CHAPTER 6

Chemical Bonding and Molecular Geometry

Ionic Bonding

- A chemical bond is defined as the attractive force that hold two or more atoms together in a molecule or an ion.
- An ionic bond is a type of chemical bond that involves a metal and a non-metal ion (or polyatomic ions such as ammonium) through electrostatic attraction.
- It is a bond formed by the attraction between two oppositely charged ions (cations and an anions)
- It involves by complete transfer of electrons from one atom to another.
- Electrons are transferred to achieve noble gas configuration.

Properties of Ionic Compounds

1. Most are crystalline solids at room temperature.
2. High melting points.
3. Conduct electricity when melted or dissolved in water.



Formation of Ionic Compounds

❖Ionic compounds are formed by complete transfer of electrons from metals to non metals via strong electrostatic attraction between **cations** and **anions**

Electronic Structures of Cations and Anions

✓The stability of noble gases are a result of their electron configuration.

✓A filled valence shell results in stability.

✓Main-group elements either lose, gain, or share electrons in order to have a filled valence shell, making that element now isoelectronic with a noble

Electron Configuration of Main-Group Cations

- For all main group elements, the number of valence electrons is equal to the last digit of the group number.

- Main-group metals form cations by losing all of their valence electrons resulting in a filled valence shell.

  - **Exceptions**: Tl, Sn, Pb, Bi (post-transition metals)
    - Tl^{3+}, Sn^{4+}, Pb^{4+}, and Bi^{5+} do form
    - Tl^{+}, Sn^{2+}, Pb^{2+}, and Bi^{3+} also form

Electron Configuration of TMs and ITMs Cations

- Transition metals and Inner Transition metals behave differently than Main-Group metals.

- The cations formed by Transition Metals and Inner Transition Metals are typically NOT isoelectronic with a noble gas.

For example, iron ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$) forms the ion Fe^{2+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$) by the loss of the 4*s* electrons and the ion Fe^{3+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$) by the loss of the 4*s* electrons and one of the 3*d* electrons.

Electron Configuration of Anions

- Anions usually form when a non-metal atom gains enough electrons to have a filled valence shell.
- The charge of the anion is equal to the number of electrons gained by the atom.

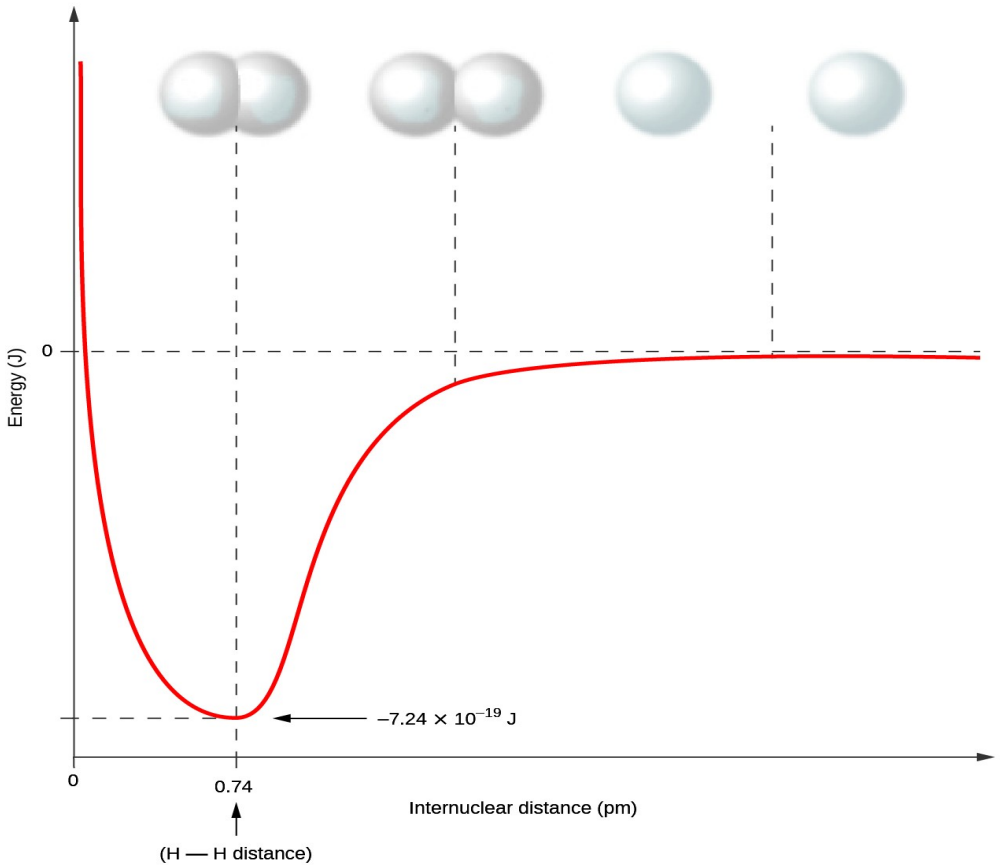
Example Write the electron configurations of the anions.

Covalent Bonding

➢ *Nonmetals tend to share electrons with each other forming covalent bonds.*

➢ Covalent bonds are formed between atoms that have similar abilities to attract electrons.

- **Consider the H_2 molecule**
  - H: $1s^1$
  - Each hydrogen contributes a 1s electron in forming a covalent bond.
  - Each H now has a first valence shell filled with 2 electrons, just like the noble gas, He.



- Formation of H_2 molecule.
- Distance of lowest potential energy is the bond length.

Figure 6.3: The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

Formation of Covalent Bonds

- To break chemical bonds, energy must be added (endothermic process).
- The formation of chemical bonds results in the release of energy (exothermic process).
  - The bond makes each atom more stable and therefore in a lo

$$H_2(g) \longrightarrow 2H(g) \quad \Delta H = 436kJ$$

Polarity of Covalent Bonds

- All covalent bonds involve the sharing of electrons. But the electrons are not always shared equally

$$2H(g) \longrightarrow H_2(g) \Delta H = -436kJ$$

Two types of covalent bonds

1)Pure Covalent bonds (Non-polar covalent bonds) – Equal sharing of electrons

2)Polar Covalent Bonds – Unequal sharing of electrons

❖These different types of covalent bonds arise from *electronegativity differences* amongst the bonded atoms.

➢*Electronegativity (EN)* is a measure of the tendency of an atom to attract electrons towards itself.

1)Pure Covalent Bonds: Pure Covalent bonds (Non-polar covalent bonds) – Equal sharing of electrons

➢Form when the atoms have the exact same or very similar electronegativity values.

- This occurs in all bonds when the atoms are the same (X-X)
- C-H bonds are a common pure covalent bond.

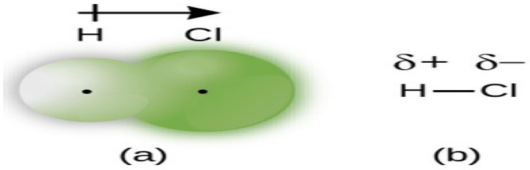
Example Cl_2, H_2, CH_4 etc

Polar Covalent Bonds

2) Polar Covalent Bonds – Unequal sharing of electrons

- Form when the atoms have significantly different EN values.
- Most covalent bonds involving different atoms (X-Y), are polar covalent bonds.
- The polarity of a bond increases with increasing EN difference between the bonded atoms.
- The polar bond is a dipole
  - Less EN atom is partially positive (δ^+), while the more EN atom is partially negative (δ^-).

Example HCl



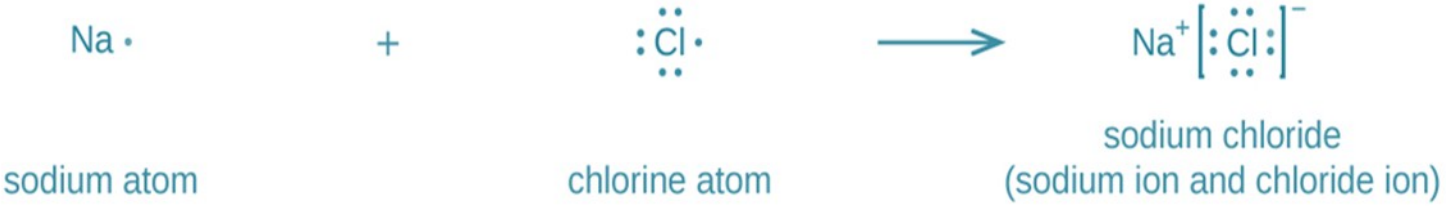
Lewis Symbols and Structures

- All bonds involve the sharing or transfer of *valence* electrons between atoms.
- Lewis Symbol – Consists of an elemental symbol surrounded by one dot for each of its valence elect

Exampl

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na ·
magnesium	$[Ne]3s^2$	· Mg ·
aluminum	$[Ne]3s^23p^1$	· Al ·
silicon	$[Ne]3s^23p^2$	· Si ·
phosphorus	$[Ne]3s^23p^3$	· P ·
sulfur	$[Ne]3s^23p^4$	: S ·
chlorine	$[Ne]3s^23p^5$	: Cl ·
argon	$[Ne]3s^23p^6$	: Ar :

Lewis Symbols of Ions



- Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.
- An ionic bond forms between Na^+ and Cl^- to form the ionic compound, NaCl.
- The valence electron from sodium is transferred to chlorine.

Lewis Structures

- Lewis Structures – Drawings that use Lewis Symbols to describe the bonding in molecules and polyatomic ions.

- We will work with compounds containing only main-group elements.

- Lewis structures show the arrangement of all valence electrons in a covalent compound.

- **In the Lewis structure of a molecule or polyatomic ion, valence electrons *ordinarily* occur in pairs.**

- A pair of shared electrons between two atoms is a covalent bond and is shown as a straight line connecting the atoms.

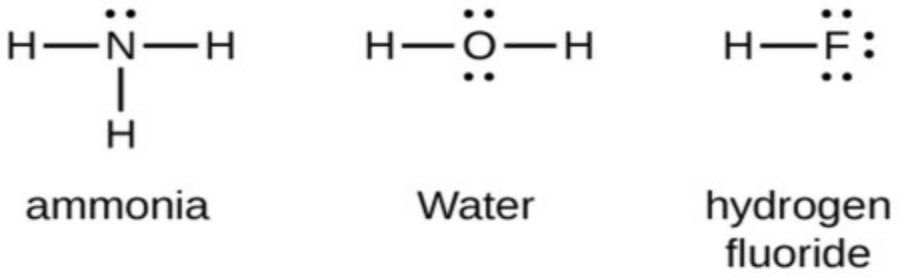
- An unshared pair, or lone pair of electrons, is shown as a pair of dots on an atom.

The Octet Rule

- *Noble gases, except for He, have 8 valence electrons.*

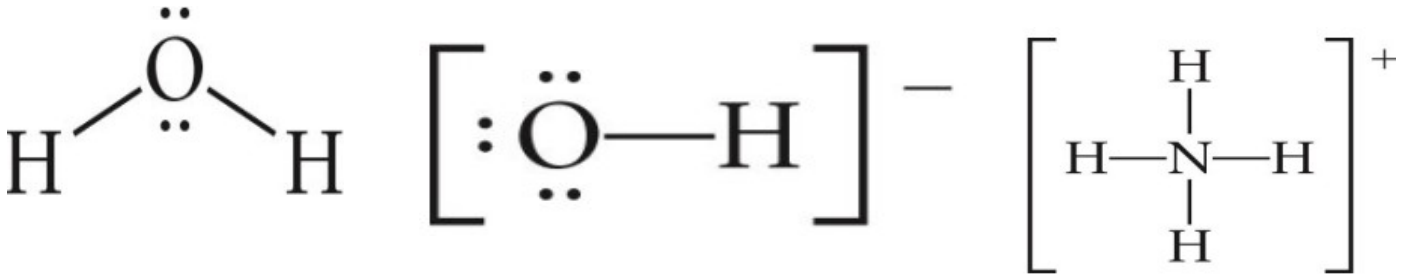
- *The Octet Rule* – Nonmetals, except for hydrogen, form molecules whereby sharing electrons allows them to be surrounded by eight valence electrons and therefore isoelectronic with a noble gas.

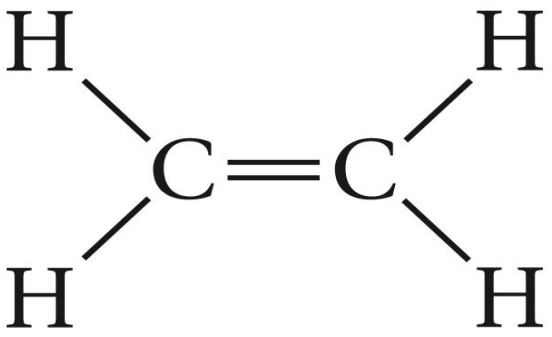
- Hydrogen is an octet rule exception, because it only needs two to have a filled valence she



Examples of Lewis Structures

H_2O, OH^-, NH_4^+ , C_2H_4, C_2H_2





ethylene, C_2H_4



acetylene, C_2H_2

Writing Lewis Structures

1) Determine the total number of valence electrons (VE).

- For cations, subtract one electron for each positive charge.
- For anions, add one electron for each negative charge.

2) Draw a skeleton structure of the molecule or ion, using single **bonds to attach terminal atoms to a central atom.**

- Generally, the least electronegative element should be the central atom.
- Many times there is only one central atom and it is written first in the formula.

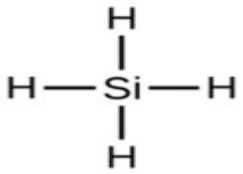
3) Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.

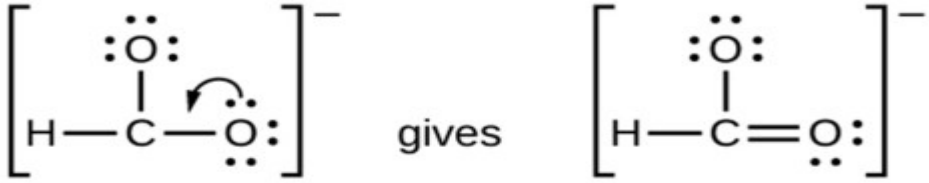
4) If any electrons remain then place on the central atom.

5) If an atom does not have an octet at this point, then rearrange the lone pairs on the terminal atoms to make multiple bonds with the central atom until an octet is obtained.

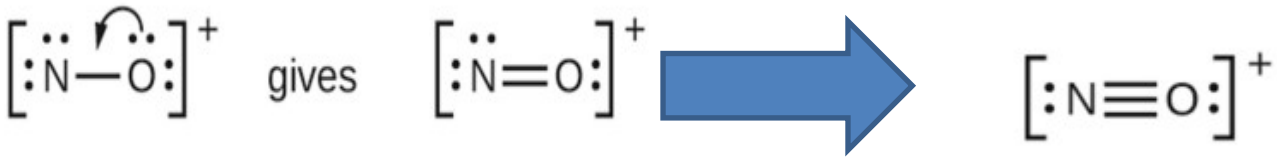
Example: Let us determine the Lewis structures of SiH_4, CHO_2^-, NO^+, OF_2 , CH_4, C_2H_2, NH_3 and HCN

1.





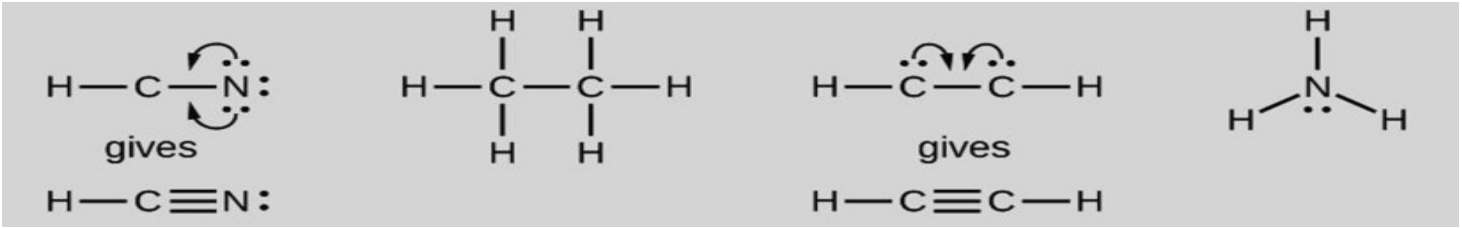
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4.

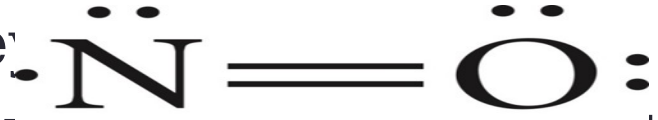


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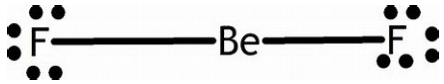
Exceptions to the Octet Rule

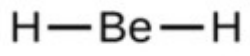
- Most molecules and polyatomic ions do follow the octet rule.
- There are some notable exceptions.
- Sometimes an atom in a Lewis structure will be surrounded by *less than 8 electrons – Electron deficient molecules.*
- ✓Sometimes an atom in a Lewis structure will be surrounded by *more than 8 electrons – Hypervalent molecules.*
  - Occasionally a molecule or ion contains an **odd number of valence electrons.**
    - **These species are known as free radicals.**
    - Impossible to write a Lewis structure with all atoms obe
  - Get each atom as close as possible to 8 electrons.
  - Example: NO

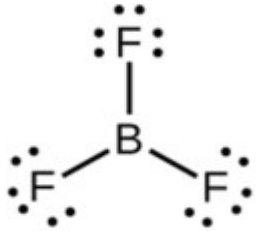


Electron Deficient Molecules

- Sometimes a central atom will violate the octet rule by only being surrounded by 4 or 6 electrons.
- This sometimes occurs in molecules where the central atom is from group 2 or 13, such as Be or B.
  - Examples: BeF_2, BeH_2, BH_3, BF_3







Hypervalent Molecules

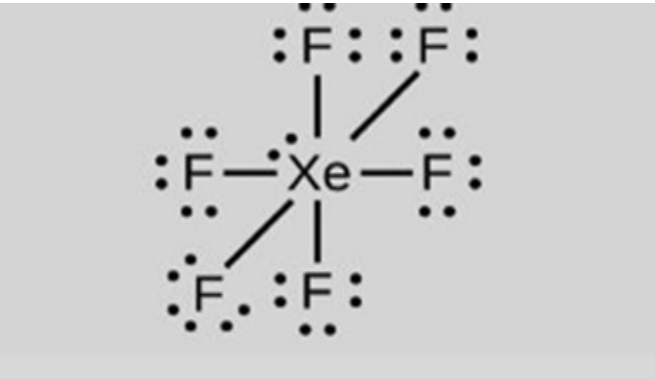
- Elements in the second period (n = 2) can only accommodate 8 electrons in their valence shell.

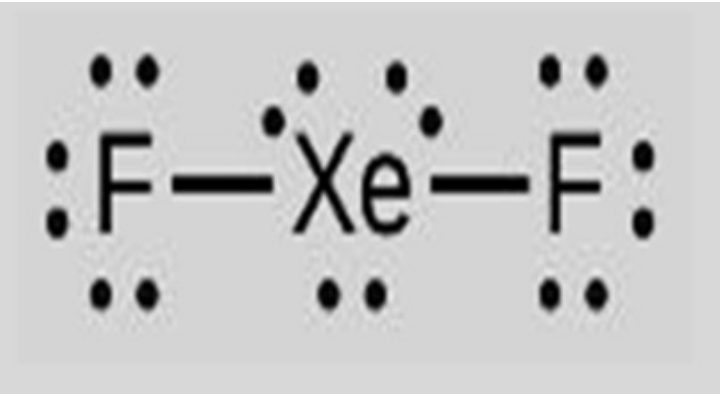
- Beginning with the third period (n = 3), the presence of empty d orbitals may allow central atoms to have *10 or 12 electrons.*

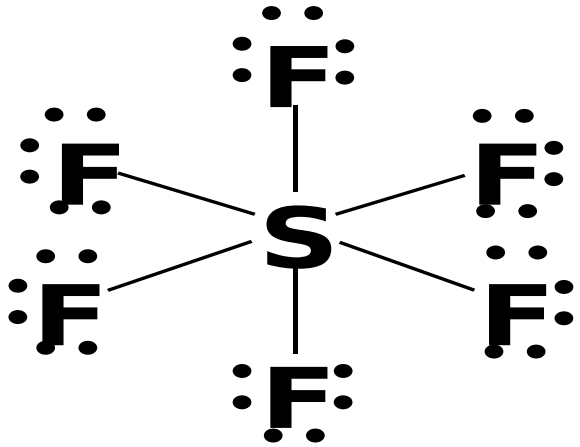
✓*Hypervalent Molecules* – Molecules with a central atom surrounded by more than 8 electrons.

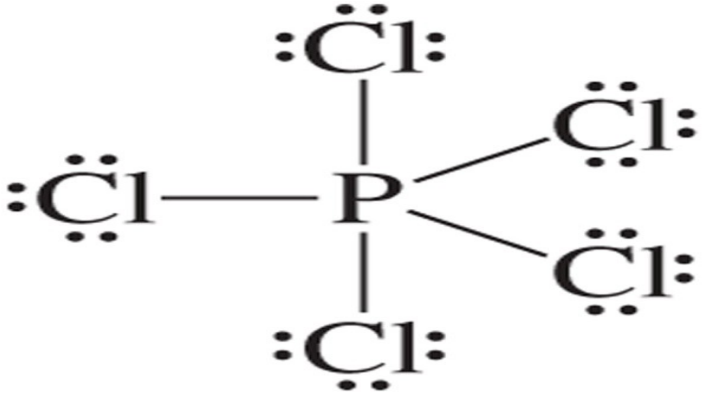
Examples: What are the Lewis structures of $XeF_{2,}$ XeF_6, SF_6 and PCl_5?

Examples of Hypervalent Molecules









Formal Charges and Resonance

- Sometimes there is more than one Lewis Structure that can be drawn from a given molecular formula.

- In these instances, the concept of formal charge can be used to help choose the most appropriate Lewis Structure.

- The Formal charge of an atom in a molecule is the hypothetical charge that the atom would have if electrons were shared equally.

- As with oxidation numbers:

  - Formal charges are NOT actual charges
  - Formal Charges help track electron ownership

Formal Charge (FC)

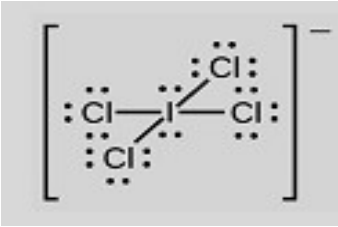
- Each atom in a Lewis structure can be assigned a formal charge.

FC = # VE – # nonbonding electrons – ½ (# bonding electrons)

- The sum of the formal charges must equal the charge of the entire species.
  - Zero for a molecule
  - For a polyatomic ions, the charge of the ion
  - This rule can be used to check your Lewis Structure.

Examples

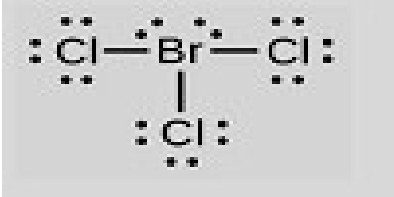
1.Assign formal charges to each atom in the interhalogen ion ICl_4^-.



FC for I = 7-4-4=-1, for Cl FC = 7-6-1 = 0

- The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).

2)Assign formal charges to each atom in the interhalogen molecule $BrCl_3$.



FC of Br = 7-4-3 = 0

FC of Cl = 7-6-1 = 0

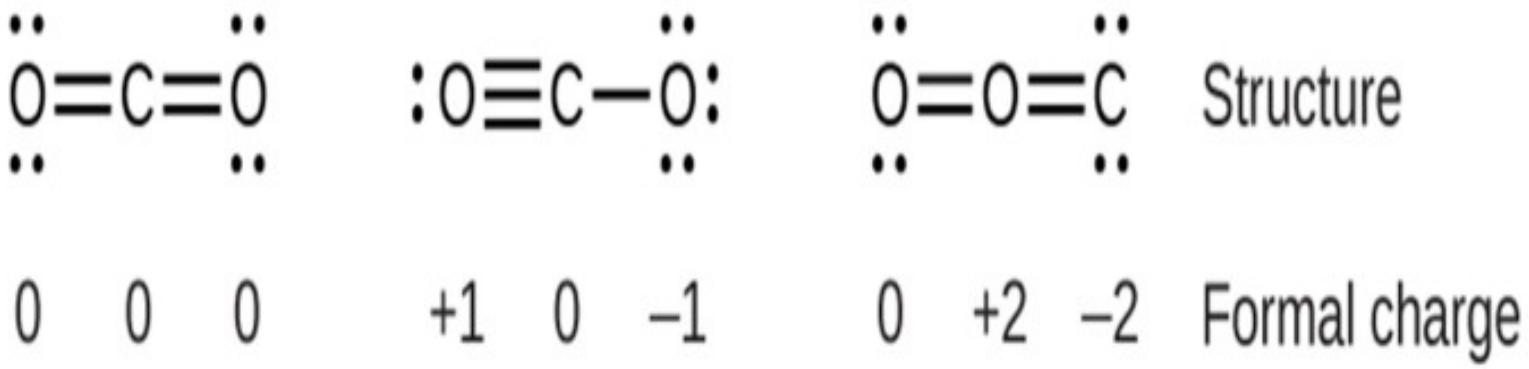
- All atoms in BrCl3 have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

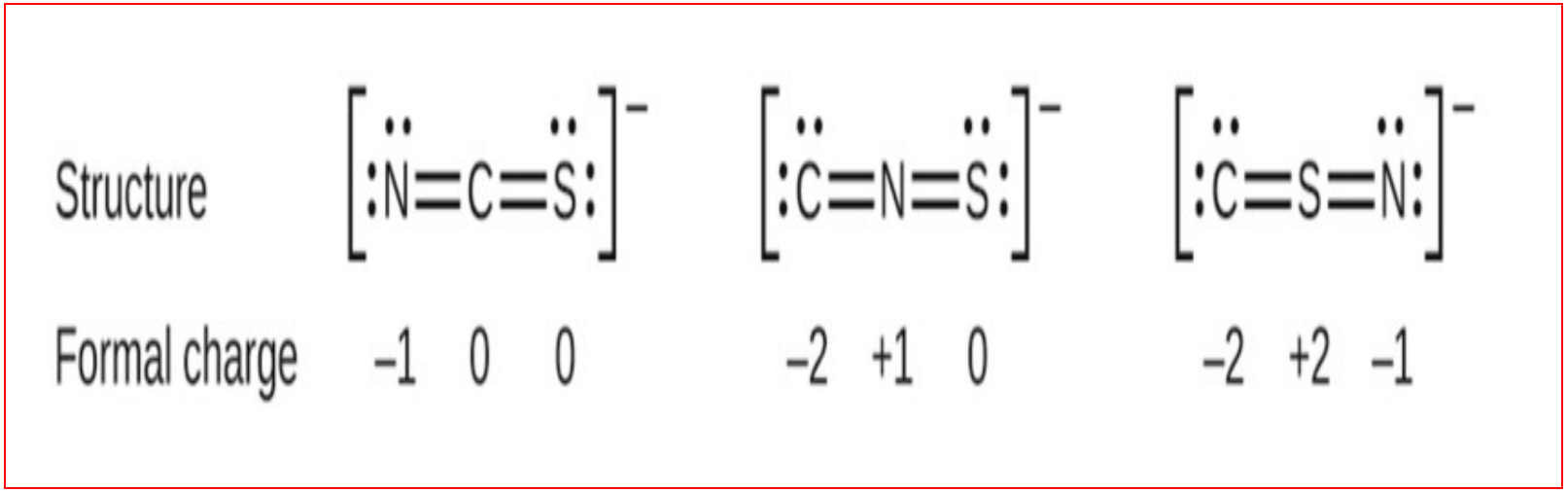
Predicting molecular structure using formal charge

- The most likely Lewis Structure will have
  1) Formal charges as close to zero as possible.
  2) Adjacent formal charges of zero or of the opposite sign.
  3) If there must be an atom with a negative formal charge, then it is assigned to the most electronegative atom in the structure.

- There are some exceptions to the octet rule.
- On rare occasion, the correct Lewis structure does not obey the octet rule.
- Formal charge can be used to help predict these instances.

Examples CO_2 and for NCS^-, CNS^-, or CSN^-.





Resonance Forms

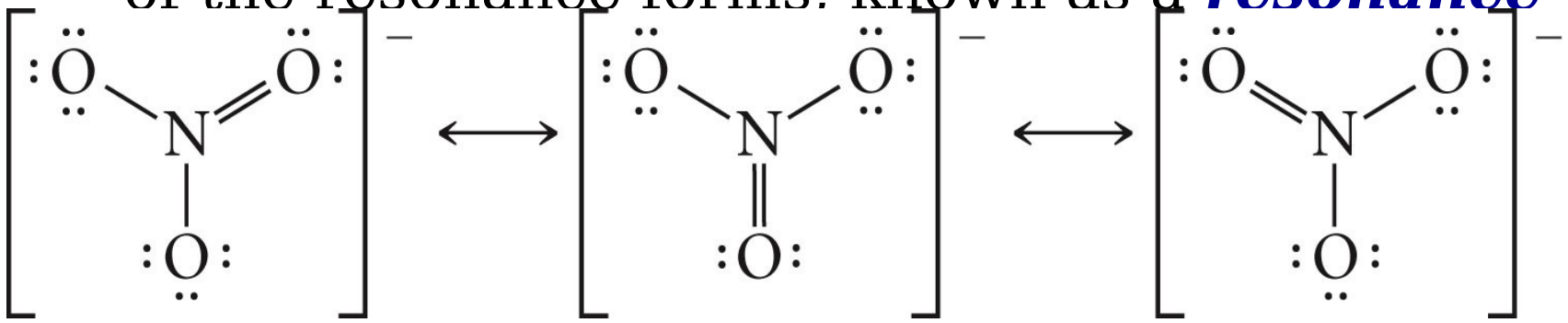
- In certain cases, a single Lewis structure does not adequately predict the properties of a molecule or ion.
- For these compounds, two or more Lewis structures can be drawn. These individual Lewis structures are called *Resonance forms.*
- *Individual resonance forms do not exist!*
- *Resonance* – If two or more Lewis Structures with the same arrangement of atoms can be drawn for a molecule or ion, then the actual distribution of electrons is an average of that shown by the various structures.

– Consider SO_2 and its resonance forms.



– Both S-O bonds are identical in all properties, as determined by experiment.

– The actual structure of the molecule is an average of the resonance forms. known as a ***resonance***



•All three N-O bonds are identical in properties.

•These bonds are intermediate in length between a single and a double bond.

Exercise:- Draw the resonance structure of NO_2^-, SO_3 and CO_3^{2-}

Notes on Resonance Hybrid Molecules

1)A resonance hybrid never posses a structure described by either resonance form.

2)A resonance hybrid does NOT fluctuate between the different resonance forms. Electrons are NOT shifting between the different structures.

3)Resonance arises when two Lewis structures are equally plausible.

4)Resonance forms only differ in the distribution of electrons. Not in the arrangement of atoms.

Strengths of ionic and covalent bonds

- Bond strength- describes how strongly each atom is joined to another atom.
- It shows How much energy is required to break the bond between the two atoms.

Ionic bond strength and lattice energy: An ionic compound is stable.

- Due to electrostatic attraction between its positive and negative ions.
- The lattice energy of a compound is a measure of the strength of this attraction.
- The lattice energy ($\Delta H_{lattice}$) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions.

- ✓ For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$MX(s) \longrightarrow Mn+(g) + Xn-(g) \quad \Delta H_{lattice}$$

$\Delta H_{lattice}$

- ✓ Positive for endothermic process
- ✓ Negative for exothermic process

EXAMPLES

- ✓ $Na(S) + Cl_2(g) \rightarrow 2NaCl(s)$, $\Delta H = -769kJ$
- ✓ $NaCl(s) \rightarrow Na+ + Cl-$, $\Delta H = +769kJ$

- ➢ The lattice energy of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

- In which C is a constant that depends on the type of crystal structure; Z^+ and Z^- are the charges on the ions; and Ro is the interionic distance (the sum of the radii of the positive and negative ions)

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

1) The lattice energy of LiF (Z^+ and Z^- = 1) is 1023 kJ/mol, whereas that of MgO (Z^+ and Z^- = 2) is 3900 kJ/mol (Ro is nearly the same-about 200 pm for both compounds).

2) Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF_2 (2957 kJ/mol) to that of MgI_2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F^- as compared to I^-.

3) The precious gem ruby is aluminum oxide, Al_2O_3, containing traces of Al^{3+}. The compound Al_2Se_3 is used in the fabrication of some semiconductor devices. Which has the larger lattice energy, Al_2O_3 or Al_2Se_3?

Solution

In these two ionic compounds, the charges Z^+ and Z^- are the same, so the difference in lattice energy will depend upon Ro. The O^{2-} ion is smaller than the Se^{2-} ion. Thus, Al_2O_3 would have a shorter interionic distance than Al_2Se_3, and Al_2O_3 would have the larger lattice energy.

The Born-Haber Cycle

➢The Born-Haber cycle is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- ΔH_f^0, the standard enthalpy of formation of the compound
- IE, the ionization energy of the metal
- EA, the electron affinity of the nonmetal
- ΔH_s^0, the enthalpy of sublimation of the metal
- D, the bond dissociation energy of the nonmetal
- $\Delta H_{lattice}$, the lattice energy of the compound

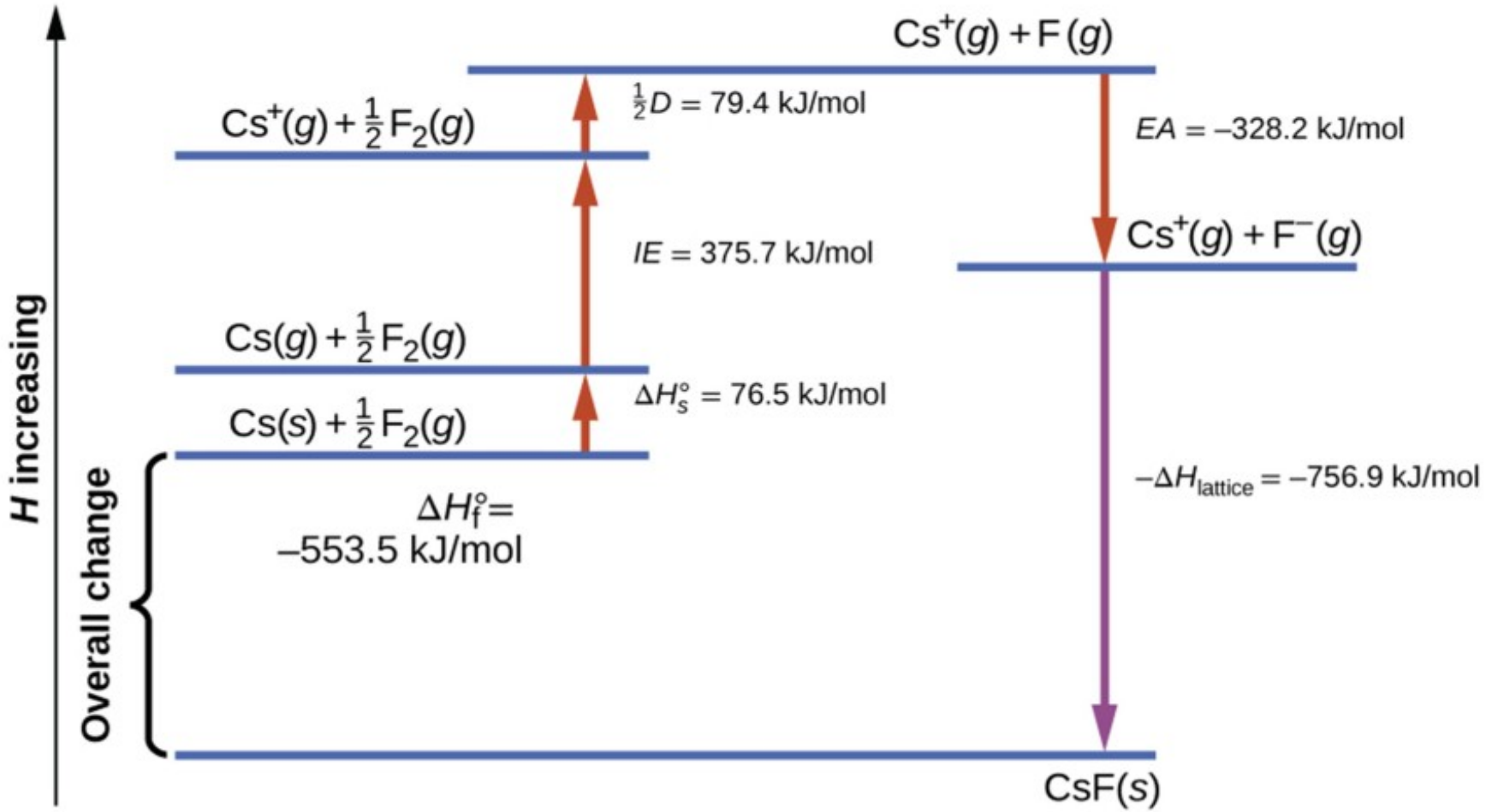


Figure 6.5: The Born-Haber cycle shows the relative energies of each step involved in the formation of solid cesium fluoride from the necessary elements in their reference states

Relationship between the enthalpies of the individual steps and the enthalpy of formation of CsF

Enthalpy of sublimation of Cs(s)	$Cs(s) \longrightarrow Cs(g)$	$\Delta H1=\Delta H^{\circ}s=76.5kJ/mol$
One-half of the bond energy of F_2	$1/2F_2(g) \longrightarrow F(g)$	$\Delta H2=1/2D=79.4kJ/mol$
Ionization energy of Cs(g)	$Cs(g) \longrightarrow Cs^{+}(g) + e^{-}$	$\Delta H3=IE=375.7kJ/mol$
Negative of the electron affinity of F	$F(g) + e^{-} \longrightarrow F^{-}(g)$	$\Delta H4 = -EA = -328.2kJ/mol$
Negative of the lattice energy of CsF(s)	$Cs^{+}(g)+F^{-}(g) \longrightarrow CsF(s)$	$\Delta H_5 = -\Delta H_{lattice} = ?$
Enthalpy of formation of CsF(s)	$\Delta H = \Delta H^{\circ}f = \Delta H^{\circ}s + \frac{1}{2} D + IE + (-EA) + (-\Delta H_{lattice}) + 1/2F_2(g) \longrightarrow CsF(s)$	$\Delta H_f=\Delta H_1+\Delta H_2+\Delta H_3+\Delta H_4+\Delta H_5$ mol

$\Delta H_{lattice}$ = $76.5+375.7+79.4+(-328.2)-(-553.5k)=756.9kJ/mol$

Bond strength of covalent bond

- The energy required to break a specific covalent bond in one mole of gaseous molecules is called the bond energy or the bond dissociation energy.

Example

$XY(g) \rightarrow X(g) + Y(g)$, $D_{X\text{-}Y} = +\Delta H^0$

$H2(g) \rightarrow 2H(g)$, $D_{H\text{-}H} = +436kJ$

- The enthalpy change, ΔH, for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy “in”, positive sign) plus the energy released when all bonds are formed in the products (energy “out,” negative sign).

$$\Delta H = \Sigma D_{bonds\ broken} - \Sigma D_{bonds\ formed}$$

Example

Consider the following reaction:

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g \quad or$$

$$H-H(g) + Cl-Cl(g) \longrightarrow 2H-Cl(g$$

$$\Delta H = [(D_{H\text{-}H} + D_{Cl\text{-}Cl}) - 2D_{H\text{-}Cl}]$$

$$= [(436 + 243) - 2(432)]kJ/mol$$

$$=(678\text{-}864)kJ/mol$$

$$= -185kJ/mol$$

Table 6.2: Bond Energies (kJ/mol)

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≡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

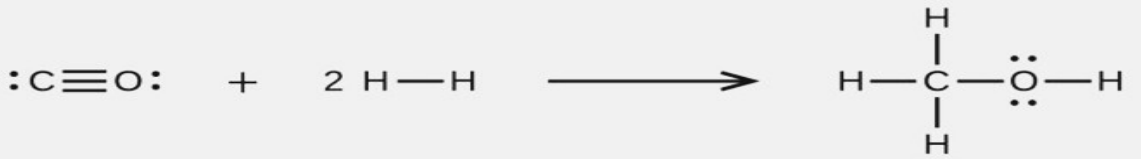
Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
C=C	611	O–O	140	P–I	215
C≡C	837	O=O	498	S–S	215
C–N	290	O–F	160	S–Cl	250
C=N	615	O–Si	370	S–Br	215
C≡N	891	O–P	350	Cl–Cl	243
C–O	350	O–Cl	205	Cl–Br	220
C=O	741	O–I	200	Cl–I	210
C≡O	1080	F–F	160	Br–Br	190
C–F	439	F–Si	540	Br–I	180
C–Si	360	F–P	489	I–I	150
C–P	265	F–S	285		

Example: Calculate the approximate enthalpy change, ΔH, for the reaction:

$$CO_2(g) + 2H_2(g) \rightarrow CH_3OH(g)$$

Lewis structure

Solution



$$\Delta H = \Sigma D_{bonds\ broken} - \Sigma D_{bonds\ formed}$$

$$[DC \equiv O + 2(DH - H)] - [3(DC - H) + DC - O + DO - H]$$

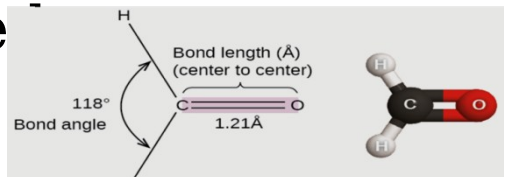
$$\Delta H = [1080 + 2(436)] - [3(415) + 350 + 464] = -107kJ$$

Ex. calculate an approximate enthalpy change, ΔH, for the following reaction. $C_2H_4 + H_2O \rightarrow CH_3CH_2OH$

Molecular Structure and Polarity

- Diatomic molecules have the easiest geometry to visualize.
- Diatomic molecules are *linear*
  - ***Examples: HCl and Cl_2***
- The molecular geometry of molecules containing three or more atoms is not always so obvious.
- Many geometries are 3-Dimensional.

Bond Distance (or Bond Length)-The distance between the nuclei of two bonde



Ångstroms ($1\ Å = 10^{-10}$ m) or picometers ($1\ pm = 10^{-12}$ m, $100\ pm = 1\ Å$).

Figure 6.6: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

Valence Shell Electron Pair Repulsion Theory (VSEPR)

- The molecular geometry of a molecule, including bond angles, is based on electron pair repulsion.
- *VSEPR Model* – The valence electron pairs surrounding an atom repel one another.
- Consequently, the orbitals containing those electron pairs become oriented so that they are as far apart from each other as possible.

Ideal Electron Pair Geometries

- Consider a central atom, A, surrounded by a certain number of electron pairs (bonded or lone pair), represented as different balloons.
- Like balloons tied at their ends, the electron pairs want to be situated as far from each other as possible.

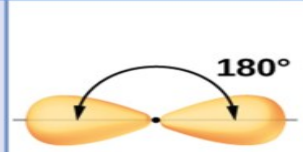
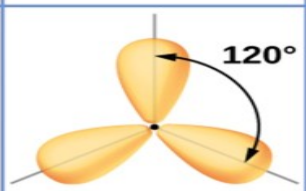
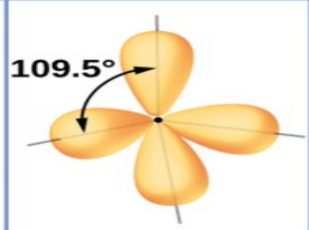
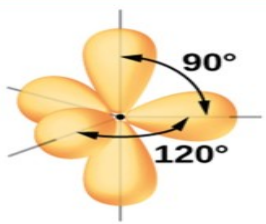
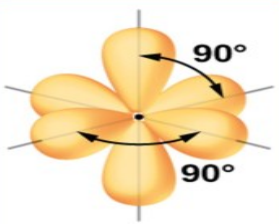
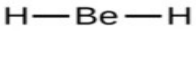
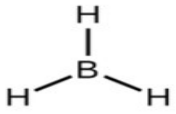
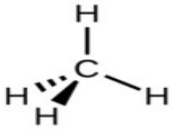
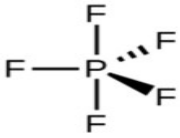
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 6.8: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Two Types of Geometries

- *We will focus primarily on the geometry that results about the central atom.*

1)Electron Pair Geometry – describes the placement of *all* electron pairs (bonded *and* unshared).

2)Molecular Structure – describes only the placement of the atoms in the molecule.

- *Molecules with the central atom has no lone pairs and therefore the electron pair geometry and molecular structure are the same,* but they will be different when there are lone pairs present on the central atom.

Example CH_4 has no lone pairs and NH_3 has lone pair electron

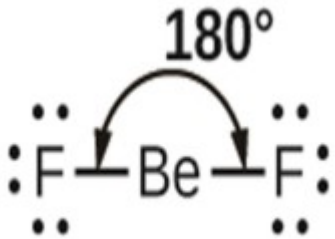
The A-X-E Notation

- A denotes a central atom
- X denotes a terminal atom
- E denotes a lone pair

Two bonded electron pairs around “A”

AX_2

- *Molecular Structure = Linear*
- *180° bond angle*
- *Central atom is electron deficient*
- *Example: BeF_2*



Three bonded electron pairs around “A”

AX_3

- Molecular Structure = Trigonal Planar
- X atoms are directed to the corners of an equilateral triangle.
- 120° bond angles
- Central atom is electron deficient

Example: BF_3

Four bonded electron pairs around “A”

AX_4

- *Molecular Structure = Tetrahedral*
- *X atoms are directed to the corners of a tetrahedron.*
- *109.5° bond angles*
- *Central atom has an octet.*
- *Example: CH_4*

Five bonded electron pairs around “A”

AX_5

- *Molecular Structure = Trigonal bipyramid*
- *Two triangular pyramids fused together base to base.*
- *Bond Angles: 90°, 120°*
- *Molecule is hypervalent*

Example: PF_5

Six bonded electron pairs around “A”

AX_6

- *Molecular Structure = Octahedral*
- *Two square pyramids fused together base to base.*
- *Bond Angles: 90°*
- *Molecule is hypervalent*
- *Example: SF_6*

Molecular Structure for when Central Atom has Lone Pairs

- When the central atom has lone pairs, the electron pair geometry and molecular structure are different.
- Lone pairs cause deviations from the ideal bond angles.

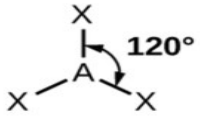
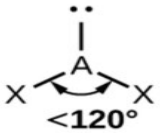
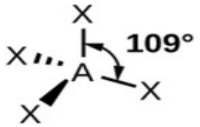
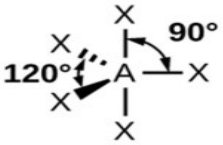
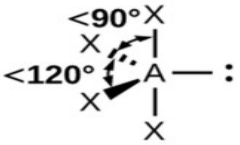
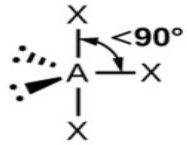
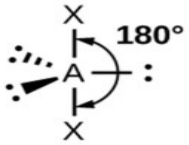
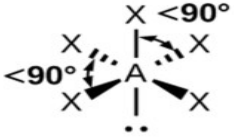
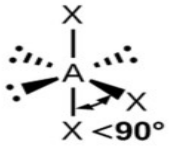
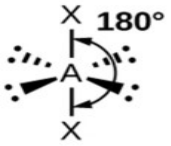
Order of electron pair repulsion:

Lone pair-lone pair>lone pair-bonding pair>bonding pair-bonding pair

Why are there Ideal Bond Angle Deviations?

- Lone pairs take up a larger region of space on the central atom.
- There is only one nucleus attracted to a lone pair so these electrons are able to spread out over a larger area of space.
- As a result, lone pair(s) takes up a larger volume and push the bonded pairs closer together, decreasing the bond angle(s).

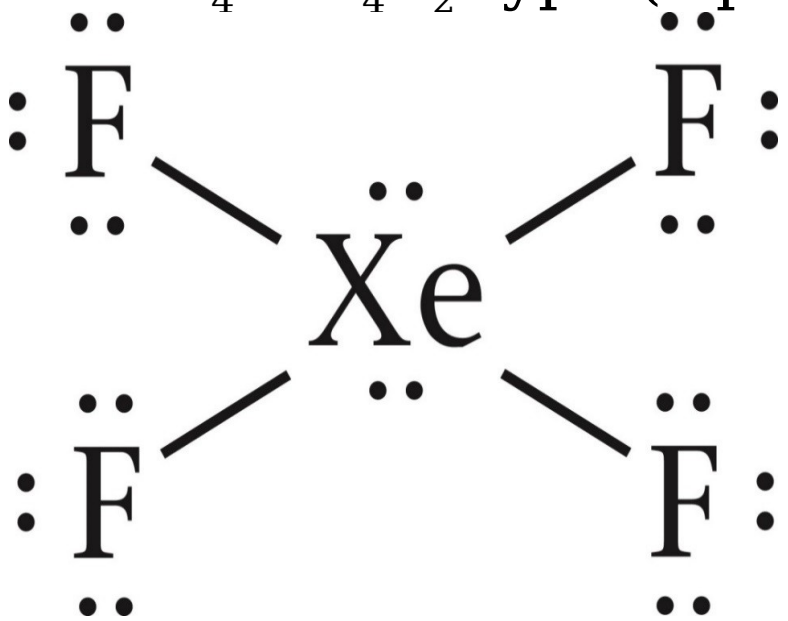
Examples: H_2CO (121^0 fro double bond and 118^0 for single bonds), (NH_3, 109.5^0 between single bonds) (H_2O, $<<109^0$)

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

Lone Pairs and Hypervalent Molecules

- In many hypervalent molecules, lone pairs are on the central atom.

Example: XeF_4 AX_4E_2 type (square planar)



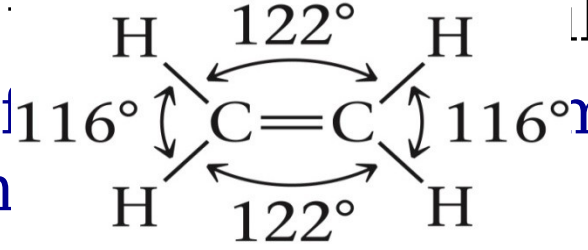
Multi Bonds and Geometry

- Multi bonds also cause deviations from ideal bond angles.
- Double and triple bonds occupy more space than a single bond.

Region of space occupied:

lone pair > [illegible] ble bond > single bond

Geometry of [illegible] nulti bonds and multiple center atom



Geometry of m $H-C\equiv C-H$ d without a single central atom

How to Determine Structure with VSEPR Theory

1)Draw Lewis Structure

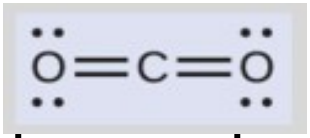
2)Count the number of regions of electron density (lone pairs and bonds) around the central atom.

- A lone pair, single bond, double bond, and triple bond all count as one region.

3)Identify the electron-pair geometry

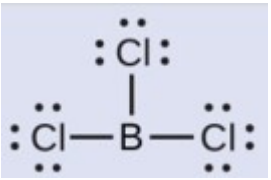
4)Determine the molecular structure. Recognize where possible deviations from ideal bond angles exist.

Example: predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3

a)Lewis structure of CO_2 

The electron-pair geometry and molecular structure are identical, and CO2 molecules are linear.

b) We write the Lewis structure of BCl_3 as:



- The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar.
- Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Molecular Polarity and Dipole Moment

- Recall, that polar bonds are dipoles.
- The separation of charge results in a bond dipole moment (m)

$$\mu = Qr$$

Q = magnitude of partial charges

r = bond distance

Bond Dipole Moment

➢The dipole moment (m) can be represented as a vector, having both direction and magnitude.



(a) There is a small difference in electronegativity between C and H, represented as a short vector.

(b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

Molecular Polarity and Dipole Moment

- If a molecule has a molecular dipole moment, then it is considered polar.
- A polar *molecule* contains a positive pole and a negative pole.
  - One end of the molecule has a partial positive charge (δ^+) - positive pole.
  - The other end of the molecule has a partial negative charge (δ^-) - negative pole.
- There are no positive or negative poles in a nonpolar molecule.

Deciding if a Molecule is Polar or Non-polar

- For diatomic molecules it is simple.
  - If the bond is polar then the molecule is polar.
  - If the bond is non-polar then the molecule is non-polar
- For molecules with three or more atoms it is not so simple. Two conditions must be satisfied in order for a molecule to be considered polar.

1)The molecule must have at least one polar bond.

2)The molecule must have an overall dipole moment.

Molecular Dipoles

- If both those criteria are NOT met then the molecule is non-polar.
- We have to consider molecular geometry when determining if a molecule has an overall dipole moment.
- Sometimes bond dipoles will cancel each other out, making the molecule non-polar.
- If the polar A-X bonds in a molecule of type AX_mE_n are arranged symmetrically around the central atom A, the molecule is nonpolar.

Properties of non-Polar and polar Molecules

- Polar molecules in an electric field the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate.
- Electrically charged object to attract polar molecules, but nonpolar molecules are not attracted.
- polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.


THE END