Skills to Develop

- Define bond length and bond energy and note the relationship between the two.
- Define bond order; explain its relationship to bond length or bond energy.
- Evaluate enthalpies of reactions using bond energies.
- Recognize covalent substances and characterize ionic character as difference in electronegativity.
- Describe trends in bond lengths of a series of related compounds.

**Bond Lengths and Bond Energies**

Distances between centers of bonded atoms are called bond lengths, or bond distances. Bond lengths vary depending on many factors, but in general, they are very consistent. Of course the bond orders affect bond length, but bond lengths of the same order for the same pair of atoms in various molecules are very consistent. Thus, there are tables of interatomic distances or bond lengths in some standard handbooks.

**Figure 1: Summary of common Bond Energies and Bond Lengths**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (pm)</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ce{H-H}$</td>
<td>74</td>
<td>436</td>
</tr>
<tr>
<td>$\ce{H-C}$</td>
<td>109</td>
<td>413</td>
</tr>
<tr>
<td>$\ce{C-C}$</td>
<td>154</td>
<td>348</td>
</tr>
<tr>
<td>$\ce{H-N}$</td>
<td>101</td>
<td>391</td>
</tr>
<tr>
<td>$\ce{N-N}$</td>
<td>145</td>
<td>170</td>
</tr>
<tr>
<td>$\ce{H-O}$</td>
<td>96</td>
<td>366</td>
</tr>
<tr>
<td>$\ce{O-O}$</td>
<td>148</td>
<td>145</td>
</tr>
<tr>
<td>$\ce{H-F}$</td>
<td>92</td>
<td>568</td>
</tr>
<tr>
<td>$\ce{F-F}$</td>
<td>142</td>
<td>158</td>
</tr>
<tr>
<td>$\ce{Cl-Cl}$</td>
<td>199</td>
<td>243</td>
</tr>
<tr>
<td>$\ce{Br-Br}$</td>
<td>228</td>
<td>193</td>
</tr>
<tr>
<td>$\ce{I-I}$</td>
<td>267</td>
<td>151</td>
</tr>
<tr>
<td>$\ce{C-C}$</td>
<td>154</td>
<td>348</td>
</tr>
</tbody>
</table>
Bond lengths are determined by X-ray diffraction of solids, by electron diffraction, and by spectroscopic methods (study the light absorbed or emitted by molecules).

The bond lengths range from the shortest of 74 pm for \(\text{H-H}\) to some 200 pm for large atoms, and the bond energies depend on bond order and lengths. Half of the bond length of a single bond of two similar atoms is called **covalent radius**. The sum of two covalent radii of two atoms is usually the single bond length. For example, the covalent radii of \(\text{C-H}\) and \(\text{C-C}\) are 37 and 77 pm respectively. The \(\text{C-H}\) bond is thus \((37+77) 114\) pm. Note that 77 pm = 154/2 pm.

The bond order is the number of electron pairs shared between two atoms in the formation of the bond. Bond order for \(\text{C=C}\) and \(\text{O=O}\) is 2. The amount of energy required to break a bond is called **bond dissociation energy** or simply **bond energy**. Since bond lengths are consistent, bond energies of similar bonds are also consistent. Thus, tables of bond energies are also of common occurrence in handbooks. Some typical bond lengths in picometers (1 pm = \(10^{-12}\) m) and bond energies in kJ/mol are given here to illustrate a general trend so that you are familiar with these quantities.

The bond energy is essentially the average enthalpy change for a gas reaction to break all the similar bonds. For the methane molecule, \(\text{C(-H)4}\), 435 kJ is required to break a single \(\text{C-H}\) bond for a mole of methane, but breaking all four \(\text{C-H}\) bonds for a mole requires 1662 kJ. Thus the average bond energy is \((1662/4) 416\) (not 436) kJ/mol.

Note
Bond energy is a measure of the strength of a chemical bond. The larger the bond energy, the stronger the bond.

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**Covalent Bonds**

Bonds between the same type of atom are **covalent bonds**, and bonds between atoms when their electronegativity differs by a little (say 0.7) are also predominantly covalent in character. There is also some covalent character between ions of what we usually call ionic solids. For example, bonds in the following substances are predominantly covalent:

- Elements: \(\text{H}_2\), \(\text{Li}_2\), \(\text{B}_2\), \(\text{C}_2\), \(\text{N}_2\), \(\text{O}_2\), \(\text{F}_2\), \(\text{Cl}_2\), \(\text{S}_8\), \(\text{P}_4\), \(\text{I}_2\), diamond, graphite, silicon etc
- Covalent compounds: \(\text{H}_2\text{O}\), \(\text{NH}_2\), \(\text{CH}_4\), \(\text{H}_3\text{C-CH}_3\), \(\text{H}_2\text{C=CH}_2\), \(\text{SiO}_2\), \(\text{CO}_2\), \(\text{N}_2\text{O}_4\), \(\text{NO}_2\), \(\text{SO}_2\) etc.

Theoretically, even ionic bonds have some covalent character. Thus, the boundary between ionic and covalent bonds is a vague one.

For covalent bonds, bond energies and bond lengths depend on many factors: electron affinities, sizes of atoms involved in the bond, differences in their electronegativity, and the overall structure of the molecule. There is a general trend in that the shorter the bond length, the higher the bond energy. However, there is no formula to show this relationship, because the variation is widespread. From a table of values, we can not grasp the trend easily. The best method to see the trend is to plot the data on a graph.

In a discussion of bond energies, this link has shown how energy varies as two H atoms approach each other in the formation of a \(\text{H-H}\) covalent bond:

Covalent bonds such as \(\text{H-Cl}\), \(\text{H-I}\) etc. are polar, because the bonding electrons are attracted to the more electronegative atoms, \(\text{Cl}\) and \(\text{I}\) in these cases. In general, the higher the electronegativity difference, the more polar are the bonds. In particular, \(\text{H-F}\) and \(\text{H-O}\) bonds are very polar.

Example 1
Use the table of bond energies to find the $\Delta H^o$ for the reaction:

$$\ce{H_{(g)} + Br_{(g)} \rightarrow 2 HBr_{(g)}}$$

**Solution**

From the Table of bond length and bond energy given above, a table below is obvious:

<table>
<thead>
<tr>
<th>Changes</th>
<th>$\Delta H^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ce{H-H \rightarrow H + H}$</td>
<td>436</td>
</tr>
<tr>
<td>$\ce{Br-Br \rightarrow Br + Br}$</td>
<td>193</td>
</tr>
<tr>
<td>$\ce{H + H + Br + Br \rightarrow 2 H-Br}$</td>
<td>$2\times(-366)$ = -732</td>
</tr>
</tbody>
</table>

**Overall (add up)**

$$\ce{H-H + Br-Br \rightarrow 2 H-Br}$$  -103

**Discussion**

Another approach is shown below. Write the bond energy below the formula, and then apply the principle of conservation of energy.

<table>
<thead>
<tr>
<th>Bonds broken</th>
<th>Bonds formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ce{H-H + Br-Br}$</td>
<td>$\ce{2 H-Br}$</td>
</tr>
<tr>
<td>$\Delta H^o$</td>
<td>436 + 193</td>
</tr>
</tbody>
</table>

$-2\times366$ energy released

$$\Delta H^o = 436 + 193 - 2\times366 = -103$$

**Exercises**

Evaluate the energy changes for the following reactions

A)

```
\[
\text{Ethylene} + \text{Hydrogen} \rightarrow \text{Ethane}
\]
```

B)
Questions

1. **Which bond in the list has the highest bond energy**, \( \text{H-H} \), \( \text{H-O} \), \( \text{H-F} \), \( \text{H-I} \) or \( \text{I-I} \)?

   Hint: \( \text{H-F} \)

   **Discussion:** Describe the trends in bond length and bond energy from the Table above.

2. **Which bond of the following list has the lowest bond energy**, \( \text{H-H} \), \( \text{C-C} \), \( \text{N-N} \), \( \text{O-O} \), \( \text{Cl-Cl} \), \( \text{Br-Br} \), \( \text{I-I} \)? Note that all these are single bonds.

   Hint: \( \text{O-O} \)

   **Discussion:** The bond lengths and energies of two possible ones are compared here. \( \text{I-I} \), 267 pm, 153 kJ/mol; \( \text{O-O} \), 148 pm, 145 kJ/mol.

3. **For carbon-carbon bonds, which one has the highest bond energy:** single bond, double bond, or triple bond?

   Hint: Triple bond has the highest bond energy.

   **Discussion:** Bond energies: single, 348; double, 614; triple, 839 kJ/mol. The higher the bond order, the more the bond energy.

4. **Define bond energy**

   Hint: The energy required to break a mole of bonds is the bond energy.

   **Discussion:** Energy is always required to break a chemical bond. Chemical bonds store energy.

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