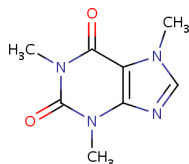
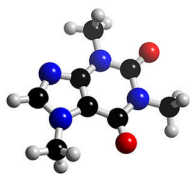


Bonding and Molecular Structure: Fundamental Concepts



Valence Electrons

Electrons in an atom are divided into two groups: Valence (involved in reactions) and Core

Main Group Elements (A groups): Valence electrons = Outer s and p electrons

The number of valence electrons = group number

Transition Elements: Valence electrons = ns and (n-1)d orbitals (for highest n number in the atom)

Lewis Electron Dot Symbols: Represent the valence electrons in an atom

Useful for examining bonding

Table 9.2 Lewis Dot Symbols for Main Group Atoms

1A ns^1	2A ns^2	3A ns^2np^1	4A ns^2np^2	5A ns^2np^3	6A ns^2np^4	7A ns^2np^5	8A ns^2np^6
Li·	·Be·	·B·	·C·	·N·	·O·	·F·	·Ne:
Na·	·Mg·	·Al·	·Si·	·P·	·S·	·Cl·	·Ar:

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Four pairs of electrons around the atomic symbol constitute an octet (8 valence electrons = filled s and p orbitals)

Stable configuration associated with noble gases (He has 2 electrons due to no 1p sublevel)

Chemical Bond Formation Ionic and Covalent

Ionic:

When one or more valence electrons are transferred from one atom to another creating positive and negative ions to form noble gas configuration.

The formation of an ionic compound can be broken down into a multi-step process involving some or all of the following:

- ΔH_f° of the ionic substance
- Enthalpy of sublimation (solid to gas) (from enthalpy of formation)
- Dissociation of molecules into atoms (bond dissociation energy) (from enthalpy of formation)
- Ionization of atoms to cations (ionization energy)
- Ionization of atoms to anions (electron affinity)
- Assembly of ions into a crystal (lattice energy)

Can you identify which processes are endothermic and which are exothermic?

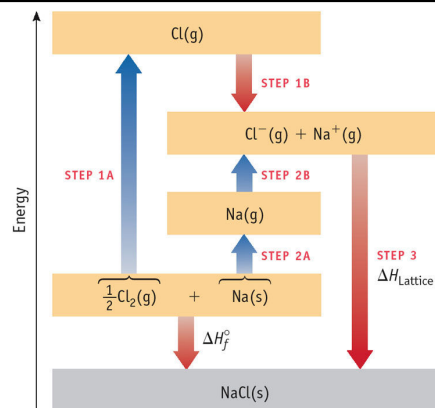
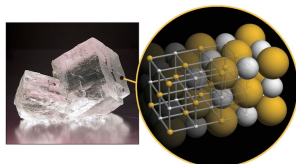
The energy associated with the formation of the ion pair is given by $(X^+_{(g)} + Y^-_{(g)} \rightarrow XY_{(g)})$

$$E_{\text{ion pair}} = C(N)[(n^+e)(n^-e) / d] \text{ (in kJ/mol)}$$

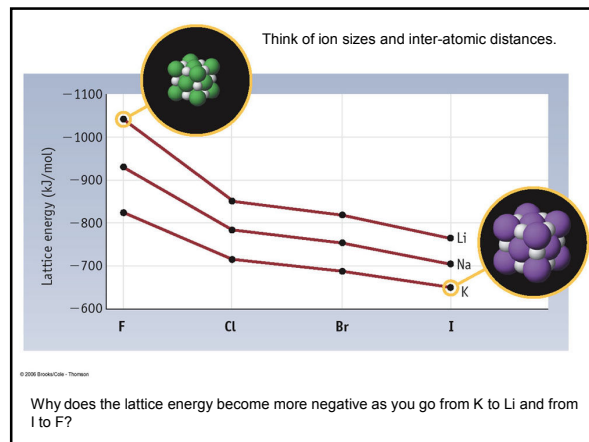
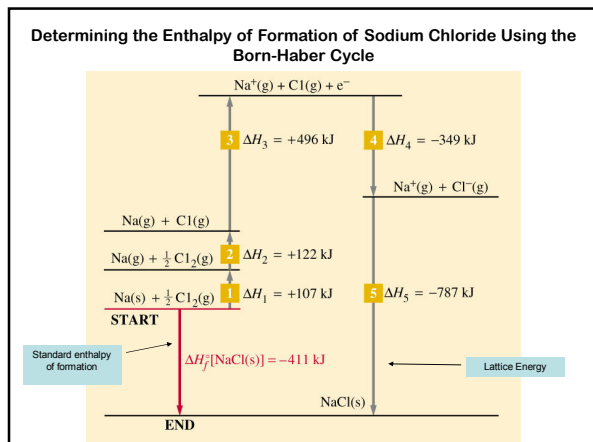
Where n is the number of positive and negative charges on an ion, e is the charge on an electron, C is a constant, d is the distance between the ion centers and N is Avogadro's number.

When the number of ions surrounding other ions in the crystal are taken into account and the fact that ionic crystals typically exist as solids, the *lattice energy* of the ionic compound can be determined.

For NaCl the ion pair energy is -498kJ/mol and the lattice energy is -787kJ/mol



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The steps of the Born-Haber cycle can be used to make predictions as to why compounds such as NaCl₂ and NaNe do not exist.

If the overall process isn't exothermic (negative enthalpy), the reaction is not likely to happen.

Example: Calculate the molar enthalpy of formation, ΔH_f° , of solid sodium iodide using the Born-Haber cycle. The required data can be found in Appendices F (A-19) and L (A-27) and in Table 9.3 (page 379)

Answer:

ΔH_f° for Na_(g) = +107.3kJ/mol (From solid sodium)
 ΔH_f° for I_(g) = +106.8kJ/mol (From solid iodine)
 ΔH° [for Na_(g) → Na⁺_(g) + e⁻] = +496kJ/mol (First ionization energy)
 ΔH° [for I_(g) + e⁻ → I_(g)⁻] = -295.2kJ/mol (Electron affinity)
 ΔH° [for Na⁺_(g) + I_(g)⁻] = -702kJ/mol (Lattice energy) (From table 9.3)
 The sum of these values $\Delta H_f^\circ[\text{NaI}(s)] = -287\text{kJ/mol}$

Example:

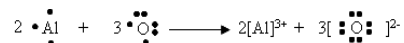
Use the following data to determine the lattice energy of MgF_{2(s)}: enthalpy of sublimation of magnesium, +146kJ/mol; IE₁ for Mg, +738kJ/mol; IE₂ for Mg, +1451kJ/mol; bond-dissociation energy of F_{2(g)}, +159kJ/mol F₂; electron affinity of F, -328kJ/mol F; enthalpy of formation of MgF_{2(s)}, -1124kJ/mol

Answer: -2962kJ/mol MgF_{2(s)}

Showing the Formation of an Ionic Compound Using Lewis Dot Structures

Example:

Show the formation of Aluminum oxide from its elements using Lewis Dot notation.



Covalent Bonding

In covalent bonding, electrons are shared to produce octets around the bonding atoms.

Bonds in which the shared electrons come from the same atom are known as *coordinate covalent bonds*.

Up to three pairs of electrons can be shared between atoms depending on the circumstances.



Using Lewis Dot Structures to Represent Molecular Bonding

Table 9.4 Common Hydrogen-Containing Compounds and Ions of the Second-Period Elements

Group 4A	Group 5A	Group 6A	Group 7A
CH ₄ methane $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	NH ₃ ammonia $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}-\text{H} \\ \\ \text{H} \end{array}$	H ₂ O water $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O}-\text{H} \\ \\ \text{H} \end{array}$	HF hydrogen fluoride $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{F} \\ \\ \text{H} \end{array}$
C ₂ H ₆ ethane $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	N ₂ H ₄ hydrazine $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{N}-\text{N}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	H ₂ O ₂ hydrogen peroxide $\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\ \quad \quad \\ \text{H}-\text{O}-\text{O}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	
C ₂ H ₄ ethylene $\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}=\text{C}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	NH ₄ ⁺ ammonium ion $\left[\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}-\text{H} \\ \\ \text{H} \end{array} \right]^+$	H ₃ O ⁺ hydronium ion $\left[\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O}-\text{H} \\ \\ \text{H} \end{array} \right]^+$	
C ₂ H ₂ acetylene $\text{H}-\text{C}\equiv\text{C}-\text{H}$	NH ₂ ⁻ amide ion $\left[\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}-\text{H} \\ \\ \text{H} \end{array} \right]^-$	OH ⁻ hydroxide ion $\left[\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O}-\text{H} \\ \\ \text{H} \end{array} \right]^-$	

Note:

Sometimes a line is used between atoms to represent a pair of electrons.

Outline for Predicting Lewis Structures

- Determine how many valence electrons you have available
 - Determine the most likely arrangement of the atoms in the molecule
 - Least electronegative (incr. →↑) atom is usually in the center
 - Hydrogen only makes one bond
 - Look for symmetry of the molecule
 - Fill in the octets of the atoms surrounding the central atom (or duet for hydrogen) by placing the dots in pairs around them.
 - Place any leftover pairs on the central atom (if there is only one electron left over it creates a "free radical")
- or
- If there is an incomplete octet on the central atom, consider multiple bonds.
 - Remember: The LDS does not tell you anything directly about the geometry of the molecule. This has to be determined by other methods.

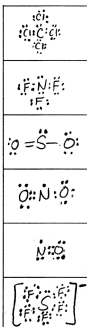
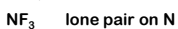
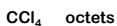
Examples

Draw Lewis Structures for the following compounds.



Examples

Draw Lewis Structures for the following compounds.



Note that only elements in the 3rd period and higher can have expanded valences, n = 1 and 2 do not have d-sublevels.

Oxoacids and Their Anions

Table 9.5 Lewis Structures of Common Oxoacids and Their Anions

HNO ₃ nitric acid $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O}-\text{N}=\text{O} \\ \\ \text{O} \end{array}$	H ₃ PO ₄ phosphoric acid $\begin{array}{c} \text{O} \\ \\ \text{H}-\text{P}-\text{O}-\text{H} \\ \quad \\ \text{O} \quad \text{O} \end{array}$	H ₂ SO ₄ sulfuric acid $\begin{array}{c} \text{O} \quad \text{H} \\ \quad \\ \text{O}-\text{S}-\text{O} \\ \quad \\ \text{O} \quad \text{H} \end{array}$
NO ₂ ⁻ nitrate ion $\left[\begin{array}{c} \text{O} \\ \\ \text{O}-\text{N}=\text{O} \\ \\ \text{O} \end{array} \right]^-$	PO ₄ ³⁻ phosphate ion $\left[\begin{array}{c} \text{O} \\ \\ \text{O}-\text{P}-\text{O} \\ \quad \\ \text{O} \quad \text{O} \end{array} \right]^{3-}$	HSO ₄ ⁻ hydrogen sulfate ion $\left[\begin{array}{c} \text{O} \quad \text{H} \\ \quad \\ \text{O}-\text{S}-\text{O} \\ \quad \\ \text{O} \quad \text{O} \end{array} \right]^-$
HClO ₄ perchloric acid $\begin{array}{c} \text{O} \\ \\ \text{H}-\text{Cl}-\text{O} \\ \\ \text{O} \end{array}$	HOCl hypochlorous acid $\begin{array}{c} \text{H} \\ \\ \text{H}-\text{O}-\text{Cl} \\ \\ \text{O} \end{array}$	SO ₄ ²⁻ sulfate ion $\left[\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{O}-\text{S}-\text{O} \\ \quad \\ \text{O} \quad \text{O} \end{array} \right]^{2-}$
ClO ₄ ⁻ perchlorate ion $\left[\begin{array}{c} \text{O} \\ \\ \text{O}-\text{Cl}-\text{O} \\ \\ \text{O} \end{array} \right]^-$	OCl ⁻ hypochlorite ion $\left[\begin{array}{c} \text{O} \\ \\ \text{O}-\text{Cl} \\ \\ \text{O} \end{array} \right]^-$	

Isoelectronic Species

Table 9.6 Some Common Isoelectronic Molecules and Ions

Formulas	Representative Lewis Structure	Formulas	Representative Lewis Structure
BH_4^- , CH_4 , NH_4^+		CO_3^{2-} , NO_3^-	
NH_3 , H_3O^+		PO_4^{3-} , SO_4^{2-} , ClO_4^-	
CO_2 , OCN^- , SCN^- , N_2O NO_2^+ , OCS , CS_2			

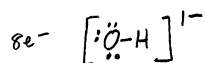
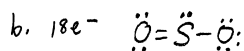
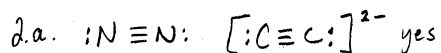
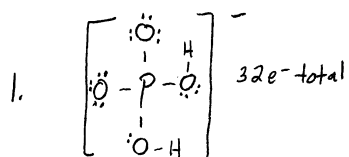
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Having the same number of valence electrons and the same structure

Examples:

1. Draw a Lewis structure for the anion H_2PO_4^- , which is derived from phosphoric acid.

2. a) Is the acetylide ion, C_2^{2-} , isoelectronic with N_2 ?
b) Identify a common molecular (uncharged) species that is isoelectronic with the nitrite ion, NO_2^- . Identify a common ion that is isoelectronic with HF.

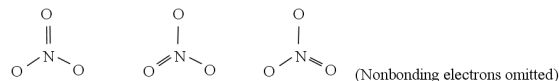


Resonance

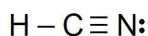
When multiple bonding conditions can occur between two atoms the molecule is said to be resonant (resonance structures).

A portion of the multiple bond is shared between all of the bond possibilities.

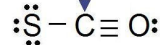
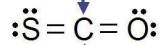
The **bond order** gives the amount of bonding that occurs between two atoms. For instance, in the NO_3^- polyatomic ion, three different equivalent structures are possible:



The bond order between the nitrogen and each oxygen is $1 \frac{1}{3}$



Isomeric Structures
Hydrogen cyanide
and hydrogen
isocyanide



Resonance Structures
Some structures may be more "significant" than others. The true structure is likely a hybrid.

Formal Charge

Used to determine the most plausible Lewis structure for a molecule among multiple acceptable arrangements.

The equation is:

$$\text{Formal Charge} = \text{Total valence electrons} - \text{nonbonding electrons} - \frac{1}{2} \text{bonding electrons}$$

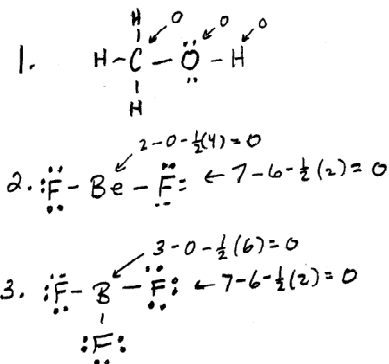
This should not be confused with the ionization state of atoms in an ionic compound where the more electronegative atom is assigned all of the bonding electrons.

1. Ideally you want formal charges to be 0 or very close to zero
2. If there must be a charge you want the more electronegative atom to have the negative charge.
3. The formal charge should be determined for each atom in the compound.

Sample Problems

Using formal charges:

- Determine the best possible arrangement for methyl alcohol between CH_3OH and CH_2OH_2
- Determine the best possible arrangement for BeF_2 , between single bonds between beryllium and fluorine vs double bonds between both.
- Determine the best possible arrangement for BF_3 between single bonds between the boron and fluorine atoms vs a resonance structure in which the octet of boron is fulfilled.

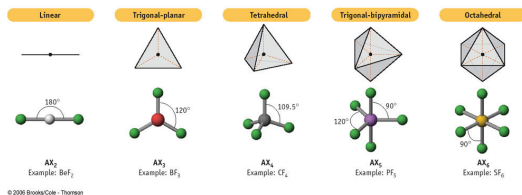


VSEPR Theory

Valence shell electron pair repulsion theory: Electron pairs around the central atom geometrically arrange themselves to minimize repulsions (i.e. as far away from each other as possible)

Determine the geometry of the molecule with respect to a central atom.

Major Classes and associated bond angles:




- Geometrically, treat multiple bonds as though they were single bonds.



- Be able to differentiate between electronic geometry (always a major class) and molecular geometry (Major class or subclass)

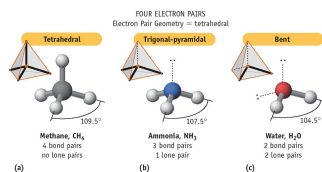
- Lone pairs on the central atom will affect the geometry of the molecule.

Subclasses of *Trigonal Planar* electronic geometries

Lewis Structure	Molecular Geometry	Bond Angle(s)
	Bent	$<120^\circ$ (AX_2E_2)




Subclasses of *Tetrahedral* electronic geometries

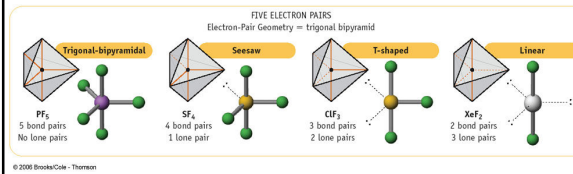
Lewis Structure	Molecular Geometry	Bond Angle(s)
	Trigonal pyramidal	$<109.5^\circ$ (AX_3E)
	Bent	$<109.5^\circ$ (AX_2E_2)



Subclasses of *Trigonal bipyramidal* electronic geometries

NOTE: Nonbonding electron pairs MUST be on the equatorial region of the molecule.

Lewis Structure	Molecular Geometry	Bond Angle(s)
	See Saw (Distorted tetrahedron)	$<120^\circ, <90^\circ$ (AX_4E)
	T-shaped	$<90^\circ$ (AX_2E_2)
	Linear	180° (AX_2E_3)



Subclasses of *Octahedral* electronic geometries
NOTE: Remove electrons from the axial regions BEFORE the equatorial regions.

Lewis Structure	Molecular Geometry	Bond Angle(s)
	Square Pyramidal	<math><90^\circ, <180^\circ</math> (AX ₅ E)
	Square Planar	<math><90^\circ</math> (AX ₄ E ₂)
	T-Shaped	<math><90^\circ</math> (AX ₃ E ₃)
	Linear	180° (AX ₂ E ₄)

SIX ELECTRON PAIRS
Electron-Pair Geometry = octahedron

SF ₆ 6 bond pairs No lone pairs	BrF ₅ 5 bond pairs 1 lone pair	XeF ₄ 4 bond pairs 2 lone pairs

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Determine the electronic and molecular geometries of the following molecules:

- CH₃⁻
- SF₂
- I₃⁻
- NO₃⁻
- XeF₄
- BrF₅
- H₂O
- H₃O⁺
- OPF (Phosphorous fluoride)

a. tetrahedral
trigonal pyramidal

b. tetrahedral
bent

c. trigonal bipyramidal
linear

d. octahedral
square planar

e. tetrahedral
trigonal pyramidal

f. octahedral
square pyramidal

g. tetrahedral
bent

h. tetrahedral
trigonal pyramidal

i. tetrahedral
tetrahedral

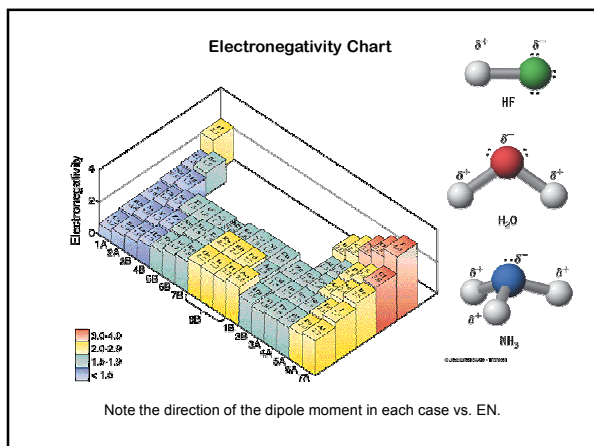
Molecular Geometry and Bond Polarity

Melting point, boiling point, electrostatic properties and more are affected by bond polarity

The strength of the polarity (dipole moment) depends on the amount of charge on either end of the molecule (brought about by the electronegativity difference) times the distance between the bonding atoms

Dipole moment (μ) = Product of the magnitude of the partial charges (δ^+ and δ^-) and the distance by which they are separated. Units are in Cm (coulomb-meters) usually written by the derived unit of the Debye (D; 1D = 3.34x10⁻³⁰Cm)

— Dipolar Molecule



Electronegativity is represented by the symbol χ

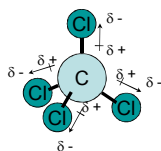
The difference in EN between two atoms $\Delta\chi$ determines bond character between the atoms.

A $\Delta\chi$ of 0 would indicate pure covalent, whereas values greater than about 1.7 are considered primarily ionic (with polar covalent falling in between).

Note from box on page 410 of text that "Even compounds with high electronegativity differences are not 100% ionic."

Cancellation of dipoles

- Many times, the geometry will cause the molecule to be nonpolar overall even though individual dipoles may exist within the molecule.



Example: Carbon tetrachloride is nonpolar even though there are individual dipoles between the central carbon and the chlorines. The net effect of the geometry is to cancel out the dipole nature of the molecule

Bond Order, Bond Length and Bond Dissociation Energy

Bond Dissociation Energy (D): The enthalpy change for breaking a bond in a molecule with the reactants and products in the gas phase.

Trends in Bond length and energy:

As bond order increases
Bond length decreases
Bond energy increases

Bond length is proportional to the relative sizes of the combining atoms.

H-F < H-Cl < H-Br < H-I

C-C > C-N > C-O > C-F

C=O < C=S

C=N < C=C

Note:

Breaking bonds in a molecule is always endothermic

Forming bonds from atoms or radicals in a gas phase is always exothermic

Using a table of average bond energies, the enthalpy of a reaction can be estimated by the equation given by:

$$\Delta H^\circ_{\text{rxn}} = \sum D(\text{bonds broken}) - \sum D(\text{bonds formed})$$

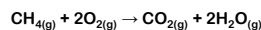
Where D represents the bond dissociation energy

Table 9.10 page 422 (Ave. Bond Energies, kJ/mol)

Example:

Using the bond energies in Table 9.10 (p 422), estimate the heat of combustion of gaseous methane, CH₄. That is, estimate $\Delta H^\circ_{\text{rxn}}$ for the reaction of methane with O₂ to give water vapor and carbon dioxide gas.

Answer:



$$4x \text{ C-H} = 4(413) = 1652 \text{ kJ/mol}$$

$$2x \text{ O=O} = 2(498) = 996 \text{ kJ/mol}$$

$$2x \text{ C=O} = 2(745) = 1490 \text{ kJ/mol}$$

$$4x \text{ H-O} = 4(463) = 1852 \text{ kJ/mol}$$

$$\Delta H^\circ_{\text{rxn}} = 1652 + 996 - 1490 - 1852 = -694 \text{ kJ/mol}$$

1. Use VSEPR theory to predict the shapes of the following molecules:

- a. BrF₅ b. HCN c. BF₃ d. SO₂ e. SCl₂

2. Predict the approximate bond angles in the following:

- a. GeCl₂ b. IF₄⁻ c. TeCl₄

3. CCl₄ is a perfect tetrahedron, but AsCl₄⁻ is a distorted tetrahedron. Explain.

4. BeCl₂ and TeCl₂ are both covalent molecules, yet BeCl₂ is linear while TeCl₂ is nonlinear (bent). Explain.

5. What types of geometries can be formed by elements of the third period that cannot be formed by elements in the second period?

6. Which molecule should have the larger dipole moment, HBr or HI?

7. Which of the following molecules has a dipole moment?

- a. CCl₄ b. H₂S c. CO₂ d. BCl₃ e. Cl₂

Answers:

1. Use VSEPR theory to predict the shapes of the following molecules:

- a. BrF₅ b. HCN c. BF₃ d. SO₂ e. SCl₂

- a. Square-pyramidal
b. Linear
c. Trigonal planar
d. Bent (subclass of trigonal planar)
e. Bent (subclass of tetrahedral)

2. Predict the approximate bond angles in the following:

- a. GeCl₂ b. IF₄⁻ c. TeCl₄

- a. 120° b. 90° c. 120°/90°

Answer:

3. CCl_4 is a perfect tetrahedron, but AsCl_4^- is a distorted tetrahedron. Explain.

As has a lone pair making the molecule a subclass of trigonal bipyramidal (see-saw or distorted tetrahedron)

4. BeCl_2 and TeCl_2 are both covalent molecules, yet BeCl_2 is linear while TeCl_2 is nonlinear (bent). Explain.

Beryllium only has two bonding electron pairs, whereas Tellurium has four electron pairs (two bonding, two nonbonding) making it tetrahedral subclass bent.

5. What types of geometries can be formed by elements of the third period that cannot be formed by elements in the second period?

Elements from the 3rd period on have d-sublevels (whether empty or occupied) which can take part in the bonding process, allowing them to achieve expanded valences (sp^3d and sp^3d^2 hybridization as we will see in chapter 10) and trigonal bipyramidal and octahedral geometries (and their subclasses)

Answers:

6. Which molecule should have the larger dipole moment, HBr or HI?

HBr would have a larger dipole because $\Delta\chi$ is $3.0 - 2.2 = .8$ whereas for HI it would be $2.7 - 2.2 = .5$

7. Which of the following molecules has a dipole moment?

a. CCl_4 b. H_2S c. CO_2 d. BCl_3 e. Cl_2

- a. No. tetrahedral symmetrical
- b. Yes. Tetrahedral bent
- c. No. Linear, symmetrical
- d. No. Trigonal planar, symmetrical
- e. No. Linear, symmetrical