Chemistry 1000 Lecture 15: Covalent bonding and Lewis structures

Marc R. Roussel

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Covalent bonding

Covalent bond: a chemical bond in which electrons are shared between two atoms

Contrast:

Ionic bonding: material held together by electrostatic force between ions (no sharing of electrons)

Metallic bonding: electrons shared among all the metal atoms

- Covalent bonds are typically formed between two non-metallic elements.

Lewis diagrams

- A convenient graphical accounting system for valence electrons in molecules

- A shared electron pair is represented by a line between the two atoms.

  Bond order: number of shared electron pairs in a bond

- A nonbonding valence electron is represented by a dot.

- Dots are paired to represent their occupation of orbitals.
    Lone pair: a pair of nonbonding electrons in an "orbital"

Example:

$$\text{H} \text{---} \overset{\cdot\cdot}{\underset{|}{\text{O}}}\text{:}$$
$$\text{H}$$
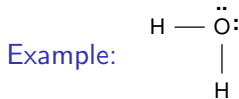
The octet rule

Typically, main-group elements in chemical compounds (except H) are surrounded by eight valence electrons (including any shared in covalent bonds).

H can only have/share two electrons.

Some elements, notably B, sometimes form electron deficient compounds in which there is less than a full octet around the atom, with important implications for their chemistry.

Figuring out the connectivity

- If you're given a chemical formula, you can usually figure out the connectivity for yourself.
- If the formula is AX_n, A is usually the central atom.
  Example: SO_3
- Neither H nor F can form more than one bond.
- C is rarely a terminal atom.
- In oxoacids (H_mAO_n), the hydrogens are almost always connected to an oxygen atom.
  Example: H_2SO_4
- If these rules aren't enough to figure it out, we will give you the connectivity in a test.

Guidelines for drawing Lewis diagrams
Part one

1. Count up the number of valence electrons in all the atoms.
   - If the species is a cation, subtract the charge.
   - If the species is an anion, add the absolute value of the charge.

   This is the total number of valence electrons to place in your Lewis diagram.

2. Draw a skeleton with one bond between each pair of atoms which are covalently bonded.

3. Complete the octets for any group 17 elements with lone pairs.

   Exception: compounds where a halogen is the central atom

Guidelines for drawing Lewis diagrams
Part one

4. Placing the remaining electrons becomes a puzzle:
   - Complete as many octets as possible with lone pairs or multiple bonds.
   - Double bonds are common for C, group 15 and group 16.
   - Triple bonds are common for C and group 15.
   - Never exceed an octet in period 2.
   - You can exceed an octet in periods 3 and up if necessary.

Examples: ammonium ion, cyanide ion, boron trifluoride, BrF_5, NO
(State bond orders for each structure.)

Resonance

- Sometimes, there is more than one reasonable Lewis diagram.

- The true (quantum mechanical) structure can be thought of as an average (not necessarily equally weighted) of all reasonable Lewis diagrams.
  $\implies$ resonance structures

- The best Lewis structure (based on the Lewis rules) sometimes consists of several equivalent resonance structures.

Examples: benzene, nitrate ion
            (State bond orders for each structure.)

Formal charges

Definition: a calculation of the charge of an atom in a Lewis diagram assuming electrons are exactly equally shared

Calculation: Draw the Lewis diagram, then count the electrons on a particular atom, counting half of any electrons shared with a neighbor.
The formal charge is the number of valence electrons of the neutral atom minus the number of electrons on the atom in the Lewis structure.

Useful fact: Sum of formal charges = charge of molecule

Nonzero formal charges should be written next to the appropriate atoms in a Lewis structure.

Examples: CO, BrF_5, nitrate ion

Guidelines for drawing Lewis diagrams
Part two

5. The best Lewis structure for a compound minimizes the formal charges even if this means violating the octet rule for atoms in the 3rd period and beyond.

   Never violate the octet rule for 2nd period elements.

   Examples: BF_3, SO_2, SO_4^{2-}, XeF_6

Concept application: Why doesn't F ever form a double bond?

A controversy: Should we stick to the octet rule or minimize formal charge?

- It is important to keep in mind that both Lewis structures and formal charge are accounting devices which provide us some guidance regarding the likely bonding arrangement in molecules.
- With that in mind, do we get better Lewis structures by sticking to the octet rule as closely as possible, or by minimizing formal charge? These two rules don't always make the same predictions!
- Chemists disagree on this point.

So what should you do?

- By default minimize formal charge.

- If asked, you should be able to produce strict octet-rule structures.

- Learn some of the patterns (e.g. the tendency for B to form electron-deficient compounds).

Bond order and bond length

- Single bond lengths can be estimated from the sum of the covalent radii of the two elements.
  Why?
- All other things being equal, higher bond orders correspond to shorter bonds.

Compound	C–C bond order	Bond length/pm
$H_3C–CH_3$	1	152.4
Benzene	$\frac{3}{2}$	139
$H_2C=CH_2$	2	133.05
$HC\equiv CH$	3	120.4

Bond dissociation enthalpies

Definition: Enthalpy change for the breaking of a covalent bond in the gas phase

Symbol: $\Delta_{bd}H$

Example: $H_{2(g)} \rightarrow 2H_{(g)}$, $\Delta_{bd}H = 435.996\,\text{kJ/mol}$

Example: $CH_{4(g)} \rightarrow CH_{3(g)} + H_{(g)}$, $\Delta_{bd}H = 438.3\,\text{kJ/mol}$

Note: So-called bond energies are almost always bond dissociation enthalpies.
The latter term is more precise and unambiguous.

- In general, bond dissociation enthalpy depends on the particular molecule in which the bond occurs, not just on the atoms involved.

Example:

Reaction	$\Delta_{bd}H/\text{kJ mol}^{-1}$
$CH_{4(g)} \rightarrow CH_{3(g)} + H_{(g)}$	438.3
$CH_{3(g)} \rightarrow CH_{2(g)} + H_{(g)}$	458.70
$CH_{2(g)} \rightarrow CH_{(g)} + H_{(g)}$	425.74
$CH_{(g)} \rightarrow C_{(g)} + H_{(g)}$	340.55
Average:	416

- Tables of bond dissociation enthalpies contain average values obtained from many different molecules (except when the bond only occurs in one molecule, e.g. H–Cl).

Bond dissociation enthalpy and bond order

- All other things being equal, the bond dissociation enthalpy increases with bond order.

Compound	C–C bond order	$\Delta_{\text{bd}}H$/kJ/mol
$H_3C–CH_3$	1	375
$H_2C=CH_2$	2	720.4
$HC\equiv CH$	3	960.9

Estimating reaction enthalpies

- We can estimate reaction enthalpies from bond dissociation enthalpies by counting up the number of bonds of each type made and broken.

- Due to Hess's law, which says that the enthalpy change of a reaction can be calculated by adding the enthalpy changes of the steps, this should be exact, except that we typically use average bond dissociation enthalpies instead of the bond dissociation enthalpies for the actual bonds made/broken.

- This works reasonably well in the gas phase, but is much less accurate in solution due to interactions of the solutes with the solvent.

Estimating reaction enthalpies: example

Estimate the enthalpy change in the reaction
$C_2H_{6(g)} + Cl_{2(g)} \rightarrow C_2H_5Cl_{(g)} + HCl_{(g)}$.
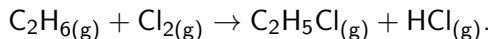
Data:

| Bond	C–Cl	C–H	Cl–Cl	H–Cl
$\Delta_{bd}H/\text{kJ mol}^{-1}$	339	414	243	431

Answer: $\Delta H = -113\,\text{kJ/mol}$

Actual (from tables of enthalpy of formation): $-117\,\text{kJ/mol}$

Why N_2 is inert, but carbon-carbon double and triple bonds are reactive

Bond	C–C	C=C	C≡C	C–Br	Br–Br
$\Delta_{bd}H/\text{kJ mol}^{-1}$	347	611	837	276	193

- The increase in C–C bond dissociation enthalpy with bond order is small.
- Tends to be enthalpically favorable to replace C–C multiple (double or triple) bonds with a single bond and bonds to other atoms
- Classic test for C–C multiple bonds:

$$-\text{C=C-} + Br_2 \rightarrow -\text{C(Br)–C(Br)-}$$
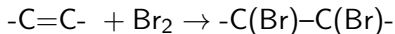
$$
\begin{aligned}
\Delta H &\approx \Delta_{bd}H(\text{C=C}) + \Delta_{bd}H(\text{Br}_2) \\
&\quad - (\Delta_{bd}H(\text{C–C}) + 2\Delta_{bd}H(\text{C–Br})) \\
&= 611 + 193 - [347 + 2(276)] \text{ kJ/mol} = -95 \text{ kJ/mol}
\end{aligned}
$$

Exercise: Try showing that brominating a carbon-carbon triple bond is also enthalpically favorable.
(Hint: You will use two equivalents of bromine.)

Bond	N–N	N=N	N≡N	N–Cl	Cl–Cl
$\Delta_{bd}H/\text{kJ mol}^{-1}$	163	418	946	200	243

- Note how quickly the bond dissociation enthalpies increase.
- It's going to be enthalpically disfavorable to replace multiple nitrogen-nitrogen bonds with an N–N single bond.
- Imagine trying the reaction $N_2 + 2Cl_2 \rightarrow N_2Cl_4$.

$$\begin{aligned} \Delta H &\approx \Delta_{bd}H(N \equiv N) + 2\Delta_{bd}H(Cl_2) \\ &\quad - (\Delta_{bd}H(N–N) + 4\Delta_{bd}H(N–Cl)) \\ &= 946 + 2(243) - [163 + 4(200)] \text{ kJ/mol} = 469 \text{ kJ/mol} \end{aligned}$$

- Consequence: N_2 is very inert (unreactive).

Bond polarity

- Recall: Electronegativity is a measure of the ability of an atom to attract electrons to itself.

- Two atoms in a covalent bond may not share the electrons in the bond equally, depending on the difference in electronegativity.

- Example: $\chi(H) = 2.1$, $\chi(Cl) = 3.0$, so in the HCl bond, the electrons tend to stay closer to the Cl atom (on average) than to the H atom. We say that the HCl bond is polar.

  $\implies$ Cl carries a partial negative charge and H carries a partial positive charge in an HCl molecule.
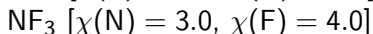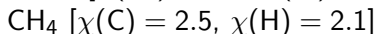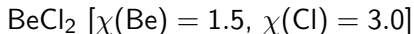
Ionic compound or covalent compound?

- In the limit of very large differences in electronegativity, the electrons are transferred from one atom to another rather than shared, and we get an ionic compound.

- As a guide, we get ionic compounds when we combine elements whose electronegativities differ by 2 units or more.

Examples of ionic compounds:

Li_2O [$\chi(Li) = 1.0$, $\chi(O) = 3.5$]
NaCl [$\chi(Na) = 0.9$, $\chi(Cl) = 3.0$]
$CaBr_2$ [$\chi(Ca) = 1.0$, $\chi(Br) = 2.8$]
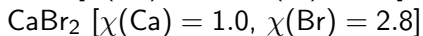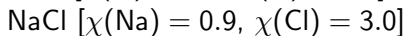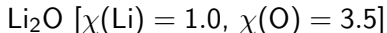
Examples of covalent compounds:

$BeCl_2$ [$\chi(Be) = 1.5$, $\chi(Cl) = 3.0$]
CH_4 [$\chi(C) = 2.5$, $\chi(H) = 2.1$]
NF_3 [$\chi(N) = 3.0$, $\chi(F) = 4.0$]

Ionic compound or covalent compound?

- Many compounds fall into a grey area:
    - HF [$\chi(H) = 2.1$, $\chi(F) = 4.0$]
    - FeCl$_3$ [$\chi(Fe) = 1.8$, $\chi(Cl) = 3.0$]
- Ultimately, the test of polar vs covalent is experimental: Does a melt conduct electricity?