Chapter 9: Molecular Structures

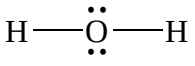
Solutions for Chapter 9

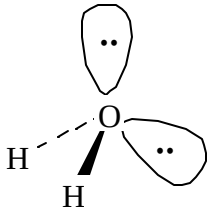
Questions for Review and Thought

Review Questions

1. VSEPR stands for "Valence-shell electron-pair repulsion." This model is used to predict the shape of molecules and ions by describing the relative orientation of atoms connected to each other with covalent bonds. The physical basis of the model is the repulsion of like charges. Because electron pairs will repel each other, they will arrange themselves to be as far from each other as possible.

2. Electron-pair geometry identifies the positions of all the electron pairs around the central atom. The molecular geometry identifies the positions of all the atoms bonded to the central atom. For example, look at H_2O:





The central O atom in H_2O has four electron pairs, two bonding pairs and two lone pairs, so its electron geometry is tetrahedral. The two atoms bonded to the O in the AX_2E_2 type are arranged with an angular molecular geometry.

3.

Number of electron pairs	electron-pair geometry
2	linear
3	triangular planar
4	tetrahedral
5	triangular bipyramidal
6	octahedral

4. (a) Two atoms bonded together must be linear.

   (b) AX_2E_2 type has angular molecular geometry.

   (c) AX_3E_1 type has trigonal pyramidal molecular geometry.

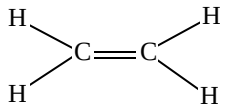
   (d) AX_4E_0 type has tetrahedral molecular geometry.

5. To have a trigonal planar molecule with three electron pairs around the central atom, the central atom must have three bonded atoms and no lone pairs. To have an angular molecule with three electron pairs around

the central atom, the central atom must have two bonded atoms and one lone pair. In the first case, the bond angles are predicted to be 120°. In the second case, they are 109.5°.

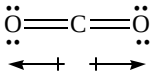
6. Following the example at the end of Section 9.2, we'll look at each atom in the molecule with more than one atom bonded to it and determine the geometry at that center, then determine the shape of the molecule from the collective shape at these centers.

   The Lewis structure for ethylene (C_2H_4) looks like this:



   Looking at the first C atom, it has three bonded atoms (two H atoms and one C atom) and no lone pairs. That makes it an AX_3E_0 type, so the atoms bonded to that C atom are arranged with a triangular planar geometry. Looking at the second C atom, it also has three bonded atoms and no lone pairs. That also makes it an AX_3E_0 type, so the atoms bonded to that C atom are also arranged with a triangular planar geometry. VESPR alone does not assure us that these two planes are coplanar, but the π bond in the double bond would not be formed unless they are. With all the atoms in a common plane, the molecule is planar.

7. A molecule with polar bonds can be nonpolar if the bond poles are equal and point in opposite directions. CO_2 is a good example of a nonpolar molecule with polar bonds.



8. Chiral drugs often have one enantiomer that is more active than another. This enantiomer interacts with certain receptor sites in the body, which are designed for one of the enantiomers found in nature.

9. A polar molecule has different atoms (specifically, atoms with different electronegativities) bonded together in any number of different asymmetric fashions. A chiral molecule has different atoms or groups of atoms bonded in a specific asymmetric fashion that provides two nonsuperimposable mirror images.

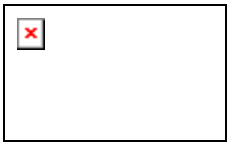
10. Infrared spectroscopy is used to characterize the structure of molecules. The infrared spectrum shows the specific frequencies absorbed when the molecule undergoes specific types of motions. Each molecule, with its unique arrangement of atoms and bonds, interacts differently with infrared light; hence, the resulting spectrum is also unique, much like the individual fingerprints of people.

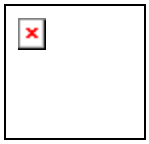
11. The frequency of motion the molecule should be in the range of 10^{12}-10^{14} s^{-1} for infrared radiation to be absorbed.

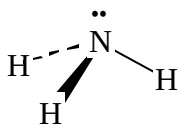
Molecular Shape

12. Ball and stick models, space filling models, and two-dimensional pictures using wedges and dashed lines:

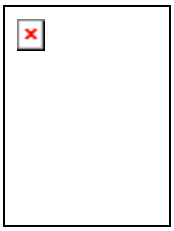
   (a)

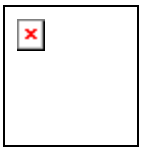


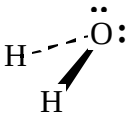




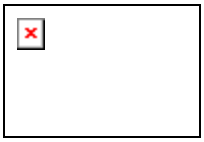
   (b)

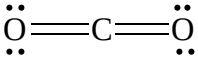






(c)





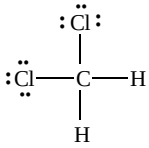
13. *Define the problem*: Write Lewis Structures for a list of formulas and identify their shape.

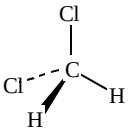
Develop a plan: Follow the systematic plan for Lewis structures given in the answers to Question 8.16, then determine the number of bonded atoms and lone pairs on the central atom, determine the designated type (AX_nE_m) and use Table 9.1. *Note: It is not important to expand the octet of a central atom solely for the purposes of lowering its formal charge, because the shape of the molecule will not change. Hence, we will write Lewis structures that follow the octet rule unless the atom needs more than eight electrons.*

Execute the plan:

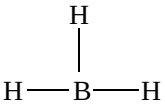
(a) BeH_2 (4 e^-) The type is AX_2E_0, so it is linear.

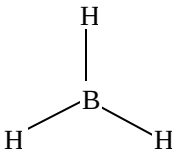
(b) CH_2Cl_2 (20 e^-) The type is AX_4E_0, so it is tetrahedral.



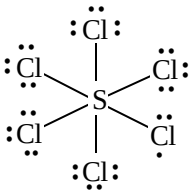


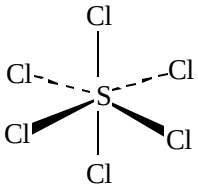
(c) BH_3 (6 e^-) The type is AX_3E_0, so it is triangular planar.



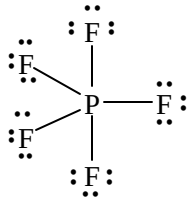
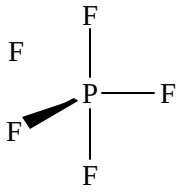


(d) SCl_6 (48 e^-) The type is AX_6E_0, so it is octahedral.





(e) PF_5 (40 e^-) The type is AX_5E_0, so it is triangular bipyramidal.

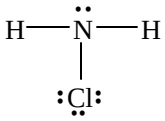
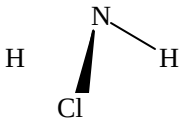



14. *Define the problem*: Write Lewis Structures for a list of formulas and identify their shape.

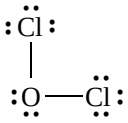
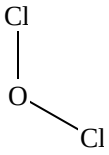
Develop a plan: Follow the systematic plan for Lewis structures given in the answers to Question 8.15, then determine the number of bonded atoms and lone pairs on the central atom, determine the designated type (AX_nE_m) and use Table 9.1.

Execute the plan:

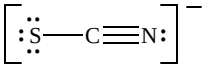
(a) NH_2Cl (14 e^-) The type is AX_3E_1, so the electron-pair geometry is tetrahedral and the molecular geometry is triangular pyramidal.

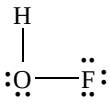
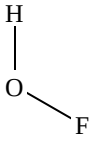
(b) OCl_2 (20 e^-) The type is AX_2E_2, so the electron-pair geometry is tetrahedral and the molecular geometry is angular (109.5°).

(c) SCN^- (16 e^-) The type is AX_2E_0, so the electron-pair geometry and the molecular geometry are both linear.

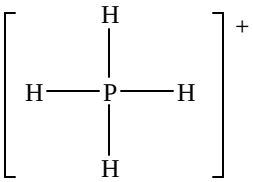


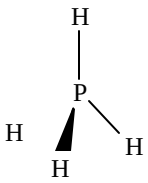
(d) HOF (14 e^-) The type is AX_2E_2, so the electron-pair geometry is tetrahedral and the molecular geometry is angular (109.5°).

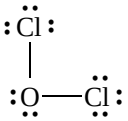
15. Adapt the method given in the answers to Question 13.

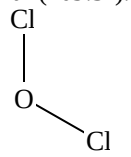
(b) PH_4^+ (8 e^-) The type is AX_4E_0, so it is tetrahedral.



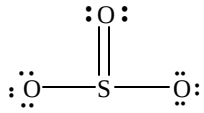


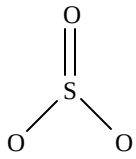
(b) OCl_2 (20 e^-) The type is AX_2E_2, so the electron-pair geometry is tetrahedral and the molecular geometry is angular (109.5°).



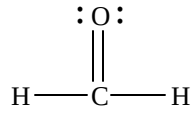


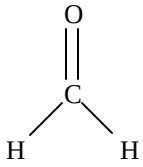
(c) SO_3 (24 e^-) The type is AX_3E_0, so it is triangular planar.





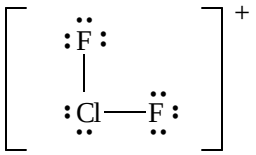
(d) H_2CO (12 e^-) The type is AX_3E_0, so it is triangular planar.

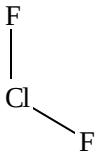




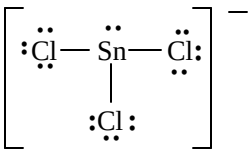
16. Adapt the method given in the answers to Question 14.

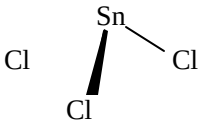
(a) ClF_2^+ (20 e^-) The type is AX_2E_2, so the electron-pair geometry is tetrahedral and the molecular geometry is angular (109.5°).



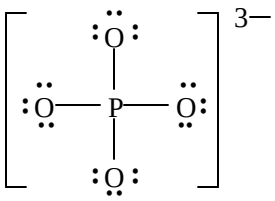


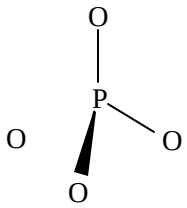
(b) $SnCl_3^-$ (26 e^-) The type is AX_3E_1, so the electron-pair geometry is tetrahedral and the molecular geometry is triangular pyramidal.



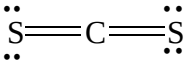


(c) PO_4^{3-} (32 e^-) The type is AX_4E_0, so the electron-pair geometry and the molecular geometry are both tetrahedral.



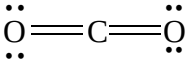


(d) CS_2 (16 e^-) The type is AX_2E_0, so the electron-pair geometry and the molecular geometry are both linear.

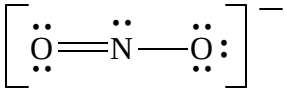


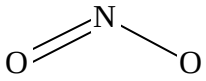
16. Adapt the method given in the answers to Question 14.

(a) CO_2 (16 e^-) The type is AX_2E_0, so the electron-pair geometry and the molecular geometry are both linear.

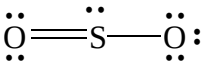


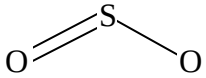
(b) NO_2^- (18 e^-) The type is AX_2E_1, so the electron-pair geometry is triangular planar and the molecular geometry is angular (120°).



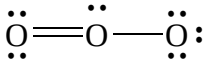


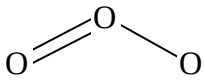
(c) SO_2 (18 e^-) The type is AX_2E_1, so the electron-pair geometry is triangular planar and the molecular geometry is angular (120°).



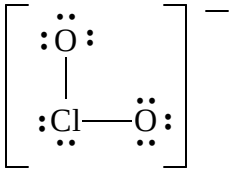


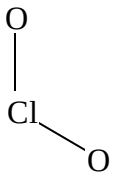
(d) O_3 (18 e^-) The type is AX_2E_1, so the electron-pair geometry is triangular planar and the molecular geometry is angular (120°).





(e) ClO_2^- (20 e^-) The type is AX_2E_2, so the electron-pair geometry is tetrahedral and the molecular geometry is angular (109.5°).

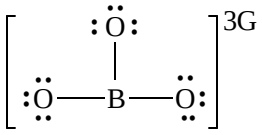


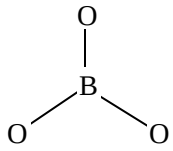


All of these ions and molecules have one central atom with two O atoms bonded to it. The number and type of bonded atoms is constant. The geometries vary depending on how many lone pairs are on the central atom. The structures with the same number of valance electrons all have the same geometry.

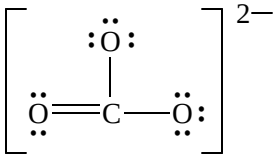
17. Adapt the method given in the answers to Question 13.

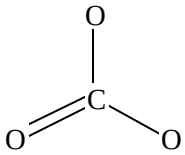
(a) BO_3^{3-} (24 e^-) The type is AX_3E_0, so both the electron-pair geometry and the molecular geometry are triangular planar.



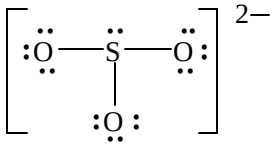


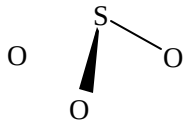
(b) CO_3^{2-} (24 e^-) AX_3E_0, so both the electron-pair geometry and the molecular geometry are triangular planar.



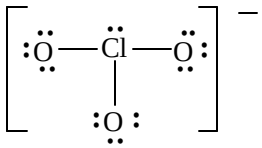


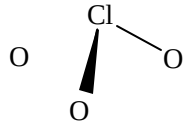
(c) SO_3^{2-} (26 e^-) AX_3E_1, so the electron-pair geometry is tetrahedral and the molecular geometry is triangular pyramidal.





(d) ClO_3^- (26 e^-) AX_3E_1, so the electron-pair geometry is tetrahedral and the molecular geometry is triangular pyramidal.

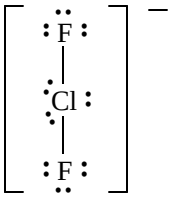


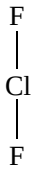


All of these ions and molecules have one central atom with three O atoms bonded to it. The number and type of bonded atoms is constant. The geometries vary depending on how many lone pairs are on the central atom. The structures with the same number of valance electrons all have the same geometry.

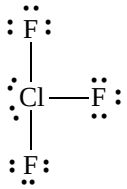
18. Adapt the method given in the answers to Question 14.

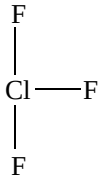
(a) ClF_2^- (22 e^-) The type is AX_2E_3, so the electron-pair geometry is triangular bipyramid and the molecular geometry is linear.



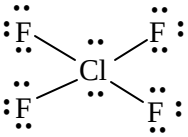


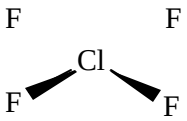
(b) ClF_3 (28 e^-) The type is AX_3E_2, so the electron-pair geometry is triangular bipyramid and the molecular geometry is T-shaped.



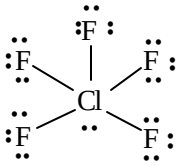


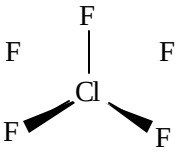
(c) ClF_4^- (36 e^-) The type is AX_4E_2, so the electron-pair geometry is octahedral and the molecular geometry is square planar.





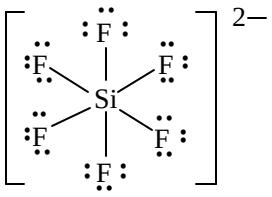
(d) ClF_5 (42 e^-) The type is AX_5E_1, so the electron-pair geometry is octahedral and the molecular geometry is square pyramidal.

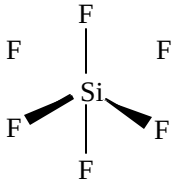




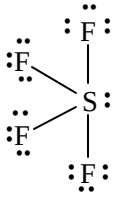
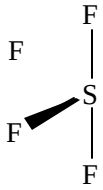
19. Adapt the method given in the answers to Question 13.

(a) SiF_6^{2-} (48 e^-) The type is AX_6E_0, so both the electron-pair geometry and the molecular geometry are octahedral.

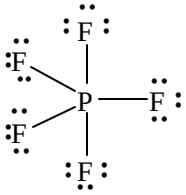
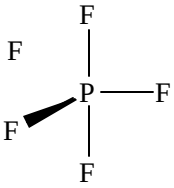




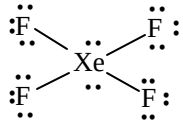
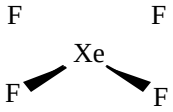
(b) SF_4 (34 e^-) The type is AX_4E_1, so the electron-pair geometry is triangular bipyramid and the molecular geometry is seesaw.

(c) PF_5 (40 e^-) The type is AX_5E_0, so the electron-pair geometry is triangular bipyramidal and the molecular geometry is triangular bipyramidal.

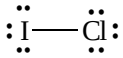
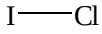



(d) XeF_4 (36 e^-) The type is AX_4E_2, so the electron-pair geometry is octahedral and the molecular geometry is square pyramidal.

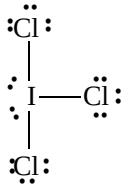
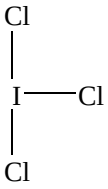



20. Adapt the method given in the answers to Question 14.

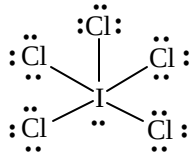
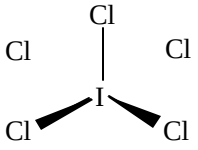
ICl (14 e^-) Two atoms bonded together. The molecular geometry is linear.

ICl_3 (28 e^-) The type is AX_3E_2, so the molecular geometry is T-shaped.

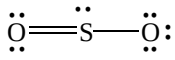



ICl_5 (42 e^-) The type is AX_5E_1, so the molecular geometry is square pyramidal.

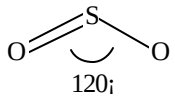



27. Adapt the method given in the answers to Question 13 to get the electron-pair geometry of the second atom in the bond. Use this to predict the approximate bond angle.

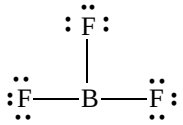
(a) SO_2 (18 e^-)



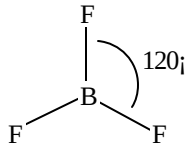
The type is AX_2E_1, so the electron-pair geometry is triangular planar and the approximate O–S–O angle is 120°.



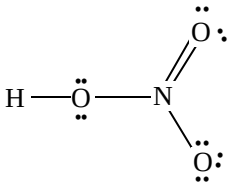
(b) BF_3 (24 e^-)



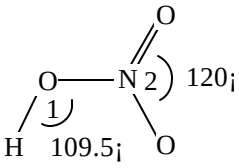
The type is AX_3E_0, so the electron-pair geometry is triangular planar and the approximate F–B–F angle is 120°.



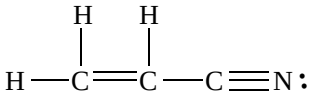
(c) HNO_3 (24 e^-)



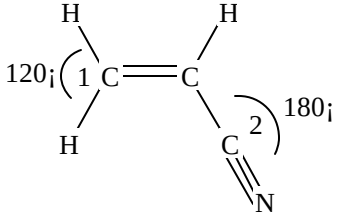
Look at the first O atom: The type is AX_2E_2, so the electron-pair geometry is tetrahedral and the approximate N–O–H angle is 109.5°. Look at the N atom: The type is AX_3E_0, so the electron-pair geometry is triangular planar and the approximate O–N–O angle is 120°.



(c) CH_2CHCN (20 e^-)

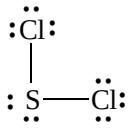


Look at the first C atom: The type is AX_3E_0, so the electron-pair geometry is triangular planar and the approximate H–C–H angle is 120°. Look at the third C atom: The type is AX_2E_0, so the electron-pair geometry is linear and the approximate C–C–N angle is 180°.

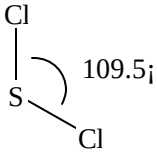


22. Adapt the method given in the answers to Question 14 to get the electron-pair geometry of the second atom in the bond description (e.g., A in X–A–Y). Use this to predict the approximate bond angle.

(a) SCl_2 (20 e^-)

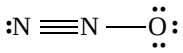


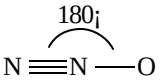
The type is AX_2E_2, so the electron-pair geometry is tetrahedral and the approximate Cl–S–Cl angle is 109.5°.



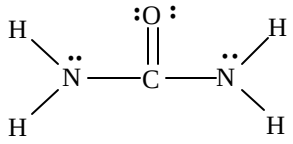
(b) N_2O (16 e^-)

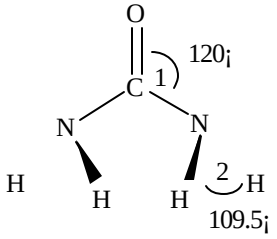
The type is AX_2E_0, so the electron-pair geometry is linear and the approximate N–N–O angle is 180°.



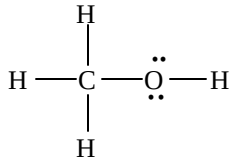


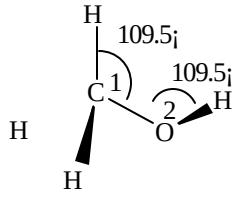
(c) NH_2CONH_2 (24 e^-) Look at the C atom: The type is AX_3E_0, so the electron-pair geometry is triangular planar and the approximate O–C–N angle is 120°. Look at the second N atom: The type is AX_3E_1, so the electron-pair geometry is tetrahedral and the approximate H–N–H angle is 109.5°.





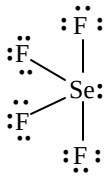
(c) CH_3OH (14 e^-) Look at the C atom: The type is AX_4E_0, so the electron-pair geometry is tetrahedral and the approximate H–C–O angle is 109.5°. Look at the O atom: The type is AX_2E_2, so the electron-pair geometry is tetrahedral and the approximate C–O–H angle is 109.5°.

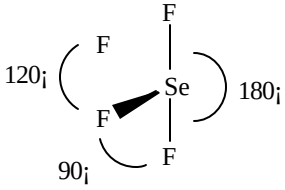




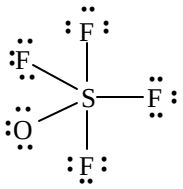
23. Adapt the method given in the answers to Question 21.

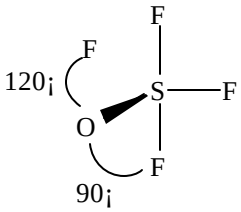
(a) SeF_4 (34 e^-) The type is AX_4E_1, so the electron-pair geometry is trigonal bipyramid. The $F_{equitorial}$–Se–$F_{equitorial}$ angle is 120°, the $F_{equitorial}$–Se–F_{axial} angles are 90° and F_{axial}–Se–F_{axial} angle is 180°.



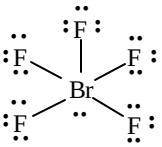


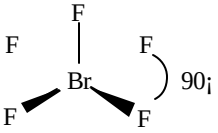
(b) SOF_4 (40 e^-) The type is AX_5E_0, so the electron-pair geometry is triangular bipyramidal, equatorial-F–S–O angles are 120° and the axial-F–S–O angles are 90°.





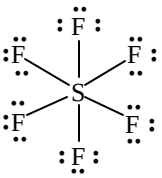
(c) BrF_5 (42 e^-) The type is AX_5E_1, so the electron-pair geometry is octahedral and all the F–Br–F angles are 90°.

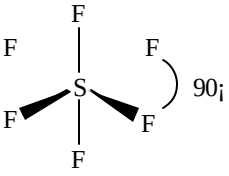




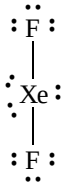
24. Adapt the method given in the answers to Question 22.

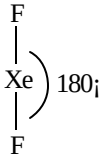
(a) SF_6 (48 e^-) The type is AX_6E_0, so the electron-pair geometry is octahedral and all the F–S–F angles are 90°.



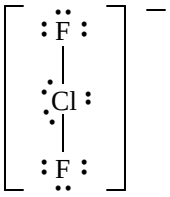


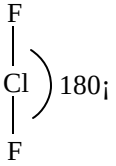
(b) XeF_2 (22 e^-) The type is AX_2E_3, so the electron-pair geometry is triangular bipyramidal, and the F–Xe–F angle is 180°.



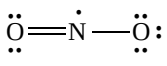


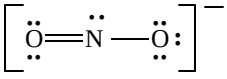
(c) ClF_2^- (22 e^-) The type is AX_2E_3, so the electron-pair geometry is triangular bipyramidal, and the F–Cl–F angle is 180°.





25. NO_2 molecule and NO_2^- ion differ by only one electron. NO_2 has 17 electrons and NO_2^- has 18 electrons. Their Lewis structures are quite similar:

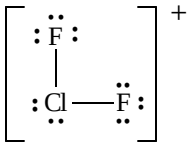


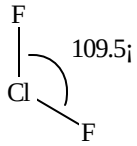


According to VESPR, both of these are triangular planar (AX_2E_1), where the O–N–O angle is approximately 120°. However, the single unpaired electron in NO_2 molecule is not as good at repelling other electrons as a full pair would be. When a nonbonded pair of electrons is repelling the bonding pairs, it pushes them closer together making a narrower angle. Hence, we will predict that the O–N–O angle in NO_2^- ion is slightly smaller than the angle in NO_2 molecule.

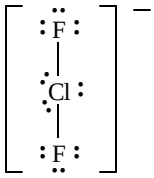
26. ClF_2^+ cation and ClF_2^- anion differ by two electrons. ClF_2^+ has 20 electrons and ClF_2^- has 22 electrons. Use the VSEPR model on each of them.

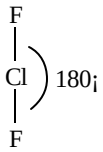
ClF_2^+ cation has type AX_2E_2..The electron-pair geometry is tetrahedral, and the F–Cl–F angle is 109.5° as shown below:





ClF_2^- anion has type AX_2E_3. The electron-pair geometry is triangular bipyramidal, and the F–Cl–F angle is 180° as shown below:





According to the VESPR model, we predict that the F–Cl–F angle in a ClF_2^- anion is a greater angle than the angle in a ClF_2^+ cation.

Hybridization and Multiple Bonds

27. (a) One s and three p orbitals combine to make sp^3 hybrid orbitals.

(b) One s, three p, and two d orbitals combine to make sp^3d^2 hybrid orbitals.

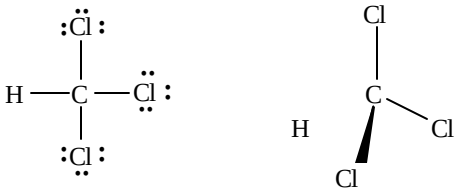
(c) One s and two p orbitals combine to make sp^2 hybrid orbitals.

28. (a) When four atomic orbitals (one s and three p orbitals) combine to make hybrid orbitals, **four** sp^3 hybrid orbitals are formed.

(b) When six atomic orbitals (one s, three p, and two d orbitals) combine to make hybrid orbitals, **six** sp^3d^2 hybrid orbitals are formed.

(c) When three atomic orbitals (one s and two p orbitals) combine to make hybrid orbitals, **three** sp^2 hybrid orbitals are formed.

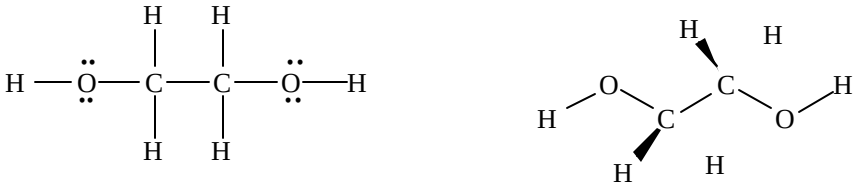
29. Write a Lewis structure for $HCCl_3$ and use VSEPR to determine the molecular geometry as described in the answer to Question 13. Use Table 9.2 to determine the hybridization of the central atom using the electron-pair geometry. The molecule is AX_4E_0 type, so its electron-pair geometry and its molecular geometry are tetrahedral.



To make four equal bonds with an electron-pair geometry of tetrahedral, the C atom must be sp^3 hybridized, according to Table 9.2. The H atom and Cl atoms are not hybridized.

30. Write a Lewis structure for $HOCH_2CH_2OH$ and use VSEPR to determine the geometry of the inner atoms – namely, each of the O atoms and C atoms as described in the answer to Question 14. Use Table 9.2 to determine the hybridization of each inner atom using the electron-pair geometry.

The O atoms are AX_2E_2 type, so the H–O–C angles will be approximately the tetrahedral angle of 109.5°. The C atoms are AX_4E_0 type, so the O–C–C, O–C–H, H–C–C and H–C–H angles will also be approximately the tetrahedral angle of 109.5°.



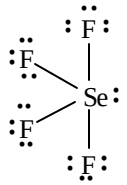
The O atoms must be sp^3 hybridized, according to Table 9.2, to make two bonds and two lone pairs with an electron-pair geometry of tetrahedral. The C atoms must be sp^3 hybridized, according to Table 9.2, to make four bonds with an electron-pair geometry of tetrahedral.

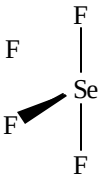
31. Follow the procedure described in the answer to Question 29, except use Table 9.3. SF_4 structure and geometry is provided in the answer to Questions 19(b) and 92. The S atom must be sp^3d hybridized, according to Table 9.3. SF_6 structure and geometry is provided in the answer to Questions 24 and 92. The S atom must be sp^3d^2 hybridized, according to Table 9.3.

32. Draw the Lewis structure and use VSEPR to determine the geometry of the central atom as described in the answer to Question 16. Use Table 9.2 or Table 9.3 to determine the hybridization of the central atom using the electron-pair geometry.

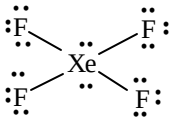
(a) GeF_4 (32 e^-) The type is AX_4E_0, so both the electron-pair geometry and the molecular geometry are tetrahedral. The Ge atom must be sp^3 hybridized, according to Table 9.2, to make these four bonds.

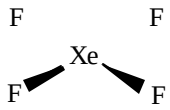
(b) SeF_4 (34 e^-) The type is AX_4E_1, so the electron-pair geometry is triangular bipyramidal and the molecular geometry is seesaw. The Se atom must be sp^3d hybridized, according to Table 9.3, to make these four bonds and to have one lone pair.





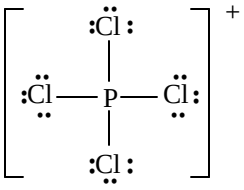
(c) XeF_4 (36 e^-) The type is AX_4E_2, so the electron-pair geometry is octahedral and the molecular geometry is square pyramidal. The Xe atom must be sp^3d^2 hybridized, according to Table 9.3, to make these four bonds and to have two lone pairs.

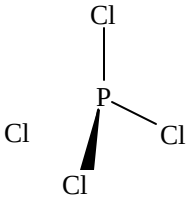




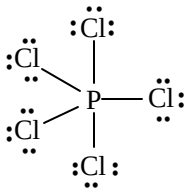
33. Draw the Lewis structure and use VSEPR to determine the geometry of the central atom as described in the answer to Question 17. Use Table 9.2 or Table 9.3 to determine the hybridization of the central atom using the electron-pair geometry.

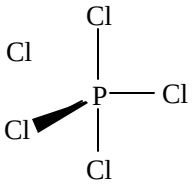
(a) PCl_4^+ (32 e^-) The type is AX_4E_0, so both the electron-pair geometry and the molecular geometry are tetrahedral. The P atom must be sp^3 hybridized, according to Table 9.2, to make these four bonds.



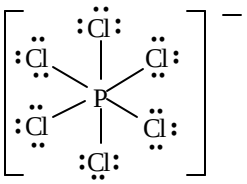


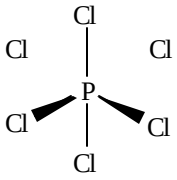
(b) PCl_5 (40 e^-) The type is AX_5E_0, so the electron-pair geometry and the molecular geometry are triangular bipyramidal. The P atom must be sp^3d hybridized, according to Table 9.3, to make these five bonds.





(c) PCl_6^- (48 e^-) The type is AX_4E_2, so the electron-pair geometry and the molecular geometry are octahedral. The P atom must be sp^3d^2 hybridized, according to Table 9.3, to make these six bonds.





34. The bond angles are associated with the electron-pair geometry, so use Figure 9.4.

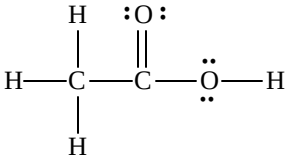
    (a) Tetrahedral sp^3 hybrid orbitals are generally associated with bond angles of 109.5°.

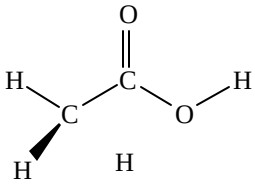
    (b) Octahedral sp^3d^2 hybrid orbitals are generally associated with bond angles of 90°.

    (c) Triangular planar sp^2 hybrid orbitals are generally associated with bond angles of 120°.

35. There are two mistakes described here. First, the n = 2 shell does not contain d orbitals, therefore it is inappropriate to use a "2d atomic orbital" to make any hybrid orbital. Secondly, there is no mention of sp^2d hybrid orbitals in this chapter; the student probably meant to use three p orbitals to make sp^3d hybrid orbitals.

36. Draw the Lewis structure and use VSEPR to determine the electron-pair geometry of each of the C atoms. Use Table 9.2 or Table 9.3 to determine the hybridization of the central atom using the electron-pair geometry. The bond angles are associated with the electron-pair geometry, also, so use Figure 9.4.

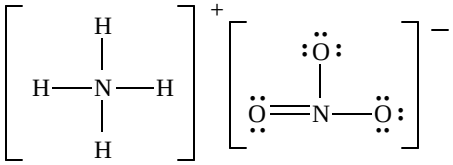


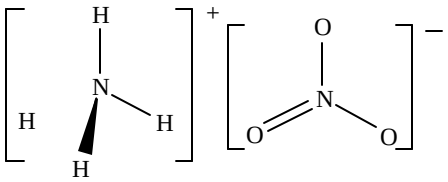


    (a) Look at the first C atom: The type is AX_4E_0, so the electron-pair geometry is tetrahedral and this C atom's hybridization is sp^3. Look at the second C atom: The type is AX_3E_0, so the electron-pair geometry is triangular planar and this C atom's hybridization is sp^2.

    (b) The sp^3-hybridized C atom has tetrahedral H–C–H and H–C–C bond angles of approximately 109.5°. The sp^2-hybridized C atom has triangular planar C–C–O and O–C–O bond angles of approximately 120°.

37. Draw the Lewis structure for the ions in this ionic compound and use VSEPR separately on the cation and the anion to determine the electron-pair geometry of each of the N atoms. Use Table 9.2 or Table 9.3 to determine the hybridization of the central atom using the electron-pair geometry. The bond angles are associated with the electron-pair geometry, also, so use Figure 9.4.





(a) Look at the first N atom: The type is AX_4E_0, so the electron-pair geometry is tetrahedral and this N atom's hybridization is sp^3. Look at the second N atom: The type is AX_3E_0, so the electron-pair geometry is triangular planar and this N atom's hybridization is sp^2.

(b) The sp^3-hybridized N atom has tetrahedral H–N–H bond angles of approximately 109.5°. The sp^2-hybridized N atom has triangular planar O–N–O bond angles of approximately 120°.

38. Use the Lewis structure of alanine and the VSEPR model to determine the electron-pair geometry of each of the atoms. Use Table 9.2 to determine the hybridization of the central atom using the electron-pair geometry. The bond angles are associated with the electron-pair geometry also, so use Figure 9.4.

Look at the first C atom (the one farthest to the left): The type is AX_4E_0, so the electron-pair geometry is tetrahedral and this C atom's hybridization is sp^3. The sp^3-hybridized C atom has tetrahedral bond angles of approximately 109.5°.

Look at the second C atom (the center one): The type is AX_4E_0, so the electron-pair geometry is tetrahedral and this C atom's hybridization is sp^3. The sp^3-hybridized C atom has tetrahedral bond angles of approximately 109.5°.

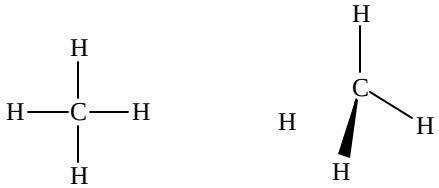
Look at the third C atom (the one farthest to the right): The type is AX_3E_0, so the electron-pair geometry is triangular planar and this C atom's hybridization is sp^2. The sp^2-hybridized C atom has triangular planar bond angles of approximately 120°.

Look at the N atom: The type is AX_3E_1, so the electron-pair geometry is tetrahedral and this N atom's hybridization is sp^3. The sp^3-hybridized N atom has tetrahedral bond angles of approximately 109.5°.

Look at the O atom on the right: The type is AX_2E_2, so the electron-pair geometry is tetrahedral and this O atom's hybridization is sp^3. The sp^3-hybridized O atom has tetrahedral bond angles of approximately 109.5°.

The top O atom has only one atom bonded to it. It is not hybridized and has no bond angles.

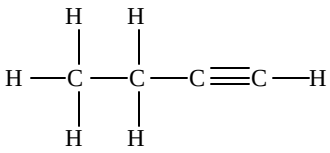
39. Choose an alkane, such as methane, CH_4, and write its Lewis structure. Use the VSEPR model to determine the electron-pair geometry of each of the atoms. Use Table 9.2 to determine the hybridization of the central atom using the electron-pair geometry. The bond angles are associated with the electron-pair geometry, also, so use Figure 9.4.

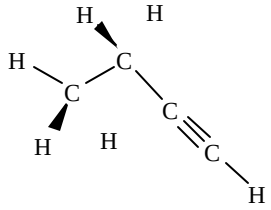


Look at the C atom: The type is AX_4E_0, so the electron-pair geometry is tetrahedral and its hybridization is sp^3. The sp^3-hybridized C atom has tetrahedral bond angles of approximately 109.5°.

Larger alkanes will all follow the same pattern. Since they are saturated, all the carbon atoms have four bonds, and every one of them will have a tetrahedral shape and tetrahedral bond angles.

40. (a) Write the Lewis structure. Use the VSEPR model to determine the electron-pair geometry of each of the atoms. Use Table 9.2 to determine the hybridization of the central atom using the electron-pair geometry. The bond angles are associated with the electron-pair geometry also, so use Figure 9.4.





Look at the first two C atoms (the two farthest to the left): They are both of type AX_4E_0, so the electron-pair geometry is tetrahedral and these C atoms have sp^3. hybridization. The sp^3-hybridized C atoms have tetrahedral bond angles of approximately 109.5°.

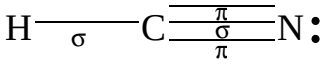
Look at the second two C atoms (the two farthest to the right): They are both of type AX_2E_0, so the electron-pair geometry is linear and these C atoms have *sp* hybridization. The *sp*-hybridized C atoms have linear bond angles of approximately 180°.

(b) The shortest carbon-carbon bond is the triple bond. That can be confirmed by looking up the bond lengths in Table 8.1.

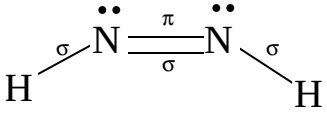
(c) The strongest carbon-carbon bond is the triple bond. That can be confirmed by looking up the bond energies in Table 8.2.

41. The first bond between two atoms must always be a σ bond. When more than one pair of electrons are shared between atoms, they are always part of π bonds. So the second bond in a double bond and the second and third bonds in a triple bond are always π bonds.

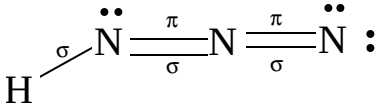
(a)



(b)

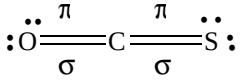


(c)

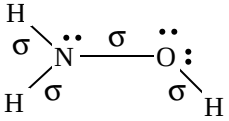


42. The first bond between two atoms must always be a σ bond. When more than one pair of electrons are shared between atoms, they are always part of π bonds. So the second bond in a double bond and the second and third bonds in a triple bond are always π bonds.

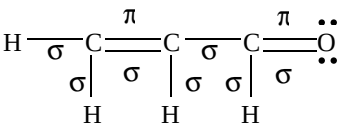
(a)



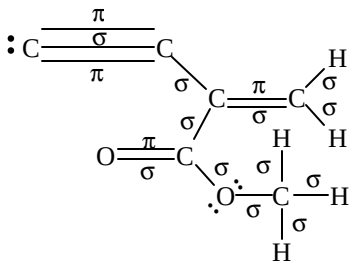
(b)



(c)



43. Use the method described in the answer to questions 38 and 41.



(a) The structure has 12 sigma bonds.

(b) The structure has four pi bonds.

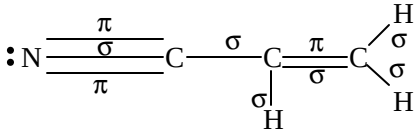
(c) Look at the C atom bonded to the N atom: It is of type AX_2E_0, so the electron-pair geometry is linear and this C atom has *sp* hybridization.

(d) Look at the C atom bonded both O atoms: It is of type AX_3E_0, so the electron-pair geometry is triangular planar and this C atom has sp^2 hybridization.

Look at the C atom bonded to only one O atom: The type is AX_4E_0, so the electron-pair geometry is tetrahedral this C atom has sp^3 hybridization.

(e) Look at the double bonded O atom: The type is AX_1E_2, so the electron-pair geometry triangular planar and this O atom has sp^2 hybridization.

44. Use the method described in the answer to questions 38 and 42.



(a) As seen above, the structure has six sigma bonds.

(b) As seen above, the structure has three pi bonds.

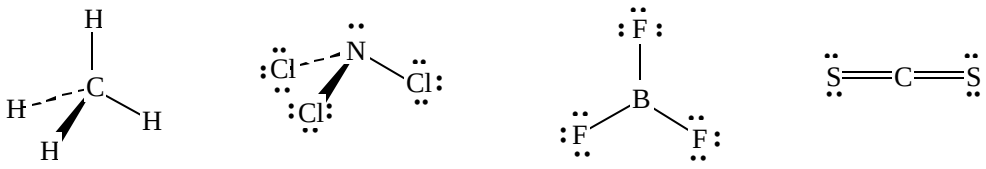
(c) Look at the C atom bonded to the N atom: It is of type AX_2E_0, so the electron-pair geometry is linear and these C atoms have *sp* hybridization.

(c) Look at the N atom: It is of type AX_1E_1, so the electron-pair geometry is linear and it has *sp* hybridization.

(e) Both H-bearing C atoms are type AX_3E_0, so the electron-pair geometry is triangular planar and both of them have a hybridization of sp^2.

Molecular Polarity

45. We need the Lewis structures and molecular shapes of CH_4, NCl_3, BF_3, and CS_2.



(a) The bond polarity is related to the difference in electronegativity. Use Figure 8.6 to get electronegativity (EN) values:

$$EN_C = 2.5,\ EN_H = 2.1,\ EN_N = 3.0,\ EN_{Cl} = 3.0,$$

$$EN_B = 2.0,\ EN_F = 4.0,\ EN_S = 2.5$$

$\Delta EN_{C-H} = EN_C - EN_H = 2.5 - 2.1 = 0.4$

$\Delta EN_{N-Cl} = EN_N - EN_{Cl} = 3.0 - 3.0 = 0.0$

$\Delta EN_{B-F} = EN_F - EN_B = 4.0 - 2.0 = 2.0$ B–F is most polar.

$\Delta EN_{S-C} = EN_C - EN_S = 2.5 - 2.5 = 0.0$

The most polar bonds are in BF_3.

(b) Use the description given in Section 9.4 to determine if the molecule is polar:

CH_4 is not polar, since the four terminal H atoms are all the same, they are symmetrically arranged (in a tetrahedral shape) around the C atom, and they all have the same partial charge.

$$\overset{\delta^+}{H} \text{—} \overset{\delta^-}{C}$$

NCl_3 is polar, since the three terminal Cl atoms are not symmetrically arranged around the N atom.

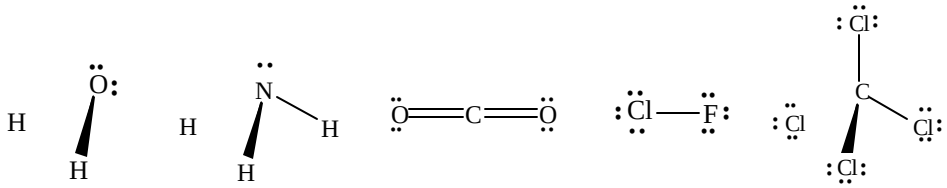
BF_3 is not polar, since the three terminal F atoms are all the same, they are symmetrically arranged (in a triangular planar shape) around the B atom, and they all have the same partial charge.

$$\overset{\delta^+}{B} \text{—} \overset{\delta^-}{F}$$

CS_2 is not polar, since the bonds are not polar and, they are symmetrically arranged (in a linear shape) around the C atom, and they all have the same partial charge of approximately zero.

So, CH_4 , BF_3 and CS_2 are the molecules in the list that are not polar.

46. We need the Lewis structures and molecular shapes of H_2O, NH_3, CS_2, ClF, and CCl_4.



(a) The bond polarity is related to the difference in electronegativity. Use Figure 8.6 to get electronegativity (EN) values:

$$EN_O = 3.5,\ EN_H = 2.1,\ EN_N = 3.0,\ EN_C = 2.5,\ EN_{Cl} = 3.0$$

$\Delta EN_{O-H} = EN_O - EN_H = 3.5 - 2.1 = 1.4$ O–H is most polar.

$\Delta EN_{N-H} = EN_N - EN_H = 3.0 - 2.1 = 0.9$

$\Delta EN_{C-O} = EN_O - EN_C = 3.5 - 2.5 = 1.0$

$\Delta EN_{Cl-F} = EN_F - EN_{Cl} = 3.5 - 3.0 = 0.5$

$$\Delta EN_{C-Cl} = EN_{Cl} - EN_C = 3.0 - 2.5 = 0.5$$

The most polar bonds are in H_2O.

(b) Use the description given in Section 9.4 to determine if the molecule is polar:

H_2O is polar, since the terminal atoms are not symmetrically arranged around the O atom.

NH_3 is polar, since the terminal atoms are not symmetrically arranged around the N atom.

CO_2 is not polar, since the two terminal atoms are all the same, they are symmetrically arranged (in a l shape) around the C atom, and they have the same partial charge.

$$\underset{\delta^+}{C} \text{——} \underset{\delta^-}{O}$$

CCl_4 is not polar, since the four terminal atoms are all the same, they are symmetrically arranged (in a tetrahedral shape) around the C atom, and they all have the same partial charge.

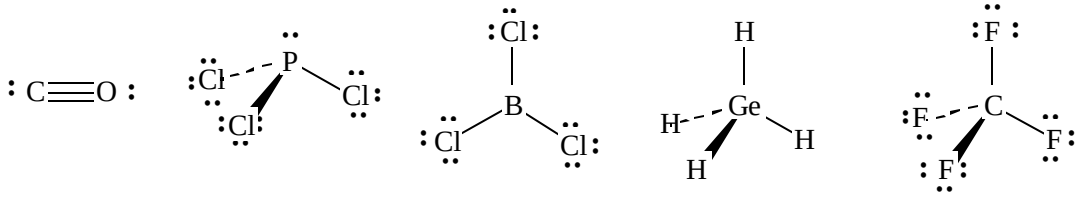
$$\underset{\delta^+}{C} \text{——} \underset{\delta^-}{Cl}$$

So, CO_2 and CCl_4 are the molecules in the list that are not polar.

(c) The more negatively charged atom of a pair of bonded atoms is the atom with the largest electronegativity. In ClF, the F atom is more negatively charged.

47. We need the Lewis structures and molecular shapes of the molecules:

(a) (b) (c) (d) (e)



The molecules that are polar have asymmetrical atom arrangement, such as (a) CO and (b) PCl_3. The others have symmetrical arrangements of identical atoms with the same partial charge and are not polar.

The bond polarity is related to the difference in electronegativity. Use Figure 8.6 to get electronegativity (EN) values:

$$EN_C = 2.5,\ EN_O = 3.5,\ EN_P = 2.1,\ EN_B = 2.0,\ EN_{Cl} = 3.0,$$

$$EN_{Ge} = 1.8,\ EN_H = 2.1,\ EN_F = 4.0$$

$$\Delta EN_{O-C} = EN_O - EN_C = 3.5 - 2.5 = 1.0$$

$$\Delta EN_{P-Cl} = EN_{Cl} - EN_P = 3.0 - 2.1 = 0.9$$

$$\Delta EN_{B-Cl} = EN_{Cl} - EN_B = 3.0 - 2.0 = 1.0$$

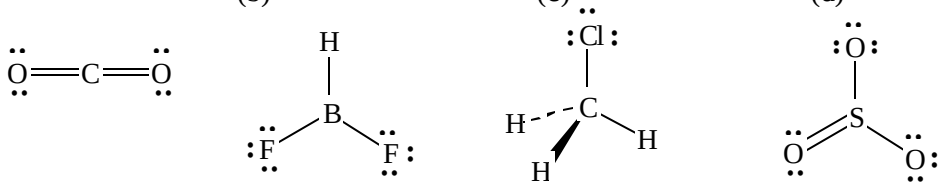
$$\Delta EN_{Ge-H} = EN_H - EN_{Ge} = 2.1 - 1.8 = 0.3$$

$$\Delta EN_{C-F} = EN_F - EN_C = 4.0 - 2.5 = 1.5$$ C–F is most polar.

The most polar bonds are in (e) CF_4.

48. We need the Lewis structures and molecular shapes of the mo lecules:

(a) (b) (c) (d)



The molecules that are not polar have asymmetrical atom arrangement, such as (b) HBF_2 and (b) CH_3Cl. The others have symmetrical arrangements of identical atoms with the same partial charge. (Note: Three equivalent resonance structures following the octet rule can be written for SO_3, making each S–O bond the same length and strength.)

The bond polarities related to the difference in electronegativity. Use Figure 8.6 to get electronegativity (EN) values:

$$EN_B = 2.0,\ EN_H = 2.1,\ EN_F = 4.0,\ EN_C = 2.5,\ EN_{Cl} = 3.0$$

$$\Delta EN_{B-H} = EN_H - EN_B = 2.1 - 2.0 = 0.1$$

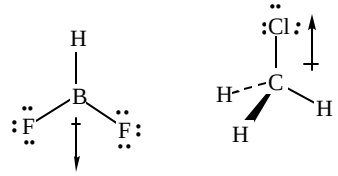
$$\Delta EN_{B-F} = EN_F - EN_B = 4.0 - 2.0 = 2.0$$

$$\Delta EN_{C-H} = EN_C - EN_H = 2.5 - 2.1 = 0.4$$

$$\Delta EN_{C-Cl} = EN_{Cl} - EN_C = 3.0 - 2.5 = 0.5$$

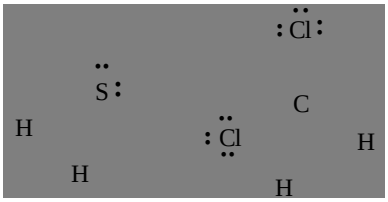
The bond pole arrows' lengths are related to their ΔEN, and points toward the atom with the more negative EN. So, the B–F arrows are much longer than the HB arrow, and a net dipole points toward the F atoms' side of the molecule, making the F atoms' side of the molecule the partial negative end and the H atom's side of the molecule the partial positive end.

The C–Cl arrow points toward Cl, and the C–H points toward the C, so all the arrows point toward the C. (Left right, and back forward cancel due to the symmetry of the triangular orientation of the H atoms). That means a net dipole points toward the Cl atom's side of the molecule, making the Cl atom's side of the molecule the partial negative end and the H atoms' side of the molecule the partial positive end.



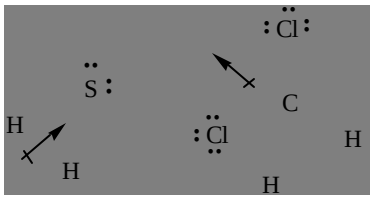
49. We need the Lewis Structures and molecular shapes for the molecules:

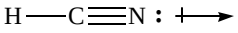
(a) (b) (c) (d)



The polar molecules have a nonzero dipole moment. These are (b) H_2S, (c) CH_2Cl_2, and (d) HCN, because they have a nonsymmetrical arrangement of the atoms in the molecule with polar bonds.

The dipole in the molecules point toward the atoms with high electronegativity and away from the atoms with low electronegativity:





50. The dipole moment relates both to the strength of the bond poles and their directionality.

The bond polarities are related to the difference in electronegativity. Use Figure 8.6 to get electronegativity (EN) values:

$$EN_{Br} = 2.8,\ EN_F = 4.0,\ EN_{Cl} = 3.0$$

$$\Delta EN_{Br-F} = EN_F - EN_{Br} = 4.0 - 2.8 = 1.2$$

$$\Delta EN_{Cl-F} = EN_F - EN_{Cl} = 4.0 - 3.5 = 0.5$$

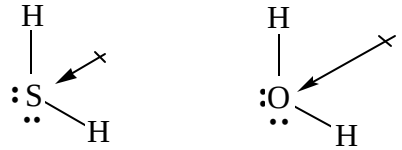
The bond polarity of the bond in BrF is much greater than that in ClF, which explains the significant dipole moment difference.

$$EN_H = 2.1,\ EN_O = 3.5,\ EN_S = 2.5$$

$$\Delta EN_{O-H} = EN_O - EN_H = 3.5 - 2.1 = 1.4$$

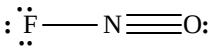
$$\Delta EN_{S-H} = EN_S - EN_H = 2.5 - 2.1 = 0.4$$

The bond polarity of the O–H bonds is greater than that of the O–S bonds, which explains the dipole moment difference.



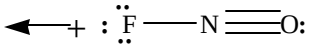
51. Follow the method described in the answer to Question 49.

(a) 18 e^-. The Lewis Structure looks like this:

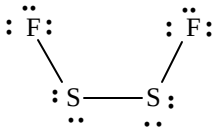


$$\Delta EN_{F-N} = EN_F - EN_N = 4.0 - 3.0 = 1.0$$

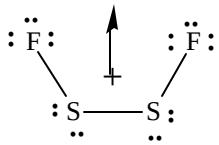
$$\Delta EN_{N-O} = EN_O - EN_N = 3.5 - 3.0 = 0.5$$



(b) 26 e^- . The Lewis Structure looks like this:

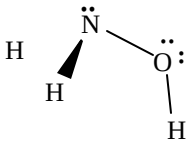


$\Delta EN_{F-S} = EN_F - EN_S = 4.0 - 2.5 = 1.5$



52. Follow the method described in the answer to Question 50.

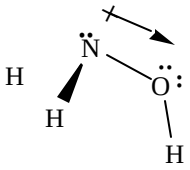
(a) 14 e^- . The Lewis Structure looks like this:



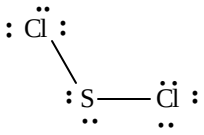
$\Delta EN_{O-H} = EN_O - EN_H = 3.5 - 2.1 = 1.4$

$\Delta EN_{N-H} = EN_N - EN_H = 3.0 - 2.1 = 0.9$

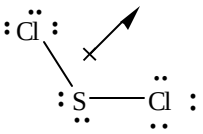
$\Delta EN_{N-O} = EN_O - EN_N = 3.5 - 3.0 = 0.5$



(b) 20 e^- . The Lewis Structure looks like this:



$\Delta EN_{Cl-S} = EN_{Cl} - EN_S = 3.5 - 2.5 = 1.0$



Noncovalent Interactions

53. Water and ethanol can both form hydrogen bonds, hence they have similar strong interactive hydrogen bonding forces. These two substances would easily interact, hence they would mix readily (i.e., they are miscible).

Cyclohexane, a six-carbon-ring hydrocarbon, has no capability for forming hydrogen bonds. Because of its size, it interacts primarily with London forces. The symmetry of the molecule and the only slightly polar bonds give it very little capacity for dipole-dipole interactions. Water molecules would have to give up hydrogen bonds between other water molecules to interact with cyclohexane using only much weaker London forces. These two substances would not interact very well, hence they would not mix readily (i.e., they are not miscible).

54.

Interaction	Distance	Example
ion-ion	longest range	Na^+ interaction with Cl^-
ion-dipole	long range	Na^+ ions in H_2O
dipole-dipole	medium range	H_2O interaction with H_2O
dipole-induced dipole	short range	H_2O interaction with Br_2
induced dipole-induced dipole	shortest range	Br_2 interaction with Br_2

55. Boiling points increase as the strength of the interactive forces increases. The strongest interactive force is hydrogen bonding, then dipole-dipole, then London forces. London forces increase with increasing number of electrons (found in larger atoms) and increased molecular complexity.

(a) Group IV hydrides all interact by London forces. The larger the Group IV atom, the stronger the London forces and the higher the boiling point, because it has more electrons.

(b) NH_3 molecules interact via hydrogen bonding so its boiling point is quite high compared to the other Group V hydrides. The other Group V hydrides interact mostly by London forces and dipole-dipole forces. Dipole forces are not very different between one and the next; however, the larger the Group V atom, and the stronger the London forces the higher the boiling point.

(c) H_2O molecules interact via hydrogen bonding, so its boiling point is quite high compared to the other Group VI hydrides. The other Group VI hydrides interact mostly by London forces and dipole-dipole forces. Dipole forces are not very different between one and the next; however, the larger the Group VI atom, and the stronger the London forces, the higher the boiling point.

(d) HF molecules interact via hydrogen bonding, so its boiling point is quite high compared to the other Group VII hydrides. The other Group VII hydrides interact mostly by dipole-dipole and London forces. Dipole forces are not very different between one and the next; however, the larger the Group VII atom, and the stronger the London forces, the higher the boiling point.

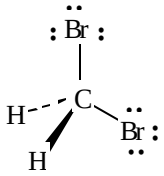
56. Wax is made up of nonpolar molecules that interact almost exclusively by London forces. The water molecules are highly polar and would have to give up hydrogen bonds between other water molecules to interact with wax using only much weaker London forces. These two substances would not interact very well. The water "beads up" in an attempt to have the smallest possible necessary surface interaction with the wax. On a dirty, unwaxed car, the soils and salts that are often found on cars contain ions and polar

compounds. They interact much more readily with water, so the water would not "bead up" on the dirty surface.

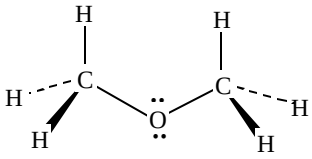
57. Tar is made up of nonpolar molecules that interact almost exclusively by London forces. The water molecules are highly polar and would have to give up hydrogen bonds between other water molecules to interact with tar using only much weaker London forces. Water would not dissolve tar, so it would not be a good solvent to use. The kerosene molecules are non-polar and would interact using London forces. These two substances would be miscible, and kerosene would be a good solvent to remove tar.

58. Hydrogen bonds form between very electronegative atoms in one molecule to H atoms bonded to a very electronegative atom (EN = 3.0) in another molecule. If H atoms are present in a molecule but they are bonded to lower electronegativity atoms, such as C atoms, the molecule cannot use those H atoms for hydrogen bonding.

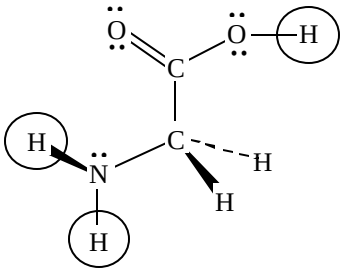
(a) No, the H atoms are bonded to C atoms and the highest electronegativity atom in the molecule is Br (EN = 2.8), so this molecule cannot form hydrogen bonds.



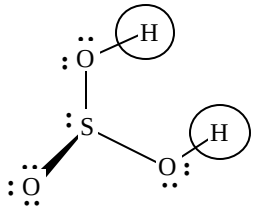
(b) No, the H atoms are bonded to C atoms, so this molecule cannot form hydrogen bonds with other molecules of the same compound. It does have a high electronegativity O atom (EN = 3.5), so this molecule could interact with other molecules, such as H_2O, which can provide the H atoms for hydrogen bonding to the O atom on this molecule.



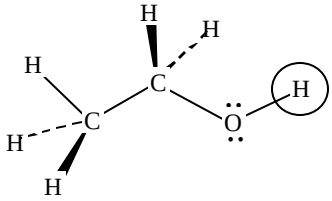
(c) Yes, three H atoms are bonded to high electronegativity atoms (EN_O = 3.5 and EN_N = 3.0). Those H atoms (circled in the structure below) can form hydrogen bonds with the N and O atoms in neighboring molecules.



(d) Yes, two H atoms are bonded to high electronegativity O atoms (EN = 3.5). Those H atoms (circled in the structure below) can form hydrogen bonds with the O atoms in neighboring molecules.



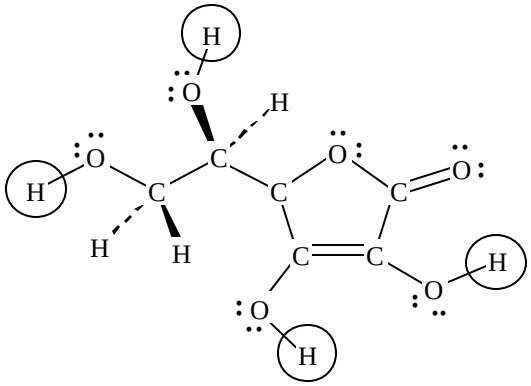
(e) Yes, one H atom is bonded to a high electronegativity O atom (EN = 3.5). That H atom (circled in the structure below) can form hydrogen bonds with the O atoms in neighboring molecules.



59. The noble gases are Group 8 elements: He, Ne, Ar, Kr, Xe, and Rn. These substances are monatomic, so they interact exclusively using London forces. London forces increase as the size of the atom increases. On the periodic table, the atoms lower in the group are larger than the atoms higher in the group, so Rn is the largest and He is the smallest. Boiling points increase as the interactive forces increase, so the order of the noble gases' boiling points, from lowest to highest is as follows:

$$He > Ne > Ar > Kr > Xe > Rn$$

60. Vitamin C is capable of forming hydrogen bonds with water. Four H atoms are bonded to high electronegativity O atoms (EN = 3.5). Those H atoms (circled in the structure below) can form hydrogen bonds with H_2O molecules.



This molecule is quite polar and would not interact well with fats, because they interact primarily using weaker London forces.

61. Cyclohexane, a six-carbon-ring hydrocarbon, has no capability of forming hydrogen bonds. Because of its size, it interacts primarily with London forces. The symmetry of the molecule and the only slightly polar bonds give it very little capacity for dipole-dipole interactions.

Molecule (c), C_3H_8, is also an alkane, and for the same reasons, interacts with the same types of forces as cyclohexane. It would be more soluble in cyclohexane than NaCl or CH_3CH_2OH.

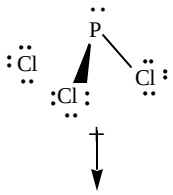
NaCl is composed of ions, which would interact well only with other ions or highly polar substances. While CH_3CH_2OH does have the capability of forming hydrogen bonds, it also has a hydrocarbon end, which interacts with the same types of forces as cyclohexane. Therefore, the least soluble is NaCl.

62. (a) Hydrocarbons have no capability of forming hydrogen bonds and the bonds are close to non-polar. The molecules interact primarily with London forces. The London forces between the molecules must be overcome to sublime $C_{10}H_8$.

(b) As described in (a), propane molecules, a hydrocarbon, would need to overcome London forces to melt.

(c) Decomposing molecules of nitrogen and oxygen require breaking covalent bonds, so the forces that must be overcome are the intramolecular (covalent) forces.

(d) To evaporate polar PCl_3 requires that the molecules overcome dipole-dipole forces.



(e) The double strands of DNA are shown in Figure 9.25. The interaction between the two strands are hydrogen bonds. These hydrogen bonding forces must be overcome to "unzip" the DNA double helix.

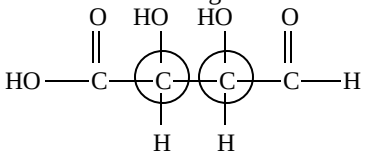
63. Vitamin E is a large molecule that contains a long hydrocarbon chain. Comparatively, its structure provides very few ways to undergo dipole-dipole or hydrogen bonding interactions. Because of its size and composition, it interacts primarily with London forces. Fats interact primarily using the same London forces, so Vitamin E would dissolve in fats.

In contrast, water molecules would have to give up hydrogen bonds between other water molecules and use only much weaker London forces to interact with at large part of the Vitamin E molecule. Hence Vitamin E would not dissolve in water.

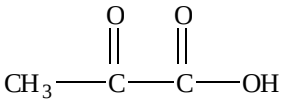
Chirality in Organic Compounds

64. Chiral centers are C atoms with four bonds, where each fragment bonded is different.

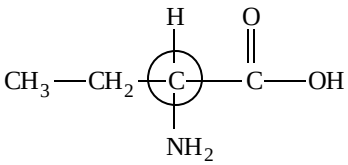
(a) The second and third C atoms have four different fragments: HOOC–, HO–, –H, and –CH(OH)COOH.



(b) This molecule has no chiral centers. The two inner C atoms do not have four bonds. The first C atom has three H atoms bonded.

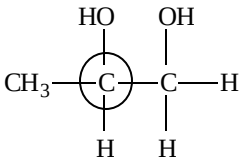


(c) The third C atom has four different fragments: CH_3CH_2–, –H, –COOH, and $–NH_2$. The first and second C atoms have three and two H atoms bonded, respectively, so they are not chiral centers.

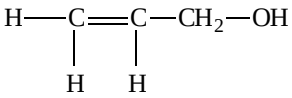


65. Chiral centers are C atoms with four bonds, where each fragment bonded is different.

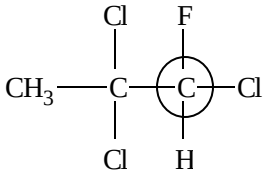
(a) The second C atom has four different fragments: CH_3–, HO–, $–CH_2OH$, and –H. The first C atom has three H atoms bonded and the third C atom has two H atoms bonded, so they are not chiral centers.



(b) This molecule has no chiral centers. The first two C atoms do not have four bonds. The third C atom has two H atoms bonded.

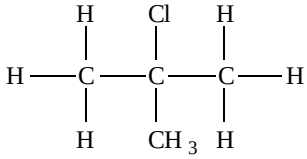


(c) The third C atom has four different fragments: CH_3CCl_2–, F–, –Cl, and –H. The first C atom has two H atoms bonded. The second C atom has two Cl atoms bonded, so they are not chiral centers.

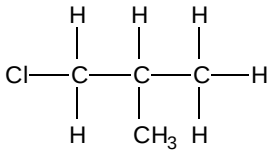


66. Chiral centers are C atoms with four bonds, where each fragment bonded is different.

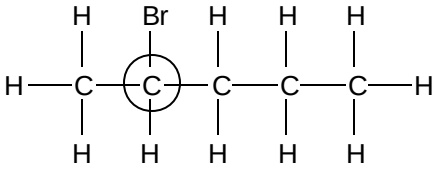
(a) This molecule has no chiral centers. The end C atoms have three H atoms bonded, and the second C atom has three CH_3 fragments.



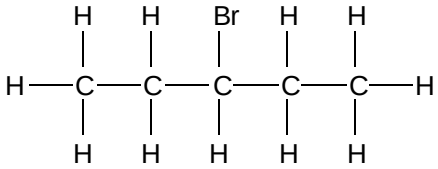
(b) This molecule has no chiral centers. The end C atoms have two or three H atoms bonded, and the second C atom has two CH_3 fragments.



(c) The second C atom has four different fragments: CH_3–, Br–, $–CH_2CH_2CH_3$, and –H. The other C atoms have more than one H atom bonded, so they are not chiral centers.

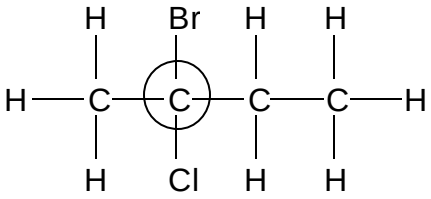


(d) This molecule has no chiral centers. Most of the C atoms have two or three H atoms, and the second C atom has two $–CH_2CH_3$ fragments.

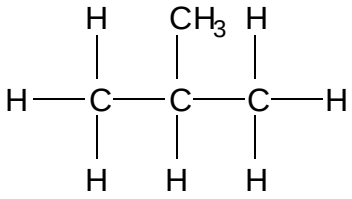


67. Chiral centers are C atoms with four bonds, where each fragment bonded is different.

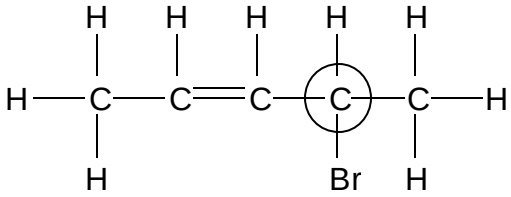
(a) The second C atom has four different fragments: $CH_3–$, Br–, $–CH_2CH_3$, and –Cl. The other C atoms have more than one H atoms bonded, so they are not chiral centers.



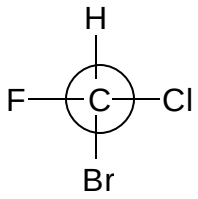
(b) This molecule has no chiral centers. The end C atoms have three H atoms bonded, and the third C atom has three $–CH_3$ fragments.



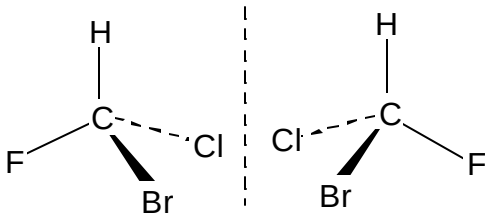
(c) The fourth C atom has four different fragments: $CH_3CH=CH–$, H–, $–CH_3$, and –Br. The end C atoms have three H atoms bonded, and the second and third C atoms have only three bonds, so they are not chiral centers.



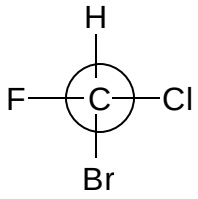
68. A compound can exist as a pair of enantiomers if it has one or more chiral centers, so look at the structural formula and find an atom with four different fragments bonded to it. For example:



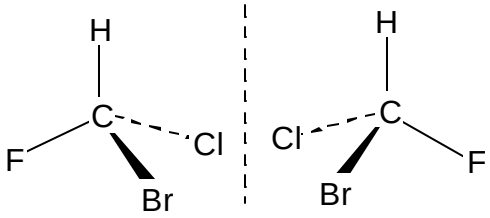
The C in this formula (circled) has four different fragments: F–, H–, –Cl, and –Br. This chiral center allows for the creation of two nonsuperimposeable mirror images of the same molecule, making them enantiomers of each other:



69. A molecule is chiral if it has one or more chiral centers, so look at the structural formula and find an atom with four different fragments bonded to it. For example:



The C in this formula (circled) has four different fragments: F–, H–, –Cl, and –Br. This chiral center makes the molecule chiral and allows for the creation of two nonsuperimposeable mirror images of the same molecule:



70. If something looks different from its own reflection in a mirror then it cannot be superimposed on its mirror image.

(a) A nail looks the same in a mirror, that makes it superimposable.

(b) A screw has the grooves spiraling in a specific direction. Its mirror image would have the grooves spiraling in the opposite direction, so it cannot be superimposed on its mirror image.

(c) A left shoe's arch is on the left side, its mirror image would have the arch on the right side, so it cannot be superimposed on its mirror image.

(d) Most socks look the same in a mirror; that makes them superimpoeable. (A sock just taken off a foot might still retain the asymmetric shape of the foot and could be considered to be not superimposed on its mirror image under these conditions.)

(e) A right-handed golf club has the head facing the left hand, so that the ball can be hit to the left by a right handed person. In a mirror that head would be facing left, so it cannot be superimposed on its mirror image.

(f) A football looks the same in a mirror, that makes it superimposable.

(g) Your left ear widens into a cone facing left. If you look at the person in the mirror that same ear would be facing to their right. So your ear cannot be superimposed on its mirror image.

(h) A helix spirals in a specific direction. Its mirror image would spiral in the opposite direction, so it cannot be superimposed on its mirror image.

(i) An unadorned baseball bat looks the same in a mirror; that makes it superimposable. However, if it has markings or some sort of label such as the name of the manufacturer, the symbols or lettering would be backwards in the mirror, and then it would not be superimposable.

(j) For clarity, let's face north while wearing the sweater. If you look at the person in the mirror, the part of the sweater that was furthest north is now the back of that person's sweater. Another more obvious way of looking at it is if the left sleeve is red and the right sleeve is blue. The person in the mirror has a left sleeve that is blue and a right sleeve that is red. So a sweater cannot be superimposed on its mirror image.

Molecular Structure Determination by Spectroscopy

71. The “Tools of Chemistry” box in Section 9.2 describes infrared spectroscopy. The “Tools of Chemistry” box in Section 9.4 describes ultraviolet-visible spectroscopy.

(a) Ultraviolet and visible spectroscopy are described together and some of the given examples that specifically talk about what electrons are involved refer to visible light. The electrons that would be affected by ultraviolet light (or high-energy visible light) are d electrons in some transition metals and pi electrons in the double bonds of organic compounds.

(b) Infrared spectroscopy tells us about the frequencies of specific vibrational motions in molecules.

72. The "Tools of Chemistry" box in Section 9.2 describes infrared spectroscopy. Wavelength, λ, is the variable on the horizontal axis of the spectrum shown. Wavelength is inversely proportional to the energy. So, longer wavelength light has lower energy and shorter wavelength light has higher energy.

(a) The lowest energy motion described in the spectrum is C–C stretch.

(b) The highest energy motion described in the spectrum is O–H stretch.

73. (a) IR radiation is lower in energy than UV radiation. (IR is below the visible speactrum and UV is above).

(b) IR radiation have longer wavelength than UV radiation. (Lower energy waves have longer wavelength than higher energy waves.).

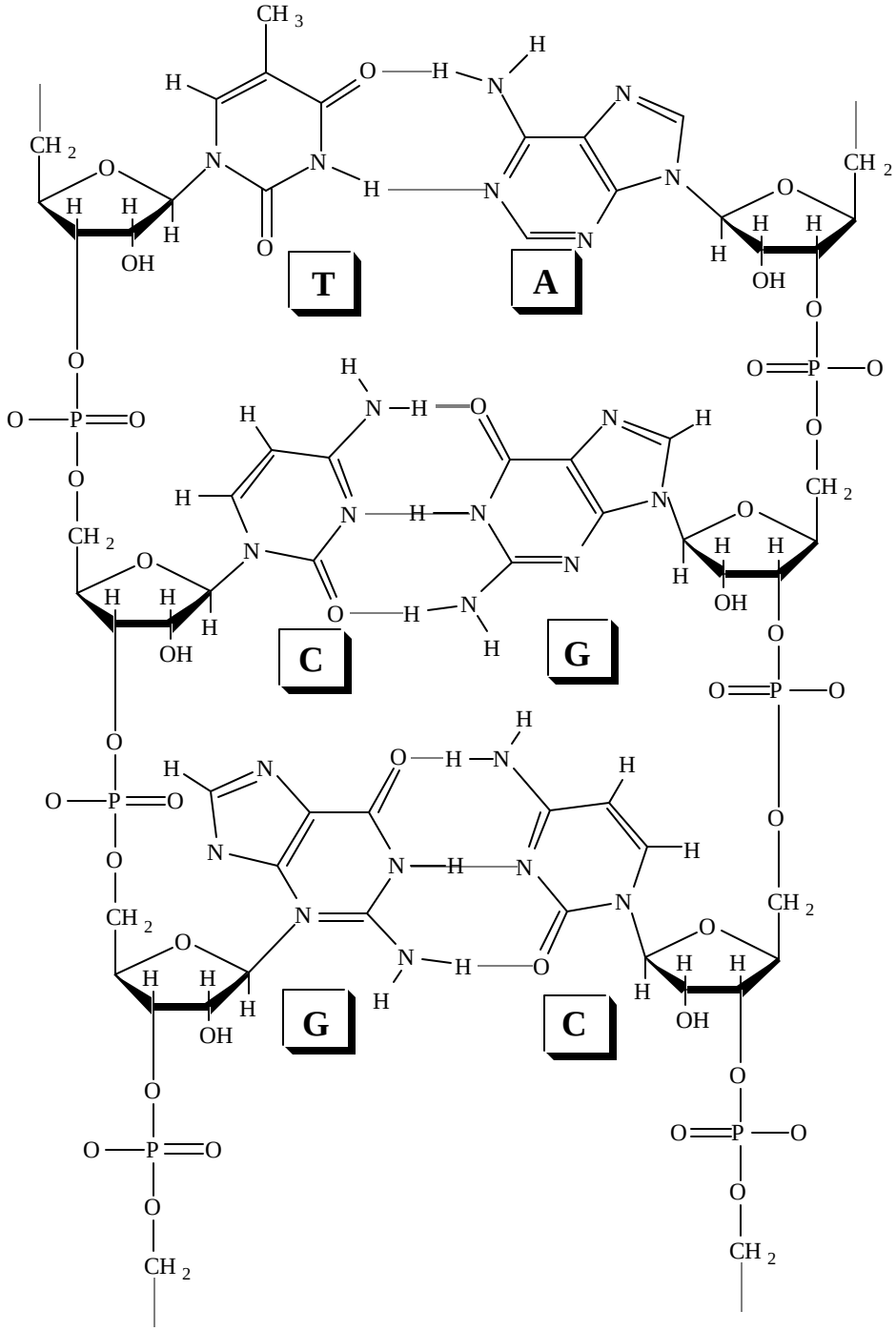
(c) IR radiation has lower frequency than UV radiation. (Lower energy waves have smaller frequency than higher energy waves).

74. NOTE: The UV-spectrum of beta carotene is on page 408, not on page 410. Two “shoulders” on either side of the main peak can be estimated to be found at 427 nm and 483 nm. Because shorter wavelength indicates higher energy light, the 427 nm peak is the more energetic transition.

Biomolecules

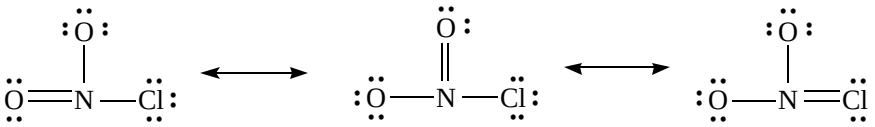
75. G-C interacts with three hydrogen bonds; whereas, A-T interacts with only two hydrogen bonds. Stronger attractive forces require higher melting temperature.

76.

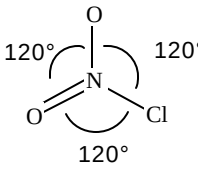


General Questions

77. NO_2Cl has three resonance structures. The first two are equivalent and the third is not as good because the formal charges are higher.



The central N atom has three atoms bonded to it and no lone pairs, so the type is AX_3E_0. The electron-pair geometry and the molecular geometry are both triangular planar. The triangular planar electron geometry indicates approximate O–N–O and O–N–Cl angles of 120°.



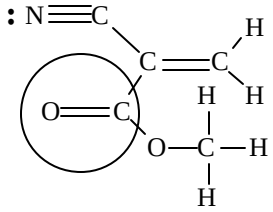
78. (a) Follow the method described in the answer to Questions 38 and 40.

Angle 1: Look at the C atom bonded to the N atom: It is of type AX_2E_0, so the electron-pair geometry is linear and this C atom has *sp* hybridization. The *sp*-hybridized C atoms have linear bond angles of approximately 180°. So, the CCN angle is 180°.

Angles 2 and 3: Look at the C atom bonded to only one O atom: The type is AX_4E_0, so the electron-pair geometry is tetrahedral this C atom has sp^3 hybridization. The sp^3-hybridized C atom has tetrahedral bond angles of approximately 109.5°. So, the HCH angle (Angle 2) and the OCH angle (Angle 3) are both 109.5°.

(b) Follow the method described in the answer to Question 46. The most polar bond is the C=O bond.

(c) Multiple bonds are shorter than single bonds, so the C=O bond is the shortest CO bond:

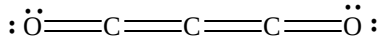


79. (a) Follow the method described in the answer to Questions 38 and 40.

Angle 1: Look at the C atom bonded to the N atom: It is of type AX_2E_0, so the electron-pair geometry is linear and this C atom has *sp* hybridization. The *sp*-hybridized C atoms have linear bond angles of approximately 180°. So, the NCC angle is 180°.

Angles 2 and 3: Look at the C atoms double bonded to each other: The type for each C atom is AX_3E_0, so the electron-pair geometry is trigonal planar and each of these C atom has sp^2 hybridization. The sp^2-hybridized C atom has trigonal planar bond angles of approximately 120°. So, the HCH angle (Angle 2) and the CCH angle (Angle 3) are both 120°.

(b) Follow the method described in the answer to Question 46. The most polar bond is the C≡N bond.

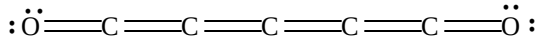
80. (a) 

(b) Follow the method described in the answer to Questions 38 and 40.

Angle 1: Look at the C atom bonded to the O atom: It is of type AX_2E_0, so the electron-pair geometry is linear and this C atom has *sp* hybridization. The *sp*-hybridized C atoms have linear bond angles of approximately 180°. So, the CCO angle is 180°.

(b) Follow the method described in the answer to Questions 38 and 40.

Angle 2: Look at the C atom bonded only to the C atoms: It is of type AX_2E_0, so the electron-pair geometry is linear and this C atom has *sp* hybridization. The *sp*-hybridized C atoms have linear bond angles of approximately 180°. So, the CCO angle is 180°.

81. (a) 

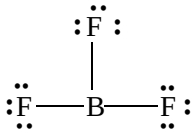
Follow the method described in the answer to Questions 38 and 40.

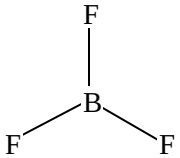
(b) Angle 1: Look at the C atom bonded to the O atom: It is of type AX_2E_0, so the electron-pair geometry is linear and this C atom has *sp* hybridization. The *sp*-hybridized C atoms have linear bond angles of approximately 180°. So, the CCO angle is 180°.

(c) Angle 2: Look at the C atom bonded only to the C atoms: It is of type AX_2E_0, so the electron-pair geometry is linear and this C atom has *sp* hybridization. The *sp*-hybridized C atoms have linear bond angles of approximately 180°. So, the CCO angle is 180°.

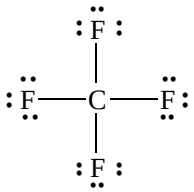
82. The "Tools of Chemistry" box in Section 9.5 (page 408) describes ultraviolet-visible spectroscopy. Compounds with an extended pi system formed by conjugation between a series of alternating double bonds absorb visible light. This molecule also has a extended pi system, so we would predict it absorbs visible light.

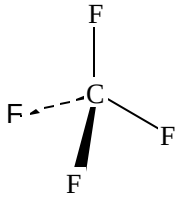
83. (a) BF_3 (24 e^-) The type is AX_3E_0, so the electron-pair geometry and the molecular geometry are both triangular planar.



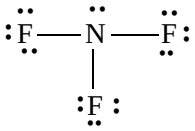


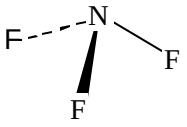
(b) CF_4 (32 e^-) The type is AX_4E_0, so both the electron-pair geometry and the molecular geometry are tetrahedral.



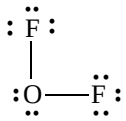


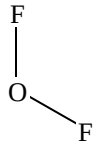
(c) NF_3 (26 e^-) The type is AX_3E_1, so the electron-pair geometry is tetrahedral and the molecular geometry is triangular pyramidal.



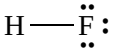


(d) OF_2 (20 e^-) The type is AX_2E_2, so the electron-pair geometry is tetrahedral and the molecular geometry is angular (109.5°).



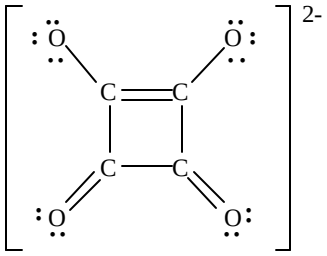


(e) HF (8 e^-) There are two atoms in the molecule so the electron-pair geometry is not defined by VSEPR. The electrons have the geometry of the atomic orbitals. The molecular geometry is linear.



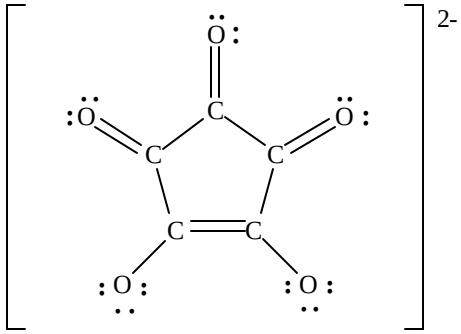
The similarities are that all of the molecules have F atoms in terminal positions (except HF),. The different geometries result in the differences between the central atoms and the number of F atoms.

84. (a) $C_4O_4^{2-}$ (42 e^-) has four equivalent resonance structures. One of these resonance structures looks like this:



(b) Look at each C atom: The type for each C atom is AX_3E_0, so the electron-pair geometry is trigonal planar and each of these C atom has sp^2 hybridization.

85. (a) $C_5O_5^{2-}$ (52 e^-) has five equivalent resonance structures. One of these resonance structures looks like this:



(b) Look at each C atom: The type for each C atom is AX_3E_0, so the electron-pair geometry is trigonal planar and each of these C atom has sp^2 hybridization.

86. The dipole moment is determined by multiplying the partial charge by the bond length.

$$\mu = (\delta^+) \times (\text{bond length})$$

For HCl: $$\delta^+ = \frac{\mu}{\text{bond length}} = \frac{3.43 \times 10^{-30}\ \text{C} \cdot \text{m}}{127.4\ \text{pm}} \times \frac{1\ \text{pm}}{10^{-12}\ \text{m}} = 2.69 \times 10^{-20}\ \text{C}$$

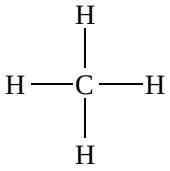
For HF: $$\delta^+ = \frac{\mu}{\text{bond length}} = \frac{6.37 \times 10^{-30}\ \text{C} \cdot \text{m}}{91.68\ \text{pm}} \times \frac{1\ \text{pm}}{10^{-12}\ \text{m}} = 6.95 \times 10^{-20}\ \text{C}$$

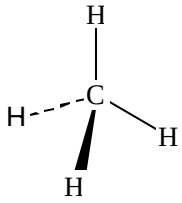
The partial charges in the HF bond are larger than those of the HCl bond, indicating that the fluorine is more electronegative than chlorine.

87. Many correct answers exist for this question. What are given here are examples of suitable answers. Other answers will also be completely correct.

(a) An example of a carbon-containing molecule in which the angle between two atoms bonded to carbon is 109.5°.

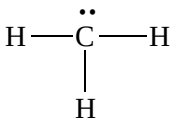
CH_4 (8 e^-) The type is AX_4E_0, so the electron-pair geometry is tetrahedral and the H–C–H angles are predicted to be 109.5°.

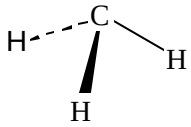




(b) An example of a carbon-containing ion in which the angle between two atoms bonded to carbon is slightly different from 109.5°.

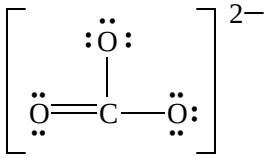
CH_3^- (8 e^-) The type is AX_3E_1, so the electron-pair geometry is tetrahedral and the molecular geometry is triangular pyramidal and the H–C–H angles are predicted to be slightly less than 109.5° because of the lone pair effect.

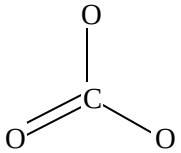




(c) An example of a carbon-containing ion in which the angle between two atoms bonded to carbon is 120°.

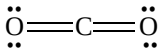
CO_3^{2-} (24 e^-) AX_3E_0, so both the electron-pair geometry and the molecular geometry are triangular planar and the O–C–O angles are predicted to be 120°.





(d) An example of a carbon-containing ion in which the angle between two atoms bonded to carbon is 180°.

CO_2 (16 e^-) AX_2E_2, so both the electron-pair geometry and the molecular geometry are linear and the O–C–O angle is predicted to be 180°.



88. The definition of dipole moment was given in Question 86:

$$\mu = (\delta^+) \times (\text{bond length})$$

For KF: $$\delta^+ = \frac{\mu}{\text{bond length}} = \frac{28.7 \times 10^{-30}\ \text{C} \cdot \text{m}}{217.2\ \text{pm}} \times \frac{1\ \text{pm}}{10^{-12}\ \text{m}} = 1.32 \times 10^{-19}\ \text{C}$$

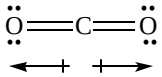
$$\delta^- = -1.32 \times 10^{-19}\ \text{C}$$

If the bond were completely ionic, then the partial negative charge on fluorine would be the same as the charge on the electron (-1.62×10^{-19} C). So, KF is not completely ionic.

Percent of full negative charge = $\frac{-1.32 \times 10^{-19}\ \text{C}}{-1.62 \times 10^{-19}\ \text{C}} \times 100\,\% = 81.6\,\%$ = 81.6 % of a full negative charge.

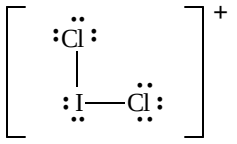
89. A diatomic molecule is nonpolar if the atoms that it is composed of have the same electronegativity. The only way to be sure of identical electronegativity is for the two atoms to be the same. A diatomic molecule is polar when the two atoms it is composed of have different electronegativities.

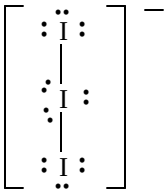
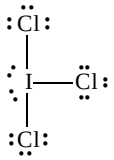
90. A molecule with polar bonds can have a dipole moment of zero if the bond poles are equal and point in opposite directions. CO_2 is a good example of a nonpolar molecule with polar bonds.



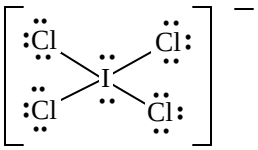
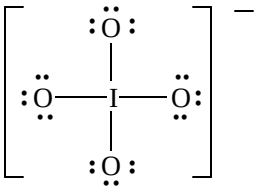
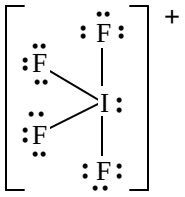
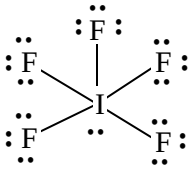
Applying Concepts

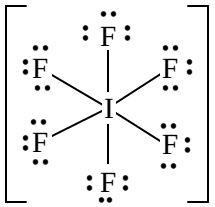
91.

Molecule or Ion	Number of electrons	Lewis Structure	Type AX_nE_m	electron-pair geometry	molecular geometry	hybrid-ization
ICl_2^+	7 + 2(7) – 1 = 20		AX_2E_2	tetrahe-dral	angular	sp^3

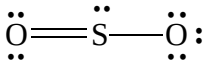
I_3^-	3(7) + 1 = 22		AX_2E_3	triangular bipyra-midal	linear	sp^3d
ICl_3	7 + 3(7) = 28		AX_3E_2	triangular bipyra-midal	T-shaped	sp^3d

91. continued

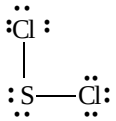
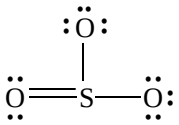
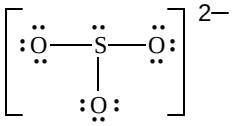
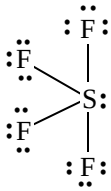
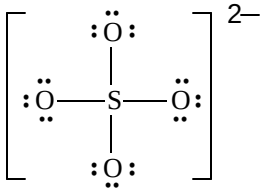
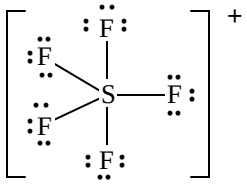
Molecule or Ion	Number of electrons	Lewis Structure	Type AX_nE_m	electron-pair geometry	molecular geometry	hybrid-ization
ICl_4^-	7 + 4(7) + 1 = 36		AX_4E_2	octahedral	square planar	sp^3d^2
IO_4^-	7 + 4(6) + 1 = 32		AX_4E_0	tetrahe-dral	tetrahe-dral	sp^3
IF_4^+	7 + 4(7) – 1 = 34		AX_4E_1	triangular bipyra-midal	seesaw	sp^3d
IF_5	7 + 5(7) = 42		AX_4E_1	octahedral	square pyramid	sp^3d^2

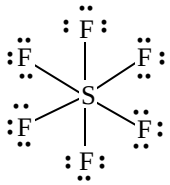
IF_6^+	7 + 6(7) – 1 = 48		AX_6E_0	octahedral	octahedral	sp^3d^2

92.

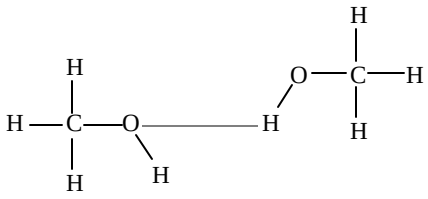
Molecule or Ion	Number of electrons	Lewis Structure	Type AX_nE_m	electron-pair geometry	molecular geometry	hybrid-ization
SO_2	6 + 2(6) = 18		AX_2E_1	triangular planar	angular (120°)	sp^2

92. (continued)

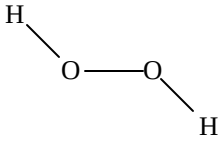
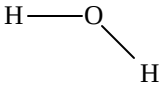
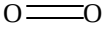
Molecule or Ion	Number of electrons	Lewis Structure	Type AX_nE_m	electron-pair geometry	molecular geometry	hybrid-ization
SCl_2	6 + 2(7) = 20		AX_2E_2	tetrahe-dral	angular (109.5°)	sp^3
SO_3	6 + 3(6) = 24		AX_3E_0	triangular planar	triangular planar	sp^2
SO_3^{2-}	6 + 3(6) + 2 = 26		AX_3E_1	tetrahe-dral	triangular pyramidal	sp^3
SF_4	6 + 4(7) = 34		AX_4E_1	triangular bipyra-midal	seesaw	sp^3d
SO_4^{2-}	6 + 4(6) + 2 = 32		AX_4E_0	tetrahe-dral	tetrahe-dral	sp^3
SF_5^+	6 + 5(7) – 1 = 40		AX_5E_0	triangular bipyra-midal	triangular bipyra-midal	sp^3d

SF_6	6 + 6(7) = 48		AX_6E_0	octahedral	octahedral	sp^3d^2

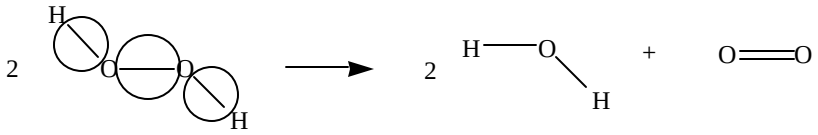
93. (a) Molecules of liquid methanol (CH_3OH) interact via dipole-dipole interactions and hydrogen bonding. These intermolecular forces must be overcome to evaporate liquid methanol.



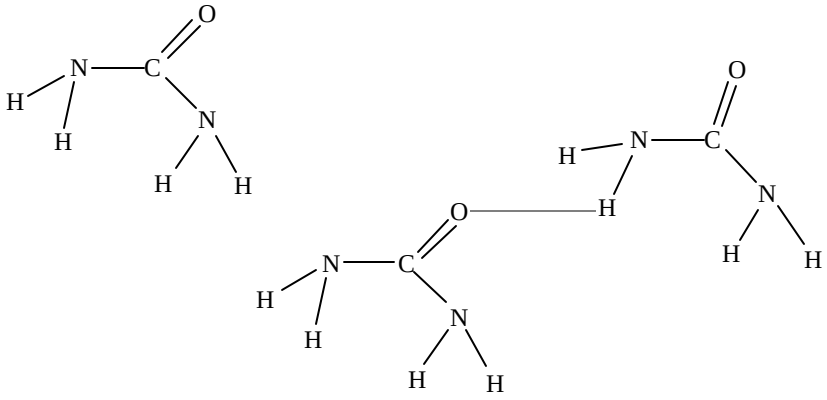
(b) Decomposing molecules into other molecules requires breaking covalent bonds, so the forces that must be overcome are the intramolecular (covalent) forces. The reactant molecule looks like this:

 and the product molecules look like this:  and  .

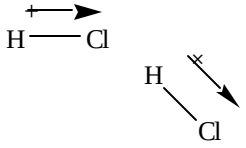
So, all the polar covalent bonds in the reactants have to be broken to make some of the new bonds in the products:



(c) Molecules of solid urea (H_2NCONH_2) interact via dipole-dipole interactions and hydrogen bonding. Some of these intermolecular forces must be overcome to melt solid urea.

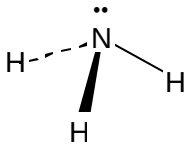


(d) Molecules of liquid HCl interact via dipole-dipole interactions. These intermolecular forces must be overcome to boil liquid HCl.

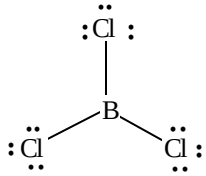


94. The answers given here are not the only correct answers. They are only examples.

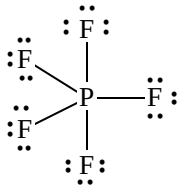
(a) XH_3 would have a central atom with one lone pair of electrons, if X = N.



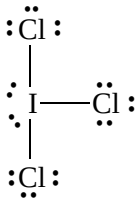
(b) XCl_3 would have no lone pairs on the central atom, if X = B.



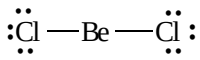
(c) XF_5 would have no lone pairs on the central atom, if X = P.



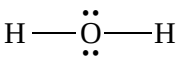
(d) XCl_3 would have two lone pairs on the central atom, if X = I.



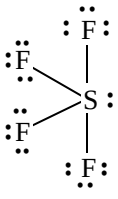
95. (a) XCl_2 would have a central atom with no lone pair of electrons, if X = Be.



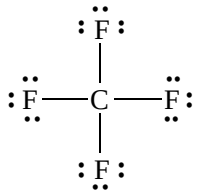
(b) XH_2 would have two lone pairs on the central atom, if X = O.



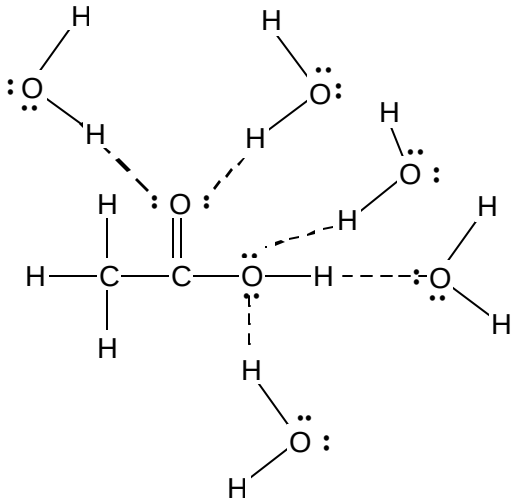
(c) XF_4 would have one lone pair on the central atom, if X = S.



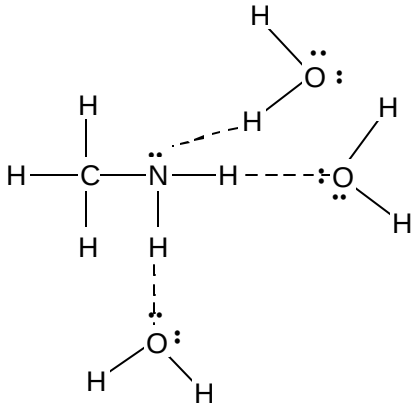
(d) XCl_4 would have no lone pairs on the central atom, if X = C.



96. Five water molecules could hydrogen bond to an acetic acid molecule: one to each of the four lone pairs on O atoms in acetic acid and one to the H atom bonded to an O atom in acetic acid.



97. Three water molecules could hydrogen bond to an ethylamine molecule. One to the lone pair on the N atom in ethylamine and one to each of the H atoms bonded to the N atom in ethylamine.



98. (a) This is incorrect, because the H atoms are not bonded to highly electronegative atoms.

(b) This is correct. The H atom is bonded to an O atom (EN = 3.5) and is hydrogen bonding to another O atom.

(c) This is incorrect. The H atom is bonded F. This is a covalent bond, not an example of the noncovalent interactive force called a hydrogen bond.

(d) This is incorrect. The H atoms are bonded to O atom (EN = 3.5), but they will not form a hydrogen bond to each other!

The only answer that is correct is (b).

99. (a) This is correct. The H atom is bonded to an O atom (EN = 3.5) and is hydrogen bonding to an N atom (EN = 3.0).

(b) This is incorrect. The H atom is bonded H. This is a covalent bond, not an example of the noncovalent interactive force called a hydrogen bond.

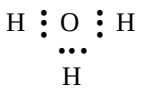
(c) This is incorrect. The H atoms are bonded to O atom (EN = 3.5), but they will not form a hydrogen bond to each other!

(d) This is incorrect. The H atoms are bonded to highly electronegative atoms ($EN_F = 4.0$ and $EN_N = 3.5$), but N will not form a hydrogen bond to an F!

The only answers that is correct is (a).

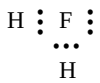
100. In this fictional universe, a nonet is nine electrons. We will assume that the number of electrons in the atom called "O" in the other universe is still six, the number of electrons in the atom called "H" is still one, and the number of electrons in the atom called "F" is still seven. The equivalent to our VSEPR model is the VSTPR model (Valence Shell Electron Trio Repulsion Theory), where electron trios repel each other.

The 6 electrons in the O atom would need three more electrons to make a total of nine. That means it would combine with three H atoms to make this molecule:



In this H_3O molecule, the central atom has three bonded atoms and no lone trios. That would make it AX_3E_0 type. As a result, the electron-trio geometry and the molecular geometry would be triangular planar.

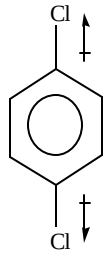
The 7 electrons in the F atom would need two more electrons to make a total of nine. That means it would combine with two H atoms to make this molecule:



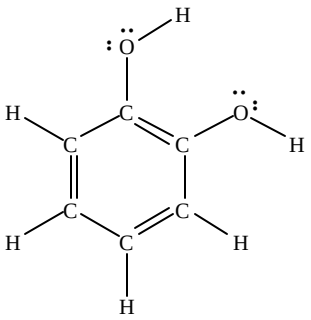
In this H_3F molecule, the central atom has two bonded atoms and one lone trio. That would make it AX_2E_1 type. As a result, the electron-trio geometry would be triangular planar and the molecular geometry would be angular at somewhat less than 120° due to the electron trio repelling the bonding trios somewhat better.

More Challenging Problems

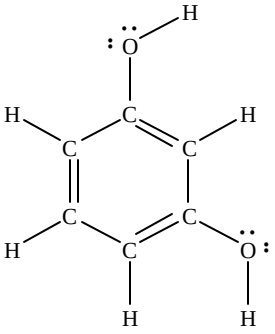
101. The *para*-isomer of dichlorobenzene is non polar, since the polar bonds C-Cl are directly opposite each other in this structure:



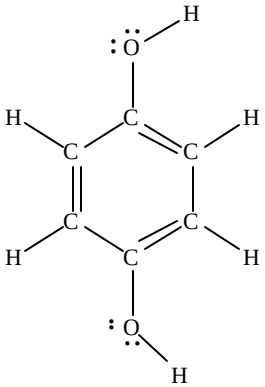
102. (a) The Lewis structures for the three isomers of $C_6H_6O_2$ (each with one benzene ring and two –OH groups attached) look like this:



(i)



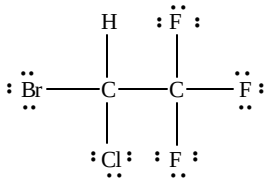
(ii)



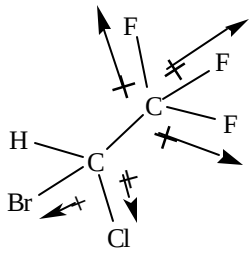
(iii)

(b) All of these molecules have the same kind and strength of hydrogen bonding; however, because of the proximity of the two –OH groups in structure (i), these molecules are able to experience intramolecular hydrogen bonding (that is hydrogen bonding between H atoms and O atoms within the same molecule). Less hydrogen bonding disruption will be experienced when the molecules undergo a transition to the liquid state; hence, (i) will melt at a lower temperature than the other two. The asymmetry of structure (ii) might suggest that the intermolecular forces could be a little bit weaker in the solid, compared to those experienced among the higher-symmetry molecules in structure (iii). Therefore, the predicted order of for melting points of these three solids would be (i) < (ii) > (iii).

103. (a) Halomethane, $CHBrClCF_3$ (44 e^-) has the following Lewis Structure.

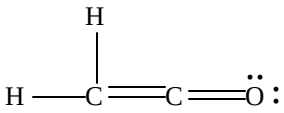


(b) As a asymmetric molecule with polar bonds, Halomethane is a polar structure.



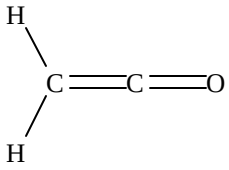
(c) No, halomethane molecules cannot interact via hydrogen bonding, since the only H atom in the molecule is bonded to a C atom and the C–H bond is not polar enough for the H to have a high enough partial positive charge.

104. (a) Ketene, C_2H_2O (16 e^-) has the following Lewis Structure.



(b) Look at the first C atom: It is of type AX_3E_0, so the electron-pair geometry is trigonal planar with H–C–C and H–C–H bond angles of 120°.

Look at the second C atom: It is of type AX_2E_0, so the electron-pair geometry is linear with a C–C–O bond angle of 180°.

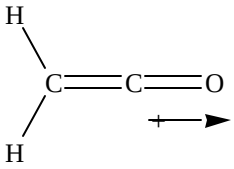


(c) Look at the first C atom: It is of type AX_3E_0, so the C atom must be sp^2-hybridized.

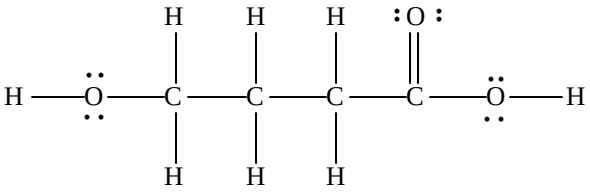
Look at the second C atom: It is of type AX_2E_0, so the C atom must be *sp*-hybridized.

Look at the O atom: It is of type AX_1E_2, so the O atom must be sp^2-hybridized.

(d) The C=O bond in this asymmetric molecule is a significantly polar bond which makes the molecule polar.



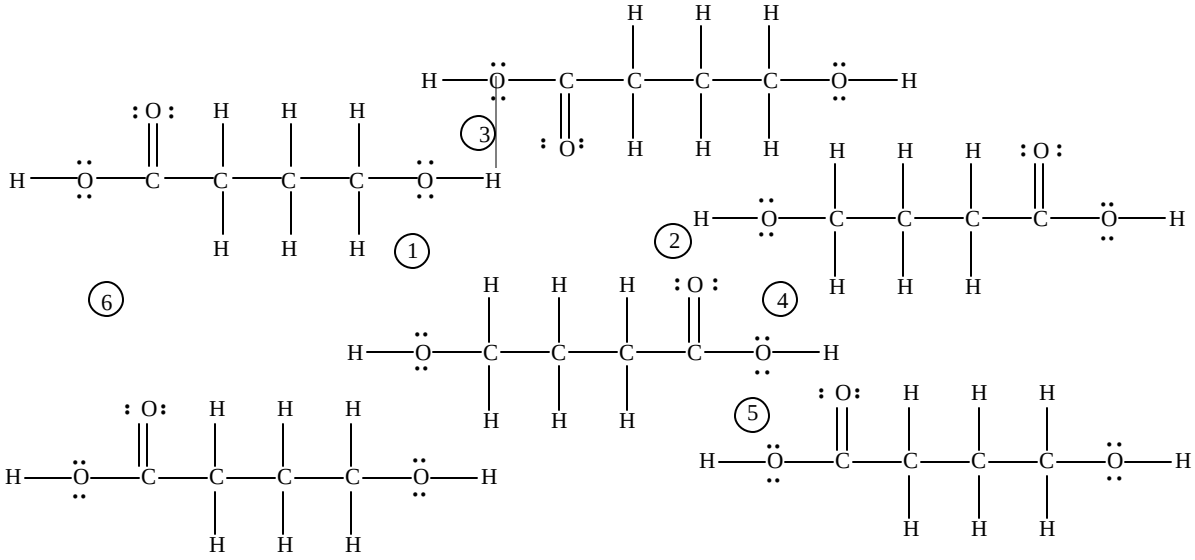
105. (a) $HO(CH_2)_3COOH$ (42 e^-) has the following Lewis Structure.



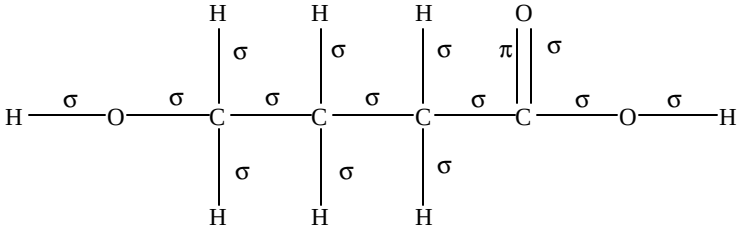
(b) Look at the C atoms in the CH_2 groups: They are each of type AX_4E_0, so each of the three C atoms must be sp^3-hybridized.

Look at the terminal C atom: It is of type AX_3E_0, so the C atom must be sp^2-hybridized.

(c) Yes, hydrogen bonding is possible in GHB. Two different H atoms and three different O atoms can contribute to six different hydrogen bonding interactions. One of each of these six is show below. Answers may vary in appearance, but should show the six different ways these atoms can interact: The H on the –OH group can hydrogen bond to one of three O atoms (shown below, labeled 1, 2, 3). The H atom on the COOH group can hydrogen bond to one of three O atom (shown below, labeled 4, 5, 6).



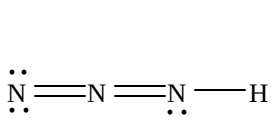
For (d) and (e) Every single bond is a sigma-bond and every double bond is one sigma bond and one pi bond. So the sigma and pi bonds in this molecule are shown here:



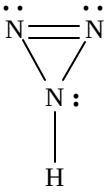
(d) All of the C atoms in the molecule are involved in sigma bonds. The terminal C atom is involved in one pi bond.

(e) All of the O atoms in the molecule are involved in sigma bonds. The double bonded O atom is involved in one pi bond.

106. (a) The two isomers of N_3H (16 e^-) have the following Lewis Structures.



hydrogen azide



cyclotriazene

(b) Look at the first N atom (the left-most one) in hydrogen azide: It is of type AX_1E_2, so this N atom must be sp^2-hybridized.

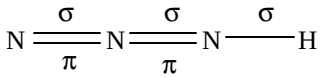
Look at the second N atom in hydrogen azide: It is of type AX_2E_0, so this N atom must be *sp*-hybridized.

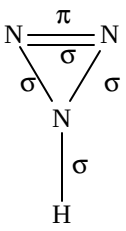
Look at the third N atom in hydrogen azide: It is of type AX_2E_1, so this N atom must be sp^2-hybridized.

(c) Look at the first two N atom (the two on top of the triangle) in cyclotriazene: Each N atom is of type AX_2E_1, so each N atom must be sp^2-hybridized.

Look at the third N atom in cyclotriazene: It is of type AX_3E_1, so this N atom must be sp^3-hybridized.

For (d) and (e) Every single bond is a sigma-bond and every double bond is one sigma bond and one pi bond. So the sigma and pi bonds in this molecule are shown here:





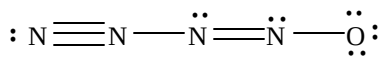
(d) In hydrogen azide, there are three sigma bonds. In cyclotriazene, there are four sigma bonds.

(e) In hydrogen azide, there are two pi bonds. In cyclotriazene, there is one pi bond.

(f) In hydrogen azide, the second N dictates the N–N–N bond angle. In (b), we ascertained that this N atom is sp hybridized, so the bond angle must be 180°.

In cyclotriazene, the methods of this chapter indicate that the bond angles should be 120° (for the two angles represented by [left N-right N-bottom N], or [right N-left N- bottom N]) and 109.5° (for the angle represented by [left N-bottom N-right N]); however, since the three N atoms form a triangle, geometric constraints dictate that the bond angles will be approximately 60°.

107. (a) Nitrosyl azide, N_4O (26 e^-) has the following Lewis Structure.

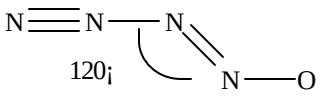


(b) Look at the "terminal" N atom (the left-most one): It is of type AX_1E_1, so this N atom must be *sp*-hybridized.

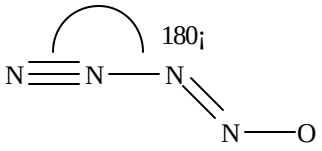
(c) Look at the "central" N atom (the third one from the left; the third of five atoms): It is of type AX_2E_1, so it must be sp^2-hybridized.

(d) The shortest bond between two atoms of given type is a triple bond. So, in nutrosyl azide, the shortest nitrogen-nitrogen bond is the N≡N bond.

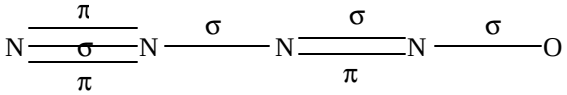
(e) To determine the N–N–N angle starting with the N atom bonded to the O atom, we have to look at the third N atom from the left. As identified in (c), this atom is of type AX_2E_1, so it must have trigonal planar electron geometry, and the bond angle is approximately 120°.



(f) To determine the N–N–N angle using the N atoms not bonded to the O atom, we have to look at the second N atom from the left. This atom is of type AX_2E_0, so it must have linear electron geometry, and the bond angle is 180°.



(g) Every single bond is a sigma bond, every double bond is one sigma bond and one pi bond. Every triple bond is one sigma bond, and two pi bonds. In this molecule, therefore, we have:



So, there are four sigma bonds and three pi bonds.

108. (a) Angle 1: Look at the C atom: It is of type AX_3E_0, so it must have trigonal planar electron geometry, and the bond angle is approximately 120°.

Angle 2: Look at the second of the three carbon atoms: It is of type AX_3E_0, so it must have trigonal planar electron geometry, and the bond angle is approximately 120°.

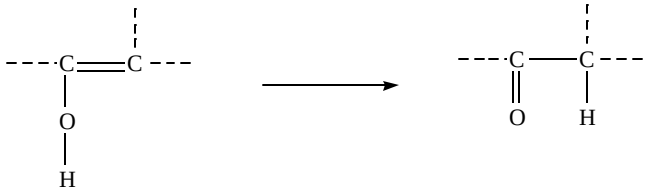
Angle 3: Look at the C atom: It is of type AX_4E_0, so it must have tetrahedral electron geometry, and the bond angle is approximately 109.5°.

(b) The N atom is of type AX_3E_1, so it must be sp^2-hybridized.

(c) Look at the O atoms with two single bonds: Each of them are of type AX_2E_2, so they must each be sp^3-hybridized.

Look at the double bonded O atom: It is of type AX_1E_2, so it must be sp^2-hybridized.

109. (a) The bonds that are changed during the conversion of *enol* form to *keto* form are these:



None of the other bonds change, so only break and form these bonds:

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

$\Delta H = (1\text{ mol}) \times D_{O-H} + (1\text{ mol}) \times D_{C-O} + (1\text{ mol}) \times D_{C=C}$

$- [(1\text{ mol}) \times D_{C=O} + (1\text{ mol}) \times D_{C-C} + (1\text{ mol}) \times D_{C-H}]$

Look up the bond energies in Table 8.2.

$= (1\text{ mol}) \times (463\text{ kJ/mol}) + (1\text{ mol}) \times (351\text{ kJ/mol}) + (1\text{ mol}) \times (611\text{ kJ/mol})$

$- [(1\text{ mol}) \times (745\text{ kJ/mol}) + (1\text{ mol}) \times (347\text{ kJ/mol}) + (1\text{ mol}) \times (414\text{ kJ/mol})]$

$\Delta H = -81$ kJ exothermic reaction

(b) The methyl C atoms (CH_3) in both forms are the same. The electron-pair and molecular geometries about those C atoms are tetrahedral. The fourth C atom in both molecules is the same. They each have three bonded atoms and no lone pairs, so the electron-pair and molecular geometries are both triangular planar.

The left-most carbons shown in the *enol* and *keto* forms in (a) above have the same geometries. These C atoms have three bonded atoms and no lone pairs so the electron-pair and molecular geometries are both triangular planar.

The right-most carbons shown in the *enol* and *keto* forms in (a) above have different geometries. Look first at the *enol* form: The right-most C atom has three bonded atoms and no lone pairs so the electron-pair and molecular geometries are both triangular planar. Now look at the *keto* form: The right-most C atom has four bonded atoms and no lone pairs, so the electron-pair and molecular geometries about that C atom is tetrahedral.

When there is a shift from the *enol* to the *keto* form, one of the chain carbons shifts from triangular planar to tetrahedral. That means the bond angle will narrow and the molecule will pucker more than it did before.

(c) Use methods described in Chapter 4, such as given in the answer to Question 4.53.

Cr(acac)3 is $Cr(C_5O_2H_7)_3$, with a calculated molar mass of:

$51.9961\text{ g} + 3 \times [5 \times (12.0107\text{g}) + 2 \times (15.9994\text{g}) + 7 \times (1.0079\text{g})] = 349.9189\text{ g/mol}.$

Similarly, the reactants are $CrCl_3$ (with a calculated molar mass of 158.355 g/mol) and $HC_5O_2H_7$ (with a calculated molar mass of 100.1076 g/mol).

Calculate the number of moles of product:

$$15.0\text{ g } Cr(acac)_3 \times \frac{1\text{ mol } Cr(acac)_3}{349.9189\text{ g } Cr(acac)_3} = 0.0429\text{ mol } Cr(acac)_3$$

The balanced equation says: 1 mol $Cr(acac)_3$ requires 1 mole of $CrCl_3$.

$$0.0429 \text{ mol } Cr(acac)_3 \times \frac{1 \text{ mol } CrCl_3}{1 \text{ mol } Cr(acac)_3} \times \frac{158.355 \text{ g } CrCl_3}{1 \text{ mol } CrCl_3} = 6.79 \text{ g } CrCl_3$$

The balanced equation says: 1 mol $Cr(acac)_3$ requires 3 moles $HC_5O_2H_7$.

$$0.0429 \text{ mol } Cr(acac)_3 \times \frac{3 \text{ mol } HC_5O_2H_7}{1 \text{ mol } Cr(acac)_3} \times \frac{100.1076 \text{ g } HC_5O_2H_7}{1 \text{ mol } HC_5O_2H_7} = 12.9 \text{ g } HC_5O_2H_7$$

We need 6.79 grams of $CrCl_3$ and 12.9 grams of $HC_5O_2H_7$, assuming the reaction has a 100% yield.