

CHEMISTRY

Chapter 7

Chemical Bonding and Molecular Geometry



Chem-
istry

CHAPTER 7: ELECTRONIC STRUCTURE

7.1 Ionic Bonding

7.2 Covalent Bonding

7.3 Lewis Symbols and Structures

7.4 Formal Charges and Resonance

7.5 Strengths of Ionic and Covalent Bonds

7.6 Molecular Structure and Polarity

7.1 IONIC BONDING

Properties of Ionic Compounds

- Ionic compounds, also known as salts, are held together by electrostatic forces of attraction between cations and anions.
- Ionic compounds have distinct chemical and physical properties.
 - crystalline
 - high melting points
 - conduct electricity in aqueous solution
 - rigid and brittle
 - dissolve readily in water
- The properties of ionic compounds are very different from those of its constituent neutral atoms.



Na(s)



Cl₂ (g)



NaCl(s)

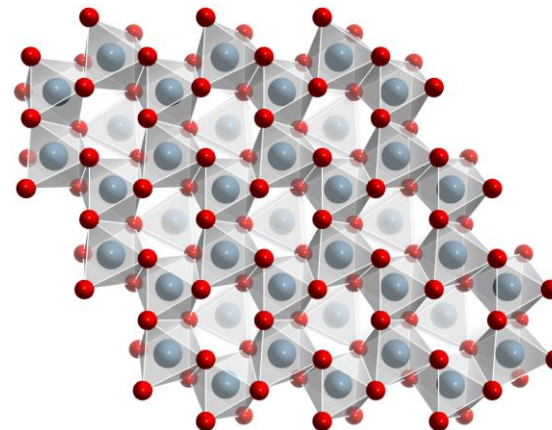
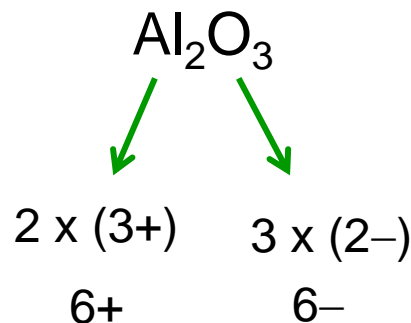
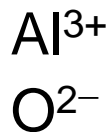
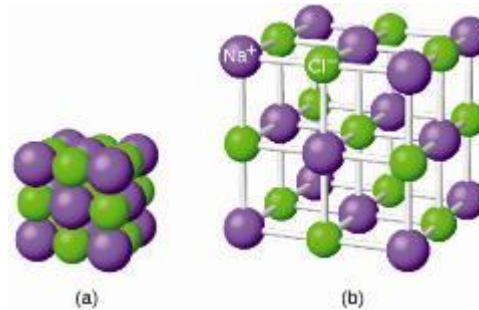
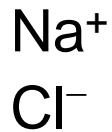


NaCl(aq)

7.1 IONIC BONDING

Formation of Ionic Compounds

- Ionic compounds must be electrically neutral.
- # of positive charges = # negative charges
- The simplest ratio of atoms is used for the formula.



som.web.cmu.edu

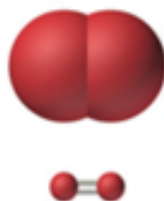
7.2 COVALENT BONDING

Properties of Covalent Bonds

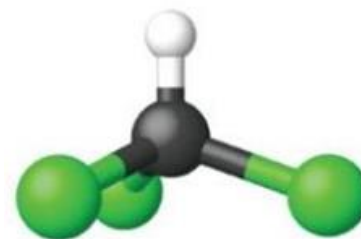
- Electrons are shared between atoms in a covalent bond.
- Both atoms have similar electron affinities.
- Covalently bonded compounds:
 - have lower melting and boiling points than ionic compounds
 - can be liquids or gases at room temperature
 - form softer solids than ionic compounds
 - are mostly insoluble in water and are poor conductors
- Nonmetals generally form covalent bonds with other nonmetals.



Hydrogen
(H₂)



Oxygen
(O₂)

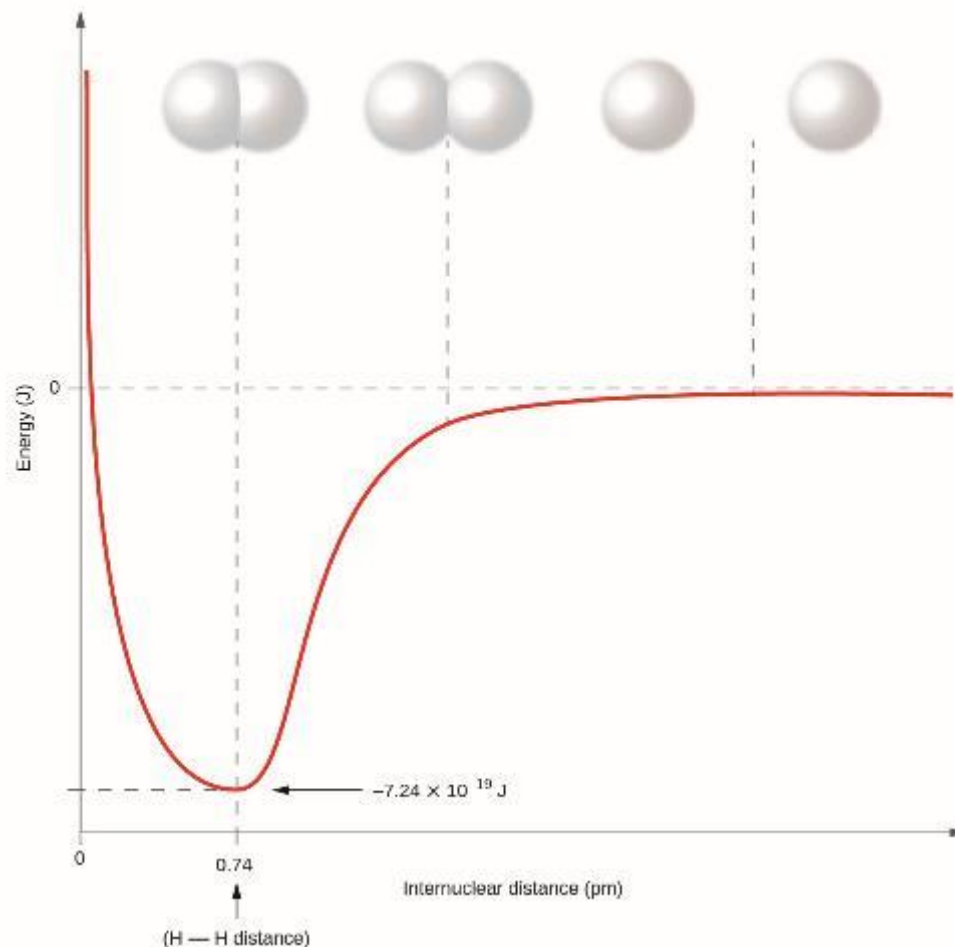


Chloroform
(CHCl₃)

7.2 COVALENT BONDING

Formation of Covalent Bonds

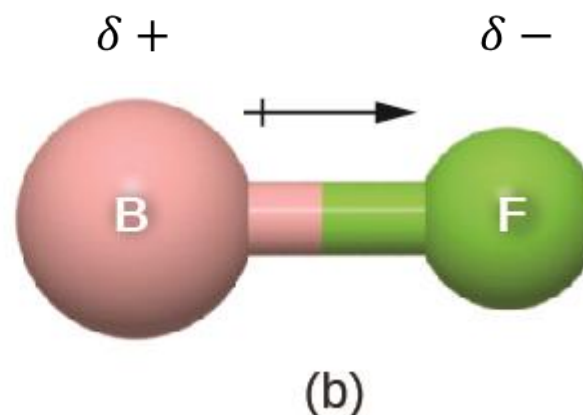
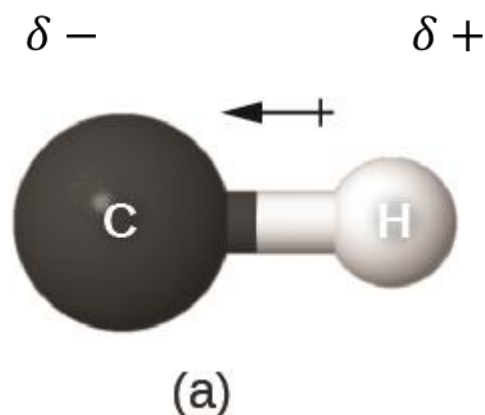
- s-orbitals of the atoms can overlap to form a covalent bond.
- Bond length is determined by the distance at which lowest potential energy is achieved.
- Energy must be added to break a chemical bond, so energy is released when one is formed.



7.2 COVALENT BONDING

Pure vs. Polar Covalent Bonds

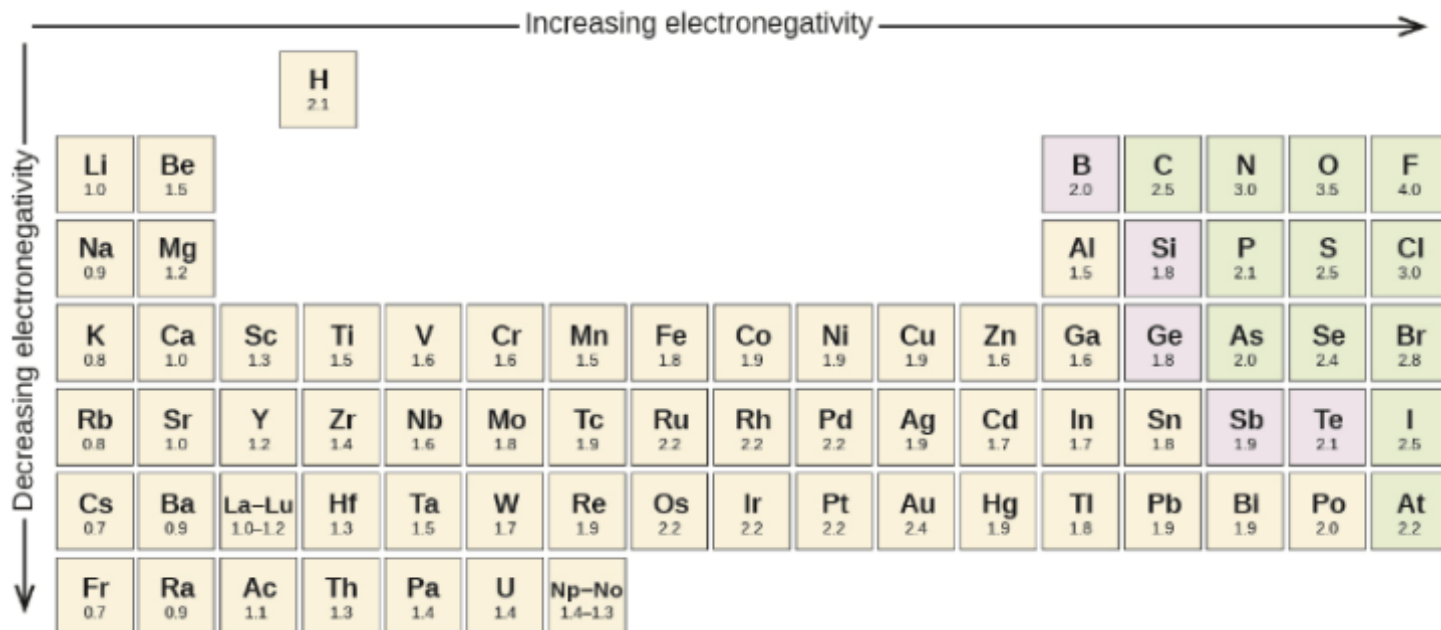
- A pure covalent bond occurs in diatomic molecules.
 - Electrons shared have equal probability of being near each nucleus.
- A polar covalent bond occurs when one atom is more electronegative than the other.
- There is partial positive charge ($\delta +$) on one atom and a partial negative charge ($\delta -$) on the other.



7.2 COVALENT BONDING

Electronegativity

- The extent that a bond is polarized is determined by the electronegativity of the atoms involved.
- Electronegativities as derived by Linus Pauling are listed in the table below.
- Consider the polarity of an N-O bond versus that of a Si-O bond.



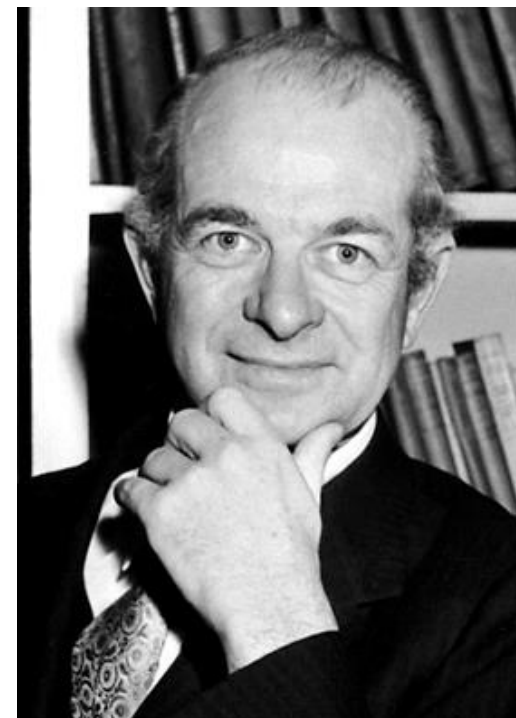
7.2 COVALENT BONDING

Reminder: Electron Affinity vs. Electronegativity

- Be careful not to confuse electronegativity and electron affinity.
- The electron affinity of an element is a measurable physical quantity: energy released or absorbed when an isolated gas-phase atom acquires an electron (kJ/mol).
- The electronegativity describes how tightly an atom attracts electrons in a bond.
 - a dimensionless quantity that is calculated, not measured.
 - derived by Pauling as he compared the amounts of energy required to break different types of bonds
 - on an arbitrary relative scale ranging from 0 to 4

LINUS PAULING

- Linus Pauling (1901-1994) is the only person to have received two unshared Nobel Prizes.
 - Chemistry in 1954 for his work on the nature of chemical bonds.
 - Peace in 1962 for his opposition to weapons of mass destruction.
- Pauling developed many fundamental chemical concepts such as electronegativity and resonance structures.
- Pauling also discovered the cause of sickle cell anemia—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics.
- Pauling was also a prominent activist, publicizing issues related to health and nuclear weapons.
 - He proved that radioactive fallout from nuclear testing posed a public health risk.

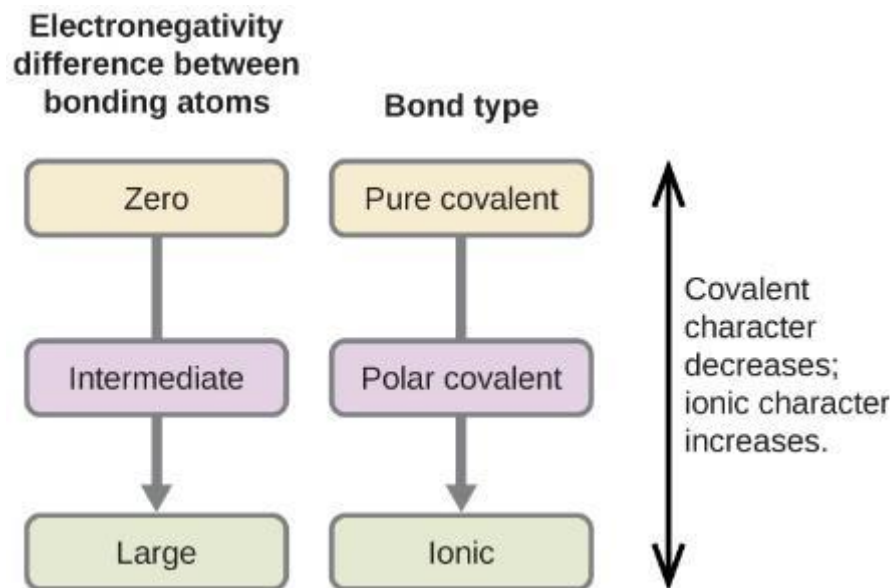


nobelprize.org

7.2 COVALENT BONDING

Electronegativity and Bond Polarity

- The absolute value of the electronegativity difference (ΔE) between two atoms provides a measure of polarity.
- When ΔE is small, the bond has more covalent character.
- A large value of ΔE means that the bond is ionic in character.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

7.3 LEWIS SYMBOLS AND STRUCTURES

Lewis Symbols

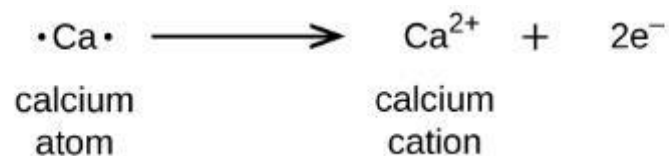
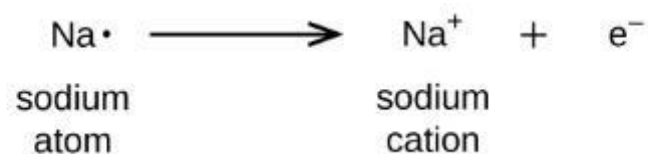
- G.N. Lewis devised a way to represent valence electrons around atoms and monatomic ions.
- A Lewis symbol consists of an elemental symbol surrounded by one dot per valence electron.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[\text{Ne}]3s^1$	$\text{Na} \cdot$
magnesium	$[\text{Ne}]3s^2$	$\cdot \text{Mg} \cdot$
aluminum	$[\text{Ne}]3s^2 3p^1$	$\cdot \overset{\cdot}{\underset{\cdot}{\text{Al}}} \cdot$
silicon	$[\text{Ne}]3s^2 3p^2$	$\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Si}}}} \cdot$
phosphorus	$[\text{Ne}]3s^2 3p^3$	$\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{P}}}}} \cdot$
sulfur	$[\text{Ne}]3s^2 3p^4$	$\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{S}}}}} \cdot$
chlorine	$[\text{Ne}]3s^2 3p^5$	$\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Cl}}}}} \cdot$
argon	$[\text{Ne}]3s^2 3p^6$	$\cdot \overset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\underset{\cdot}{\text{Ar}}}}} \cdot$

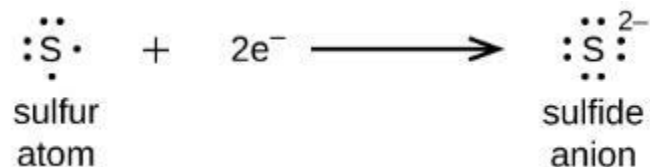
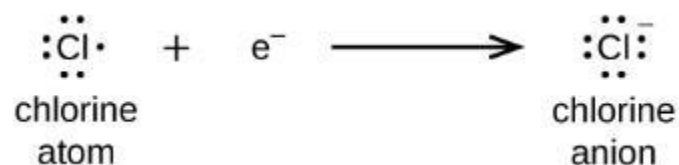
7.3 LEWIS SYMBOLS AND STRUCTURES

Lewis Symbols

- For ions, Lewis symbols are used as well.
- For cations:



- For anions:



7.3 LEWIS SYMBOLS AND STRUCTURES

Lewis Symbols for Ionic Compounds

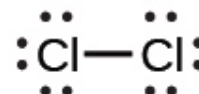
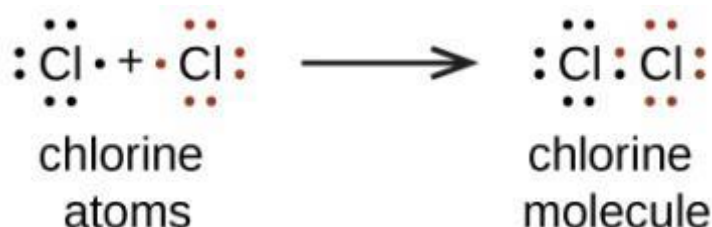
- The metal (cation) and nonmetal (anion) must be considered.
 - The cation loses electrons.
 - The anion gains electrons.
- The total number of electrons does not change.

Metal		Nonmetal		Ionic Compound
$\text{Na} \cdot$ sodium atom	+	$:\ddot{\text{Cl}} \cdot$ chlorine atom	\longrightarrow	$\text{Na}^+ \left[:\ddot{\text{Cl}}: \right]^-$ sodium chloride (sodium ion and chloride ion)
$\cdot \text{Mg} \cdot$ magnesium atom	+	$:\ddot{\text{O}} \cdot$ oxygen atom	\longrightarrow	$\text{Mg}^{2+} \left[:\ddot{\text{O}}: \right]^{2-}$ magnesium oxide (magnesium ion and oxide ion)
$\cdot \text{Ca} \cdot$ calcium atom	+	$2 :\ddot{\text{F}} \cdot$ fluorine atoms	\longrightarrow	$\text{Ca}^{2+} \left[:\ddot{\text{F}}: \right]_2^-$ calcium fluoride (calcium ion and two fluoride ions)

7.3 LEWIS SYMBOLS AND STRUCTURES

Lewis Structures

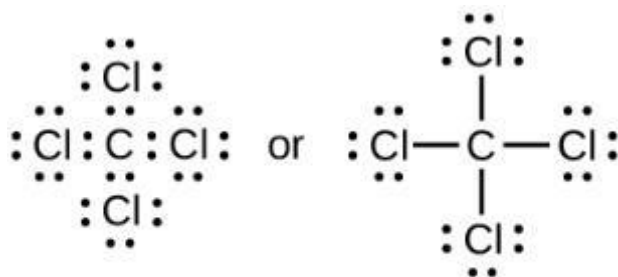
- Covalent compounds can be represented as Lewis structures.
- A bond requires that an electron pair be shared between atoms.
 - One pair of electrons shared → single bond.
 - Two pairs → double bond
 - Three pairs → triple bond
- Electrons not involved in bonding are called lone pairs and are drawn on the outside of each atom.



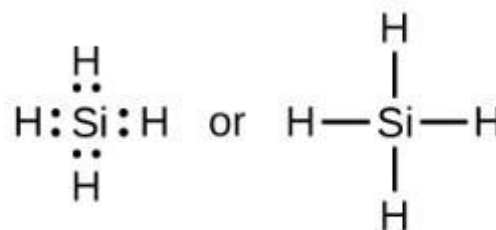
7.3 LEWIS SYMBOLS AND STRUCTURES

The Octet Rule

- The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.
- The number of bonds an atom can form can be predicted from the number of electrons needed to reach an octet.
- Carbon atoms require four electrons to reach an octet and can do this by forming four covalent bonds.
- Locate silicon on the periodic table. Does the silane structure make sense?



carbon tetrachloride

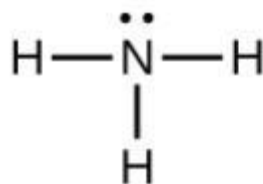


silane

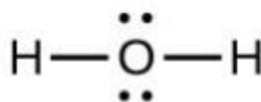
7.3 LEWIS SYMBOLS AND STRUCTURES

The Octet Rule

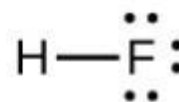
- Group 15 elements require three bonds to reach an octet.
- Group 16 elements require two bonds.
- Group 17 elements require one bond.



ammonia



water

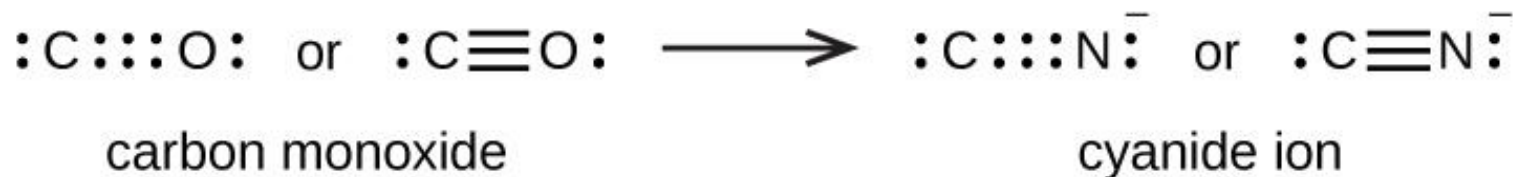
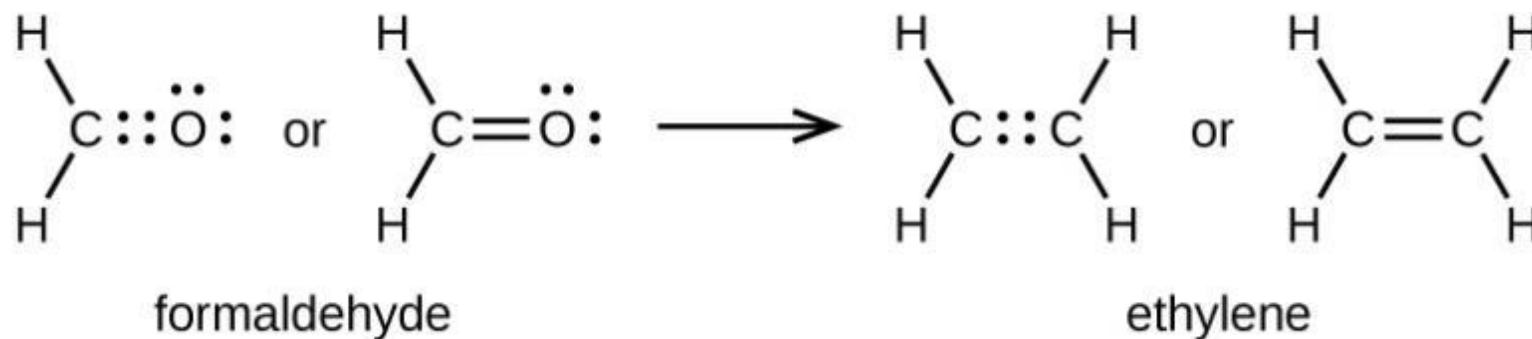


*hydrogen
fluoride*

7.3 LEWIS SYMBOLS AND STRUCTURES

Double and Triple Bonds

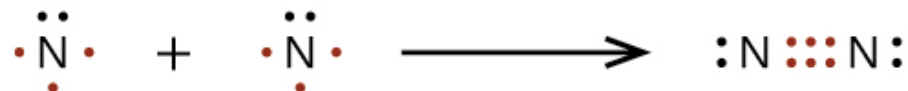
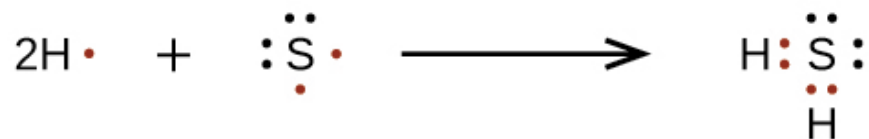
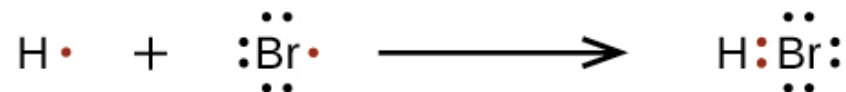
- When two atoms share multiple electrons pairs, double and triple bonds can form.



7.3 LEWIS SYMBOLS AND STRUCTURES

Writing Lewis Structures

- For simple molecules, Lewis structures can be drawn by pairing up the unpaired electrons on each atom.



- For more complicated molecules, a step-by-step procedure can be used.

7.3 LEWIS SYMBOLS AND STRUCTURES

Procedure for Writing Lewis Structures

1. Determine the total # of valence electrons.
2. Draw a skeleton structure with the least electronegative atom (generally) in the center. Connect to outer atoms with a single bond.
3. Distribute the remaining valence electrons on outer atoms.
4. Place any remaining electrons on the central atom.
5. Rearrange atoms/bonds so that all atoms have an octet.



7.3 LEWIS SYMBOLS AND STRUCTURES

Example 7.4

NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?



7.3 LEWIS SYMBOLS AND STRUCTURES

Exceptions to the Octet Rule

- Many covalent molecules have central atoms that do not have octets.
- If a molecule has an odd number of valence electrons, it will have an unpaired electron or a free radical.
- *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible.

Draw Lewis structures for:



nitric oxide



*hydroxyl
radical*

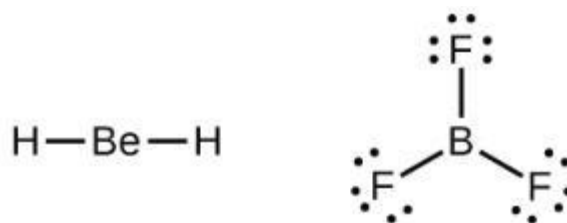


*methyl
radical*

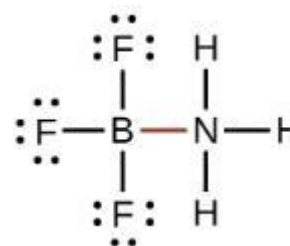
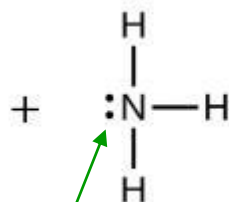
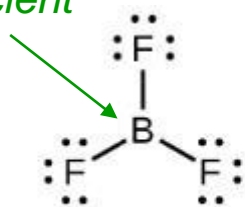
7.3 LEWIS SYMBOLS AND STRUCTURES

Exceptions to the Octet Rule

- Electron deficient molecules have a central atom with fewer than eight electrons.
- Hydrogen is usually a terminal atom and does not have an octet.
- Be and B also form molecules with fewer than eight electrons around the central atom.



electron deficient

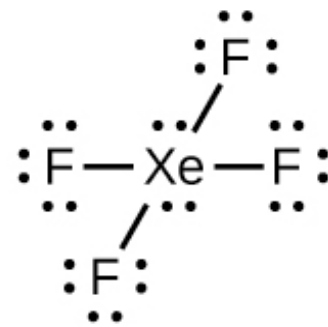
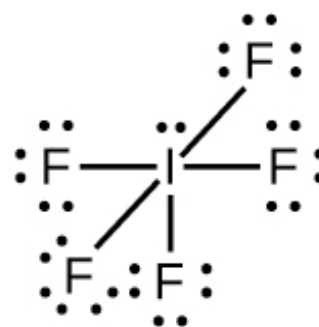
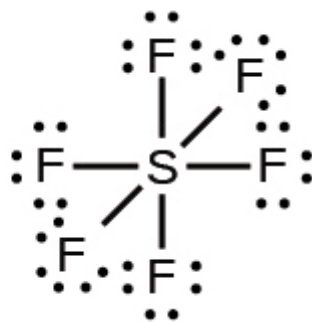
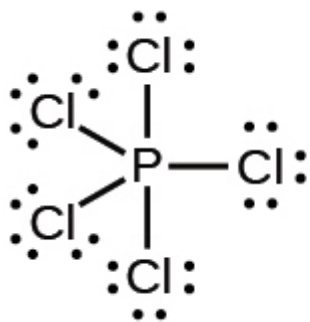


lone pair can be shared

7.3 LEWIS SYMBOLS AND STRUCTURES

Exceptions to the Octet Rule

- Hypervalent molecules have more than eight electrons, an expanded octet, around the central atom.
- Atoms with $n \geq 3$ can have expanded octets.
- Drawing these Lewis structures correctly will be crucial when we study molecular geometry.



7.4 FORMAL CHARGES AND RESONANCE

Formal Charge

- The formal charge of an atom in a molecule is the hypothetical charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms.
- # valence shell electrons (free atom) – # lone pair electrons
– $\frac{1}{2}$ # bonding electrons
- The formal charge is hypothetical and not the actual charge on an atom.
- Formal charges are useful for predicting molecular structure, as we shall see.

Draw Lewis structures and assign formal charges for:



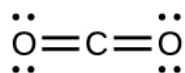
7.4 FORMAL CHARGES AND RESONANCE

Formal Charge and Molecular Structure

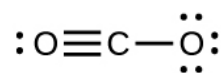
- The arrangement of atoms in a molecule or ion is called its molecular structure.
- For a molecular structure:
 - formal charges of zero preferred
 - adjacent formal charges should be zero or opposite sign
 - a negative formal charge should reside on an electronegative atom and a positive on the least electronegative atom.
 - charge separation should be minimized

Choose the favored Lewis structure from the possibilities given:

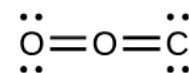
CO₂



0 0 0

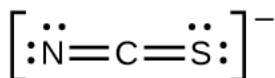


+1 0 -1

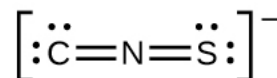


0 +2 -2

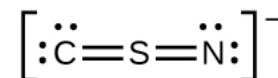
[NCS]⁻



-1 0 0



-2 +1 0



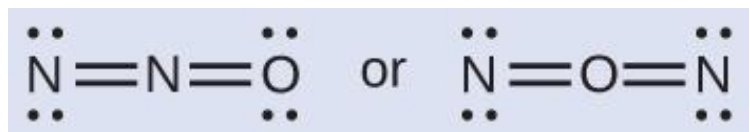
-2 +2 -1

Skeleton: N—C—S

7.4 FORMAL CHARGES AND RESONANCE

Example 7.8

Nitrous oxide, N_2O , commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



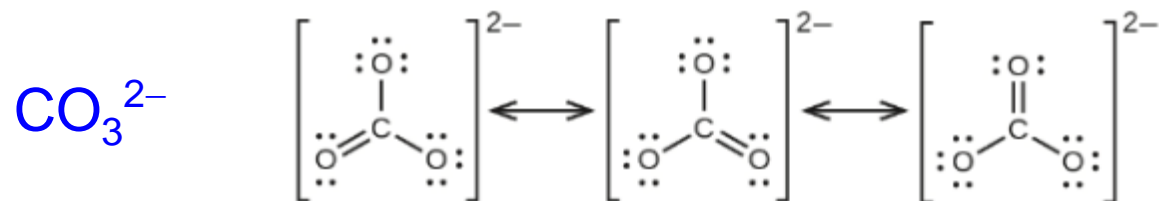
Draw all possible Lewis structures for NO_2^- . Choose the most favored structure.

7.4 FORMAL CHARGES AND RESONANCE

Resonance

- If two or more Lewis structures with the same arrangement of atoms can be drawn for a molecule or ion, the actual distribution of electrons is an average of the two.
- The individual arrangements are called resonance structures.
- The average is called a resonance hybrid.

Draw the resonance structures and the resonance hybrid for CO_3^{2-} and O_3 .

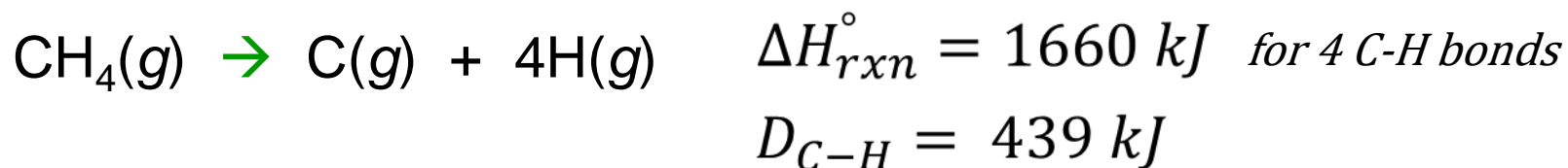
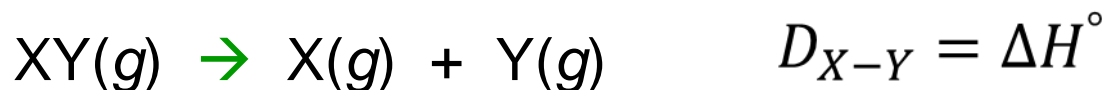


Skeleton: $\text{O} - \text{O} - \text{O}$

7.5 STRENGTHS OF IONIC AND COVALENT BONDS

Bond Strength: Covalent Bonds

- The strength of a covalent bond is measured by the energy required to break it.
- The energy required to break a covalent bond in one mole of gaseous molecules is the bond energy, or bond dissociation energy.
- The bond energy for a molecule is the standard enthalpy of change for the endothermic process required to break the bond.



7.5 STRENGTHS OF IONIC AND COVALENT BONDS

Bond Strength: Covalent Bonds

- In general, as bond strength increases, bond length decreases.
- Triple bonds are shorter and stronger than double bonds.
- Double bonds are shorter and stronger than single bonds.

Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C = C	1.34	611
C ≡ C	1.20	837
C–N	1.43	290
C = N	1.38	615
C ≡ N	1.16	891
C–O	1.43	350
C = O	1.23	741
C ≡ O	1.13	1080

7.5 STRENGTHS OF IONIC AND COVALENT BONDS

Bond Strength: Covalent Bonds

- What periodic trends can be noted from the bond energies (kJ/mol) in the table?

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H-H	436	C-S	260	F-Cl	255
H-C	415	C-Cl	330	F-Br	235
H-N	390	C-Br	275	Si-Si	230
H-O	464	C-I	240	Si-P	215
H-F	569	N-N	160	Si-S	225
H-Si	395	N = N	418	Si-Cl	359
H-P	320	N \equiv N	946	Si-Br	290
H-S	340	N-O	200	Si-I	215
H-Cl	432	N-F	270	P-P	215
H-Br	370	N-P	210	P-S	230
H-I	295	N-Cl	200	P-Cl	330
C-C	345	N-Br	245	P-Br	270
C = C	611	O-O	140	P-I	215
C \equiv C	837	O = O	498	S-S	215
C-N	290	O-F	160	S-Cl	250
C = N	615	O-Si	370	S-Br	215
C \equiv N	891	O-P	350	Cl-Cl	243
C-O	350	O-Cl	205	Cl-Br	220
C = O	741	O-I	200	Cl-I	210
C \equiv O	1080	F-F	160	Br-Br	190
C-F	439	F-Si	540	Br-I	180
C-Si	360	F-P	489	I-I	150
C-P	265	F-S	285		

7.5 STRENGTHS OF IONIC AND COVALENT BONDS

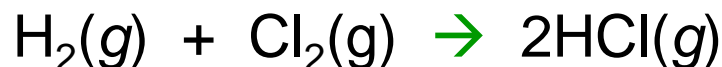
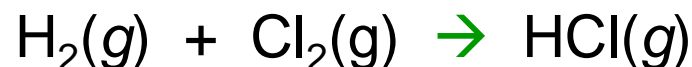
Covalent Bond Energies and Enthalpy

- Bond energies can be used to calculate enthalpy changes for reactions where enthalpies of formation are not available.
- Such a calculation will also show whether a reaction is exothermic or endothermic.
- An exothermic reaction ($\Delta H < 0$) results when the bonds in the products are stronger than the bonds in the reactants.
- An endothermic reaction ($\Delta H > 0$) results when the bonds in the products are weaker than those in the reactants.
- $\Delta H_{rxn} = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$ D = bond energy (kJ/mol)

7.5 STRENGTHS OF IONIC AND COVALENT BONDS

Bond Energies and Enthalpy

- Consider the reaction between hydrogen gas and chlorine gas to form hydrochloric acid.



one mole H-H one mole Cl-Cl two moles H-Cl
bonds *broken* bonds *broken* bonds *formed*

$$\Delta H_{\text{rxn}} = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$$

$$\Delta H_{\text{rxn}} = \Sigma[D_{\text{H-H}} + D_{\text{Cl-Cl}}] - \Sigma[2D_{\text{H-Cl}}]$$

Values are tabulated
in the textbook.

$$\Delta H_{\text{rxn}} = [436 + 243] - [2(432)] = -185 \text{ kJ}$$

7.5 STRENGTHS OF IONIC AND COVALENT BONDS

Bond Strength: Ionic Bonds and Lattice Energy

- Ionic bonds are held together by electrostatic interactions between positive and negative ions.
- The energy required to convert one mole of an ionic compound into gaseous ions is called the lattice energy, $\Delta H_{\text{lattice}}$.
- Lattice energies will always be positive.
- Energy is released when a lattice forms.

$$\Delta H_{\text{lattice}} = 769 \text{ kJ}$$

$$\Delta H_{\text{lattice}} = \frac{C(Z^+)(Z^-)}{R_0}$$

constant \nearrow
distance \nearrow between ions R_0
ion charges \nearrow

- It requires 769 kJ to separate one mole of solid **NaCl** into gaseous Na^+ and Cl^- ions.
- When one mole each of gaseous Na^+ and Cl^- ions form solid NaCl, 769 kJ of heat is released.
- How would the lattice energy change for a compound like **MgO**?

7.5 STRENGTHS OF IONIC AND COVALENT BONDS

The Born-Haber Cycle

- Lattice energies cannot be measured directly, but it can be calculated using a thermochemical cycle.
- The Born-Haber Cycle is an application of Hess's Law.
- Individual steps for the formation of ionic solids are considered.
 - standard enthalpy of formation of compound
 - ionization energy of the metal
 - electron affinity of the nonmetal
 - enthalpy of sublimation of the metal
 - bond dissociation energy of the nonmetal
 - lattice energy of the compound

$$\Delta H_{\text{formation}}^{\circ}$$

$$IE_{\text{metal}}$$

$$EA_{\text{nonmetal}}$$

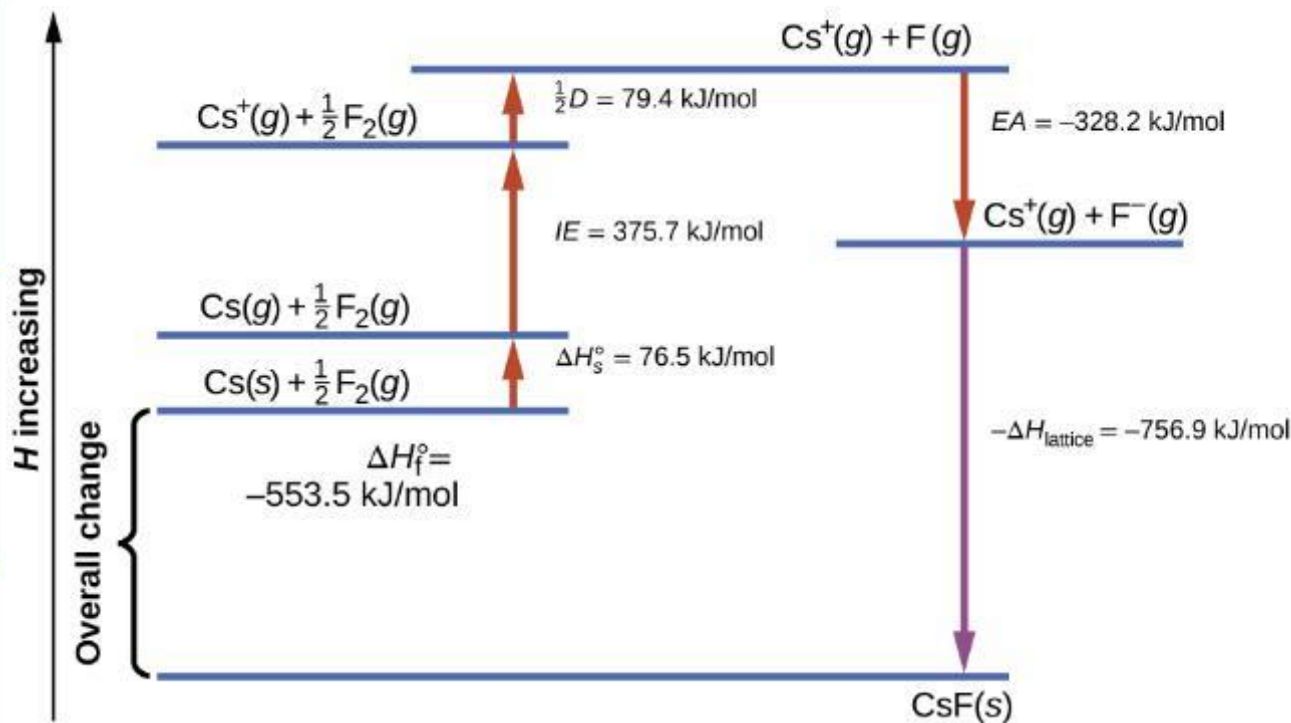
$$\Delta H_{\text{sublimation}}^{\circ}$$

$$D_{\text{nonmetal}}$$

$$\Delta H_{\text{lattice}}$$

7.5 STRENGTHS OF IONIC AND COVALENT BONDS

The Born-Haber Cycle: Cesium Fluoride



$\Delta H_{\text{formation}}^\circ$
 IE_{metal}
 EA_{nonmetal}
 $\Delta H_{\text{sublimation}}^\circ$
 D_{nonmetal}
 $\Delta H_{\text{lattice}}$

The lattice energy or heat of formation may be calculated from the other values.

$$\Delta H_f^\circ = \Delta H_s^\circ + \frac{1}{2}D_{\text{nonmetal}} + IE_{\text{metal}} - EA_{\text{nonmetal}} - \Delta H_{\text{lattice}}$$

$$\Delta H_{\text{lattice}} = -\Delta H_f^\circ + \Delta H_s^\circ + \frac{1}{2}D_{\text{nonmetal}} + IE_{\text{metal}} - EA_{\text{nonmetal}}$$

$$\Delta H_{\text{lattice}} = [-(-553.5) + 76.5 + 79.4 + 375.76 - 328.2] \text{ kJ} = 756.9 \text{ kJ}$$

7.5 STRENGTHS OF IONIC AND COVALENT BONDS

The Born-Haber Cycle: Cesium Chloride

Enthalpy of sublimation of Cs(s)	$\text{Cs}(s) \longrightarrow \text{Cs}(g) \quad \Delta H = \Delta H_s^\circ = 76.5\text{kJ}$
One-half of the bond energy of Cl ₂	$\frac{1}{2} \text{Cl}_2(g) \longrightarrow \text{Cl}(g) \quad \Delta H = \frac{1}{2} D = 122\text{kJ}$
Ionization energy of Na(g)	$\text{Na}(g) \longrightarrow \text{Na}^+(g) + e^- \quad \Delta H = IE = 496\text{kJ}$
Negative of the electron affinity of Cl	$\text{Cl}(g) + e^- \longrightarrow \text{Cl}^-(g) \quad \Delta H = -EA = -368\text{kJ}$
Negative of the lattice energy of NaCl(s)	$\text{Na}^+(g) + \text{Cl}^-(g) \longrightarrow \text{NaCl}(s) \quad \Delta H = -\Delta H_{\text{lattice}} = ?$
Enthalpy of formation of NaCl(s), add steps 1–5	$\Delta H = \Delta H_f^\circ = \Delta H_s^\circ + \frac{1}{2} D + IE + (-EA) + (-\Delta H_{\text{lattice}})$ $\text{Na}(s) + \frac{1}{2} \text{Cl}_2(g) \longrightarrow \text{NaCl}(s) = -411\text{kJ}$

The lattice energy can be calculated from other values.

$$\Delta H_f^\circ = \Delta H_s^\circ + \frac{1}{2} D_{\text{nonmetal}} + IE_{\text{metal}} - EA_{\text{nonmetal}} - \Delta H_{\text{lattice}}$$

$$\Delta H_{\text{lattice}} = -\Delta H_f^\circ + \Delta H_s^\circ + \frac{1}{2} D_{\text{nonmetal}} + IE_{\text{metal}} - EA_{\text{nonmetal}}$$

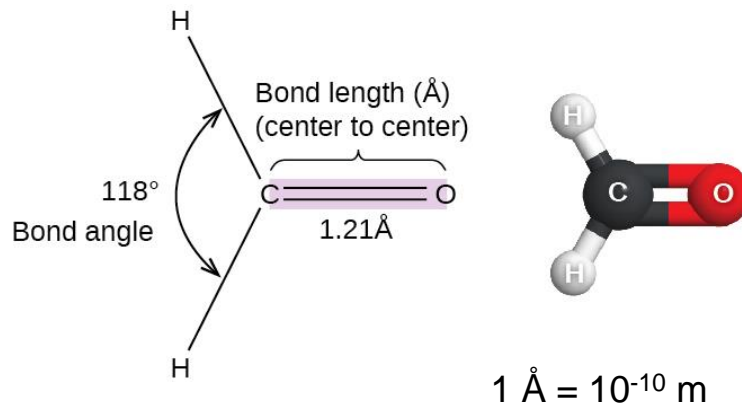
$$\Delta H_{\text{lattice}} = [-(-411) + 77 + 122 + 496 - 368] \text{ kJ} = 738 \text{ kJ}$$

$$\begin{aligned} &\Delta H_f^\circ \\ &IE_{\text{metal}} \\ &EA_{\text{nonmetal}} \\ &\Delta H_s^\circ \\ &D_{\text{nonmetal}} \\ &\Delta H_{\text{lattice}} \end{aligned}$$

7.6 MOLECULAR STRUCTURE AND POLARITY

Depicting Molecules in Three Dimensions

- Molecules can be represented by Lewis structures, but a more complete representation includes three-dimensional geometries.
- The distances between atoms, bond angles, and relative arrangements in space are critical for understanding molecular structures.
- A bond angle (degrees) is the angle between two bonds that have a common atom.
- A bond length (Ångstroms) is the distance between the nuclei of two bonded atoms.



7.6 MOLECULAR STRUCTURE AND POLARITY

VSEPR Theory

- The molecular structure of molecules can be predicted by using valence shell electron pair repulsion theory (VSEPR).
- Electron pairs in the valence shell of the central atom will adopt an arrangement so that they are as far apart in space as possible.
- This minimizes repulsion between electron pairs.

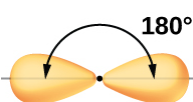
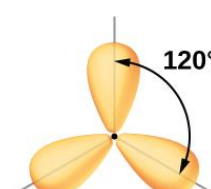
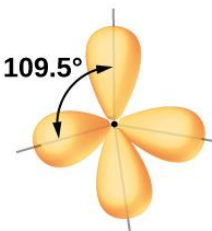
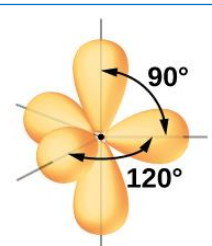
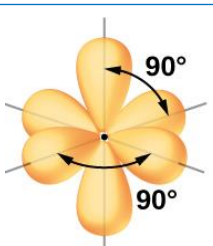
Draw the Lewis structure for each molecule and predict a geometry that will minimize electron pair repulsion.



7.6 MOLECULAR STRUCTURE AND POLARITY

Electron Density and Geometry


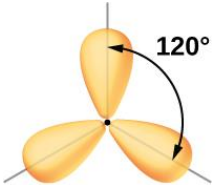
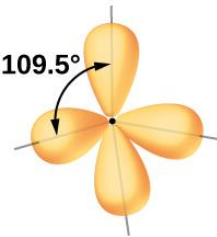
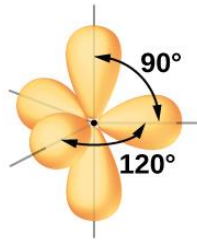
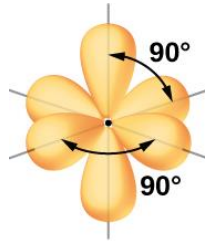
- For more complicated molecules, all regions of high electron density around a central atom need to be considered.
- Both bonded atoms and electron pairs on a central atom are considered regions of high electron density must be considered when starting to determine molecular geometry.

Regions	2	3	4	5	6
Arrangement					

7.6 MOLECULAR STRUCTURE AND POLARITY

Electron Density and Geometry

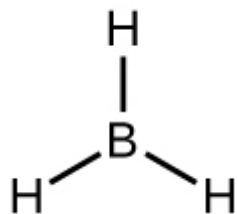
- When considering regions of high electron density, bonding atoms and lone pairs must be considered.
- The arrangement of these regions in space is referred to as the electron pair geometry.
- The possible arrangements for electron pair geometry are limited and fall into five general categories.

Regions	2	3	4	5	6
Arrangement					
Electron Pair Geometry	<i>linear</i>	<i>trigonal planar</i>	<i>tetrahedral</i>	<i>trigonal bipyramidal</i>	<i>octahedral</i>

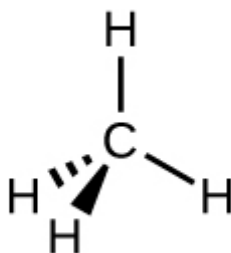
7.6 MOLECULAR STRUCTURE AND POLARITY

From Electron Pair Geometry to Molecular Structure

- The electron pairs cannot be “seen” so the actual molecular geometry is determined by the placement of atoms.
- The electron pairs are critical, however, because each occupies a relatively large region in space.
- The groups with two regions of electron densities are linear and do not involve lone pairs.
- Lone pair arrangements must be considered in higher order groups.



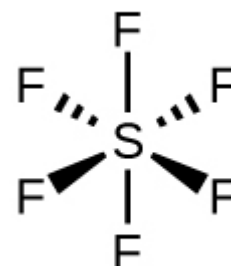
*Trigonal Planar
Group*



*Tetrahedral
Group*



*Trigonal Bipyramidal
Group*



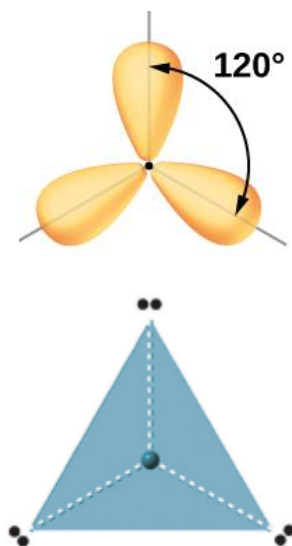
*Octahedral
Group*

7.6 MOLECULAR STRUCTURE AND POLARITY

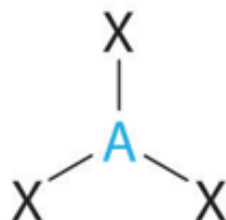
Trigonal Planar Group

- If there are three regions of electron density around a central atom, the best arrangement in space is trigonal planar.
- The molecular geometries depend on the combination of atoms and electron pairs arrayed about the central atom.

Trigonal Planar
Group



3 atoms
0 lone pairs



trigonal planar



2 atoms
1 lone pair



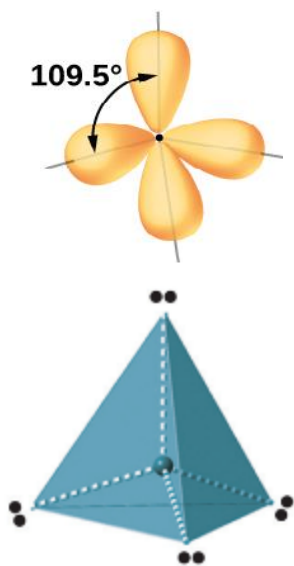
bent

7.6 MOLECULAR STRUCTURE AND POLARITY

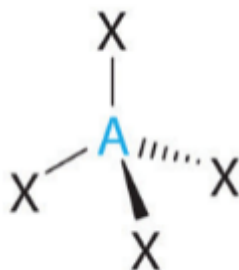
Tetrahedral Group

- If there are four regions of electron density around a central atom, the best arrangement in space is tetrahedral.
- The molecular geometries depend on the combination of atoms and electron pairs arrayed about the central atom.

Tetrahedral Group



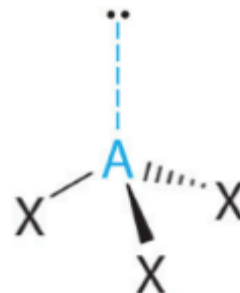
4 atoms
0 lone pairs



tetrahedral



3 atoms
1 lone pair



*trigonal
pyramidal*



2 atoms
2 lone pairs



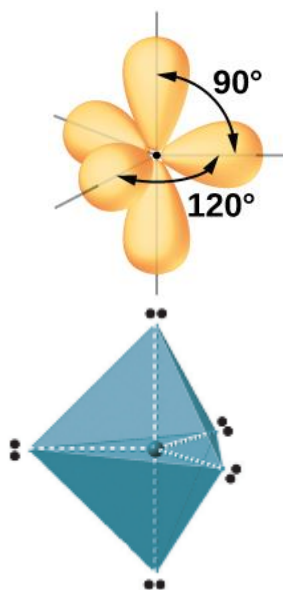
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7.6 MOLECULAR STRUCTURE AND POLARITY

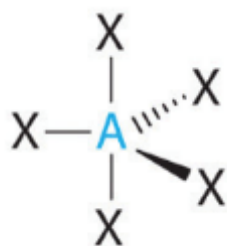
Trigonal Bipyramidal

- If there are five regions of electron density around a central atom, the best arrangement in space is trigonal bipyramidal.
- The molecular geometries depend on the combination of atoms and electron pairs arrayed about the central atom.

Trigonal Bipyramidal Group

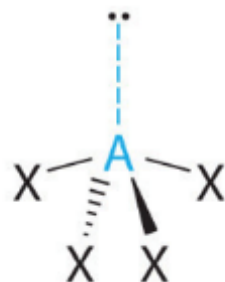


AX_5
5 atoms
0 lone pairs



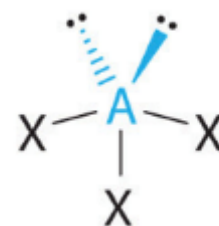
*trigonal
bipyramidal*

AX_4
4 atoms
1 lone pair



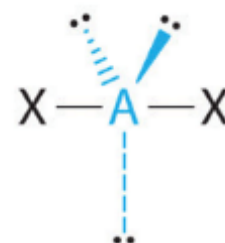
see-saw

AX_3
3 atoms
2 lone pairs



t-shaped

AX_2
2 atoms
3 lone pairs



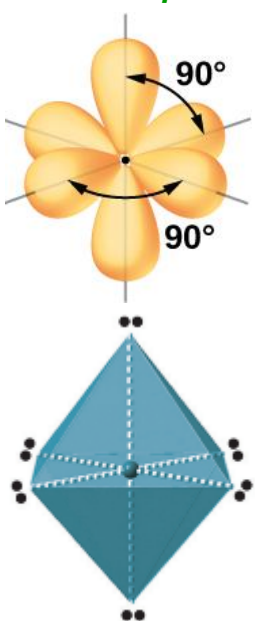
linear

7.6 MOLECULAR STRUCTURE AND POLARITY

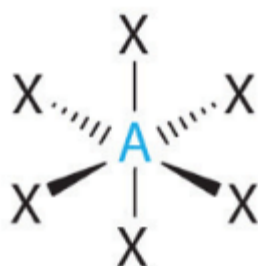
Octahedral

- If there are six regions of electron density around a central atom, the best arrangement in space is octahedral.
- The molecular geometries depend on the combination of atoms and electron pairs arrayed about the central atom.

Octahedral Group



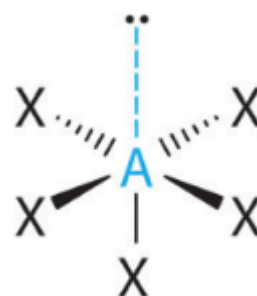
6 atoms
0 lone pairs



octahedral



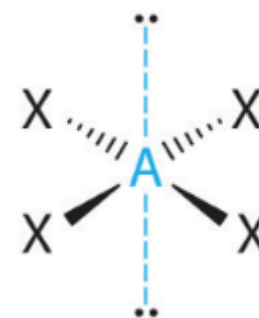
5 atoms
1 lone pair



square
pyramidal






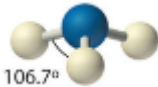
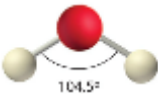
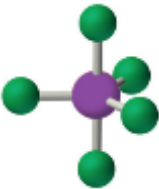
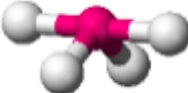
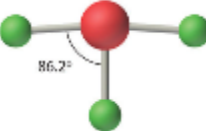

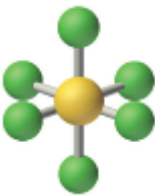

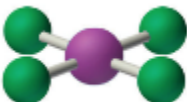
4 atoms
2 lone pairs

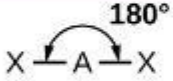
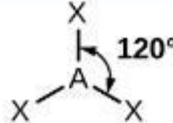

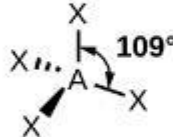
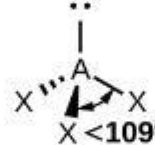

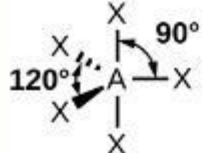
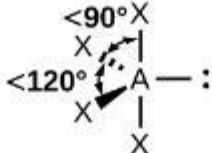
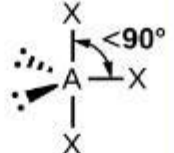
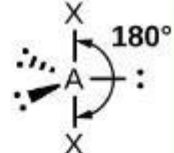
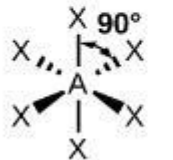
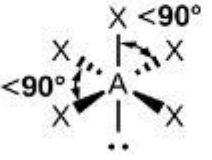
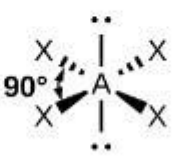
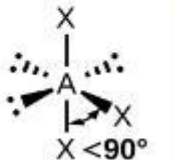
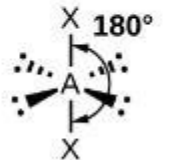


square
planar

7.6 MOLECULAR STRUCTURE AND POLARITY

Summary of Molecular Geometries

Geometry	0 lone pairs	1 lone pair	2 lone pairs	3 lone pairs
linear				
trigonal planar				
tetrahedral				
trigonal bipyramidal				
octahedral				

Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 <p>Linear</p>				
3	 <p>Trigonal planar</p>	 <p>Bent or angular</p>			
4	 <p>Tetrahedral</p>	 <p>Trigonal pyramid</p>	 <p>Bent or angular</p>		
5	 <p>Trigonal bipyramid</p>	 <p>Sawhorse or seesaw</p>	 <p>T-shape</p>	 <p>Linear</p>	
6	 <p>Octahedral</p>	 <p>Square pyramid</p>	 <p>Square planar</p>	 <p>T-shape</p>	 <p>Linear</p>

7.6 MOLECULAR STRUCTURE AND POLARITY

Example 7.14

Sulfur tetrafluoride, SF_4 , is extremely valuable for the preparation of fluorine-containing compounds used as herbicides. Predict the electron-pair geometry and the molecular geometry of the SF_4 molecule.

Hint: For this molecule, consider the difference between axial and equatorial positions.

7.6 MOLECULAR STRUCTURE AND POLARITY

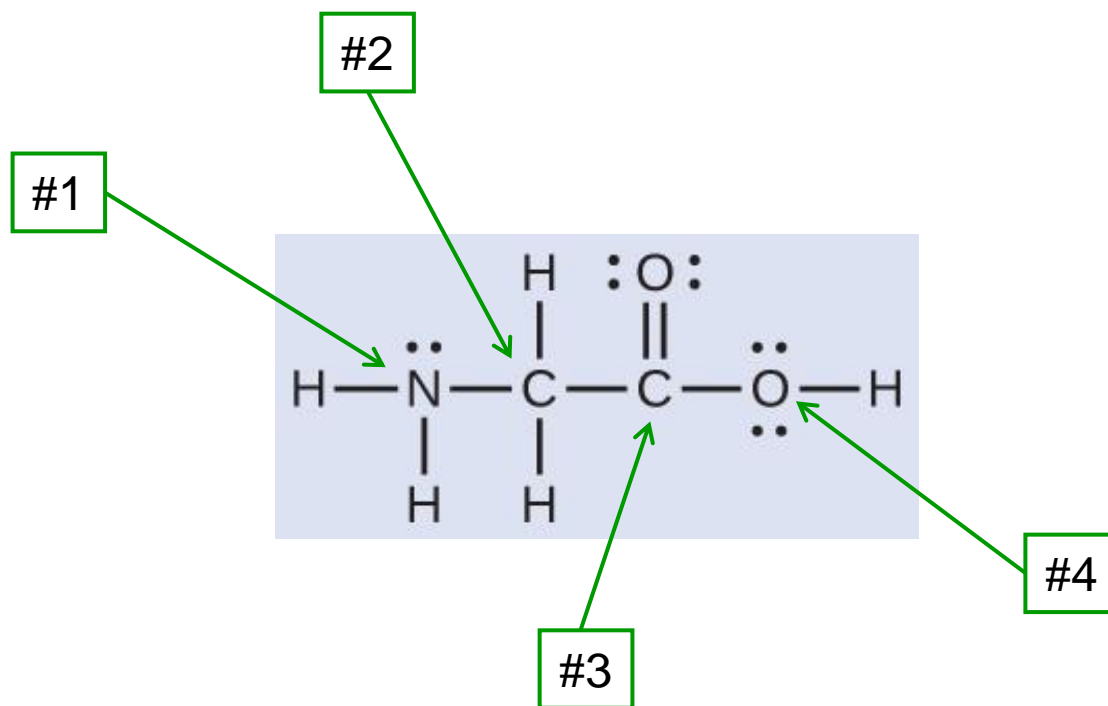
Example 7.15

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF_4 molecule.

7.6 MOLECULAR STRUCTURE AND POLARITY

Example 7.16 – The Structure of a Multicenter Molecule

The Lewis structure for the amino acid glycine, $\text{H}_2\text{NCH}_2\text{CO}_2\text{H}$ is shown. Predict the local geometry of the atoms indicated.

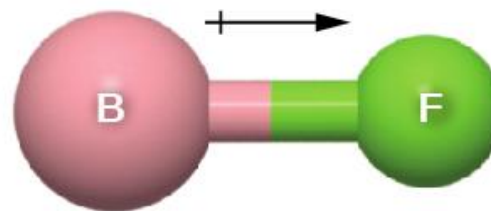
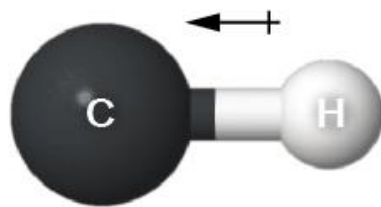


7.6 MOLECULAR STRUCTURE AND POLARITY

From Molecular Geometry to Polarity

- When two atoms of differing electronegativities are connected by a covalent bond, one atom has a partial positive charge ($\delta +$) and the other has a partial negative charge ($\delta -$).
- The separation of charge gives rise to a bond dipole moment.
- The dipole moment is represented as a vector, a quantity having both direction and magnitude, pointing from the partial positive charge to the partial negative charge.

A small difference in electronegativity for C vs. H is represented by a short vector.

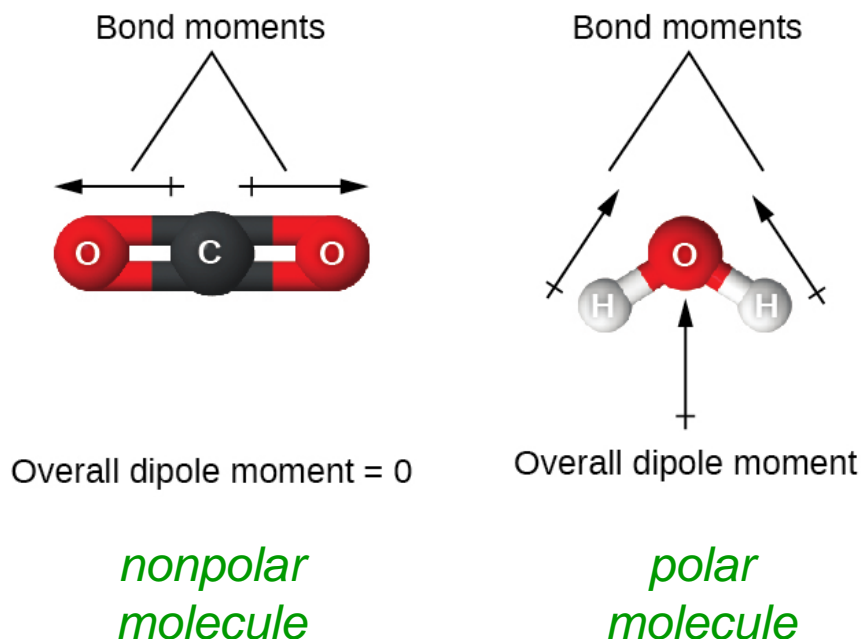


A larger difference in electronegativity between B and F is represented by a longer vector.

7.6 MOLECULAR STRUCTURE AND POLARITY

From Molecular Geometry to Polarity

- A molecule with an overall dipole moment is said to be polar.
- The vectors for each polar bond must be added to get the overall polarity of the molecule.
- *Why is it useful to know whether a molecule is polar or not?*



7.6 MOLECULAR STRUCTURE AND POLARITY

Example Structures

Determine the molecular geometry of each molecule. State whether the molecule is polar or not.



END OF CHAPTER PROBLEMS – CHAPTER 7

Lewis Structure and Formal Charges: #23, 29a-h, 51

Polarity and Bonds: #15, 17, 21, 97

VSEPR: #85, 91, 95

For detailed solutions to these problems, go to the OpenStax Chemistry website and download the [Student Solution Guide](#).

VIDEOS – CHAPTER 7

Lattice Energy

<http://screencast.com/t/3tODFuL7rZ>

Lewis Dot Structures for Individual Atoms

<http://screencast.com/t/j5dnOkm3D>

Drawing Lewis Dot Structures for Molecules

<http://youtu.be/Vio5mlzvYW8>

<http://screencast-o-matic.com/watch/cDfXfl1AoN>

Simple Resonance Structures

<http://screencast.com/t/yJikVInxjxU>

Assigning Formal Charges

<http://youtu.be/Xp3a6GJ8aUE>

VSEPR – General Shapes of Molecules

<http://screencast.com/t/nYK2Hzm9>

Drawing Orbital Overlap Diagrams (Sigma and Pi Bonds)

<http://screencast.com/t/XoxiDNDV7JMW>

**All videos were created by MC Chemistry faculty unless otherwise indicated.*

SIMULATIONS – CHAPTER 7

Molecule Polarity (Polarity, Electronegativity)

<https://phet.colorado.edu/en/simulation/legacy/molecule-polarity>