# Chapter 8: Concepts of Chemical Bonding

Learning Outcomes:

➢Write Lewis symbols for atoms and ions.

➢Define lattice energy and be able to arrange compounds in order of increasing lattice energy based on the charges and sizes of the ions involved.

➢Use atomic electron configurations and the octet rule to draw Lewis structures for molecules.

➢Use electronegativity differences to identify nonpolar covalent, polar covalent, and ionic bonds.

➢Calculate charge separation in diatomic molecules based on the experimentally measured dipole moment and bond length.

➢Calculate formal charges from Lewis structures and use those formal charges to identify the dominant Lewis structure for a molecule or ion.

➢Recognize molecules where resonance structures are needed to describe the bonding and draw the dominant resonance structures.

➢Recognize exceptions to the octet rule and draw accurate Lewis structures even when the octet rule is not obeyed.

➢Predict the relationship between bond type (single, double, and triple), bond strength (or enthalpy), and bond length.

➢Use bond enthalpies to estimate enthalpy changes for reactions involving gas-phase reactants and products.

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Chemical Bonds

Metallic
Electrons delocalized

Ionic
Electrostatic attraction
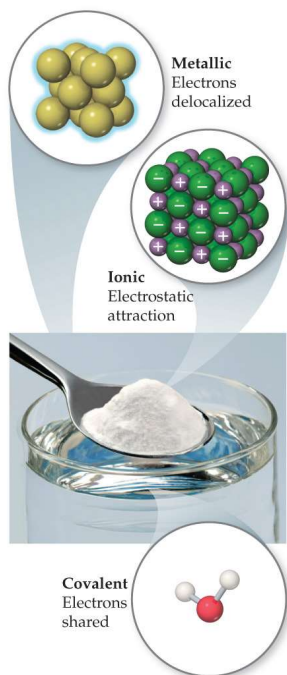
Covalent
Electrons shared

Three basic types of bonds:

– Ionic
  - Electrostatic attraction between ions
– Covalent
  - Sharing of electrons
– Metallic
  - Metal atoms bonded by free electrons

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Lewis symbol for an element consists of the element's chemical symbol plus a dot for each valence electron.

Group	1A	2A		3A	4A	5A	6A	7A	8A
Element	Li	Be		B	C	N	O	F	Ne
Electron Configuration	$[He]2s^1$	$[He]2s^2$		$[He]2s^22p^1$	$[He]2s^22p^2$	$[He]2s^22p^3$	$[He]2s^22p^4$	$[He]2s^22p^5$	$[He]2s^22p^6$
Lewis Symbol	Li·	·Be·		·Ḃ·	·Ċ·	·N̈·	:Ö:	:F̈·	:N̈e:
	Na	Mg		Al	Si	P	S	Cl	Ar
	$[Ne]3s^1$	$[Ne]3s^2$		$[Ne]3s^23p^1$	$[Ne]3s^23p^2$	$[Ne]3s^23p^3$	$[Ne]3s^23p^4$	$[Ne]3s^23p^5$	$[Ne]3s^23p^6$
	Na·	·Mg·		·Äl·	·Si·	·P̈·	·S̈·	·C̈l:	:Är:

When forming compounds, atoms tend to gain, lose, or share electrons until they are surrounded by eight valence electrons (the **octet rule**).

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Energetics of Ionic Bonding

$$\text{Na·} + \text{·C̈l:} \longrightarrow \text{Na}^+ + [\text{:C̈l:}]^-$$

TABLE 7.2 Successive

As we saw in the last chapter, it takes 495 kJ/mol to remove electrons from sodium.

Element	I_1
Na	495
Mg	738

We get 349 kJ/mol back by giving electrons to chlorine.

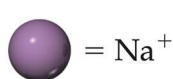| O	F	Ne
−141	−328	> 0
S	**Cl**	Ar
−200	**−349**	> 0
Se	Br	Kr
−195	−325	> 0
	I	

4

Energetics of Ionic Bonding

But these numbers don't explain why the reaction of sodium metal and chlorine gas to form sodium chloride is so exothermic.
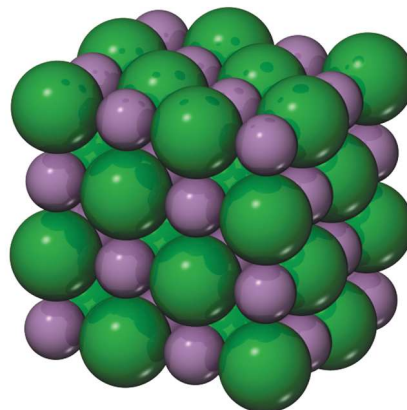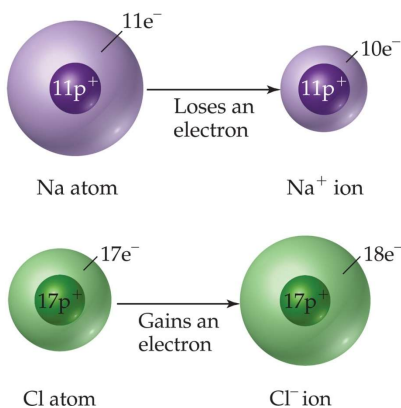
$$Na(s) + \tfrac{1}{2}\,Cl_2(g) \rightarrow NaCl(s) \qquad \Delta H°_f = -410.9 \text{ kJ/mol}$$

Na(s)

Cl₂(g)

Electrons transfer from Na(s) to Cl₂(g), forming Na⁺ and Cl⁻

Highly exothermic reaction forming sodium chloride, an ionic compound composed of sodium ions, Na⁺, and chloride ions, Cl⁻

NaCl(s) forms
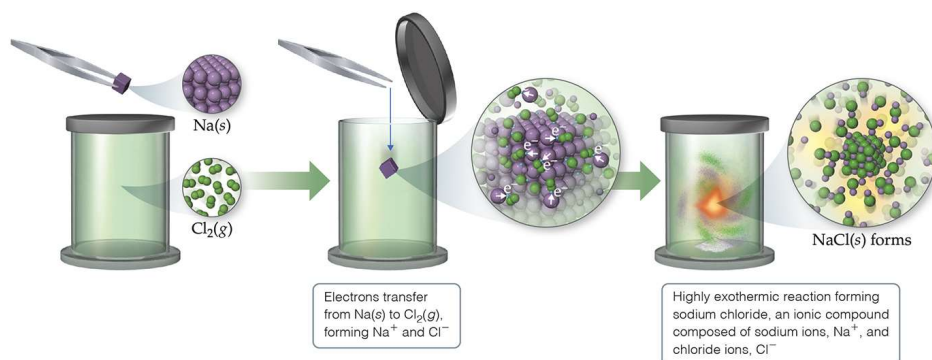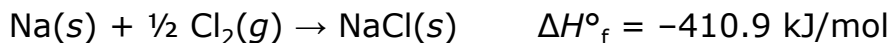
5

What is as yet unaccounted for is the electrostatic attraction between the newly formed sodium cation and chloride anion.

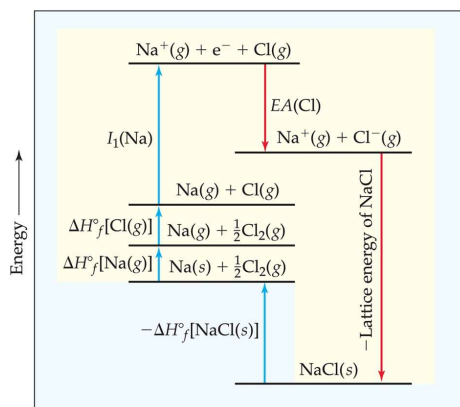$\bigcirc$ = Na⁺ $\bigcirc$ = Cl⁻

Each Na⁺ ion surrounded by six Cl⁻ ions

Each Cl⁻ ion surrounded by six Na⁺ ions

$11e^-$

$11p^+$ — Loses an electron → $11p^+$ $10e^-$

Na atom   Na⁺ ion

$17e^-$

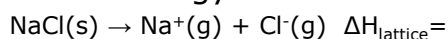$17p^+$ — Gains an electron → $17p^+$ $18e^-$

Cl atom   Cl⁻ ion

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Born–Haber Cycle

By accounting for enthalpy of formation, sublimation, bond dissociation, ionization energy, electron affinity, we can determine lattice energy.

$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$ $\Delta H_{lattice}=$

- Application of Hess's Law

It takes energy to convert the elements to atoms (endothermic).
It takes energy to create a cation (endothermic).
Energy is released by making the anion (exothermic).
The formation of the solid from gaseous ions releases a large amount of energy (exothermic), the reverse process requires a large amount of energy (endothermic).
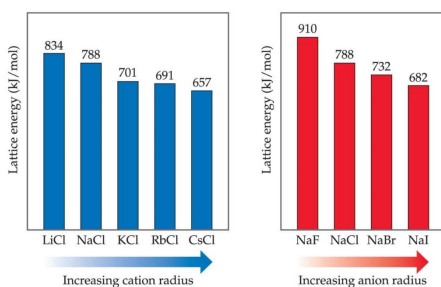
7

Lattice Energy

The energy required to completely separate a mole of a solid ionic compound into gaseous ions.

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g) \qquad \Delta H_{lattice} = +788 \, kJ/mol$$
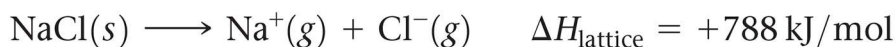
- That amount of energy is RELEASED to MAKE the ionic compound (in the Born–Haber cycle).
- The energy associated with electrostatic interactions is governed by the equation:

$$E_{el} = \frac{\kappa Q_1 Q_2}{d}$$

where $\kappa = 8.99 \times 10^9$ J-m/C^2

Lattice energy increases with the charge on the ions and decreasing size of ions.

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Lattice Energy
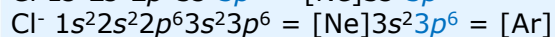
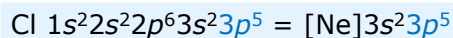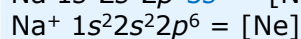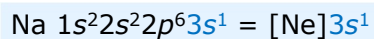**TABLE 8.1   Lattice Energies for Some Ionic Compounds**

Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	$MgCl_2$	2526
LiCl	834	$SrCl_2$	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

Electron Configurations of Ions

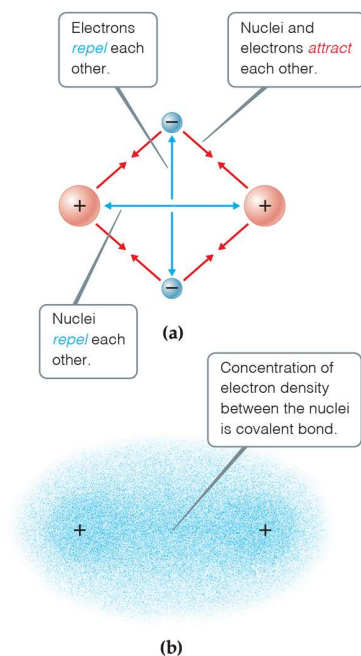Main group metals tend to stop losing electrons once they attain a noble gas configuration.
- Energy to remove electrons from an inner shell is not compensated by lattice energy.
- Nonmetals gain electrons to form the electron configuration of the nearest noble gas.

$$Na\ 1s^22s^22p^63s^1 = [Ne]3s^1$$
$$Na^+\ 1s^22s^22p^6 = [Ne]$$

$$Cl\ 1s^22s^22p^63s^23p^5 = [Ne]3s^23p^5$$
$$Cl^-\ 1s^22s^22p^63s^23p^6 = [Ne]3s^23p^6 = [Ar]$$

Transition metals don't follow the octet rule. Transition metals lose ns valence electrons with highest n first, then lose $(n-1)d$ electrons to attain the given charge.
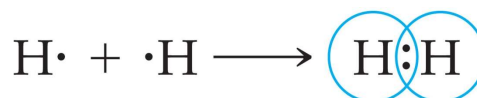
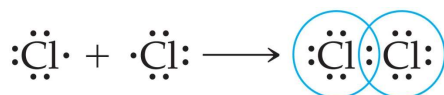Write the electron configurations for Zn^{2+}, Mn^{2+}, and Mn^{3+}.

Covalent Bonding

Electrons *repel* each other.

Nuclei and electrons *attract* each other.

Nuclei *repel* each other.

(a)

Concentration of electron density between the nuclei is covalent bond.

(b)

- Bond between nonmetals
- In these bonds atoms share electrons.

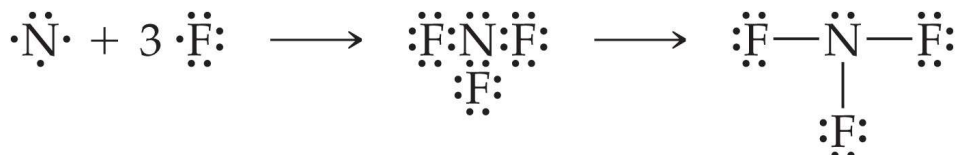$$H\cdot \; + \; \cdot H \longrightarrow H\!:\!H$$

- There are several electrostatic interactions in these bonds:
  - Attractions between electrons and nuclei
  - Repulsions between electrons
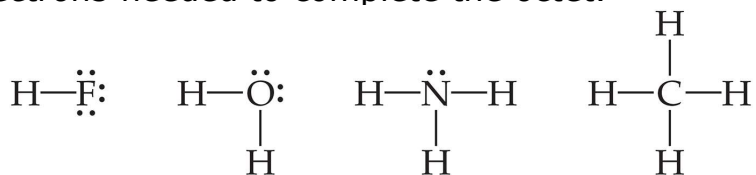 - Repulsions between nuclei

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Lewis Structures

$$:\!\overset{..}{\underset{..}{Cl}}\!\cdot \; + \; \cdot\overset{..}{\underset{..}{Cl}}\!: \longrightarrow \;\; :\!\overset{..}{\underset{..}{Cl}}\!:\!\overset{..}{\underset{..}{Cl}}\!:$$

Lewis structures are representations of molecules showing all electrons, bonding and nonbonding.

$$\cdot\overset{..}{N}\cdot \; + \; 3\,\cdot\overset{..}{\underset{..}{F}}\!: \longrightarrow \;\; :\!\overset{..}{\underset{..}{F}}\!:\!\overset{..}{N}\!:\!\overset{..}{\underset{..}{F}}\!: \;\; \longrightarrow \;\; :\!\overset{..}{\underset{..}{F}}\!-\!\overset{..}{N}\!-\!\overset{..}{\underset{..}{F}}\!:$$

$$:\!\overset{..}{\underset{..}{O}}\!: \; + \; \cdot\overset{.}{\underset{.}{C}}\cdot \; + \; :\!\overset{..}{\underset{..}{O}}\!: \longrightarrow \overset{..}{\underset{..}{O}}\!:\!:\!C\!:\!:\!\overset{..}{\underset{..}{O}} \quad (\text{or } \overset{..}{\underset{..}{O}}\!=\!C\!=\!\overset{..}{\underset{..}{O}})$$

$$:\!\overset{.}{\underset{.}{N}}\cdot \; + \; \cdot\overset{.}{\underset{.}{N}}\!: \longrightarrow \;\; :\!N\!:\!:\!:\!N\!: \quad (\text{or } :\!N\!\equiv\!N\!:)$$

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Lewis Structures

- The group number is the number of valence electrons.
- To get an octet, like the nearest noble gas, in the simplest covalent molecules for nonmetals, the number of *bonds* needed will be the same as the *electrons* needed to complete the octet.

$$H\!-\!\ddot{\underset{..}{F}}\colon \qquad H\!-\!\underset{\underset{H}{|}}{\overset{..}{O}}\colon \qquad H\!-\!\underset{\underset{H}{|}}{\overset{..}{N}}\!-\!H \qquad H\!-\!\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}\!-\!H$$

- **Lone pairs**: electrons located on *only one* atom in a Lewis structure
- **Bonding pairs**: shared electrons in a Lewis structure and can be represented by two dots *or* one line.

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Multiple Bonds

- **Single bonds** share only one pair of electrons.
- **Double bonds** share two pairs of electrons.
- Three bonds are shared between two atoms. in **triple bonds**.

$$:\!\overset{.}{\underset{.}{O}}\!: \; + \; \cdot\overset{.}{\underset{.}{C}}\cdot \; + \; :\!\overset{.}{\underset{.}{O}}\!: \; \longrightarrow \; \overset{.}{\underset{.}{O}}\!::\!C\!::\!\overset{.}{\underset{.}{O}} \qquad (\text{or } \overset{..}{\underset{..}{O}}\!=\!C\!=\!\overset{..}{\underset{..}{O}})$$

$$:\!\overset{.}{\underset{.}{N}}\!\cdot \; + \; \cdot\overset{.}{\underset{.}{N}}\!: \; \longrightarrow \; :\!N\!:::\!N\!: \qquad (\text{or } :\!N\!\equiv\!N\!:)$$
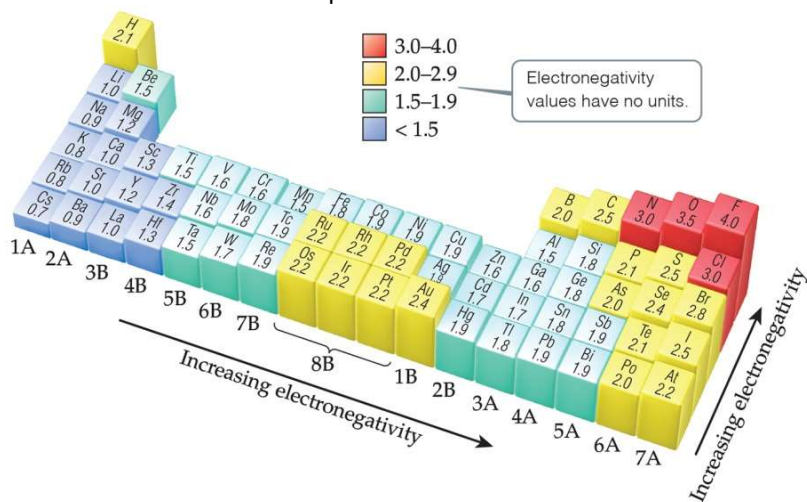
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Polarity of Bonds

- Electrons in a covalent bond are not always shared equally between two atoms.
- **Bond polarity** is a measure of how equally or unequally the electrons in a covalent bond are shared.
- In a **nonpolar covalent bond**, the electrons are shared equally.
- In a **polar covalent bond**, one of the atoms attracts electrons to itself with a greater force.
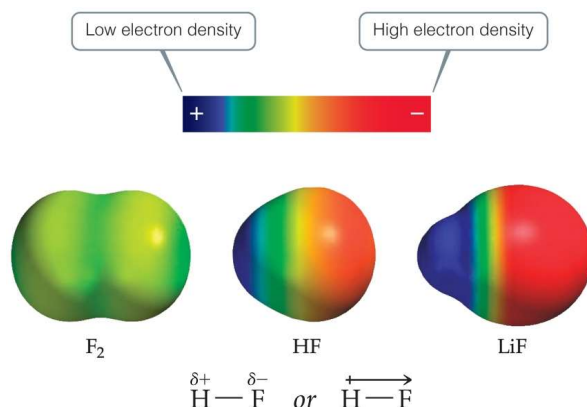
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Electronegativity

- The ability of atoms in a molecule to attract electrons to itself.
- On the periodic table, electronegativity increases as you go…
  - …from left to right across a row.
  - …from the bottom to the top of a column.

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Polar or Nonpolar Covalent Bonds

Low electron density   High electron density

F₂   HF   LiF

$$\overset{\delta+}{H}-\overset{\delta-}{F} \quad or \quad \overset{\longleftarrow}{H-F}$$

- Although atoms often form compounds by sharing electrons, the electrons are not always shared equally.
- Fluorine has a greater attraction on the electrons it shares with hydrogen than hydrogen does, therefore, the fluorine end of the molecule has more electron density than the hydrogen end in the HF molecule.

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Is a bond covalent, polar covalent, or ionic?

- Simplest approach: metal + nonmetal is ionic; nonmetal + nonmetal is covalent.
- However, this simple approach doesn't take into account oxidation number of a metal (higher oxidation numbers can give covalent bonding).
- There is a continuum between the extremes of ionic and covalent bonding.
- Electronegativity difference (ΔEN) can be used.
  - Nonpolar covalent bond, $\Delta EN = 0$
  - Polar covalent bond, $0 < \Delta EN < 2$
  - Ionic bond, $\Delta EN \geq 2$

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Example

Rank the following bonds formed between atoms in order of increasing polarity:

F and H, F and Ca, N and Se, and O and Si.

Which, if any, of the bonds are ionic?

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Dipole

$$Q-\quad\quad\quad\quad\quad\quad Q+$$

$$\overleftarrow{\quad\quad r \quad\quad}\rightarrow$$
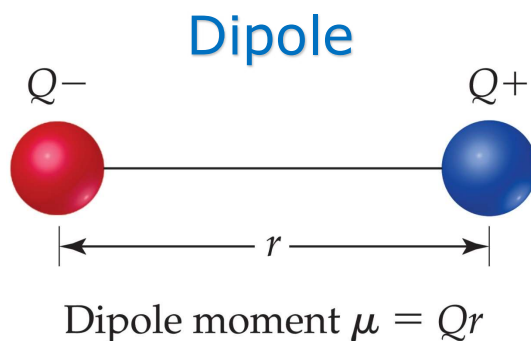
Dipole moment $\mu = Qr$

- When two atoms share electrons unequally, a bond dipole results.
- The dipole moment, μ, produced by two equal but opposite charges separated by a distance, r, is calculated: $\mu = Qr$
- The dipole moment is measured in debyes (D).
  - 1 Debye = 3.34×10^{-30} C·m

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Polar Covalent Bonds

TABLE 8.2 Bond Lengths, Electronegativity Differences, and Dipole Moments of the Hydrogen Halides

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

| + | − |

| HF | HCl | HBr | HI |
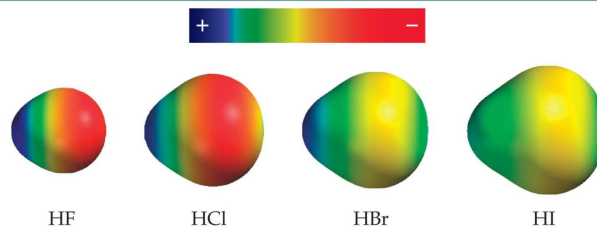
The greater the difference in electronegativity, the more polar is the bond.

Example: Calculate the partial charges on the H and F atoms in HF.

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Drawing Lewis Structures
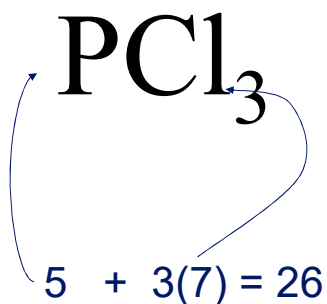
$$PCl_3$$

$$5 \ + \ 3(7) = 26$$

1. Find the sum of *valence* electrons of all atoms in the polyatomic ion or molecule.
   - If it is an anion, add one electron for each negative charge.
   - If it is a cation, subtract one electron for each positive charge.

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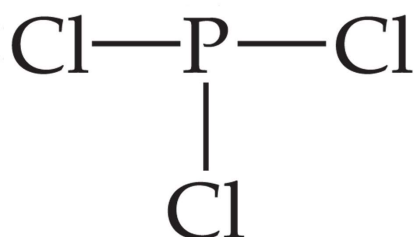
Cl—P—Cl

|

Cl

2. The central atom is the *least* electronegative element that isn't hydrogen. Connect the outer atoms to it by single bonds (lines).
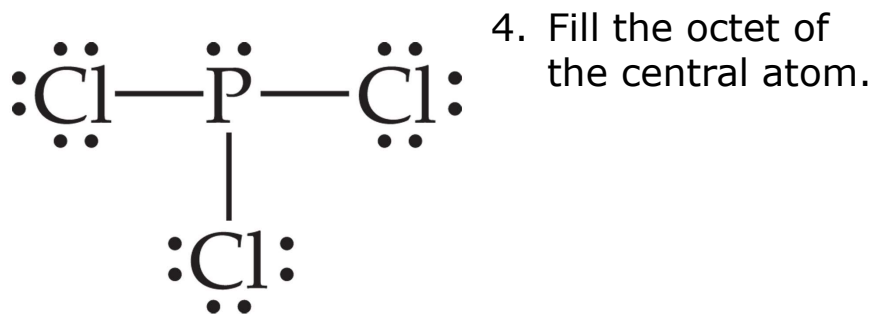
Keep track of the electrons:

26 − 6 = 20

:Cl̈—P—C̈l:

|

:C̈l:
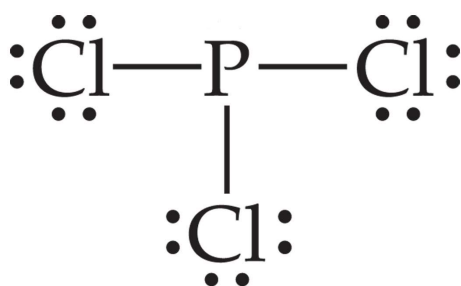
3. Complete the octets of the outer atoms.

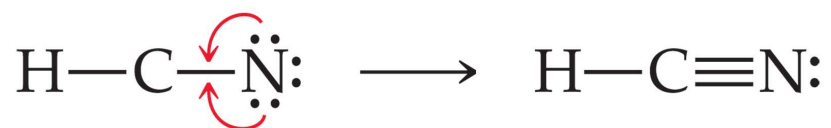Keep track of the electrons:

26 − 6 = 20 − 18 = 2

4. Fill the octet of the central atom.

Keep track of the electrons:

$$26 - 6 = 20 - 18 = 2 - 2 = 0$$

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5. If you run out of electrons before the central atom has an octet...

...form multiple bonds until it does.

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13
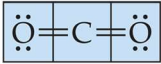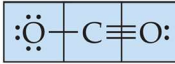
Writing Lewis Structures

Assign formal charges.

   – For each atom, count the electrons in lone pairs and half the electrons it shares with other atoms.

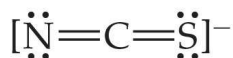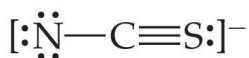   – Subtract that from the number of valence electrons for that atom: The difference is its formal charge.

Formal charge = (valence e⁻) – ½ (bonding e⁻) – (*all* nonbonding e⁻)

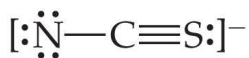|	$\ddot{O}=C=\ddot{O}$			$:\ddot{O}-C\equiv O:$		
Valence electrons:	6	4	6	6	4	6
−(Electrons assigned to atom):	6	4	6	7	4	5
Formal charge:	0	0	0	−1	0	+1

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The best Lewis structure…

   – …is the one with the fewest charges.

   – …puts a negative charge on the most electronegative atom.

$[:\ddot{N}-C\equiv S:]^-$ $[\ddot{N}=C=\ddot{S}]^-$ $[:N\equiv C-\ddot{S}:]^-$

   −2   0   +1   −1   0   0   0   0   −1

$[:\ddot{N}-C\equiv S:]^-$ $[\ddot{N}=C=\ddot{S}]^-$ $[:N\equiv C-\ddot{S}:]^-$

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14

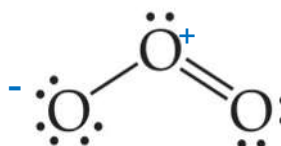# Writing Lewis Structures

1. Find the sum of valence electrons of all atoms in the polyatomic ion or molecule.
   - If it is an anion, add one electron for each negative charge.
   - If it is a cation, subtract one electron for each positive charge.

2. The central atom is the *least* electronegative element that isn't hydrogen. Connect the outer atoms to it by single bonds.
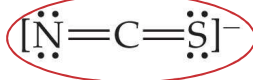
3. Fill the octets of the outer atoms.

4. Fill the octet of the central atom.

5. If you run out of electrons before the central atom has an octet - form multiple bonds until it does.

- Then assign formal charges.
  - For each atom, count the electrons in lone pairs and half the electrons it shares with other atoms.
  - Subtract that from the number of valence electrons for that atom: The difference is its formal charge.
- The best Lewis structure…
  - …is the one with the fewest charges.
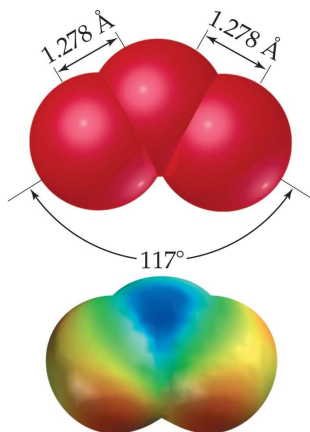 - …puts a negative charge on the most electronegative atom.

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Resonance

This is the Lewis structure we would draw for ozone, O_3.

But this is at odds with the true, observed structure of ozone, O_3, in which…
  - …both O—O bonds are the same length.
 - …both outer oxygen atoms have a charge of $-1/2$.

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Resonance

- Resonance structures are Lewis structures that differ only with respect to placement of the electrons.
- One Lewis structure cannot accurately depict a molecule such as ozone. We use multiple structures, resonance structures, to describe the molecule.

- Two identical bonds with a bond order = 1.5 for O_3
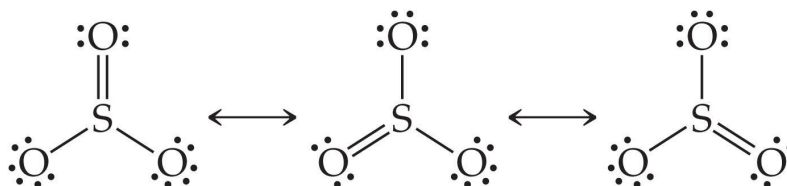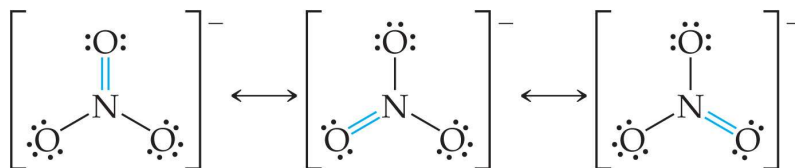- Electrons not localized, but rather are delocalized.
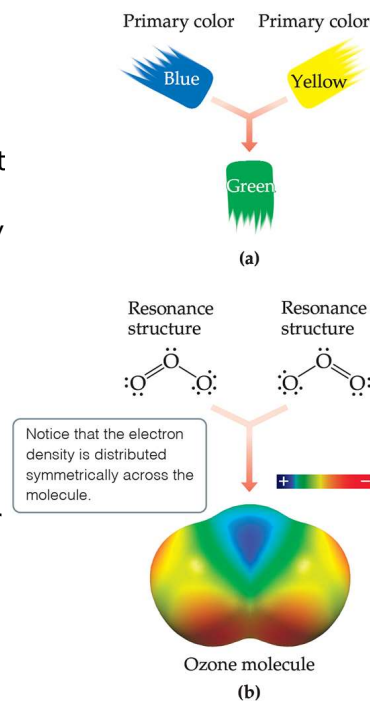
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Example

Be able to determine how many, if any, resonance structures are exhibited by a molecule or polyatomic ion.
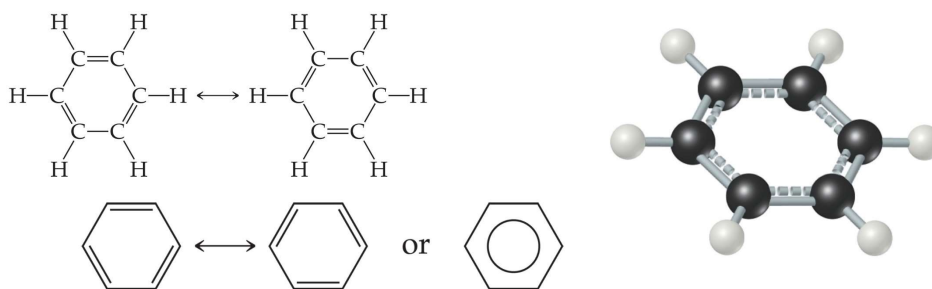
a) nitrate ion
b) sulfur trioxide

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Resonance

- The organic compound benzene, C_6H_6, has two resonance structures.
- It is commonly depicted as a hexagon with a circle inside to signify the delocalized electrons in the ring.
- *Localized* electrons are specifically on one atom or shared between two atoms; *delocalized* electrons are shared by multiple atoms.

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Average formal charge and average bond order

$$\text{average formal charge} = \frac{\text{sum of formal charges on an oxygen atom as it appears in all resonance structures}}{\text{number of resonance structures}}$$

$$\text{average bond order} = \frac{\text{total number of bonds between an atom pair as it appears in all resonance structures}}{\text{number of resonance structures}}$$
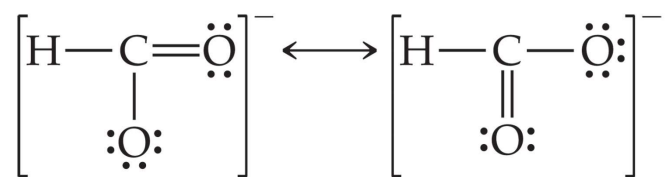
Average formal charge on O = -1/2

Average bond order = 3/2

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Exceptions to the Octet Rule

There are three types of ions or molecules that do not follow the octet rule:

- Ions or molecules with an *odd* number of electrons.

$$\dot{\ddot{N}}{=}\ddot{O} \quad \text{and} \quad \ddot{\dot{N}}{=}\dot{O}$$

- Ions or molecules with *less than* an octet.
- Ions or molecules with *more than* an octet.

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Fewer than an Octet of Electrons

Example: For boron trifluoride, draw Lewis structures in which
1) the octet rule is obeyed.
2) the formal charges are minimized.

Giving boron a filled octet places a *negative* charge on the boron and a *positive* charge on fluorine. This would not be an accurate picture of the distribution of electrons in BF_3.
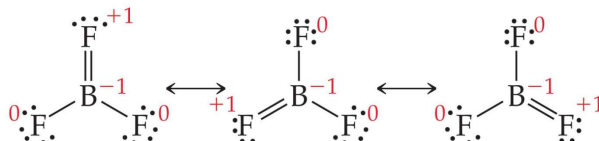
Therefore, structures that put a double bond between boron and fluorine are less important than the one that leaves boron with 6 valence electrons.

Dominant   Less important

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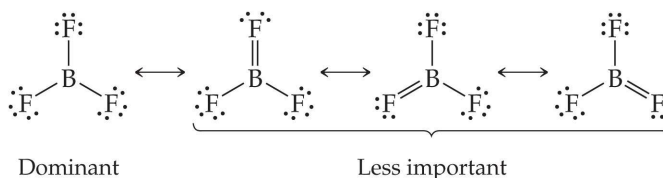
Fewer than an Octet of Electrons
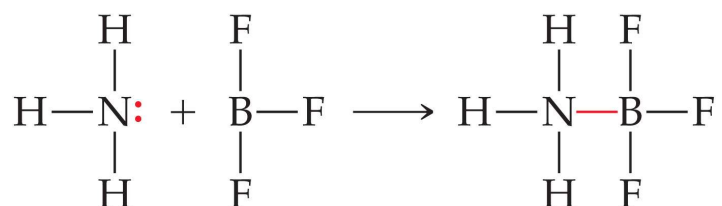
Tends to react with lone pair from another species having an unshared pair of electrons.

$$\text{H}-\overset{\displaystyle \text{H}}{\underset{\displaystyle \text{H}}{\text{N}:}} \ + \ \overset{\displaystyle \text{F}}{\underset{\displaystyle \text{F}}{\text{B}-\text{F}}} \ \longrightarrow \ \text{H}-\overset{\displaystyle \text{H}}{\underset{\displaystyle \text{H}}{\text{N}}}-\overset{\displaystyle \text{F}}{\underset{\displaystyle \text{F}}{\text{B}-\text{F}}}$$

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More Than Octet of Electrons

When an element is in periods 3 through 6, it can make *more* than four bonds and be *hypervalent* and use an expanded valence shell.
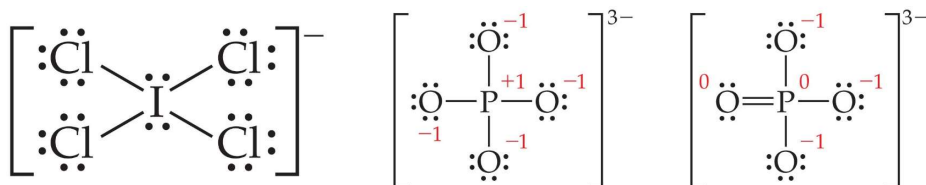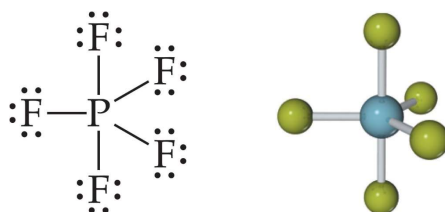
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Covalent Bond Strength

$$:\overset{..}{\underset{..}{Cl}}\!\!-\!\!\overset{..}{\underset{..}{Cl}}:(g) \longrightarrow 2 :\overset{..}{\underset{..}{Cl}}\!\cdot(g)$$

- The strength of a bond is measured by determining how much energy is required to break the bond. This is the bond enthalpy.
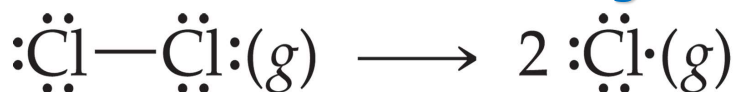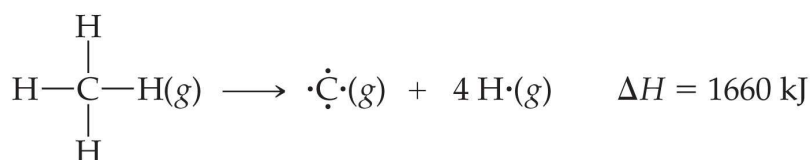- The bond dissociation enthalpy for a Cl—Cl bond, D(Cl—Cl), is 242 kJ/mol.

$$H\!-\!\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}\!-\!H(g) \longrightarrow \cdot\overset{.}{\underset{.}{C}}\cdot(g) \;+\; 4\,H\cdot(g) \qquad \Delta H = 1660\ \text{kJ}$$

Average Bond Enthalpies

- This table lists the *average* bond enthalpies for many different types of bonds.
- *Average* bond enthalpies are positive, because bond breaking is an endothermic process.

TABLE 8.3 Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						

Multiple Bonds

C=C	614	N=N	418	O=O	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

$\Delta H = \Sigma$ (bond enthalpies of bonds broken) $- \Sigma$ (bond enthalpies of bonds formed)
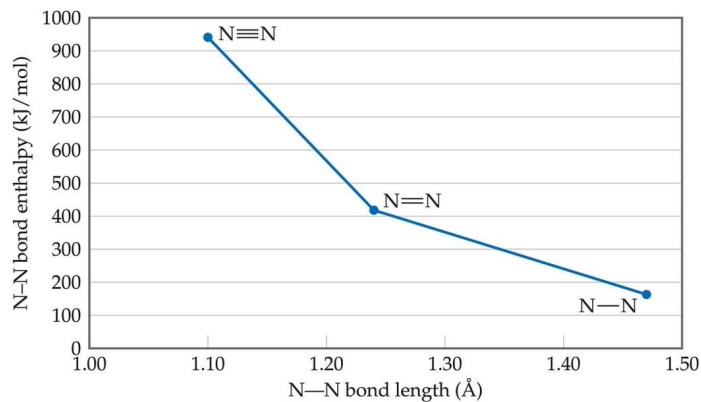
Example

Using bond enthalpies from table 8.3, estimate the enthalpy (ΔH) of the gas phase combustion reaction of methane.

Bond Enthalpy and Bond Length

$$C-C \qquad C=C \qquad C\equiv C$$

1.54 Å   1.34 Å   1.20 Å

348 kJ/mol   614 kJ/mol   839 kJ/mol

A stronger bond is a shorter bond and takes more energy to break.

Bond Length

TABLE 8.4   Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

- We can also measure an average bond length for different bond types.
- As the number of bonds between two atoms increases, the bond length decreases.

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