A general chemistry Libretexts Textmap organized around the textbook

**Chemistry: The Central Science**

by Brown, LeMay, Busten, Murphy, and Woodward

1. **Chapter 1: Introduction: Matter and Measurement**
   2. 1.1: The Study of Chemistry
   3. 1.2: Classification of Matter
   4. 1.3: Properties of Matter
   5. 1.4: Units of Measurement
   6. 1.5: Uncertainty in Measurement
   7. 1.6: Dimensional Analysis
8. 1.E: Matter and Measurement (Exercises)
9. 1.S: Matter and Measurement (Summary)

• 2

1. **Chapter 2: Atoms, Molecules, and Ions**
   2. 2.1: The Atomic Theory of Matter
   3. 2.2: The Discovery of Atomic Structure
   4. 2.3: The Modern View of Atomic Structure
   5. 2.4: Atomic Mass
   6. 2.5: The Periodic Table
   7. 2.6: Molecules and Molecular Compounds
   8. 2.7: Ions and Ionic Compounds
   9. 2.8: Naming Inorganic Compounds
   10. 2.9: Some Simple Organic Compounds
11. 2.E: Atoms, Molecules, and Ions (Exercises)
12. 2.S: Atoms, Molecules, and Ions (Summary)

• 3

1. **Chapter 3: Stoichiometry: Chemical Formulas and Equations**
   2. 3.1: Chemical Equations
   3. 3.2: Some Simple Patterns of Chemical Reactivity
   4. 3.3: Formula Masses
   5. 3.4: Avogadro's Number and the Mole
   6. 3.5: Empirical Formulas from Analysis
   7. 3.6: Quantitative Information from Balanced Equations
   8. 3.7: Limiting Reactants
   9. 3.E: Stoichiometry (Exercises)
10. 3.S: Stoichiometry (Summary)

• 4

1. Chapter 4: Reactions in Aqueous Solution
2. 4.1: General Properties of Aqueous Solutions
3. 4.2: Precipitation Reactions
4. 4.3: Acid-Base Reactions
5. 4.4: Oxidation-Reduction Reactions
6. 4.5: Concentration of Solutions
7. 4.6: Solution Stoichiometry and Chemical Analysis
8. 4.E: Reactions in Aqueous Solution (Exercises)
9. 4.S: Reactions in Aqueous Solution (Summary)

• 5

1. Chapter 5: Thermochemistry
2. 5.1: The Nature of Energy
3. 5.2: The First Law of Thermodynamics
4. 5.3: Enthalpy
5. 5.4: Enthalpy of Reaction
6. 5.5: Calorimetry
7. 5.6: Hess’s Law
8. 5.7: Enthalpies of Formation
9. 5.8: Foods and Fuels
10. 5.E: Thermochemistry (Exercises)
11. 5.S: Thermochemistry (Summary)

• 6

1. Chapter 6: Electronic Structure of Atoms
2. 6.1: The Wave Nature of Light
3. 6.2: Quantized Energy and Photons
4. 6.3: Line Spectra and the Bohr Model
5. 6.4: The Wave Behavior of Matter
6. 6.5: Quantum Mechanics and Atomic Orbitals
7. 6.6: 3D Representation of Orbitals
8. 6.7: Many-Electron Atoms
9. 6.8: Electron Configurations
10. 6.9: Electron Configurations and the Periodic Table
11. 6.E: Electronic Structure of Atoms (Exercises)
12. 6.S: Electronic Structure of Atoms (Summary)
• 7

1. Chapter 7: Periodic Properties of the Elements
   2. 7.1: Development of the Periodic Table
   3. 7.2: Effective Nuclear Charge
   4. 7.3: Sizes of Atoms and Ions
   5. 7.4: Ionization Energy
   6. 7.5: Electron Affinities
   7. 7.6: Metals, Nonmetals, and Metalloids
   8. 7.7: Group Trends for the Active Metals
   9. 7.8: Group Trends for Selected Nonmetals
10. 7.E: Periodic Properties of the Elements (Exercises)
11. 7.S: Periodic Properties of the Elements (Summary)

• 8

1. Chapter 8: Basic Concepts of Chemical Bonding
   2. 8.1: Chemical Bonds, Lewis Symbols, and the Octet Rule
   3. 8.2: Ionic Bonding
   4. 8.3: Covalent Bonding
   5. 8.4: Bond Polarity and Electronegativity
   6. 8.5: Drawing Lewis Structures
   7. 8.6: Resonance Structures
   8. 8.7: Exceptions to the Octet Rule
   9. 8.8: Strength of Covalent Bonds
10. 8.E: Basic Concepts of Chemical Bonding (Exercises)
11. 8.S: Basic Concepts of Chemical Bonding (Summary)

• 9

1. Chapter 9: Molecular Geometry and Bonding Theories
   2. 9.1: Molecular Shapes
   3. 9.2: The VSEPR Model
   4. 9.3: Molecular Shape and Molecular Polarity
   5. 9.4: Covalent Bonding and Orbital Overlap
   6. 9.5: Hybrid Orbitals
   7. 9.6: Multiple Bonds
   8. 9.7: Molecular Orbitals
   9. 9.8: Second-Row Diatomic Molecules
10. 9.E: Exercises
11. 9.S: Molecular Geometry and Bonding Theories (Summary)
• 10
  1. Chapter 10: Gases
     2. 10.1: Characteristics of Gases
     3. 10.2: Pressure
     4. 10.3: The Gas Laws
     5. 10.4: The Ideal Gas Equation
     6. 10.5: Further Applications of the Ideal-Gas Equations
     7. 10.6: Gas Mixtures and Partial Pressures
     8. 10.7: Kinetic-Molecular Theory
     9. 10.8: Molecular Effusion and Diffusion
    10. 10.9: Real Gases - Deviations from Ideal Behavior
    11. 10.E: Exercises
    12. 10.S: Gases (Summary)
• 11
  1. Chapter 11: Liquids and Intermolecular Forces
     2. 11.1: A Molecular Comparison of Gases, Liquids, and Solids
     3. 11.2: Intermolecular Forces
     4. 11.3: Some Properties of Liquids
     5. 11.4: Phase Changes
     6. 11.5: Vapor Pressure
     7. 11.6: Phase Diagrams
     8. 11.7: Structure of Solids
     9. 11.8: Bonding in Solids
    10. 11.E: Liquids and Intermolecular Forces (Exercises)
    11. 11.S: Liquids and Intermolecular Forces (Summary)
• 12
  1. Chapter 12: Solids and Modern Materials
     2. 12.1: Classes of Materials
     3. 12.2: Materials for Structure
     4. 12.3: Materials for Medicine
     5. 12.4: Materials for Electronics
     6. 12.5: Materials for Optics
     7. 12.6: Materials for Nanotechnology
     8. 12.E: Solids and Modern Materials (Exercises)
5. **16.4: The pH Scale**
6. **16.5: Strong Acids and Bases**
7. **16.6: Weak Acids**
8. **16.7: Weak Bases**
9. **16.8: Relationship Between \( K_a \) and \( K_b \)**
10. **16.9: Acid-Base Properties of Salt Solutions**
11. **16.10: Acid-Base Behavior and Chemical Structure**
12. **16.11: Lewis Acids and Bases**

• **17**

1. **Chapter 17: Additional Aspects of Aqueous Equilibria**
2. **17.1: The Common-Ion Effect**
3. **17.2: Buffered Solutions**
4. **17.3: Acid-Base Titrations**
5. **17.4: Solubility Equilibria**
6. **17.5: Factors that Affect Solubility**
7. **17.6: Precipitation and Separation of Ions**
8. **17.7: Qualitative Analysis for Metallic Elements**
10. **17.S: Additional Aspects of Aqueous Equilibria (Summary)**

• **18**

1. **Chapter 18: Chemistry of the Environment**
2. **18.1: Earth's Atmosphere**
3. **18.2: Outer Regions of the Atmosphere**
4. **18.3: Ozone in the Upper Atmosphere**
5. **18.4: Chemistry of the Troposphere**
6. **18.5: The World Ocean**
7. **18.6: Fresh Water**
8. **18.7: Green Chemistry**

• **19**

1. **Chapter 19: Chemical Thermodynamics**
2. **19.1: Spontaneous Processes**
4. **19.3: The Molecular Interpretation of Entropy**
5. 19.4: Entropy Changes in Chemical Reactions
   6. 19.5: Gibbs Free Energy
   7. 19.6: Free Energy and Temperature
8. 19.7: Free Energy and the Equilibrium Constant
9. 19.E: Chemical Thermodynamics (Exercises)

• 20
1. Chapter 20: Electrochemistry
2. 20.1: Oxidation States & Redox Reactions
3. 20.2: Balanced Oxidation-Reduction Equations
4. 20.3: Voltaic Cells
5. 20.4: Cell Potential Under Standard Conditions
6. 20.5: Gibbs Energy and Redox Reactions
7. 20.6: Cell Potential Under Nonstandard Conditions
8. 20.7: Batteries and Fuel Cells
9. 20.8: Corrosion
10. 20.9: Electrolysis
11. 20.E: Electrochemistry (Exercises)

• 21
1. Chapter 21: Nuclear Chemistry
2. 21.1: Radioactivity
3. 21.2: Patterns of Nuclear Stability
4. 21.3: Nuclear Transmutations
5. 21.4: Rates of Radioactive Decay
6. 21.6: Energy Changes in Nuclear Reactions
7. 21.7: Nuclear Fission
8. 21.8: Nuclear Fusion
9. 21.9: Biological Effects of Radiation
10. 21.E: Exercises
11. 21.S: Nuclear Chemistry (Summary)

• 22
1. Chapter 22: Chemistry of the Nonmetals
2. 22.1: General Concepts: Periodic Trends and Reactions
3. 22.2: Hydrogen
4. 22.3: Group 18: Nobel Gases
5. 22.4: Group 17: The Halogens
6. 22.5: Oxygen
7. 22.6: The Other Group 16 Elements: S, Se, Te, and Po
8. 22.7: Nitrogen
9. 22.8: The Other Group 15 Elements: P, As, Sb, and Bi
10. 22.9: Carbon
11. 22.10: The Other Group 14 Elements: Si, Ge, Sn, and Pb
12. 22.11: Boron
13. 22.E: Chemistry of the Nonmetals (Exercises)
14. 22.S: Chemistry of the Nonmetals (Summary)

• 23

1. Chapter 23: Metals and Metallurgy
2. 23.1: Occurance and Distribution of Metals
   3. 23.2: Pyrometallurgy
   4. 23.3: Hydrometallurgy
   5. 23.4: Electrometallurgy
   6. 23.5: Metallic Bonding
   7. 23.6: Alloys
8. 23.7: Transition Metals
9. 23.8: Chemistry of Selected Transition Metals
10. 23.E: Metals and Metallurgy (Exercises)

• 24

1. Chapter 24: Chemistry of Coordination Chemistry
2. 24.1: Metal Complexes
3. 24.2: Ligands with more than one Donor Atom
4. 24.3: Nomenclature of Coordination Chemistry
   5. 24.4: Isomerization
   6. 24.5: Color and Magnetism
   7. 24.6: Crystal Field Theory
8. 24.E: Chemistry of Coordination Chemistry (Exercises)

• 25

1. Chapter 25: Chemistry of Life: Organic and Biological Chemistry
2. 25.1: General Characteristics of Organic Molecules
3. 25.2: Introduction to Hydrocarbons
4. 25.3: Alkanes
5. 25.4: Unsaturated Hydrocarbons
6. 25.5: Functional Groups
7. 25.6: Compounds with a Carbonyl Group
8. 25.7: Chirality in Organic Chemistry
9. 25.8: Introduction to Biochemistry
10. 25.9: Proteins
11. 25.10: Carbohydrates
12. 25.11: Nucleic Acids
13. 25.E: Organic and Biological Chemistry (Exercises)
14. 25.S: Organic and Biological Chemistry (Summary)

• Homework

1. 1.E: Matter and Measurement (Exercises)
2. 2.E: Atoms, Molecules, and Ions (Exercises)
3. 3.E: Stoichiometry (Exercises)
4. 4.E: Aqueous Reactions (Exercises)
5. 5.E: Thermochemistry (Exercises)
6. 6.E: Electronic Structure (Exercises)
7. 7.E: Periodic Trends (Exercises)
8. 8.E: Chemical Bonding Basics (Exercises)
9. 9.E: Bonding Theories (Exercises)
10. 10.E: Gases (Exercises)
11. 11.E: Liquids and Intermolecular Forces (Exercises)
13. 13.E: Properties of Solutions (Exercises)
15. 15.E: Chemical Equilibrium (Exercises)
16. 16.E: Acid–Base Equilibria (Exercises)
17. 17.E: Additional Aspects of Aqueous Equilibria (Exercises)
18. 18.E: Chemistry of the Environment (Exercises)
19. 19.E: Chemical Thermodynamics (Exercises)
20. 20.E: Electrochemistry (Exercises)
21. 21.E: Nuclear Chemistry (Exercises)
22. 22.E: Chemistry of the Nonmetals (Exercises)
23. 23.E: Metals and Metallurgy (Exercises)
24. 24.E: Chemistry of Coordination Chemistry (Exercises)
25. 25.E: Organic and Biological Chemistry (Exercises)

These are homework exercises to accompany the Textmap created for "Chemistry: The Central Science" by Brown et al. Complementary General Chemistry question banks can be found for other Textmaps and can be accessed here. In addition to these publicly available questions, access to private problems bank for use in exams and homework is available to faculty only on an individual basis; please contact Delmar Larsen for an account with access permission.
9.1: MOLECULAR SHAPES

9.2: THE VSEPR MODEL

Conceptual Problems

1. What is the main difference between the VSEPR model and Lewis electron structures?

2. What are the differences between molecular geometry and Lewis electron structures? Can two molecules with the same Lewis electron structures have different molecular geometries? Can two molecules with the same molecular geometry have different Lewis electron structures? In each case, support your answer with an example.

3. How does the VSEPR model deal with the presence of multiple bonds?

4. Three molecules have the following generic formulas: AX₂, AX₂E, and AX₂E₂. Predict the molecular geometry of each, and arrange them in order of increasing X–A–X angle.

5. Which has the smaller angles around the central atom—H₂S or SiH₄? Why? Do the Lewis electron structures of these molecules predict which has the smaller angle?

6. Discuss in your own words why lone pairs of electrons occupy more space than bonding pairs. How does the presence of lone pairs affect molecular geometry?

   • When using VSEPR to predict molecular geometry, the importance of repulsions between electron pairs decreases in the following order: LP–LP, LP–BP, BP–BP. Explain this order. Draw structures of real molecules that separately show each of these interactions.

   • How do multiple bonds affect molecular geometry? Does a multiple bond take up more or less space around an atom than a single bond? a lone pair?

   • Straight-chain alkanes do not have linear structures but are “kinked.” Using n-hexane as an example, explain why this is so. Compare the geometry of 1-hexene to that of n-hexane.

   • How is molecular geometry related to the presence or absence of a molecular dipole moment?

   • How are molecular geometry and dipole moments related to physical properties such as melting point and boiling point?

   • What two features of a molecule’s structure and bonding are required for a molecule to be considered polar? Is COF₂ likely to have a significant dipole moment? Explain your answer.

   • When a chemist says that a molecule is polar, what does this mean? What are the general physical properties of
polar molecules?

- Use the VSEPR model and your knowledge of bonding and dipole moments to predict which molecules will be liquids or solids at room temperature and which will be gases. Explain your rationale for each choice. Justify your answers.
  1. CH₃Cl
  2. PCl₃
  3. CO
  4. SF₆
  5. IF₅
  6. CH₃OCH₃
  7. CCl₃H
  8. H₃COH

- The idealized molecular geometry of BrF₅ is square pyramidal, with one lone pair. What effect does the lone pair have on the actual molecular geometry of BrF₅? If LP–BP repulsions were weaker than BP–BP repulsions, what would be the effect on the molecular geometry of BrF₅?

- Which has the smallest bond angle around the central atom—H₂S, H₂Se, or H₂Te? the largest? Justify your answers.

- Which of these molecular geometries always results in a molecule with a net dipole moment: linear, bent, trigonal planar, tetrahedral, seesaw, trigonal pyramidal, square pyramidal, and octahedral? For the geometries that do not always produce a net dipole moment, what factor(s) will result in a net dipole moment?

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**Conceptual Answers**

3. To a first approximation, the VSEPR model assumes that multiple bonds and single bonds have the same effect on electron pair geometry and molecular geometry; in other words, VSEPR treats multiple bonds like single bonds. Only when considering fine points of molecular structure does VSEPR recognize that multiple bonds occupy more space around the central atom than single bonds.

11. Physical properties like boiling point and melting point depend upon the existence and magnitude of the dipole moment of a molecule. In general, molecules that have substantial dipole moments are likely to exhibit greater intermolecular interactions, resulting in higher melting points and boiling points.

12. The term “polar” is generally used to mean that a molecule has an asymmetrical structure and contains polar bonds. The resulting dipole moment causes the substance to have a higher boiling or melting point than a nonpolar substance.

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**Numerical Problems**

1. Give the number of electron groups around the central atom and the molecular geometry for each molecule.
Classify the electron groups in each species as bonding pairs or lone pairs.

1. BF$_3$
2. PCl$_3$
3. XeF$_2$
4. AlCl$_4^-$
5. CH$_2$Cl$_2$

2. Give the number of electron groups around the central atom and the molecular geometry for each species. Classify the electron groups in each species as bonding pairs or lone pairs.

1. ICl$_3$
2. CCl$_3^+$
3. H$_2$Te
4. XeF$_4$
5. NH$_4^+$

3. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.

1. HCl
2. NF$_3$
3. ICl$_2^+$
4. N$_3^-$
5. H$_3$O$^+$

4. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.

1. SO$_3$
2. NH$_2^-$
3. NO$_3^-$
4. I$_3^-$
5. OF$_2$

5. What is the molecular geometry of ClF$_3$? Draw a three-dimensional representation of its structure and explain the effect of any lone pairs on the idealized geometry.

6. Predict the molecular geometry of each of the following.

1. ICl$_3$
2. AsF₅
3. NO₂⁻
4. TeCl₄

7. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.
   1. NO
   2. HF
   3. PCl₃
   4. CO₂
   5. SO₂
   6. SF₄

8. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.
   1. OF₂
   2. BCl₃
   3. CH₂Cl₂
   4. TeF₄
   5. CH₃OH
   6. XeO₄

9. Of the molecules Cl₂C=Cl₂, IF₃, and SF₆, which has a net dipole moment? Explain your reasoning.

10. Of the molecules SO₃, XeF₄, and H₂C=Cl₂, which has a net dipole moment? Explain your reasoning.

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**Numerical Answers**

1. 1. trigonal planar (all electron groups are bonding pairs)
   2. tetrahedral (one lone pair on P)
   3. trigonal bipyramidal (three lone pairs on Xe)
   4. tetrahedral (all electron groups on Al are bonding pairs)
2. 5. tetrahedral (all electron groups on C are bonding pairs)
3. 1. four electron groups, linear molecular geometry
   2. four electron groups, pyramidal molecular geometry
3. four electron groups, bent molecular geometry

4. two electron groups, linear molecular geometry

5. four electron groups, pyramidal molecular geometry

5. The idealized geometry is T shaped, but the two lone pairs of electrons on Cl will distort the structure, making the F−Cl−F angle less than 180°.

9. Cl₂C=CCl₂: Although the C−Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and Cl₂C=CCl₂ does not have a net dipole moment.
IF₃: In this structure, the individual I–F bond dipoles cannot cancel one another, giving IF₃ a net dipole moment.

SF₆: The S–F bonds are quite polar, but the individual bond dipoles cancel one another in an octahedral structure. Thus, SF₆ has no net dipole moment.

9.3: MOLECULAR SHAPE AND MOLECULAR POLARITY

Conceptual Problems

1. Why do ionic compounds such as KI exhibit substantially less than 100% ionic character in the gas phase?
2. Of the compounds LiI and LiF, which would you expect to behave more like a classical ionic compound? Which would have the greater dipole moment in the gas phase? Explain your answers.

Numerical Problems

1. Predict whether each compound is purely covalent, purely ionic, or polar covalent.
   1. RbCl
   2. S₈
   3. TiCl₂
   4. SbCl₃
   5. LiI
   6. Br₂
2. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.
   1. NO
   2. HF
   3. MgO
   4. AlCl₃
   5. SiO₂
   6. the C=O bond in acetone
   7. O₃

3. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.
   1. NaBr
   2. OF₂
   3. BCl₃
   4. the S–S bond in CH₃CH₂SSCH₂CH₃
   5. the C–Cl bond in CH₂Cl₂
   6. the O–H bond in CH₃OH
   7. PtCl₄²⁻

4. Classify each species as having 0%–40% ionic character, 40%–60% ionic character, or 60%–100% ionic character based on the type of bonding you would expect. Justify your reasoning.
   1. CaO
   2. S₈
   3. AlBr₃
   4. ICl
   5. Na₂S
   6. SiO₂
   7. LiBr

5. If the bond distance in HCl (dipole moment = 1.109 D) were double the actual value of 127.46 pm, what would be the effect on the charge localized on each atom? What would be the percent negative charge on Cl? At the actual bond distance, how would doubling the charge on each atom affect the dipole moment? Would this represent more ionic or covalent character?

6. Calculate the percent ionic character of HF (dipole moment = 1.826 D) if the H–F bond distance is 92 pm.

7. Calculate the percent ionic character of CO (dipole moment = 0.110 D) if the C–O distance is 113 pm.

8. Calculate the percent ionic character of PbS and PbO in the gas phase, given the following information: for PbS, r = 228.69 pm and µ = 3.59 D; for PbO, r = 192.18 pm and µ = 4.64 D. Would you classify these compounds as
9.4: COVALENT BONDING AND ORBITAL OVERLAP

9.5: HYBRID ORBITALS

Conceptual Problems

1. Arrange \( sp, sp^3, \) and \( sp^2 \) in order of increasing strength of the bond formed to a hydrogen atom. Explain your reasoning.

2. What atomic orbitals are combined to form \( sp^3, sp, sp^2d^2, \) and \( sp^3d^2? \) What is the maximum number of electron-pair bonds that can be formed using each set of hybrid orbitals?

3. Why is it incorrect to say that an atom with \( sp^2 \) hybridization will form only three bonds? The carbon atom in the carbonate anion is \( sp^2 \) hybridized. How many bonds to carbon are present in the carbonate ion? Which orbitals on carbon are used to form each bond?

4. If hybridization did not occur, how many bonds would N, O, C, and B form in a neutral molecule, and what would be the approximate molecular geometry?

5. How are hybridization and molecular geometry related? Which has a stronger correlation—molecular geometry and hybridization or Lewis structures and hybridization?

6. In the valence bond approach to bonding in BeF\(_2\), which step(s) require(s) an energy input, and which release(s) energy?

7. The energies of hybrid orbitals are intermediate between the energies of the atomic orbitals from which they are formed. Why?

8. How are lone pairs on the central atom treated using hybrid orbitals?

9. Because nitrogen bonds to only three hydrogen atoms in ammonia, why doesn’t the nitrogen atom use \( sp^2 \) hybrid orbitals instead of \( sp^3 \) hybrids?

10. Using arguments based on orbital hybridization, explain why the CCl\(_6^2^-\) ion does not exist.

11. Species such as NF\(_5^2^-\) and OF\(_4^2^-\) are unknown. If 3\(d\) atomic orbitals were much lower energy, low enough to be involved in hybrid orbital formation, what effect would this have on the stability of such species? Why? What molecular geometry, electron-pair geometry, and hybridization would be expected for each molecule?
Numerical Problems

1. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH₃⁻. How does your diagram compare with that for methane? What is the molecular geometry?

2. Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH₃⁺. How does your diagram compare with that for methane? What is the molecular geometry?

3. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each molecule.
   1. BBr₃
   2. PCl₃
   3. NO₃⁻

4. Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each species.
   1. AsBr₃
   2. CF₃⁺
   3. H₂O

5. What is the hybridization of the central atom in each of the following?
   1. CF₄
   2. CCl₂²⁻
   3. IO₃⁻
   4. SiH₄

6. What is the hybridization of the central atom in each of the following?
   1. CCl₃⁺
   2. CBr₂O
   3. CO₃²⁻
   4. IBr₂⁻

7. What is the hybridization of the central atom in PF₆⁻? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?

8. What is the hybridization of the central atom in SF₅⁻? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?
1. The promotion and hybridization process is exactly the same as shown for CH₄ in the chapter. The only difference is that the C atom uses the four singly occupied sp³ hybrid orbitals to form electron-pair bonds with only three H atoms, and an electron is added to the fourth hybrid orbital to give a charge of 1−. The electron-pair geometry is tetrahedral, but the molecular geometry is pyramidal, as in NH₃.

3. 1. sp², trigonal planar

2. sp³, pyramidal

3. O

N

O

O
4. \( sp^2 \), trigonal planar

6. The central atoms in \( CF_4 \), \( CCl_2^{2−} \), \( IO_3^- \), and \( SiH_4 \) are all \( sp^3 \) hybridized.

7. The phosphorus atom in the \( PF_6^- \) ion is \( sp^3d^2 \) hybridized, and the ion is octahedral. The \( PF_6^- \) ion is isoelectronic with \( SF_6 \) and has essentially the same structure. It should therefore be a stable species.

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### 9.6: MULTIPLE BONDS

#### Conceptual Problems

1. What information is obtained by using the molecular orbital approach to bonding in \( O_3 \) that is not obtained using the VSEPR model? Can this information be obtained using a Lewis electron-pair approach?

2. How is resonance explained using the molecular orbital approach?

3. Indicate what information can be obtained by each method:

<table>
<thead>
<tr>
<th>Lewis Electron Structures</th>
<th>VSEPR Model</th>
<th>Valence Bond Theory</th>
<th>Molecular Orbital Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resonance</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Orbital Hybridization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactivity</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Expanded Valences</td>
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<tr>
<td>Bond Order</td>
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</tbody>
</table>

#### Numerical Problems

1. Using both a hybrid atomic orbital and molecular orbital approaches, describe the bonding in \( BCl_3 \) and \( CS_3^{2−} \).

2. Use both a hybrid atomic orbital and molecular orbital approaches to describe the bonding in \( CO_2 \) and \( N_3^{−} \).

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### 9.7: MOLECULAR ORBITALS
9.8: SECOND-ROW DIATOMIC MOLECULES