column, resulting in a larger distance from the nucleus to the free electrons