Nature of the Chemical Bond; Lewis Structures & Chemical Bonding

CHEM 107
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Energetics of Ionic Bonding

■ Problem #7.37: formation of KI ion pair from neutral atoms of K, I

\[
\begin{align*}
K(g) + I(g) & \rightarrow K^+(g) + I^-(g) \\
K^+(g) + I^-(g) & \rightarrow K^+I^-(g)
\end{align*}
\]

■ First step: form ions from atoms
■ Second step: combine ions to form pair
Attraction

Ion Formation

\[ K_{(g)} \rightarrow K^+_{(g)} + e^- \]

- Energy required or released?

\[ I_{(g)} + e^- \rightarrow I^-_{(g)} \]

- Energy required or released?

“Perhaps one of you gentlemen would mind telling me just what it is outside the window that you find so attractive...?”
Ion Formation

\[ K(g) \rightarrow K^+(g) + e^- \]

- \( \Delta E = IE(\text{potassium}) = 418.8 \text{ kJ/mol} \)
- \( I(g) + e^- \rightarrow I^-(g) \)
- \( \Delta E = EA(\text{iodine}) = -295.3 \text{ kJ/mol} \)

\[ \rightarrow \text{Overall, formation of ions costs energy:} \]
\[ \Delta E = 418.8 - 295.3 = 123.5 \text{ kJ/mol} \]

Ion Pair Formation

\[ K^+(g) + I^-(g) \rightarrow K^+I^-(g) \]

- Coulomb energy:
  \[ E_{\text{Coulomb}} = \frac{(1.389 \times 10^5 \text{kJ pm mol}^{-1})(q^+)(q^-)}{d} \]
- With \( q^+ = +1 \), \( q^- = -1 \), and \( d = 353 \text{ pm} \),
- \( E_{\text{Coulomb}} = -393.5 \text{ kJ/mol} \)
KI Ion Pairs

- Formation of ions *costs* energy:
  \[ \Delta E = 123.5 \text{ kJ/mol} \]

- Formation of ion pair *releases* energy:
  \[ \Delta E = -393.5 \text{ kJ/mol} \]

- Overall process *releases* energy:
  \[ \Delta E = 123.5 \text{ kJ/mol} + (-393.5 \text{ kJ/mol}) = -270.0 \text{ kJ/mol} \]

- Ion pair is stable

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Ionic Solids—Stabilized by Cation-Anion Coulomb Attractions
Other Types of Bonding

- Most compounds are not ionic. $\text{H}_2$, $\text{N}_2$, etc.

- Bonding based on electron \textit{sharing} rather than electron \textit{donation}.

- “\textit{Covalent bonding}.”

Types of Bonds

- Ionic Bonding $\rightarrow$ electron donation
- Covalent bonding $\rightarrow$ electron sharing

- These are two extremes. Most bonds are a combination of the two:

- Polar covalent $\rightarrow$ uneven electron sharing
Electronegativity

- “A measure of the ability of an atom in a molecule to attract the shared electrons in a chemical bond.”

- Related to IE and EA

- Based on your knowledge of IE and EA variations, how would you expect electronegativity to vary in the periodic table?

Electronegativity

- High electronegativity means an atom attracts electrons strongly.

- Low electronegativity means it is fairly easy to pull electron density away from an atom.
  - large EA $\rightarrow$ high electronegativity
  - small IE $\rightarrow$ low electronegativity
Electronegativity

- Values are approximate, scale arbitrary
- Highest electronegativity: $F$, $\chi = 4.0$
- Lowest electronegativity: $Cs$, $\chi = 0.7$
- Generally, electronegativity increases as you move up or to the right in the periodic table.

Electronegativity Difference

- In a purely covalent bond, the 2 atoms are identical: $H_2$, $N_2$, etc.
  same electronegativity $\rightarrow$ even sharing

- In an ionic bond, one atom has high electronegativity, one low: $NaCl$
  $\chi(\text{Na}) = 0.9$, $\chi(\text{Cl}) = 3.0$ $\Delta\chi = 2.1$
  Chlorine pulls an electron away from sodium, forming ions
Polar Covalent Bonds

■ For many bonds, $\Delta \chi$ is small but not zero

■ This gives an intermediate case: electrons are shared, but not equally.

■ CO: $\chi(C) = 2.5$, $\chi(O) = 3.5$  $\Delta \chi = 1.0$

■ Bond is not ionic, but is not purely covalent, either.

Lewis Structures

■ A simple way of representing valence electrons in a molecule.

■ Easy (compared to the real physics), but very useful

■ One electron = one dot

■ One pair of shared electrons = one line

■ Two pairs = two lines, etc.
Lewis Structures for Atoms

- We usually write these for molecules, but atoms are a good way to get started.
- Some examples:

- \( \text{H} \quad \text{C} \quad \text{F} \)

- Notice that the structures show whether electrons are paired or unpaired.

Writing Lewis Structures

- I develop a systematic method for doing this; the text’s approach is similar, but not spelled out as systematically.
- I will put some emphasis on the “octet rule”. I will use the octet rule to a greater extent than the text.
- Later, I’ll spell out the so-called VSEPR method of rationalizing structures of molecules that conform to the octet rule and some that don’t.
Lewis Structures

Systematic method
1. Treat ions separately.
2. Count the valence e⁻'s.
3. Set up the bonding framework, using two e⁻'s per bond
4. 3 pairs of nonbonding e⁻'s on each outer atom, except H (assuming enough e⁻'s)
5. Remaining e⁻'s to inner atoms

Lewis Structures, cont.

Systematic method
6. Find formal charge on each atom.
7. Minimize formal charges by shifting e⁻’s to make double and triple bonds.
   (a) 2\textsuperscript{nd} row atom → 4 occupied valence orbitals (8e⁻’s → \textit{"octet rule"})
   (b) other atoms → formal charge to zero.

Writing Lewis structures builds on way we wrote structural diagrams earlier in the course.
Formal Charges

- A useful “accounting device,” not the real electrical charge on the atoms.

\[ \text{FC} = (\# \text{ valence e}^-\text{'s in free atom}) - (\# \text{ valence e}^-\text{'s assigned in structure}) \]

- Sum of FC’s = zero for a molecule, or total charge on an ion.

- Minimize FC’s to get “best” structure.

Examples - no octet rule violations

- \( \text{CH}_4 \) (methane)
- \( \text{C}_2\text{H}_6 \) (ethane)
- \( \text{CCl}_4 \) (carbon tetrachloride)
- \( \text{Br}_2, \text{O}_2, \text{N}_2 \) (bromine, oxygen, nitrogen)
- \( \text{H}_2\text{O}, \text{NH}_3 \) (water, ammonia)
- \( \text{C}_2\text{H}_4, \text{C}_3\text{H}_6 \) (ethene, propene)
- \( \text{HCOOH} \) (formic acid)
- \( (\text{NH}_2)_2\text{CO} \) (urea)
Lewis Structures & Resonance

In many cases, no single Lewis structure adequately represents the distribution of electrons in a molecule. In such cases, we represent the electron distribution as a combination of Lewis structures.

Real molecule does NOT “bounce” between the different resonance structures!

Resonance — Examples

equivalent resonance structures:

\begin{align*}
O_3 & (ozone), \ NO_2^- , \ NH_4NO_3, \ CaCO_3, \\
C_6H_6 & (benzene)
\end{align*}

resonance structures are inequivalent, but at least two are important:

\begin{align*}
N_2O & (nitrous oxide), \ NCO^- (cyanate), \\
CH_3CONHCH_3 & (N-methylacetamide) — an example of an amide bond.
\end{align*}
Bond Lengths - an experimental test

\[
\begin{array}{c}
N_2O \\
\{ \\
\{ \\
\{ \\
N = \text{green}, \quad O = \text{red} \}
\end{array}
\]

\[
\begin{array}{c}
N_2 \\
: \text{N} = \text{N} : \\
1.094 \text{ Å}
\end{array}
\]

\[
\begin{array}{c}
NO_2^+ \\
: \text{O} = \text{N} = \text{O}^+ \\
1.150 \text{ Å (both)}
\end{array}
\]