Bonding: General Concepts

Chapter 8

Partial Ionic Character of Covalent Bonds

Percent ionic character for bonds of binary compounds in the gas phase.
There is no totally ionic bonds between discrete pairs on atoms.

% ionic characteristic of a bond = \frac{\text{Measured dipole moment } X-Y}{\text{Calculated dipole moment } X^*-Y^-} \times 100

Ionic characteristic increases with increased EN difference.
More than 50% character is considered ionic.

Compounds with Ionic Bonds and Covalent Bonds

Covalent bond

\begin{align*}
\text{NH}_3 & \quad 1^+ \\
\text{H}_2\text{O} & \quad 2^-
\end{align*}

Ionic bond

Covalent bond
The Covalent Chemical Bond: A Model

\[ \text{CH}_4 \text{ is four } \text{C} - \text{H interactions} \]

\[ \frac{1652 \text{ kJ/mol}}{4} \text{ energy of stabilization} = 413 \text{ kJ/mol} = \text{C-H bond energy} \]

\[ \text{CH}_3\text{Cl is three C-H interactions; one C-Cl interaction} \]

\[ \frac{1578 \text{ kJ/mol}}{4} \text{ energy of stabilization} \]

\[ (3 \times 413 \text{kJ}) + (1 \times \text{C-Cl}) = 1578 \text{ kJ} \]

C-Cl – 339 kJ/mol bond energy

Bond result from the tendency of natural systems to seek the lowest energy.

“It’s only a model.”

---

Covalent Bond Energies and Chemical Reactions

Bond energies vary with their environment

Table 8.4 is average bond energies

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Short</th>
<th>Strong</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Double</td>
<td>shorter</td>
<td>stronger</td>
</tr>
<tr>
<td>Triple</td>
<td>shortest</td>
<td>strongest</td>
</tr>
</tbody>
</table>

Breaking bonds is endothermic – positive

Forming bonds is exothermic – negative

\[ \Delta H = \sum \text{bonds broken} - \sum \text{bonds formed} \]

---

**TABLE 8.4 Average Bond Energies (kJ/mol)**

<table>
<thead>
<tr>
<th></th>
<th>Single Bonds</th>
<th>Multiple Bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–H</td>
<td>432</td>
<td>C=C 644</td>
</tr>
<tr>
<td>H–F</td>
<td>565</td>
<td>C=O 839</td>
</tr>
<tr>
<td>H–Cl</td>
<td>427</td>
<td>C=F 327</td>
</tr>
<tr>
<td>H–Br</td>
<td>295</td>
<td>N=O 607</td>
</tr>
<tr>
<td>H–I</td>
<td>363</td>
<td>C=O* 745</td>
</tr>
<tr>
<td>N–N</td>
<td>305</td>
<td>N=N 941</td>
</tr>
<tr>
<td>N–O</td>
<td>358</td>
<td>C=O 898</td>
</tr>
<tr>
<td>C–H</td>
<td>485</td>
<td>Si–Si 340</td>
</tr>
<tr>
<td>C–Cl</td>
<td>339</td>
<td>Si–N 393</td>
</tr>
<tr>
<td>C–Br</td>
<td>276</td>
<td>Si–C 360</td>
</tr>
<tr>
<td>C–I</td>
<td>240</td>
<td>Si–O 452</td>
</tr>
<tr>
<td>C–S</td>
<td>259</td>
<td>Cl–Cl 239</td>
</tr>
<tr>
<td>C–Br</td>
<td>218</td>
<td>Br–Br 193</td>
</tr>
</tbody>
</table>

*C=C*O*CO* = 799
Sample Exercise 8.5

\[ \text{CH}_4(g) + 2 \text{Cl}_2(g) + 2 \text{F}_2(g) \rightarrow \text{CF}_2\text{Cl}_2(g) + 2 \text{HF}(g) + 2 \text{HCl}(g) \]

Using bond energies on Table 8.4 find the \( \Delta H \)

---

<table>
<thead>
<tr>
<th>Bond Energy Calculations #53</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use bond energy values (Table 8.4) to estimate ( \Delta H ) for each of the following reactions</td>
</tr>
<tr>
<td>a. HCN + 2H(_2) \rightarrow CH(_3)NH(_2)</td>
</tr>
<tr>
<td>b. N(_2)H(_4) + 2F(_2) \rightarrow N(_2) + 4HF</td>
</tr>
</tbody>
</table>

---

<table>
<thead>
<tr>
<th>Bond Energy Calculations #55</th>
</tr>
</thead>
<tbody>
<tr>
<td>Use bond energies (Table 8.4) to predict ( \Delta H ) for the isomerization of methyl isocyanide to acetonitrile</td>
</tr>
<tr>
<td>CH(_3)NC \rightarrow CH(_3)CN</td>
</tr>
</tbody>
</table>
Bond Energy Calculations #57
Use the bond energies to predict $\Delta H$ for the combustion of ethanol.
\[ C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O \]

Bond Energy Calculations #59
Use bond energies to estimate $H$ for the following reaction
\[ H_2O_2 + CH_3OH \rightarrow H_2CO_3 + 2H_2O \]

Localized Electron Bonding Model
LE model – assumes that a molecule composed of atoms bond together by sharing pairs of electrons using the atomic orbitals of the bound atoms
Bonding pairs – electron pairs between atoms
Lone pairs – electron pairs on the atoms
LE Model has three parts:
1. Lewis Structures
2. VSEPR Model
3. Description of the type of atomic orbitals used by atoms to share electrons or hold lone pairs (covered in chapter 9)
The Duet Rule and the Octet Rule

Duet Rule – like helium

\[ \text{H : H} \]

Octet Rule – like every other noble gas

\[ \text{:O : O:} \]

Octet Rule Exceptions

- Less than 8 electrons
  - Boron
    - Three valence electrons
    - Stable with only six instead of eight
  - Beryllium
    - Two valence electrons
    - Stable with only four instead of eight

Octet Rule Exceptions

- Expanded valence - involves the d orbitals as well as s & p
  - Phosphorus
    - Five valence electrons
    - Stable with only ten instead of eight
  - Sulfur
    - Six valence electrons
    - Stable with only twelve instead of eight
Exceptions to the Octet Rule

BF$_3$, the B is “electron deficient”

Sulfur (Elements in period 3 and higher)

- 3s
- 3p
- 3d

Expected – 2 bonds

Expanded – 6 bonds

Calculate the total number of valence electrons
Put in bonds.
Distribute remaining electrons
Extra electrons should be placed on the central atom.

$I^-$
$3 \times 7 + 1 = 22$

Sample Exercise 8.8

ClF$_3$, XeO$_3$, RnCl$_2$, BeCl$_2$, ICl$_4^-$

Will these species obey the octet rule, be electron deficient or have an expanded octet?