CHAPTER NINE: IONIC AND COVALENT BONDING

Part One: Important Generalities

A. General Principles:

1. Strong attractive forces exist between atoms with incomplete valence shells causing formation of chemical bonds.

    a. Electrons of one atom are attracted to the positive nucleus of the other atom, and vice versa.

2. Electronegativity EN of an element = a numerical measure of the relative tendency of an atom to attract electrons to itself when it forms chemical bonds.

2. The relative strengths of EN give rise to two classes of bonds:

   a. Ionic bonding - electrons are <u>transferred</u> from atoms with low EN (metals) and gained by high EN atoms (nonmetals). Results in formation of cations and anions which are then attracted by <u>electrostatic</u> forces.

   b. Covalent bonding - electrons are <u>shared</u> by atoms of similar EN.

3. These two classes of bonding represent two extremes. Most bonds fall somewhere in between.

4. Outer electrons, or <u>valence electrons</u>, are most important for chemical bonding.

B. Lewis Electron Dot Formulas.

1. Gilbert Newton Lewis (1916) - symbolic method for keeping track of the <u>valence electrons</u> in bonding.

2. Lewis structures for atoms (note the pairing of e⁻):

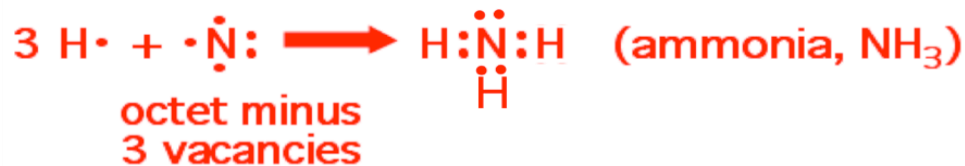| TABLE 9.1	Lewis Electron-Dot Symbols for Atoms of the Second and Third Periods						
Period	IA ns^1	IIA ns^2	IIIA ns^2np^1	IVA ns^2np^2	VA ns^2np^3	VIA ns^2np^4	VIIA ns^2np^5	VIIIA ns^2np^6
Second	Li·	·Be·	·B·	·C·	:N·	:O·	:F·	:Ne:
Third	Na·	·Mg·	·Al·	·Si·	:P·	:S·	:Cl·	:Ar:

3. All elements in same group have same outer e⁻ configuration if one looks only at the valence electrons (as does Lewis).

4. Metals tend to lose these outer e⁻:

$$Na· \longrightarrow Na^{+1} + 1e^-$$

$$Mg: \longrightarrow Mg^{2+} + 2e^-$$

5. Nonmetals tend to gain or share enough e⁻ to have an <u>octet</u> of outer e⁻. (H and He are complete with 2e⁻)

   a. Ionic bonding:

$$Na· + :\ddot{C}\!\ddot{l}: \longrightarrow Na^+, :\ddot{C}\!\ddot{l}:^-$$

octet minus one e⁻   octet

b. Covalent bonding:

$H\cdot\ +\ H\cdot\ \longrightarrow\ H\!:\!H\quad (H_2)$

$2\,H\cdot\ +\ \cdot\ddot{\underset{..}{O}}\!:\ \longrightarrow\ H\!:\!\ddot{\underset{..}{O}}\!:\!H\quad (water)$

$3\,H\cdot\ +\ \cdot\dot{\underset{..}{N}}\!:\ \longrightarrow\ H\!:\!\ddot{N}\!:\!H\quad (ammonia,\ NH_3)$
$\qquad\qquad\qquad\qquad\qquad\quad\overset{\ }{\underset{H}{\ }}$

octet minus
3 vacancies
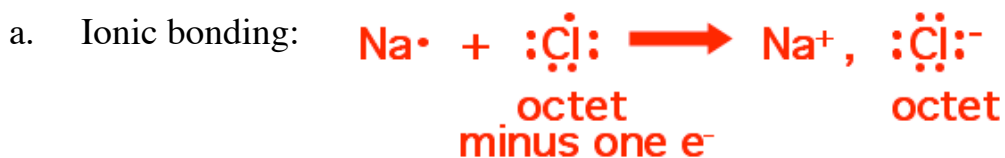
6. Vacancies in nonmetals accounts for their valence, or combining power.

O needs 2, N needs 3, etc.

Part Two: Ionic Bonding

A. Describing Ionic Bonds. (Section 9.1)

1. Ionic bond is a chemical bond formed by the electrostatic attraction between positive cations and negative anions.

2. This cation-anion pair is created by the complete transfer of one or more electrons from the more metallic atom to the lesser one.

3. Example, salts like NaCl.

    How many electrons are transferred to form NaCl?

    Which electron(s) is(are) transferred?

4. Large assemblies of these ions form an ionic solid which is a regular (spatially repeating) crystalline array.

Na^+ ●

Cl^- ●

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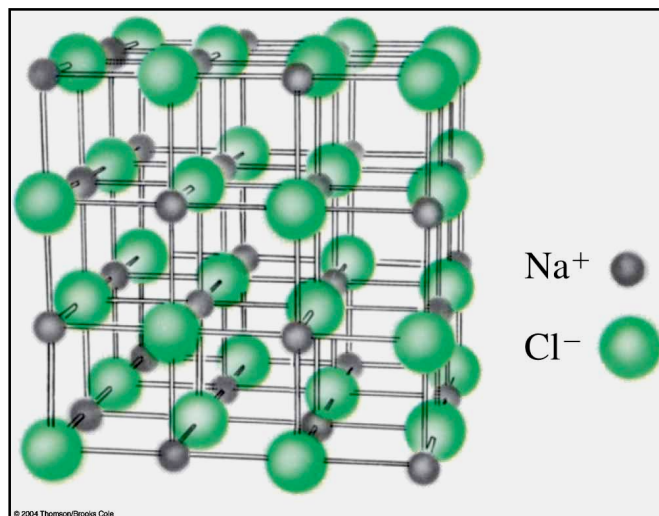
5. The exact packing pattern is dictated by the <u>sizes</u> and <u>charges</u> of the ions, and is one in which the attractive and repulsive forces are balanced to give the maximum net attractiveness.

B. Energetics of Ionic Bonds.

1. Lattice energy = energy holding the ionic lattice together.

    = U = energy required to dismember the lattice and separate the + and - ions into spatially isolated gaseous species.

    e.g. for NaCl, this is 786kJ $NaCl(s) + 786\ kJ \rightarrow Na^+(g) + Cl^-(g)$

2. This in turn is the amount of energy released then when gaseous ions combine by immense attractive forces to form the lattice.

3. This energy can be estimated using Coulomb's Law attractions and repulsions between point charges.

4. This energy is more than enough to form ions of Na^+ and Cl^- from neutral Na and Cl_2.

5. Energy accounting can be seen in the Born-Haber Cycle:
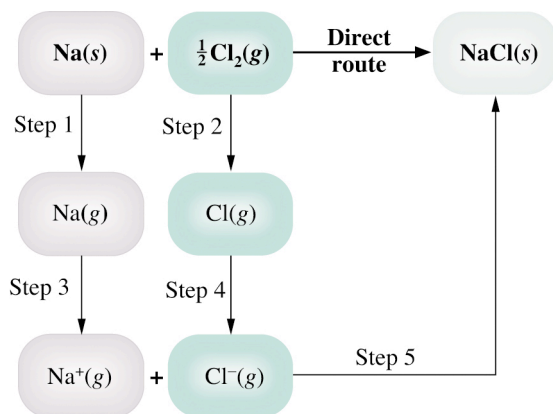
Step 1 = sublimation of Na(s)   +108 kJ/mol
Step 2 = dissociation of $Cl_2(g)$ +120 kJ/mol Cl atoms
Step 3 = ionization of Na(g)   +496 kJ/mol
Step 4 = formation of Cl^- ion   -349 kJ/mol
Step 5 = formation of lattice from ions
          = (-) Lattice Energy = -U
Sum of these steps should = heat of formation of NaCl(s) = -411 kJ/mol
Solve for Lattice Energy

    –411 kJ = +108 + 120 + 496 – 349 – U   U = +786 kJ

C. Electron Configurations of Ions. (Section 9.2)

1. In forming the most stable cation of a metal atom, it is dictated by the IE of successive ionizations:

TABLE 9.2	Ionization Energies of Na, Mg, and Al (in kJ/mol)*			
		Successive Ionization Energies		
Element	First	Second	Third	Fourth
Na	496	4,562	6,912	9,543
Mg	738	1,451	7,733	10,540
Al	578	1,817	2,745	11,577

*Energies for the ionization of valence electrons lie to the left of the colored line.

2. Three categories of ions of the A-Group elements:

a. Cations of Group IA, IIA and IIIA having noble gas configurations by losing 1, 2 and 3 electrons, resp.

    Therefore: ion charge = Group number

b. Cations of Groups IIIA, IVA, and VA having ns^2 configurations by losing 1, 2, and 3 electrons, resp.

    Therefore   ion charge = Group number - 2

c. Anions of Group VA to VIIA having noble gas configurations.

    Ion charge = Group number - 8

3. Transition Metal Ions - typically form several stable cations.

Fe^{2+} and Fe^{3+}
Cu^+ and Cu^{2+}

Cr^{3+} Fe^{2+} Co^{2+} Cu^{2+}

Mn^{2+} Fe^{3+} Ni^{2+} Zn^{2+}
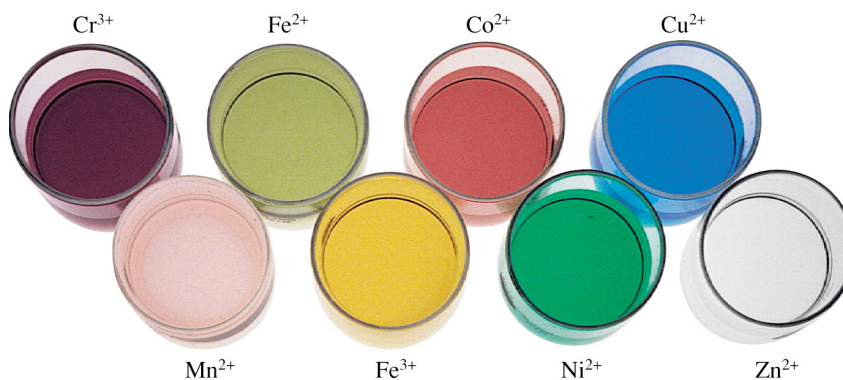
D. Ionic Radii. (Section 9.3)

1. Radius of the most stable ion of the elements.

Examples: Na^{+1} Mg^{2+} (metals)
N^{3-} O^{2-} F^{1-} (non-metals)

A   B
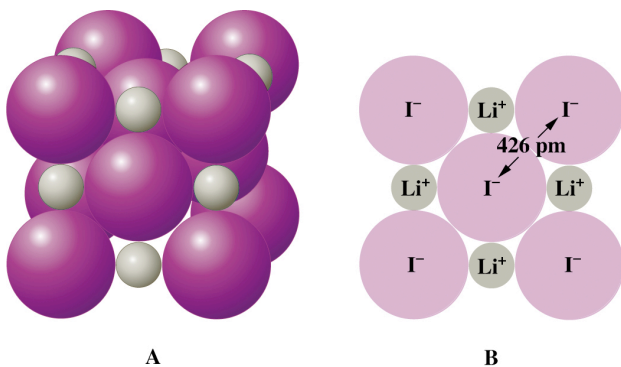
2. Trends:

a. Simple cations are always <u>smaller</u> than their neutral atoms.

Li $r = 1.52$ Å Li^+ $r = 0.90$ Å

Na $r = 1.86$ Å Na^+ $r = 1.16$ Å
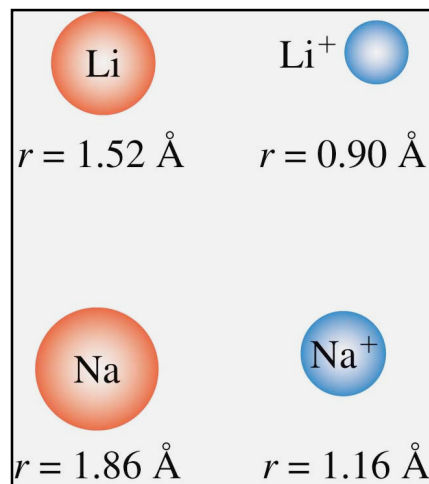
b. Simple anions are <u>larger</u> than their neutral atoms.

F $r = 0.72$ Å F^- $r = 1.19$ Å

Cl $r = 1.00$ Å Cl^- $r = 1.67$ Å
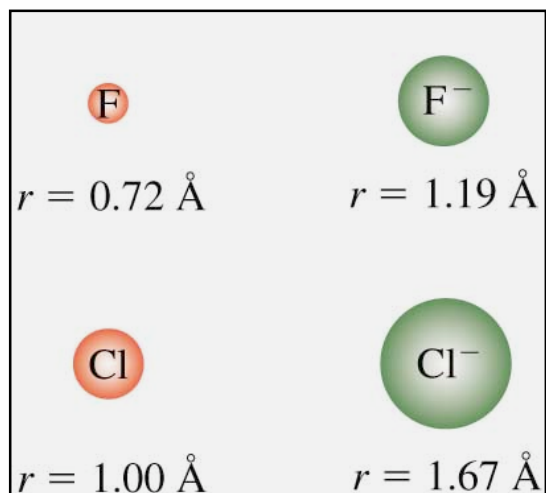
    c.   Within an isoelectronic series of ions, Ionic Radii <u>decrease</u> with increasing atomic number due to increasing nuclear charge.

isoelectronic series = series of ions having same number of e⁻

An isoelectronic series of ions

	N^{3-}	O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}
Ionic radius (Å)	1.71	1.26	1.19	1.16	0.85	0.68
No. of electrons	10	10	10	10	10	10
Nuclear charge	+7	+8	+9	+11	+12	+13

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3.   General trends in ionic radii of A-groups:

Comparison of Atomic and Ionic Radii

1A		2A		3A		5A		6A		7A	
Li 1.52	Li^+ 0.90	Be 1.12	Be^{2+} 0.59			N 0.75	N^{3-} 1.71	O 0.73	O^{2-} 1.26	F 0.72	F^- 1.19
Na 1.86	Na^+ 1.16	Mg 1.60	Mg^{2+} 0.85	Al 1.43	Al^{3+} 0.68			S 1.03	S^{2-} 1.70	Cl 1.00	Cl^- 1.67
K 2.27	K^+ 1.52	Ca 1.97	Ca^{2+} 1.14	Ga 1.35	Ga^{3+} 0.76			Se 1.19	Se^{2-} 1.84	Br 1.14	Br^- 1.82
Rb 2.48	Rb^+ 1.66	Sr 2.15	Sr^{2+} 1.32	In 1.67	In^{3+} 0.94			Te 1.42	Te^{2-} 2.07	I 1.33	I^- 2.06
Cs 2.65	Cs^+ 1.81	Ba 2.22	Ba^{2+} 1.49	Tl 1.70	Tl^{3+} 1.03						

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E.   Lewis Structures of Ionic compounds

1.   Work some examples, showing species represented by their Lewis structures.

a. NaCl(s):

$$Na\cdot \ + \ :\!\overset{\cdot}{\underset{\cdot\cdot}{Cl}}\!: \ \longrightarrow \ Na^+, \ :\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}\!:^-$$

octet
minus one e⁻   octet

b. $Li_2O(s)$:

$$2\ Li\cdot \quad \cdot\overset{\cdot}{\underset{\cdot\cdot}{O}}\!: \qquad\qquad 2\ Li^+ \quad :\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\!:^{2-}$$

c. CaO(s):

$$Ca\!: \qquad \cdot\overset{\cdot}{\underset{\cdot\cdot}{O}}\!: \qquad\qquad Ca^{2+} \quad :\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}\!:^{2-}$$

d. $Mg_3N_2(s)$:

$$3\ Mg\!: \quad 2\cdot\overset{\cdot}{\underset{\cdot}{N}}\!: \qquad 3\ Mg^{2+} \quad 2\ :\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}\!:^{3-}$$
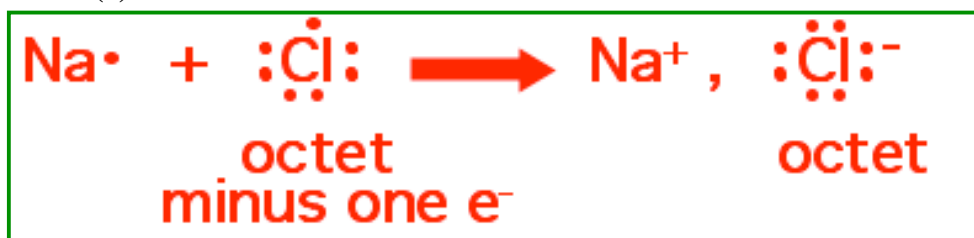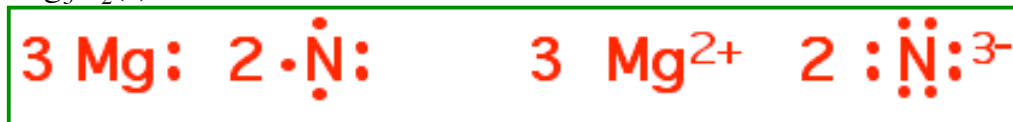
Part Three: Covalent Bonding

A. Describing Covalent Bonding. (Section 9.4)

1. Covalent bonding = atoms share one or more pairs of electrons.

2. Occurs when small EN difference between atoms.

3. Examples:

a. $H_2(g)$

H(g)   H(g)   H₂(g)

H•   H•

H:H

a single
covalent bond
H-H

H:H

each isoelectronic
with He:

Potential energy

0

Bond dissociation energy

H + H

H₂

Bond length

0   74 pm

Distance between nuclei

b.   HF(g) or HCl or HBr, etc.

H•   •F̈:

H:F̈:

a single
covalent bond
H-F

H:F̈:

iso
with He:

iso
with :N̈e:
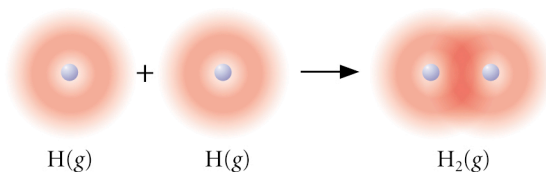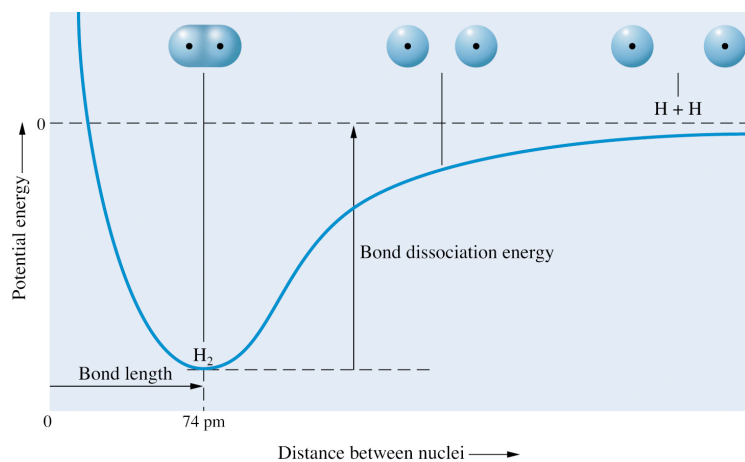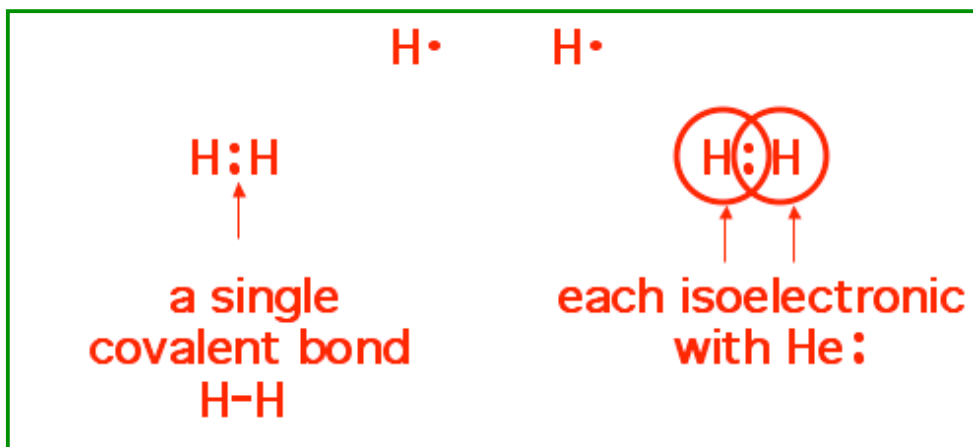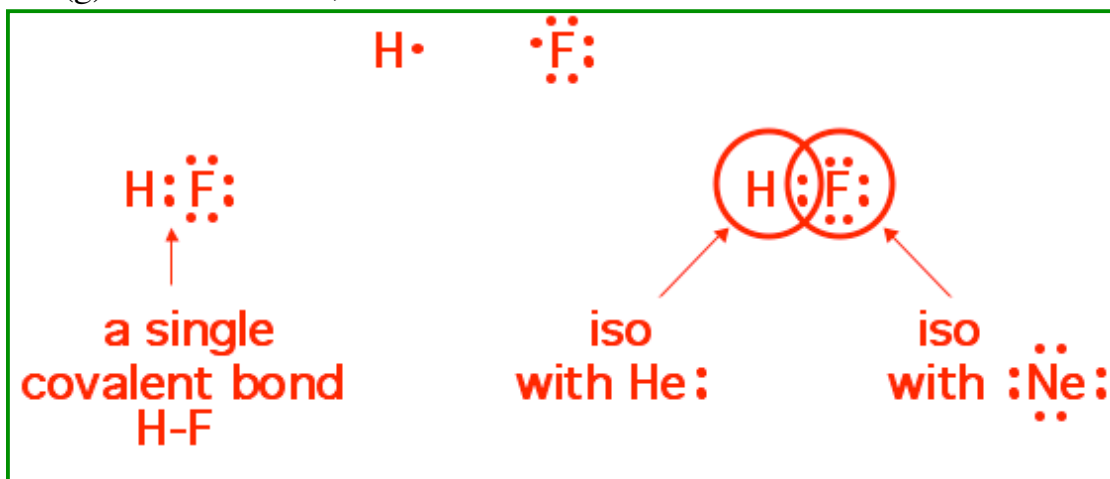
4.   Coordinate covalent bonds = bond formed when both electrons come from one atom.

A + :B → A:B

Example, forming the ammonium ion.

B. Procedure for Constructing Lewis Formulas. (Section 9.6)

1. In most of their compounds, representative elements achieve noble gas configurations. (octet rule)

2. Electrons are either:

   a. bonding pairs (shared pairs)

   b. lone pairs (unshared pairs)

3. Start by counting the total number of available valence electrons A.

4. Write the skeleton structure of the molecule with two electrons to each bond between atoms. (Symmetrical, least EN atom at center, H never center, no O-O bonds unless it's a peroxide)

5. Distribute remaining valence electrons, first to ensure the outer atoms satisfy the octet rule, then to the central atom last.

   a. CO_2 example:

   A = 4 (from C) + 6 (from O) + 6 (from O) = 16
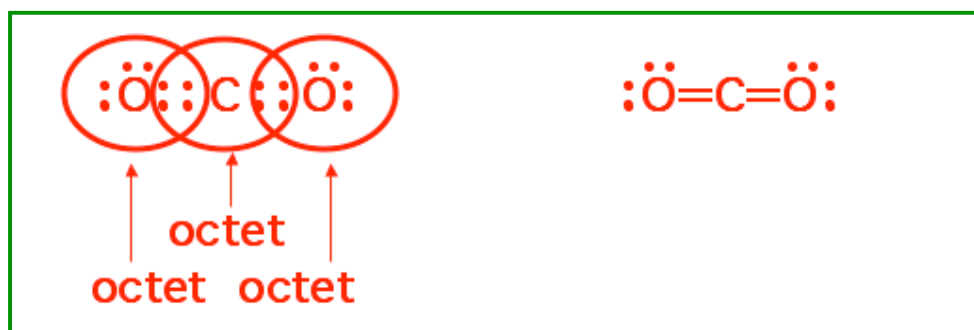
   b. SO_4^{2-} example:

   c. HNO_2 example:

d. CO example:

e. Methane, CH_4 example:

f. Ethylene, C_2H_4 example:

g. Chloromethane, CH_3Cl example:

C. Resonance Structures. (Section 9.7)

1. <u>Resonance</u> happens when 2 or more Lewis structures are equally acceptable for the <u>same skeleton</u> of atoms.

2. Example: Carbonate ion CO_3^{2-}

A = 24

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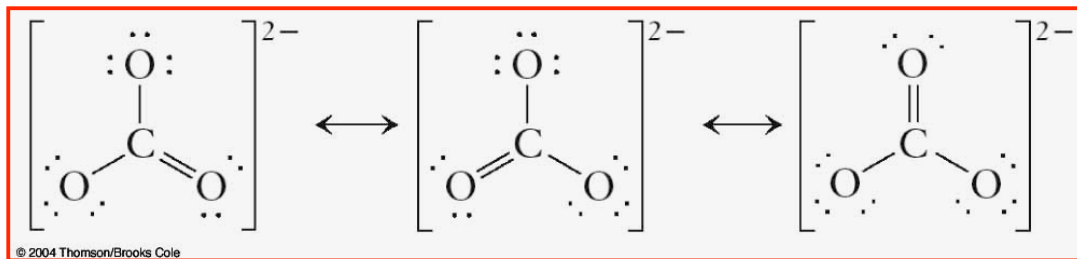
3. This means there is a <u>delocalization</u> of shared electrons, leads to greater stability.

4. Try SO_2

    A = 18

D. Violations of Octet Rule. (Section 9.8)

    1. A number of species violate the octet rule due to deficiency of electrons.

    2. These, however, are quite reactive.

    3. Be and B violate frequently.

    4. Example: BH_3

        H:B:H
         ..
          H

        will react with hydride ion H:⁻ to form stable BH_4^-
                                            (borohydride ion)

        ```
            H
            ..
       [ H:B:H ]⁻
            ..
            H
        ```

    5. Can also have <u>electron-rich</u> violations involving central atoms from Row 3.

        Examples - Phosphorus and sulfur compounds: PF_5 and SF_6 are stable.

        PF_5

        SF_6

6.   Empty 3d orbitals on the central atom are low enough in energy to get involved, so can have more than 4 atoms bonded to central P and S atom.

E.   Formal Charges. (Section 9.9)

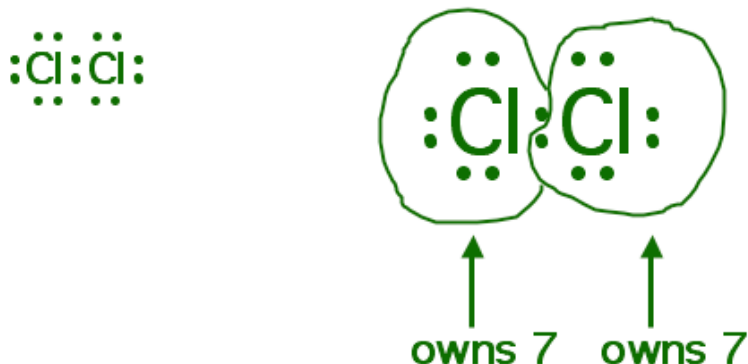   1.   The formal charge gives an indication of the extent to which atoms have gained or lost electrons in the process of covalent bond formation.

   2.   Structures with the <u>lowest</u> set of formal charges are likely to be the most stable. (lowest energy)

   3.   Calculating formal charge: divide up the electrons and figure how many electrons each atom "owns."

   4.   Examples:

      a. Cl_2

            Formal charge of any atom: FC = V – O
            (where V are the valence electrons and O are the owned electrons)

            For each Cl: FC = 7 – 7 = 0
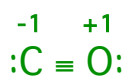
            Both Cl have formal charge of zero, since they are perfectly shared.

      b.   CO (carbon monoxide)
            :C:::O:
            for Carbon: FC = 4 – 5 = -1
            for Oxygen: FC = 6 – 5 = +1

            -1   +1
            :C ≡ O:

c. Why is this useful? Try Lewis structure of N_2O.

Is it   N   N   O

Or: N   O   N

Which is most plausible? Use FC to judge.

d. Cyanate ion. It has net −1 charge and one Carbon, one Nitrogen, and one Oxygen.

Is it: (N   C   O)$^{-1}$

Or: (C   N   O)$^{-1}$

Or: (C   O   N)$^{-1}$

F. Polar Covalent Bonds. (Section 9.5)

1. When shared electrons of a bond are shared between atoms of different electronegativity, electron density will be shifted toward the <u>higher</u> EN. Electrons are shared unequally. Creates <u>polar</u> <u>covalent</u> <u>bond</u>.

EN = 2.1 4.0

H:F:

↑

polar covalent bond

H   F

low e$^-$ high e$^-$
density   density
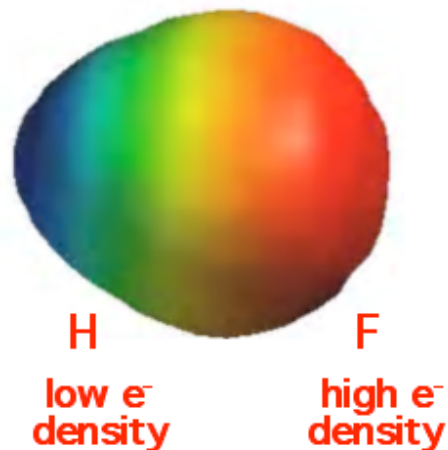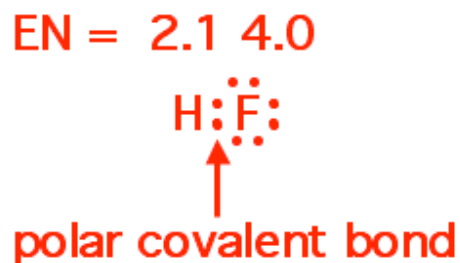
2. Creates a partial positive (δ+) and partial negative (δ-) charge.

δ+   δ-
H - F
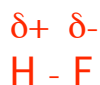
3. In molecules (such as diatomics) where polar covalent bonds cause asymmetry in charge distribution, the molecule is said to have a <u>dipole moment</u>.

4. Molecules with dipole moments are those which orient themselves in an electric field.

Field off		Field on

δ^+ ⬤ δ^- = Electrostatic Charge Potential Surface of HF δ^+ ▮▮▮ 0 ▮▮▮ δ^-
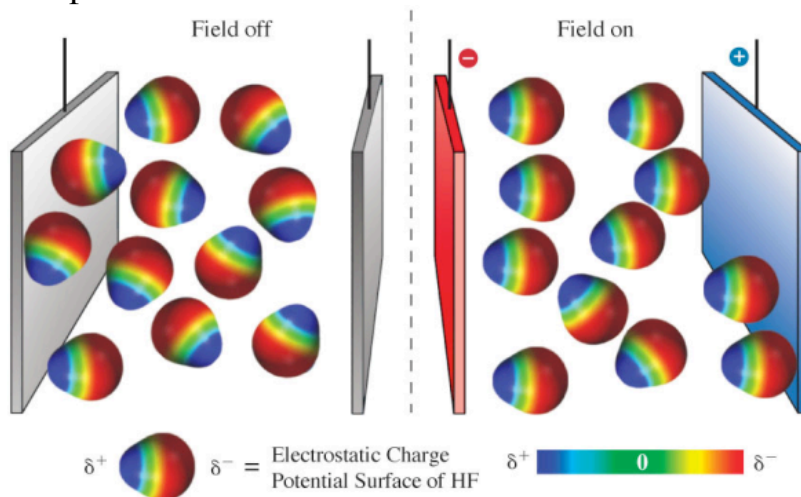
5. Now we see a whole spectrum of bonding types.

Electronegativity difference

large   small

ionic bond	polar covalent	nonpolar covalent
NaCl	HCl	H_2 or Cl_2

6. What about H_2O?

EN=3.5

O

EN=2.1   104°   EN=2.1

H   H

$\delta-$ $\delta-$

O | dipole moment

H   H

$\delta+$ $\delta+$ $\delta+$
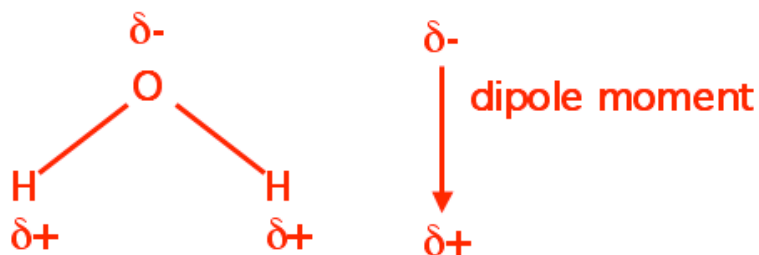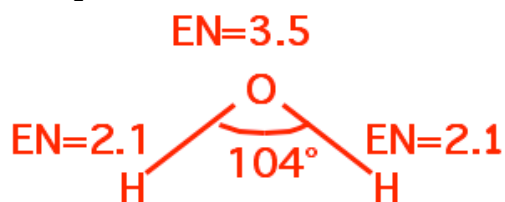
-has two polar covalent bonds, is a polar molecule.

7.   What about CO_2?

EN=3.5   EN=2.1   EN=3.5

$$O \underset{\smile}{\overset{}{\text{———}}} C \text{———} O$$

180°
(linear)

δ-   δ+   δ-
$$O \longleftarrow C \longrightarrow O$$

polar <u>bonds</u>
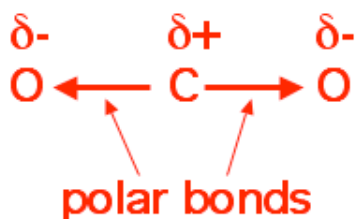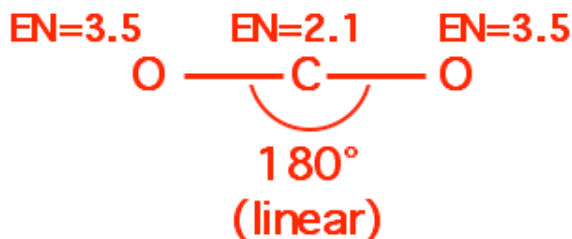
-has two polar covalent bonds, BUT is <u>not</u> a polar molecule.

G.   Bond Length and Bond Energies. (Section 9.10-11)

1.   Bond Length = distance between the nuclei at which attractive and repulsive forces balance and the bond is most stable.

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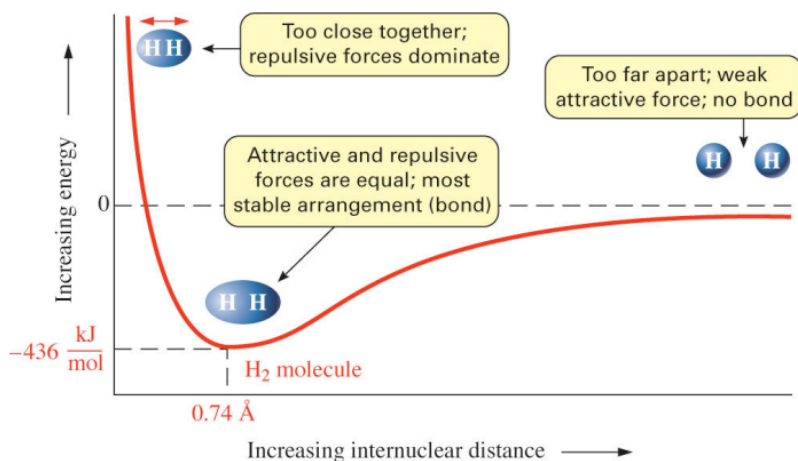
2.   Potential energy is lowered as the two atoms come from a great distance to this stable distance.

3.   That energy is released into the surroundings = bond energy, or bond dissociation energy.

     For example: H - H bond energy is 436 kJ/mol

4. Bond energy also can be defined as the energy required to break the bond.

5. Bond length and bond energy are related as follows:

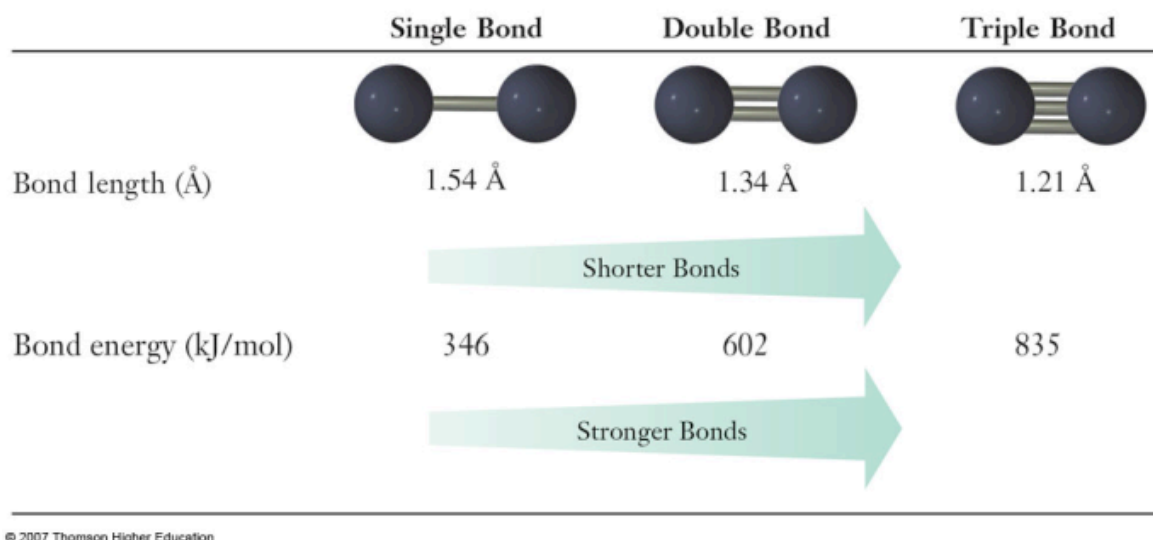|	Single Bond	Double Bond	Triple Bond
Bond length (Å)	1.54 Å	1.34 Å	1.21 Å
		Shorter Bonds →	
Bond energy (kJ/mol)	346	602	835
		Stronger Bonds →	

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6. Covalent radii = values assigned to atoms in a way that the sum of covalent radii of atoms A and B predicts an approximate A-B bond length.

TABLE 9.4

Single-Bond Covalent Radii for Nonmetallic Elements (in pm)

				H
				37
B	C	N	O	F
88	77	70	66	64
	Si	P	S	Cl
	117	110	104	99
		As	Se	Br
		121	117	114
			Te	I
			137	133

7. Bond order = number of pairs of electrons in a bond.

8. Bond energy = enthalpy required to break a chemical bond.

TABLE 9.5		**Bond Energies (in kJ/mol)***							
				Single Bonds					
	H	C	N	O	S	F	Cl	Br	I
H	432								
C	411	346							
N	386	305	167						
O	459	358	201	142					
S	363	272	—	—	226				
F	565	485	283	190	284	155			
Cl	428	327	313	218	255	249	240		
Br	362	285	—	201	217	249	216	190	
I	295	213	—	201	—	278	208	175	149

Multiple Bonds

$C=C$	602	$C=N$	615	$C=O$	745 (799 in CO_2)
$C\equiv C$	835	$C\equiv N$	887	$C\equiv O$	1072
$N=N$	418	$N=O$	607	$S=O$ (in SO_2)	532
$N\equiv N$	942	$O=O$	494	$S=O$ (in SO_3)	469

*Data are taken from J. E. Huheey, Keiter, and Keiter, *Inorganic Chemistry,* 4th ed. (New York: HarperCollins, 1993), pp. A21–A34.