Chapter 10 Bonding: Lewis electron dot structures and more

Bonding is the essence of chemistry! Not just physics!

Chemical bonds are the forces that hold atoms together in molecules, in ionic compounds, and in metals.
In molecules and polyatomic ions, bonds are the forces that hold groups of atoms together and make them act as a unit.

Only the **valence electrons** (outermost electrons of an atom) participate significantly in bonding.
valence electrons = digit in ones place of group
The term valence electrons is not well-defined and is less useful for transition metals.

The highest common oxidation number for groups 3 through 7 is the group number. OsO_4
Caution for groups 10, 11, & 12: They are often considered to have 10, 11, & 12 valence electrons respectively, although the highest common oxidation # for group 12 elements is +2, implying only two valence electrons. In group 11, only Ag^+ is common, but Cu^+ and Cu^{2+} and Au^+ and Au^{3+} are common. In group 10, Ni^{2+} and Ni^{3+} are common, and Ni(IV) and Pd(IV) and Pt(IV) all exist. But platinum does not oxidize in air at any temperature and is insoluble in HCl(*aq*) and HNO_3(*aq*), implying that Pt is rather unreactive, consistent with no valence electrons.
Remember that the heavier p-block metals such as Tl, Pb, and Bi usually form +1, +2, and +3 ions respectively despite being in Groups 13, 14, and 15—this effect is called the inert pair effect.

Lewis electron dot structures
1. Apply to main-group elements
2. Use valence electrons: *s* and *p* electrons in outermost shell

H· He: Li· Na· K· ·Be· etc.

3. Octet rule & duet rule

ionic bond example: K loses its one valence electron to form K^+,
F gains one electron to have a filled valence shell in F^-

K(*g*) + F(*g*) → KF(*g*) and K(*s*) + ½ F_2(*g*) → KF(*s*)

covalent bond: share pair of valence electrons as in H:H and F_2
Equal sharing of an electron pair gives a nonpolar covalent bond.
Unequal sharing of an electron pair gives a polar covalent bond.

Types of bonds

Ionic	full charge separation	metal-nonmetal usually
Polar covalent	partial charge separation	different nonmetals
Nonpolar covalent	no charge separation	same nonmetal usually
Metallic	mobile electrons	metals in bulk

Examples: NaCl, CaO, Fe_2S_3, $KMnO_4$, $TiCl_4$, HF, F_2

We emphasize Lewis electron dot structures because of their usefulness in explaining structure of covalent molecules, especially organic molecules.

Draw Lewis electron dot structures: CH_4 CH_3CH_3 CH_2CH_2 HCCH C_2H_2

NH_3 & NH_4^+ LiF Na_2O

HF

Electronegativity: ability of an atom in molecule to attract shared electrons to itself Figure 10-6

H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
		Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0

Fr 0.7

Central atom is usually atom of lowest <u>*electronegativity*</u>*.*
H is always a terminal atom, except in compounds such as B_2H_6.
Carbon atoms are usually central atoms, except for the isocyanide C in *n*-butylisocyanide.
$CH_3CH_2CH_2CH_2NC$ vs. $CH_3CH_2CH_2CH_2CN$ which is more stable?
Expect compact symmetrical structures for SO_4^{2-}, etc., but not for polymers such as $(CH_2CH_2)_n$
I use Strategy on pp385-6 to check rather than to generate Lewis structures; use total # valence electrons as check
Generate Lewis structures by putting together Lewis electron dot symbols, trying to create octets and duets, and move electrons as needed. My approach builds in formal charge (see pp. 388-9).

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Expect H in group 1 to form 1 bond in neutral molecules.
  "    Be "   "   2 to form 2 bonds "    "        "
  "    B  "   "  13 to form 3 bonds "    "        "
  "    C  "   "  14 to form 4 bonds "    "        "
  "    N  "   "  15 to form 3 bonds "    "        "
  "    O  "   "  16 to form 2 bonds "    "        "
  "    F  "   "  17 to form 1 bond  "    "        "
  "    Ne "   "  18 to form 0 bond.
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Resonance arises due to inadequacy of Lewis e^- dot structures
mythical unicorn ↔ dragon = rhinoceros
NO_3^-, CO_3^{2-}, benzene, O_3, CH_3COO^-

other oxoacids besides HNO_3: H_2SO_4, H_3PO_4, $HClO_4$, etc. H-O-nonmetal

Exceptions to Octet Rule
<u>Incomplete octet</u> in some compounds of Be, B, and Al: BeH_2 and BF_3 in the gas phase
central nonmetal atom comes in with < 4 valence electrons

<u>Odd-electron molecules</u>: NO and NO_2 (air pollution) These are also examples of free radicals.

<u>Expanded octet</u> for 3rd row elements and lower:
both PCl_3 & PCl_5
XeF_2 & XeF_4
H_2SO_4 & H_3PO_4

Formal charge -- use to assess relative importance of different Lewis structures
but :C:::O: ::: don't come equally from C & O

Octet rule is important because it explains a lot of bonding for most organic compounds, and it only requires pencil and paper.

Write the Lewis electron dot structure for ...

CNH_5 NO_3^- & HNO_3 SO_4^{2-} OCl^- N_2O ClF_3

Be able to show resonance, incomplete octets on Be & B, expanded octets on third row elements and lower

Percent ionic character Figure 10-7

Electrostatic potential maps -- visualize charge distribution within a species

Formal charge helps us decide which Lewis structures are important.

When I bring together atoms with their valence electrons to form molecules, I automatically try to obtain formal charges of zero.

CH_3NH_2 vs CH_2NH_3

OCl^- and where H^+ would add

CN^- and where H^+ would add

BF_3 and SO_4^{2-} and H_2SO_4 and SO_2

Based on formal charge, the best Lewis structure may not have octet on central atom

§10-7 VSEPR Table 10.1; U:_SC Student File Area\Pultz\VSEPR.pdf

Look at # of different directions for valence electron pairs! **modify step #2 on p401**

This determines the geometry of the electron pairs. Figure 10-12 shows balloons

Now note where atoms are attached to the central atom; this determines the molecular shape.

model kits

Molecular polarity put VSEPR & bond polarity together

Bond polarity & charge distribution in covalent compounds

Usually do not have equal sharing of electrons due to differences in electronegativity ==> partial charges δ+ and δ-

HOH HCl

Show the direction of *polarity* of each of the following bonds, using partial charges:

H-O, H-N, C-Cl, C-Mg

Difference in electronegativity ==> polar or ionic bond

Which bond is more polar? H-F or H-I? B-C or B-F? C-Si or C-S? K&T4Exer9.12

Which bond is most polar? N-H or N-O or N-C

If polar bond, **symmetry determines whether molecule is polar**.

CO_2 HCN BF_3 SO_2 CCl_4 HOH C_2H_6 C_2H_4 C_2H_2 SF_4

↖octet & expanded octet

O=C=O vs O=C=S HCl CCl_4 (Figure 10-15)

§10-8 & 10-9 Bond Properties
bond order in H_3PO_4, NO_2^-, CO, O_3
Bond length & bond energy depend on: Tables 10.2 & 10.3
• identity of atoms H-H 74 pm H-C 110 pm C-O 143 pm Bond length depends on atomic sizes
• bond order C=O 120 pm As bond order increases, bond length ↓
• hybridization (§11-3)
bond energy changes across period are unpredictable
bond energy decreases going down group & increases with bond order

Expanded octets normally on central atom only.
Note species which are isoelectronic, such as XeF_2 and I_3^-
Note bond angles for linear arrangement of electron pairs, trigonal planar arrangement of electron pairs, tetrahedral arrangement of electron pairs, etc.

work on Practice Examples & Concept Assessments in §9-6, §9-7, & Ch. 10.
Concept Assessment on p. 407: I find answer in back confusing. NO_2^- is isoelectronic with O_3 whose structure is on p391, & the bond order is 1½. NO_2^+ is shown in (10.14) on p388, & the bond order is 2. The higher the bond order, the shorter the bond length. NO_2^+ has shorter N-O bonds.

Some Chapter 10 problems
1a. Write the best Lewis formula, including formal charges if any, for the cyanide ion, CN^-.
b. If a hydrogen ion, H^+, attaches to a cyanide ion, does it attach to the C or to the N? Explain.

2. Do Pre-lab for *Molecular Models* exp't at U:_SC Student File Area\Pultz\Molecular_Models.doc

3. Predict molecular shape &/or overall polarity (**p**olar/**n**onpolar) for species in *Molecular Models* exp't

4. Predict the order of increasing electronegativity in each of the following groups of elements:
a. C, N, O b. S, Si, Sr c. F, Cl, Br, I d. S, O, F

5. Predict which bond in each of the following groups will be the most polar:
a. C-F, Si-F, Ti-F b. C-H, N-H, O-H, F-H c. C-O or Si-O

6. Write resonance structures for CO_3^{2-}. Use the correct symbol between resonance structures.

Partial answer key to **Some Chapter 10 problems**

1a. Write the best Lewis formula, including formal charges if any, for the cyanide ion, CN^-.

$[:C\equiv N:]^-$

C is assigned 5 valence electrons for the purpose of calculating formal charge (all of the 2 lone pair electrons and half of the 6 bonding electrons). A neutral individual C atom has 4 valence electrons. Since it has gained an electron, C has a formal charge of -1. N is assigned 5 valence electrons for the purpose of calculating formal charge (all of its 2 lone pair electrons and half of the 6 bonding electrons). A neutral individual N atom has 5 valence electrons. Since the number of electrons is unchanged, N has a formal charge of 0. We can check our assignment of formal charges by adding them up: -1 + 0 = -1 which is the overall charge on the cyanide ion.

b. If a hydrogen ion, H^+, attaches to a cyanide ion, does it attach to the C or to the N? Explain your answer.

It attaches to the C.

1st explanation: C has a -1 formal charge and H has a +1 charge. Unlike charges attract.

2nd explanation: The two possible Lewis electron dot structures are H-C≡N: and :C≡N-H

In neutral molecules we expect 4 bonds for C and 3 bonds for N, and this is what we find in H-C≡N: but not in :C≡N-H

3rd explanation: The two possible Lewis electron dot structures are H-C≡N: and :C≡N-H

In H-C≡N: the formal charges are 0 for H (since it brings in 1 valence electron and is assigned half of the 2 bonding electrons between H and C), 0 for C (since it brings in 4 valence electrons and is assigned half of the 8 bonding electrons around C), and 0 for N (since it brings in 5 valence electrons and is assigned half of the 6 bonding electrons between it and C, and all of its 2 lone pair electrons). All formal charges are zero, and this is desired for Lewis electron dot structures. In :C≡N-H we calculate a formal charge of -1 for C, +1 for N, and 0 for H. Two of the formal charges are nonzero, making this structure less likely. Furthermore, the most electronegative element in the molecule, N, has the positive formal charge, contrary to expectations.

3. Predict the molecular shape and/or the overall polarity (**p**olar or **n**onpolar) for the species in the "Molecular Models" experiment.

CH_4	tetrahedral	nonpolar
$SiCl_4$	tetrahedral	nonpolar
NH_3	trigonal pyramidal	polar
H_2O	bent	polar
HCN	linear	polar
CO_2	linear	nonpolar
F_2	linear	nonpolar
O_2	linear	nonpolar
N_2	linear	nonpolar
HCl	linear	polar
PCl_3	trigonal pyramidal	polar
PCl_5	trigonal bipyramidal	nonpolar
SF_4	seesaw	polar
SF_6	octahedral	nonpolar
BF_3	trigonal planar	nonpolar
ClF_3	T-shaped	polar
IF_5	square pyramidal	polar
XeF_2	linear	nonpolar
XeF_4	square planar	nonpolar

SO_2	bent	polar
O_3	bent	nonpolar
N_2O	linear	polar
C_2H_2	linear	nonpolar
C_2H_4		nonpolar
C_2H_6		nonpolar
$CH_3CH_2CH_3$		nonpolar
CH_3F		polar
CH_2Cl_2		polar
CH_3OH		polar
H_2CO		polar
H_2NNH_2		polar, except anti conformation is nonpolar
CH_3COOH		polar
HNO_3		
NH_4^+	tetrahedral	
ICl_2^-	linear	
IF_4^-	square planar	
CH_3O^-	tetrahedral	
CO_3^{2-}	trigonal planar	
NO_2^-	bent	
NO_3^-	trigonal planar	
SO_4^{2-}	tetrahedral	
OCN^-	linear	
I_3^-	linear	
NO_2^+	linear	

4. Predict the order of increasing electronegativity in each of the following groups of elements:
a. C, N, O b. S, Si, Sr c. F, Cl, Br, I d. S, O, F Z3-8.7,8

C < N < O Sr < Si < S I < Br < Cl < F S < O < F

5. Predict which bond in each of the following groups will be the most polar:
a. C-F, Si-F, Ti-F **Ti-F Ti & F have the greatest electronegativity difference.**
b. C-H, N-H, O-H, F-H **F-H**
c. C-O or Si-O **Si-O**

6. Write resonance structures for the carbonate ion, CO_3^{2-}. Use the correct symbol between resonance structures.