

Summary

13.1 Bonds in Space

1. The structure of a molecule or a polyatomic ion can be represented by a Lewis electron dot diagram, which shows the pattern of shared and unshared pairs of electrons.
2. The shape of a molecule can be predicted by taking into account the mutual repulsion of electron pairs due to the same electrostatic charge and the Pauli exclusion principle. Electron pairs spread as far apart as possible.
3. The shape of a molecule containing three or more atoms is determined by the number and type of electron clouds in outer levels of the atoms.
4. The actual bond angles may vary from predicted angles. Unshared electron pairs occupy the most space. Shared pairs occupy the least space.
5. The *s* and *p* orbitals of the same atom can combine to form hybrid orbitals. One *s* and three *p* orbitals can merge to form four tetrahedral sp^3 hybrid orbitals. One *s* and two *p* orbitals can merge to form three planar sp^2 hybrid orbitals. One *s* and one *p* orbital can merge to form two linear *sp* hybrid orbitals.
6. If two *s* orbitals or an *s* and a *p* orbital overlap, a sigma (σ) bond is formed. If two *p* orbitals overlap end to end, a sigma bond is formed. If two *p* orbitals overlap sideways, a pi (π) bond is formed. Pi electrons are farther from the nucleus.
7. Two atoms sometimes share more than one pair of electrons, forming double and triple bonds. This possibility must be considered when predicting geometry of a molecule.
8. Delocalization of pi electrons in conjugated chain and ring compounds such as benzene increases the stability of the structure.

13.2 Molecular Arrangements

9. Names of organic compounds carry a suffix to indicate how the atoms are bonded. The ending *-ane* is used for compounds in which all bonds are single bonds. The ending *-ene* is used for compounds with a carbon-carbon double bond. The ending *-yne* is used for compounds with a carbon-carbon triple bond.
10. Cyclic compounds may be represented using skeletal outlines with double and triple lines representing double and triple bonds respectively.
11. Isomers are compounds with the same molecular formula but with different arrangements of atoms and bonds.
12. Compounds may have several types of isomers including structural, geometric, positional, and functional.
13. Electron-pair repulsion is the simplest model used in predicting the structure of a molecule. Therefore, it should be applied before more complex explanations are tried.

Key Terms

shared pair	delocalization
unshared pair	conjugated system
hybridization	saturated compound
hybrid orbital	isomerism
sigma bond	isomer
pi bond	structural isomer
double bond	positional isomer
triple bond	functional group
unsaturated	functional isomer
compound	geometric isomer

Review and Practice

15. Draw Lewis electron dot structures for the following substances.

a. H_2S c. HBr e. NH_3 b. Br_2 d. CH_2Cl_2 f. $AlBr_3$

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16. Using the ammonia molecule as an example, distinguish between shared pairs and unshared pairs of electrons.

17. Predict shapes for the following ions.

- a. IO_4^- c. SiF_6^{2-} e. PO_4^{3-}
b. ClO_3^- d. SO_4^{2-} f. ClF_4^-

18. Predict the shapes of the following molecules. See Table 13.1.

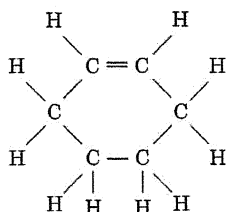
- a. H_2CO c. BF_3 e. S_2Cl_2
b. SeO_2 d. SF_6 f. SF_4

19. What is meant by hybrid in the term hybrid orbital?

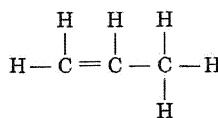
20. Sketch a molecular diagram of butyne and one of pentyne, showing all bonds.

21. Name the following compounds.

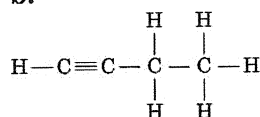
a.



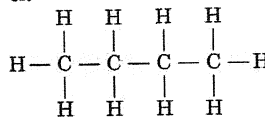
c.



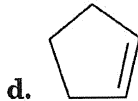
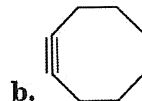
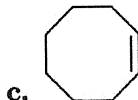
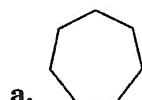
b.



d.



22. Name the following compounds.



23. Draw structural formulas for each of the following hydrocarbons.

- a. cycloheptene c. cyclobutene
b. cyclobutane d. cyclononyne

24. Draw structural formulas for each of the following hydrocarbons.

- a. propene c. heptane
b. octyne d. ethyne

25. Sketch a molecular diagram of butene, showing its orbitals and bonds.

26. Predict the bond angles indicated in the following compounds. Use Table 13.2.

- a. $\text{H}-\text{Se}-\text{H}$ in H_2Se
b. $\text{H}-\text{P}-\text{H}$ in PH_3
c. $\text{C}-\text{N}-\text{C}$ in $\text{N}(\text{CH}_3)_3$
d. $\text{Cl}-\text{P}-\text{Cl}$ in PCl_3
e. $\text{F}-\text{C}-\text{F}$ in CF_4
f. $\text{C}-\text{Pb}-\text{C}$ in $\text{Pb}(\text{C}_2\text{H}_5)_4$

27. How many pairs of electrons are shared by two atoms with each of the following bonds between them?

- a. single b. double c. triple

28. In the HCN molecule, the bonds are $\text{H}-\text{C}$ and $\text{C}\equiv\text{N}$. Predict the shape of the molecule, the hybridization of the orbitals on the carbon atom, and the type (σ , π) of each bond.

29. A conjugated system stabilizes a molecule. Define "conjugated system" and give an example of one.

30. Why is benzene a particularly stable compound?

31. Define isomerism. Draw examples of two isomers of hydrocarbons containing five carbon atoms each.

32. Draw the structural isomers of the compound with the formula C_6H_{14} .

33. How do positional and functional isomers differ?

34. In what kinds of molecules do geometrical isomers occur? Draw examples using hydrocarbon molecules with five carbon atoms and one double bond.

35. What are functional isomers? Draw an example and include names.

36. Phosphorus pentachloride occurs as PCl_5 molecules in the gaseous state. As a solid, it is an ionic compound, $\text{PCl}_4^+ \text{PCl}_6^-$. Describe the shape and bonding in each of these species. See Table 13.1.

37. Draw two possible structural formulas for decyne and one for cyclononene.

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Concept Mastery

38. How do forces resulting from the Pauli exclusion principle affect the shape of molecules? How do these forces compare with the electrostatic repulsions in a molecule? Taking both kinds of forces into account, state the general rule that applies to the shape of molecules when considering electron-pair repulsions.

39. What accounts for the difference in shape between the electron clouds of shared pairs and unshared pairs of electrons?

40. Why is the bond angle in NH_3 only 107° when the bond angle for BF_3 is 120° ?

41. Explain why water has a bond angle of 104.5° instead of the predicted 109.5° .

42. In general, what effect does the presence of unshared pairs in an atom have on the orientation of bonds to the same atom?

43. Explain why the carbon atom forms four equal bonds instead of just two bonds involving electrons from p orbitals.

44. One might expect the bond angle for each $\text{C}-\text{H}$ bond in methane to be 90° . Why is this prediction incorrect?

45. How are covalent bonds formed?

46. What is the major difference between sigma and pi bonds?

47. What kinds of orbital arrangements contribute to the bonding in ethene, $\text{H}_2\text{C}=\text{CH}_2$?

48. In what characteristics do multiple bonds differ from single bonds?

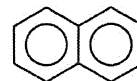
49. In general, how does the presence of double or triple bonds affect the geometry of adjacent single bonds?

50. What is meant by electrons being delocalized? In the case of benzene, describe how electrons are delocalized.

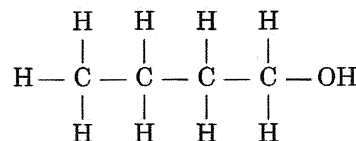
51. What is an unsaturated compound? Draw structural formulas of a saturated and an unsaturated organic hydrocarbon, each containing five carbon atoms.

52. How can isomers with very similar properties be distinguished from each other?

53. Explain the significance of the circles in the structural formula for naphthalene, C_{10}H_8 .

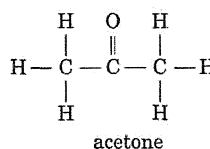


54. Butanol is an alcohol. One of its positional isomers is shown. Draw another positional isomer of butanol. Are there still other positional isomers? Explain your answer.

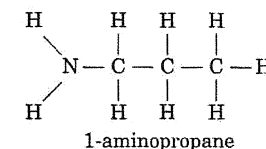


55. Draw functional isomers of the following compounds.

a.



b.



Application

56. Acetylene, ethyne, is widely used as fuel for welding torches and as a raw material for synthetic fibers and rubber. Sketch a molecular diagram of an ethyne molecule showing its bonds. Describe how these bonds are formed.

57. The largest moon of Saturn, Titan, has an atmosphere containing methane, ethane, ethene, propyne, hydrogen cyanide, and the compound diacetylene, C_4H_2 , which contains two triple bonds. Draw the structural formula of each compound.

58. Fumaric acid, $\text{C}_2\text{H}_2(\text{COOH})_2$, is used commercially in beverages. It occurs naturally in the metabolism of glucose in animal and plant cells. The structural formula of the *trans* isomer is shown.

Summary

14.1 Molecular Attraction

1. A polar bond is one in which a shared pair of electrons is attracted to one atom more strongly than to the other atom.
2. A molecule containing polar bonds can itself be polar or nonpolar depending on its bond arrangement. A molecule is polar if the polar bonds are arranged asymmetrically and nonpolar if the polar bonds are arranged symmetrically.
3. Van der Waals forces are the net result of dipole-dipole, dipole-induced dipole, and dispersion forces.

14.2 Coordination Chemistry

4. A complex ion is composed of molecular or negative-ion ligands clustered around a central positive ion.
5. The number of points of attachment of ligands around the central ion in a complex is called the coordination number.
6. A coordination compound consists of a complex ion and other ions or a neutral central atom and neutral ligands combined to form a compound.
7. Transition metals, because of their partially filled *d* orbitals, characteristically form complex ions.
8. The bonds of complex ions have both ionic and covalent bonding characteristics.

14.3 Chromatography

9. Chromatography is a method of separating a mixture of substances into identifiable chemical fractions based on differences in polarity of the individual fractions.

van der Waals force
 intramolecular force
 intermolecular force
 dipole-dipole force
 induced dipole
 dipole-induced dipole force
 temporary dipole
 dispersion force
 complex ion
 ligand
 coordination number
 coordinate covalent bond
 fractionation
 chromatography
 mobile phase
 stationary phase
 column chromatography
 high performance liquid chromatography (HPLC)
 ion chromatography
 paper chromatography
 thin layer chromatography
 gas chromatography

Review and Practice

24. The following pairs of atoms are all covalently bonded. Arrange the pairs in order of decreasing polarity of the bonds using Table 12.1, page 303.
 - a. phosphorus and sodium
 - b. fluorine and nitrogen
 - c. nitrogen and oxygen
 - d. arsenic and iodine
 - e. chlorine and tellurium
 - f. antimony and sulfur
25. What forces hold molecular substances in the liquid and solid states?
26. What are dipole-dipole forces? Give an example.
27. Water has a bond angle of 104.5° between the two O—H bonds. Sketch a diagram of a water molecule, indicating the positive and negative ends of the molecule.
28. Classify each of the following as either an intramolecular force or an intermolecular

Key Terms

polar covalent
 dipole
 dipole moment

Chapter 14 REVIEW

- ↑ force. Explain each answer.
- van der Waals forces
 - covalent bonds
29. Describe two ways that a nonpolar molecule can become dipolar. Give an example of each.
30. Chloroform, CHCl_3 , is a polar molecule. When considering intermolecular forces between CHCl_3 molecules, explain why dispersion forces may be more important than dipole-dipole forces.
31. Define central ion, ligand, and coordination number. Give an example of each.
32. What factors determine coordination number?
33. What is the coordination number in each of the following ions?
- $[\text{PtCl}_6]^{2-}$
 - $[\text{PdCl}_4]^{2-}$
 - $[\text{Sb}(\text{OH})_6]^-$
 - $[\text{Cu}(\text{CN})_2]^-$
34. What is the coordination number in each of the following ions?
- $[\text{Fe}(\text{CN})_5(\text{CO})]^{3-}$
 - $[\text{CoCl}(\text{H}_2\text{O})(\text{NH}_3)_4]^{2+}$
 - $[\text{FeCl}_2(\text{C}_2\text{O}_4)]^{2-}$
 - $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+}$
 - $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$
 - $[\text{Co}(\text{CO})_3(\text{NH}_3)_4]^+$
35. What is a didentate ligand? Give an example.
36. Predict and sketch the shape of the $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ complex.
37. Sketch the shape of the complex ion $[\text{PdCl}_4]^{2-}$.
38. What is the oxidation number of the central metal in each item of Problem 33?
39. What is the oxidation number of the central metal in each item of Problem 34?
40. Determine the oxidation number of the central metal in each of the following complex ions.
- $[\text{CrCl}_2(\text{NH}_3)_4]^+$
 - $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$
 - $[\text{Mn}(\text{CN})_6]^{2-}$
 - $[\text{CrBr}_4(\text{C}_2\text{O}_4)]^{3-}$
41. Name the following complex ions.
- $[\text{GaF}_5]^{2-}$
 - $[\text{SbS}_4]^{3-}$
 - $[\text{Au}(\text{CN})_2]^-$
 - $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$
42. Write the formula for each of the following complex ions.
- tetraamminecopper(II)
 - hexaaquanickel(II)
 - tetracyanonickelate(II)
 - pentaaquachlorochromium(III)
43. Name the following coordination compounds.
- $[\text{VCl}_2(\text{H}_2\text{O})_4]$
 - $[\text{CrBr}_2(\text{NH}_3)_4]\text{NO}_3$
 - $\text{Na}_2[\text{Ni}(\text{CN})_4]$
 - $\text{K}_3[\text{Rh}(\text{CN})_6]$
44. Write the formulas for the following coordination compounds.
- sodium tetrafluorocobaltate(II)
 - hexaaquavanadium(III) bromide
 - potassium tetrachloroferrate(III)
 - cesium trioxalatoferrate(III)
45. Why do transition metals make effective central ions in complexes?
46. How do complex ions form compounds?
47. What is fractionation?
48. What is thin layer chromatography? How is it used?
49. What is a monodentate ligand? Give an example.
50. Define tridentate ligand and tetradentate ligand.
51. Write the name for $[\text{Pt}(\text{NH}_3)_4][\text{CoCl}_4(\text{NH}_3)_2]_2$.
52. Write both names and formulas for the complex ions or coordination compounds made up of the following ions and molecules. Be sure to show the correct charges for ions.
- one chloride ion, one ruthenium(III) ion, and five ammonia molecules
 - four ammonia molecules, two chloride ions, and one platinum(IV) ion
 - one manganese(II) ion and six water molecules
 - one rhodium(III) ion and six cyanide ions
 - six carbon monoxide molecules and one chromium atom

- f. two chloride ions, four ammonia molecules, and one iridium(III) ion
- g. one thiocyanate ion, one iron(III) ion, and five water molecules

Concept Mastery

53. Covalent bonds may be polar, as in H_2O , or nonpolar, as in I_2 . Explain the differences and similarities between polar and nonpolar covalent bonds.
54. What is a dipole? Explain how some molecules with polar bonds are dipoles while other molecules are not. Explain why water is a dipole and carbon dioxide is not.
55. Explain how a nonpolar molecule can contain polar bonds. Give an example.
56. Describe the nature of a coordinate covalent bond. What conditions lead to formation of a coordinate covalent bond?
57. Describe the process of chromatography in terms of the mobile phase and stationary phase.
58. How are column and paper chromatography similar? How are they different?
59. Why would paper chromatography be impractical in an industry that must separate the components of large quantities of a mixture?
60. Carbon dioxide has a dipole moment of 0. The dipole moment of sulfur dioxide is 1.6×10^{-30} C·m. Draw structural diagrams for both molecules and use them to explain the difference in polarity.
61. Compare the structures of complex ions with those of covalent compounds.
62. What is the difference between ordinary covalent bonds such as the H—N bonds in ammonia molecules and coordinate covalent bonds such as the Co—N bond in the $[\text{Co}(\text{NH}_3)_6]^{2+}$ ion?
63. Would the use of chromatography be more effective in separating a mixture of polar substances or a mixture of nonpolar substances? Explain your answer.

64. Helium is the most common carrier gas used in gas chromatography. Why do you think helium is used rather than oxygen, methane, or another gas?

Application

65. Ethoxyethane was commonly used as a surgical anesthetic until safer, less flammable, materials were available. Methanol, called wood alcohol, is used as an industrial solvent although it is poisonous. Using Table 14.1, compare the following properties of these solvents.
 - a. polarity
 - b. melting point
 - c. boiling point
66. $[\text{PtCl}_2(\text{NH}_3)_2]$ has been found to be a powerful anti-cancer drug. Write the name of this coordination compound.
67. Forming a complex ion in solution is often easier than dissolving the metal salt. For example, AgBr, the photosensitive substance in photographic film, will not dissolve in water. However, when $\text{Na}_2\text{S}_2\text{O}_3$ is added, $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ is formed and the AgBr is now dissolved. What is the name of the $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ ion?
68. When complex ions and their compounds were first discovered, they were frequently named after the scientists who discovered them. $\text{NH}_4[\text{Cr}(\text{SCN})_4(\text{NH}_3)_2] \cdot \text{H}_2\text{O}$, for example, was named Rienecke's salt. What is the present name of the $[\text{Cr}(\text{SCN})_4(\text{NH}_3)_2]^-$ ion?
69. Some complexes were originally given names based on their colors. For example, $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$ was named purpureocobaltic chloride because the compound is purple. What is the present name of this compound?
70. Carbon monoxide is a deadly gas even in relatively low concentrations in air. Use reference books to find out how carbon monoxide acts in the human body and use your knowledge from this chapter to suggest a reason for its danger.

Critical Thinking

71. Determine whether each of the following would more likely be formed by polar or nonpolar molecules.
- a solid at room temperature
 - a liquid with a high boiling point
 - a gas at room temperature
 - a liquid with a low boiling point
72. Why is gas chromatography primarily used to separate mixtures of organic compounds?
73. Considering what you have learned about forces between atoms and molecules, why do you think all of the elements in Group 18 (VIIIA) exist as gases at room temperature?
74. Purple dye could result from a mixture of red and blue dyes. How could it be determined whether the color was obtained by using one purple dye or a mixture of red and blue?
75. Suppose you rub a balloon on a wool sweater. The balloon becomes negatively charged by gaining electrons during the rubbing. Next, you place the balloon on a wall and it stays in place. Evidently the wall now has a positive charge because there is a force holding the negatively charged balloon to the wall. Propose an explanation for the wall becoming positively charged.

76. The noble gas elements, Group 18 (VIIIA), have low boiling points and freezing points that are very close to their boiling points. Using your knowledge of bonding and forces, formulate a statement that explains this observation.
77. The dipole moment of compound X_2A equals 1.84×10^{-30} C·m. Compound X_3D has a dipole moment of 1.50×10^{-30} C·m. Which compound is more polar? If they have approximately the same formula mass, which compound would you predict to have the higher melting point?
78. Even though cyanide compounds are poisonous, they are used in the reclamation of silver from film and in other processes in the refining of precious metals. Suggest a reason that these compounds are useful despite their toxicity.

Readings

- Bertholf, Roger L. "Confirmatory Testing for Drugs of Abuse in Urine by Gas Chromatography/Mass Spectrometry." *The Chemist* 67, no. 5 (May 1990): 7-20
- McClure, M. W. "Saving Arnold." *ChemMatters* 6, no. 4 (December 1988): 4-6.
- Rouvray, Dennis H. "Predicting Chemistry from Topology." *Scientific American* 255, no. 3 (September 1986): 40-47.

Cumulative Review

- What shape would you predict for the NI_3 molecule? For CCl_4 ?
- Describe the shapes of s and p orbitals.
- Explain why carbon, which has a predicted outer configuration of $2s^2 2p^2$, can form four equivalent bonds.
- Why is benzene more stable than a compound with three single and three double bonds?
- What shape would you predict for H_2Se ? Why?
- Draw as many isomers of C_5H_{10} as you can. Hint: There are 12 isomers. All contain a $C=C$ double bond or are cyclic.
- Predict the $N-C=O$ bond angle in $(NH_2)_2CO$.