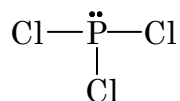


CHAPTER 10

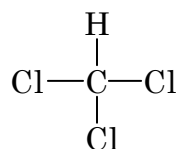
CHEMICAL BONDING II

- 10.1** Molecular geometry is the three-dimensional arrangement of atoms in a molecule. A molecule's geometry affects its physical and chemical properties, such as melting point, boiling point, density, and the types of reactions it undergoes.
- 10.2** See Table 10.1 of the text. Linear angle (180°), trigonal planar angle (120°), tetrahedral angle (109.5°), trigonal bipyramidal angles (90° , 120°), and octahedral angle (90°).
- 10.3** Four atoms are directly bonded to the central atom in a tetrahedral molecule. Five atoms are directly bonded to the central atom in a trigonal bipyramidal molecule. Six atoms are directly bonded to the central atom in an octahedral molecule.
- 10.4** The VSEPR model accounts for the geometric arrangements of electron pairs around a central atom in terms of the electrostatic repulsion between electron pairs. Electrons in a bond are held by the attractive forces exerted by the nuclei of the two bonded atoms. These electrons have less "spatial distribution" than lone pairs; that is, they take up less space than lone-pair electrons, which are associated with only one particular atom. Because lone-pair electrons in a molecule occupy more space, they experience greater repulsion from neighboring lone pairs and bonding pairs.
- 10.5** The axial position has three neighboring pairs at 90° and one at 180° , while the equatorial position has two neighboring pairs at 90° and two more at 120° . The repulsion for an electron-pair in the equatorial position is smaller.
- 10.6** A square planar geometry is shown in Table 10.2 of the text. The square planar geometry is less stable than a tetrahedral geometry for methane due to bond angles of 90° , compared to tetrahedral angles of 109.5° .
- 10.7 (a)** The Lewis structure of PCl_3 is shown below. Since in the VSEPR method the number of bonding pairs and lone pairs of electrons around the *central atom* (phosphorus, in this case) is important in determining the structure, the lone pairs of electrons around the chlorine atoms have been omitted for simplicity. There are three bonds and one lone electron pair around the central atom, phosphorus, which makes this an AB_3E case. The information in Table 10.2 shows that the structure is a **trigonal pyramid** like ammonia.

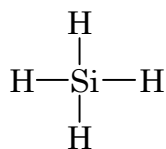


What would be the structure of the molecule if there were no lone pairs and only three bonds?

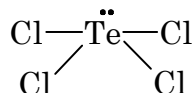
- (b)** The Lewis structure of CHCl_3 is shown below. There are four bonds and no lone pairs around carbon which makes this an AB_4 case. The molecule should be **tetrahedral** like methane (Table 10.1).



(c) The Lewis structure of SiH_4 is shown below. Like part (b), it is a **tetrahedral** AB_4 molecule.



(d) The Lewis structure of TeCl_4 is shown below. There are four bonds and one lone pair which make this an AB_4E case. Consulting Table 10.2 shows that the structure should be that of a **distorted tetrahedron** like SF_4 .



Are TeCl_4 and SF_4 isoelectronic? Should isoelectronic molecules have similar VSEPR structures?

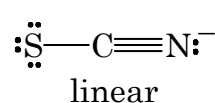
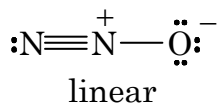
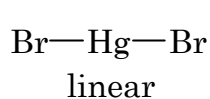
10.8 Strategy: The sequence of steps in determining molecular geometry is as follows:

draw Lewis structure \longrightarrow find arrangement of electrons pairs \longrightarrow find arrangement of bonding pairs \longrightarrow determine geometry based on bonding pairs

Solution:

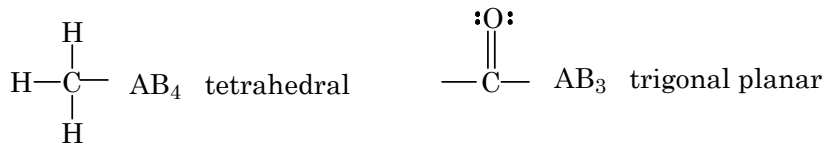
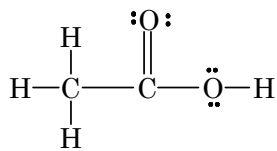
Lewis structure	Electron pairs on central atom	Electron arrangement	Lone pairs	Geometry
(a) $\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{Al}-\text{Cl} \end{array}$	3	trigonal planar	0	trigonal planar , AB_3
(b) $\text{Cl}-\text{Zn}-\text{Cl}$	2	linear	0	linear , AB_2
(c) $\left[\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{Zn}-\text{Cl} \\ \\ \text{Cl} \end{array} \right]^{2-}$	4	tetrahedral	0	tetrahedral , AB_4

10.9 The lone pairs of electrons on the bromine atoms have been omitted for simplicity.

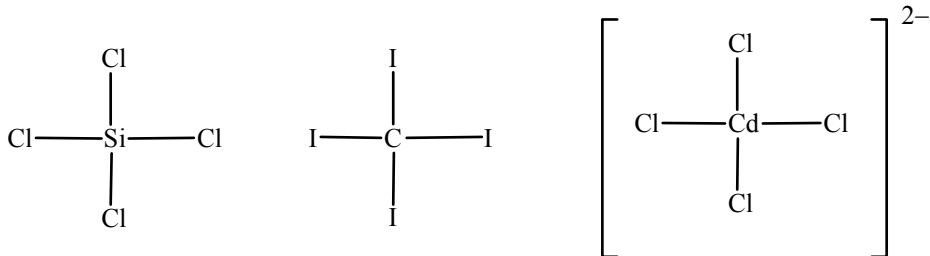


- 10.10**
- | | | | |
|-----------------------------|-----------------|---------------------------|----------------------|
| (a) AB_4 | tetrahedral | (f) AB_4 | tetrahedral |
| (b) AB_2E_2 | bent | (g) AB_5 | trigonal bipyramidal |
| (c) AB_3 | trigonal planar | (h) AB_3E | trigonal pyramidal |
| (d) AB_2E_3 | linear | (i) AB_4 | tetrahedral |
| (e) AB_4E_2 | square planar | | |

10.11 The Lewis structure is:



10.12 Only molecules with four bonds to the central atom and no lone pairs are tetrahedral (AB₄).



What are the Lewis structures and shapes for XeF₄ and SeF₄?

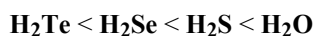
10.13 A quantitative measure of the polarity of a bond is its dipole moment, which is the product of the charge Q and the distance r between the charges. The unit of dipole moment is the Debye unit, D ($1 D = 3.336 \times 10^{-30} \text{ C}\cdot\text{m}$). The symbol for dipole moment is μ .

10.14 A dipole moment is the charge separation for a molecule, while a bond moment is the charge separation for a bond in the molecule. Based on the geometry of the molecule, the bond moments (a vector quantity) can cancel giving a molecule with no net dipole moment (a nonpolar molecule).

10.15 The electron distribution of an atom is symmetrical; therefore, an atom cannot have a permanent dipole moment.

10.16 The geometry of BeH₂ is linear. The two bond moments (a vector quantity) cancel giving a molecule with no net dipole moment ($\mu = 0$).

10.17 All four molecules have two bonds and two lone pairs (AB₂E₂) and therefore the bond angles are not linear. Since electronegativity decreases going down a column (group) in the periodic table, the electronegativity differences between hydrogen and the other Group 6 element will increase in the order Te < Se < S < O. The dipole moments will increase in the same order.



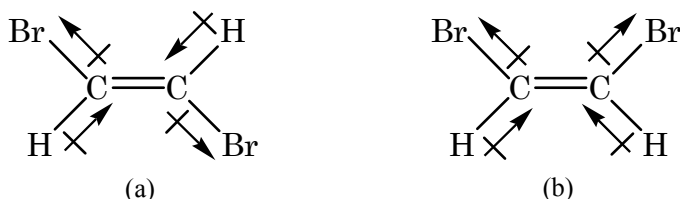
Would this conclusion be as easy if the elements were in different groups?

10.18 The electronegativity of the halogens decreases from F to I. Thus, the polarity of the H–X bond (where X denotes a halogen atom) also decreases from HF to HI. This difference in electronegativity accounts for the decrease in dipole moment.

10.19 $\text{CO}_2 = \text{CBr}_4 (\mu = 0 \text{ for both}) < \text{H}_2\text{S} < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$

10.20 Draw the Lewis structures. Both molecules are linear (AB_2). In CS_2 , the two C–S bond moments are equal in magnitude and opposite in direction. The sum or resultant dipole moment will be *zero*. Hence, CS_2 is a nonpolar molecule. Even though OCS is linear, the C–O and C–S bond moments are not exactly equal, and there will be a small net dipole moment. Hence, OCS has a **larger** dipole moment than CS_2 (zero).

10.21 Molecule (b) will have a higher dipole moment. In molecule (a), the *trans* arrangement cancels the bond dipoles and the molecule is nonpolar.

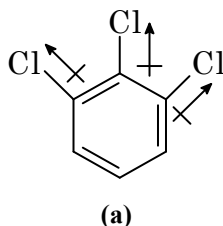


10.22 Strategy: Keep in mind that the dipole moment of a molecule depends on both the difference in electronegativities of the elements present and its geometry. A molecule can have polar bonds (if the bonded atoms have different electronegativities), but it may not possess a dipole moment if it has a highly symmetrical geometry.

Solution: Each vertex of the hexagonal structure of benzene represents the location of a C atom. Around the ring, there is no difference in electronegativity between C atoms, so the only bonds we need to consider are the polar C–Cl bonds.

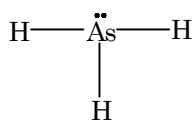
The molecules shown in (b) and (d) are nonpolar. Due to the high symmetry of the molecules and the equal magnitude of the bond moments, the bond moments in each molecule cancel one another. The resultant dipole moment will be *zero*. For the molecules shown in (a) and (c), the bond moments do not cancel and there will be net dipole moments. The dipole moment of the molecule in (a) is larger than that in (c), because in (a) all the bond moments point in the same relative direction, reinforcing each other (see Lewis structure below). Therefore, the order of increasing dipole moments is:

$$(b) = (d) < (c) < (a).$$



10.23 The Lewis theory is a classical theory that deals with chemical bond formation in terms of the pairing of electrons. In this respect, it treats all the bonds in the same way. There is also no consideration of the energetics involved. Valence bond theory treats the bond formation as the overlap of atomic orbitals of the two bonding atoms. A stable bond is formed when the potential energy of the system reaches a minimum. Because different atomic orbitals (s, p, d, \dots) may be involved, we see that not all the chemical bonds are equivalent in length and strength

- 10.24** Valence bond theory states that a stable molecule forms from reacting atoms when the potential energy of the system has decreased to a minimum. As the Cl atoms approach to form the Cl_2 molecule, an electron in a p orbital of each atom is attracted to the nucleus of the other atom. As the atoms get closer together, a distance is reached at which the potential energy reaches a minimum value (see Figure 10.4 of the text). In HCl, as the H and Cl atoms approach to form the HCl molecule, an electron in the s orbital of hydrogen and an electron in a p orbital of chlorine is attracted to the nucleus of the other atom. As the atoms get closer together, a distance is reached at which the potential energy reaches a minimum value.
- 10.25** Please see Figure 10.4 of the text.
- 10.26** Hybridization is the term applied to the mixing of atomic orbitals in an atom (usually a central atom) to generate a set of hybrid orbitals. The concept of hybridization is not applied to isolated atoms. It is a theoretical model used only to explain covalent bonding.
- 10.27** Hybrid orbitals are atomic orbitals obtained when two or more nonequivalent orbitals of the same atom combine in preparation for covalent bond formation. Hybrid orbitals are formed from pure atomic orbitals. Two $2p$ orbitals cannot hybridize; the orbitals must be nonequivalent.
- 10.28** (a) 180° (b) 120° (c) 109.5°
- 10.29** Sigma bonds (σ bonds) are covalent bonds formed by orbitals overlapping end-to-end, with the electron density concentrated between the nuclei of the bonding atoms. A pi bond (π bond) is defined as a covalent bond formed by sideways overlapping orbitals with electron density concentrated above and below the plane of the nuclei of the bonding atoms.
- 10.30** (a) sigma bond (b) sigma bond (c) cannot overlap (d) pi bond
(e) sigma bond (f) sigma bond
- 10.31** AsH_3 has the Lewis structure shown below. There are three bond pairs and one lone pair. The four electron pairs have a tetrahedral arrangement, and the molecular geometry is trigonal pyramidal (AB_3E) like ammonia (See Table 10.2). The As (arsenic) atom is in an sp^3 hybridization state.



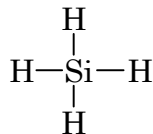
Three of the sp^3 hybrid orbitals form bonds to the hydrogen atoms by overlapping with the hydrogen $1s$ orbitals. The fourth sp^3 hybrid orbital holds the lone pair.

- 10.32 Strategy:** The steps for determining the hybridization of the central atom in a molecule are:

draw Lewis Structure of the molecule	→	use VSEPR to determine the electron pair arrangement surrounding the central atom (Table 10.1 of the text)	→	use Table 10.4 of the text to determine the hybridization state of the central atom
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Solution:

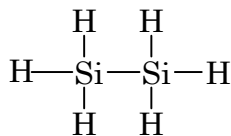
- (a) Write the Lewis structure of the molecule.



Count the number of electron pairs around the central atom. Since there are four electron pairs around Si, the electron arrangement that minimizes electron-pair repulsion is tetrahedral.

We conclude that Si is sp^3 hybridized because it has the electron arrangement of four sp^3 hybrid orbitals.

- (b) Write the Lewis structure of the molecule.



Count the number of electron pairs around the “central atoms”. Since there are four electron pairs around each Si, the electron arrangement that minimizes electron-pair repulsion for each Si is tetrahedral.

We conclude that each Si is sp^3 hybridized because it has the electron arrangement of four sp^3 hybrid orbitals.

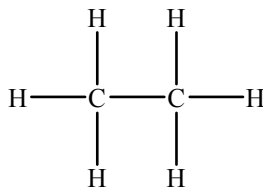
- 10.33** The Lewis structures of AlCl_3 and AlCl_4^- are shown below. The hybridization of Al changes from sp^2 in AlCl_3 to sp^3 in AlCl_4^- .



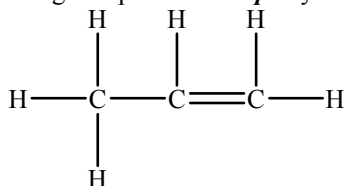
What are the geometries of these molecules?

- 10.34** Draw the Lewis structures. Before the reaction, boron is sp^2 hybridized (trigonal planar electron arrangement) in BF_3 and nitrogen is sp^3 hybridized (tetrahedral electron arrangement) in NH_3 . After the reaction, boron and nitrogen are both sp^3 hybridized (tetrahedral electron arrangement).
- 10.35** (a) NH_3 is an AB_3E type molecule just as AsH_3 in Problem 10.31. Referring to Table 10.4 of the text, the nitrogen is sp^3 hybridized.
- (b) N_2H_4 has two equivalent nitrogen atoms. Centering attention on just one nitrogen atom shows that it is an AB_3E molecule, so the nitrogen atoms are sp^3 hybridized. From structural considerations, how can N_2H_4 be considered to be a derivative of NH_3 ?
- (c) The nitrate anion NO_3^- is isoelectronic and isostructural with the carbonate anion CO_3^{2-} that is discussed in Example 9.5 of the text. There are three resonance structures, and the ion is of type AB_3 ; thus, the nitrogen is sp^2 hybridized.

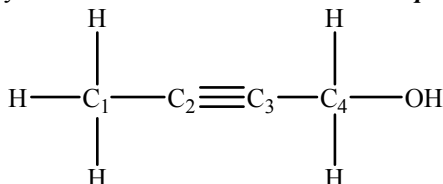
- 10.36 (a) Each carbon has four bond pairs and no lone pairs and therefore has a tetrahedral electron pair arrangement. This implies sp^3 hybrid orbitals.



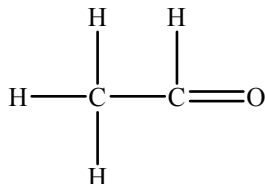
- (b) The left-most carbon is tetrahedral and therefore has sp^3 hybrid orbitals. The two carbon atoms connected by the double bond are trigonal planar with sp^2 hybrid orbitals.



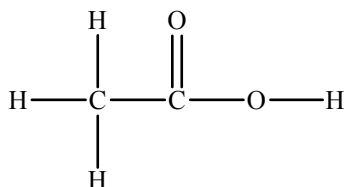
- (c) Carbons 1 and 4 have sp^3 hybrid orbitals. Carbons 2 and 3 have sp hybrid orbitals.



- (d) The left-most carbon is tetrahedral (sp^3 hybrid orbitals). The carbon connected to oxygen is trigonal planar (why?) and has sp^2 hybrid orbitals.

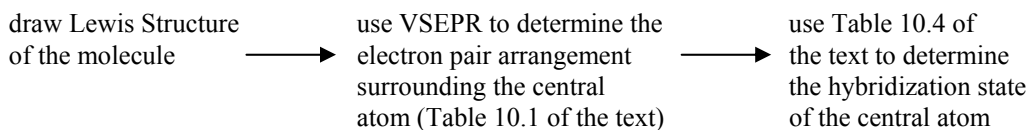


- (e) The left-most carbon is tetrahedral (sp^3 hybrid orbitals). The other carbon is trigonal planar with sp^2 hybridized orbitals.



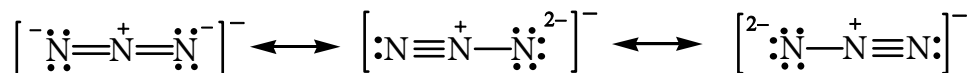
- 10.37 (a) sp (b) sp (c) sp

- 10.38 **Strategy:** The steps for determining the hybridization of the central atom in a molecule are:



Solution:

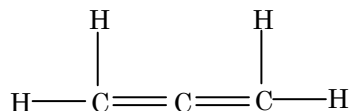
Write the Lewis structure of the molecule. Several resonance forms with formal charges are shown.



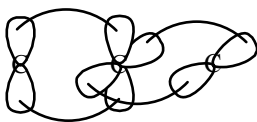
Count the number of electron pairs around the central atom. Since there are two electron pairs around N, the electron arrangement that minimizes electron-pair repulsion is linear (AB_2). Remember, for VSEPR purposes a multiple bond counts the same as a single bond.

We conclude that N is **sp hybridized** because it has the electron arrangement of two sp hybrid orbitals.

- 10.39** The Lewis structure is shown below. The two end carbons are trigonal planar and therefore use sp^2 hybrid orbitals. The central carbon is linear and must use sp hybrid orbitals.



A Lewis drawing does not necessarily show actual molecular geometry. Notice that the two CH_2 groups at the ends of the molecule must be perpendicular. This is because the two double bonds must use different $2p$ orbitals on the middle carbon, and these two $2p$ orbitals are perpendicular. The overlap of the $2p$ orbitals on each carbon is shown below.



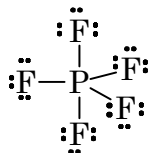
Is the allene molecule polar?

- 10.40 Strategy:** The steps for determining the hybridization of the central atom in a molecule are:

draw Lewis Structure of the molecule	→	use VSEPR to determine the electron pair arrangement surrounding the central atom (Table 10.1 of the text)	→	use Table 10.4 of the text to determine the hybridization state of the central atom
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Solution:

Write the Lewis structure of the molecule.



Count the number of electron pairs around the central atom. Since there are five electron pairs around P, the electron arrangement that minimizes electron-pair repulsion is trigonal bipyramidal (AB_5).

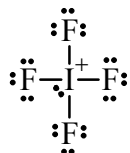
We conclude that P is **sp^3d hybridized** because it has the electron arrangement of five sp^3d hybrid orbitals.

- 10.41** It is almost always true that a single bond is a sigma bond, that a double bond is a sigma bond and a pi bond, and that a triple bond is *always* a sigma bond and two pi bonds.

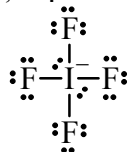
(a) sigma bonds: 4; pi bonds: 0 (b) sigma bonds: 5; pi bonds: 1
 (c) sigma bonds: 10; pi bonds: 3

10.42 A single bond is usually a sigma bond, a double bond is usually a sigma bond and a pi bond, and a triple bond is always a sigma bond and two pi bonds. Therefore, there are **nine pi bonds** and **nine sigma bonds** in the molecule.

10.43 An sp^3d hybridization indicates that the electron-pair arrangement about iodine is trigonal bipyramidal. If four fluorines are placed around iodine, the total number of valence electrons is 35. Only 34 electrons are required to complete a trigonal bipyramidal electron-pair arrangement with four bonds and one lone pair of electrons. Taking one valence electron away gives the cation, IF_4^+ .



10.44 An sp^3d^2 hybridization indicates that the electron-pair arrangement about iodine is octahedral. If four fluorines are placed around iodine, the total number of valence electrons is 35. Thirty-six electrons are required to complete an octahedral electron-pair arrangement with four bonds and two lone pairs of electrons. Adding one valence electron gives the anion, IF_4^- .



10.45 Molecular orbital theory describes covalent bonds in terms of molecular orbitals, which result from interaction of the atomic orbitals of the bonding atoms and are associated with the entire molecule. In valence bond theory, the assumption is made that electrons in a molecule occupy atomic orbitals of the individual atoms. This can only be an approximation, because each bonding electron in a molecule must be in an orbital that is characteristic of the molecule as a whole.

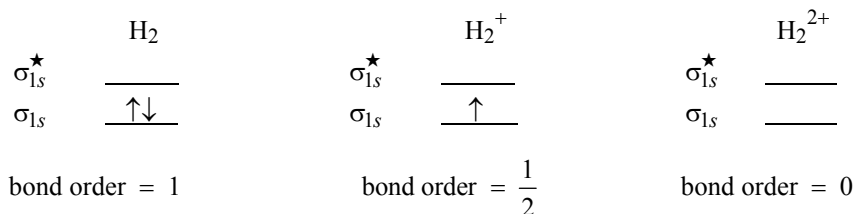
10.46 A bonding molecular orbital has lower energy and greater stability than the atomic orbitals from which it was formed. An antibonding molecular orbital has higher energy and lower stability than the atomic orbitals from which it was formed. In a pi molecular orbital (bonding or antibonding), the electron density is concentrated above and below a line joining the two nuclei of the bonding atoms. In a sigma molecular orbital (bonding or antibonding) the electron density is concentrated symmetrically around a line between the two nuclei of the bonding atoms.

10.47 Please see Figures 10.22 and 10.23 of the text. In order of increasing energy, we have:

$$\sigma_{1s} < \sigma_{1s}^* < \pi_{2p} < \pi_{2p}^*$$

10.48 The bond order is used to evaluate the stability of species. The bond order indicates the approximate strength of a bond, and therefore can only be used qualitatively.

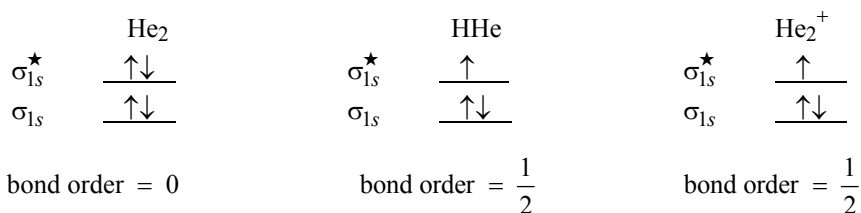
10.49 The molecular orbital electron configuration and bond order of each species is shown below.



The internuclear distance in the $+1$ ion should be greater than that in the neutral hydrogen molecule. The distance in the $+2$ ion will be arbitrarily large because there is no bond (bond order zero).

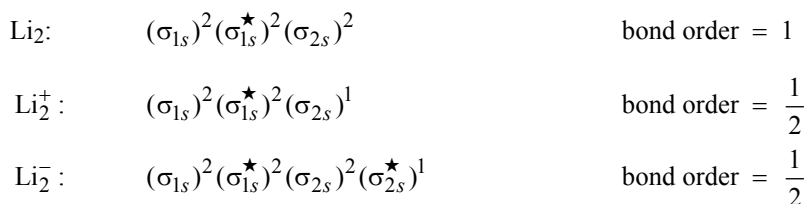
10.50 In order for the two hydrogen atoms to combine to form a H_2 molecule, the electrons must have opposite spins. Furthermore, the combined energy of the two atoms must not be too great. Otherwise, the H_2 molecule will possess too much energy and will break apart into two hydrogen atoms.

10.51 The energy level diagrams are shown below.



He_2 has a bond order of zero; the other two have bond orders of $1/2$. Based on bond orders alone, He_2 has no stability, while the other two have roughly equal stabilities.

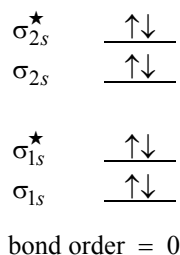
10.52 The electron configurations are listed. Refer to Table 10.5 of the text for the molecular orbital diagram.



Order of increasing stability: $Li_2^- = Li_2^+ < Li_2$

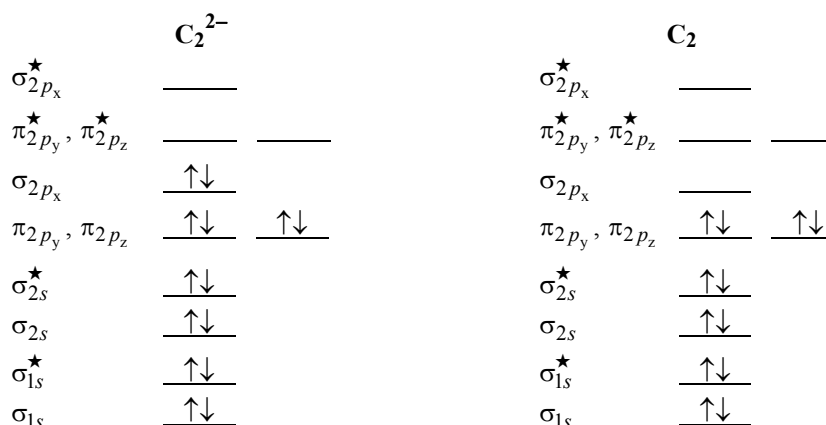
In reality, Li_2^+ is more stable than Li_2^- because there is less electrostatic repulsion in Li_2^+ .

10.53 The Be_2 molecule does not exist because there are equal numbers of electrons in bonding and antibonding molecular orbitals, making the bond order zero.



10.54 See Table 10.5 of the text. Removing an electron from B_2 (bond order = 1) gives B_2^+ , which has a bond order of $(1/2)$. Therefore, B_2^+ has a weaker and longer bond than B_2 .

10.55 The energy level diagrams are shown below.



The bond order of the carbide ion is 3 and that of C_2 is only 2. With what homonuclear diatomic molecule is the carbide ion isoelectronic?

10.56 In both the Lewis structure and the molecular orbital energy level diagram (Table 10.5 of the text), the oxygen molecule has a double bond (bond order = 2). The principal difference is that the molecular orbital treatment predicts that the molecule will have two unpaired electrons (paramagnetic). Experimentally this is found to be true.

10.57 In forming the N_2^+ from N_2 , an electron is removed from the sigma *bonding* molecular orbital. Consequently, the bond order decreases to 2.5 from 3.0. In forming the O_2^+ ion from O_2 , an electron is removed from the pi *antibonding* molecular orbital. Consequently, the bond order increases to 2.5 from 2.0.

10.58 We refer to Table 10.5 of the text.

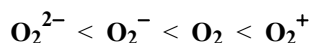
O_2 has a bond order of 2 and is paramagnetic (two unpaired electrons).

O_2^+ has a bond order of 2.5 and is paramagnetic (one unpaired electron).

O_2^- has a bond order of 1.5 and is paramagnetic (one unpaired electron).

O_2^{2-} has a bond order of 1 and is diamagnetic.

Based on molecular orbital theory, the stability of these molecules increases as follows:



10.59 From Table 10.5 we see that the bond order of F_2^+ is 1.5 compared to 1 for F_2 . Therefore, F_2^+ should be more stable than F_2 (stronger bond) and should also have a shorter bond length.

10.60 As discussed in the text (see Table 10.5), the single bond in B_2 is a pi bond (the electrons are in a pi *bonding* molecular orbital) and the double bond in C_2 is made up of two pi bonds (the electrons are in the pi *bonding* molecular orbitals).

10.61 Only (c) will not be tetrahedral. All the others have AB_4 -type Lewis structures and will therefore be tetrahedral. For SF_4 the Lewis structure is of the AB_4E type which gives rise to a distorted tetrahedral geometry (Table 10.2 of the text).

10.62 Strategy: The sequence of steps in determining molecular geometry is as follows:

draw Lewis structure \longrightarrow find arrangement of electrons pairs \longrightarrow find arrangement of bonding pairs \longrightarrow determine geometry based on bonding pairs

Solution:

Write the Lewis structure of the molecule.



Count the number of electron pairs around the central atom. There are two electron pairs around Hg.

Since there are two electron pairs around Hg, the electron-pair arrangement that minimizes electron-pair repulsion is **linear**.

In addition, since there are no lone pairs around the central atom, the geometry is also **linear** (AB₂).

You could establish the geometry of HgBr₂ by measuring its dipole moment. If mercury(II) bromide were bent, it would have a measurable dipole moment. Experimentally, it has no dipole moment and therefore must be linear.

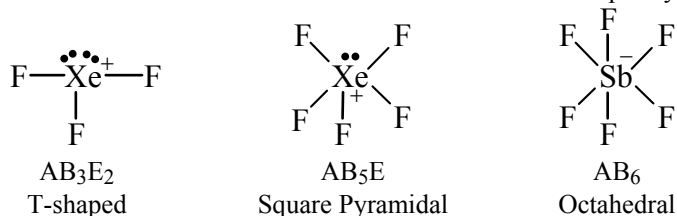
10.63	Dot structure	Label	Shape	Bond dipole	Resultant	Dipole Moment
		AB ₂ E ₂	bent			$\mu > 0$
		AB ₃ E	trigonal pyramidal			$\mu > 0$
		AB ₄ E ₂	square planar			$\mu = 0$
		AB ₅	trigonal bipyramid			$\mu = 0$
		AB ₆	octahedral			$\mu = 0$

Why do the bond dipoles add to zero in PCl₅?

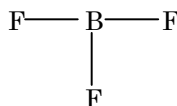
10.64 According to valence bond theory, a pi bond is formed through the side-to-side overlap of a pair of p orbitals. As atomic size increases, the distance between atoms is too large for p orbitals to overlap effectively in a side-to-side fashion. If two orbitals overlap poorly, that is, they share very little space in common, then the resulting bond will be very weak. This situation applies in the case of pi bonds between silicon atoms as well as between any other elements not found in the second period. It is usually far more energetically favorable for silicon, or any other heavy element, to form two single (sigma) bonds to two other atoms than to form a double bond (sigma + pi) to only one other atom.

10.65 Geometry: **bent**; hybridization: sp^3 .

10.66 The Lewis structures and VSEPR geometries of these species are shown below. The three nonbonding pairs of electrons on each fluorine atom have been omitted for simplicity.

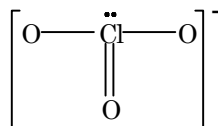


10.67 (a) The Lewis structure is:



The shape will be trigonal **planar** (AB_3)

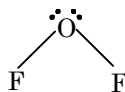
(b) The Lewis structure is:



The molecule will be a trigonal pyramid (**nonplanar**).

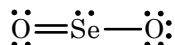
(c) The Lewis structure and the dipole moment for H_2O is presented in Problem 10.63. The dipole moment is directed from the positive hydrogen end to the more negative oxygen.

(d) The Lewis structure is:



The molecule is bent and therefore **polar**.

(e) The Lewis structure is:



The selenium atom is of the AB_2E type. The electron-pair arrangement is trigonal planar; therefore, the OSeO bond angle should be **approximately**, but smaller than, 120° .

Which of the species in this problem has resonance structures?

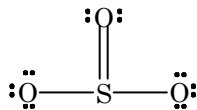
10.68 To predict the bond angles for the molecules, you would have to draw the Lewis structure and determine the geometry using the VSEPR model. From the geometry, you can predict the bond angles.

- (a) BeCl_2 : AB_2 type, 180° (linear).
 (b) BCl_3 : AB_3 type, 120° (trigonal planar).
 (c) CCl_4 : AB_4 type, 109.5° (tetrahedral).
 (d) CH_3Cl : AB_4 type, roughly 109.5° (tetrahedral with a possible slight distortion resulting from the different sizes of the chlorine and hydrogen atoms).
 (e) Hg_2Cl_2 : Each mercury atom is of the AB_2 type. The entire molecule is linear, 180° bond angles.
 (f) SnCl_2 : AB_2E type, roughly 120° (bent).
 (g) H_2O_2 : The atom arrangement is HOOH . Each oxygen atom is of the AB_2E_2 type and the $\text{H}-\text{O}-\text{O}$ angles will be roughly 109.5° .
 (h) SnH_4 : AB_4 type, 109.5° (tetrahedral).

10.69 The two approaches are discussed in Sections 10.1, 10.3, and 10.4 of the textbook.

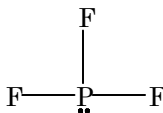
10.70 Since arsenic and phosphorus are both in the same group of the periodic table, this problem is exactly like Problem 10.40. AsF_5 is an AB_5 type molecule, so the geometry is trigonal bipyramidal. We conclude that As is sp^3d hybridized because it has the electron arrangement of five sp^3d hybrid orbitals.

10.71 (a) The Lewis structure is:



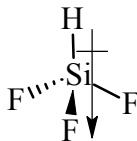
The geometry is trigonal planar; the molecule is **nonpolar**.

(b) The Lewis structure is:



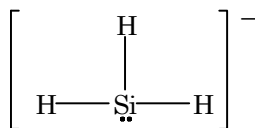
The molecule has trigonal pyramidal geometry. It is **polar**.

(c) The Lewis structure is:



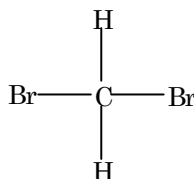
The molecule will be tetrahedral (AB_4). Both fluorine and hydrogen are more electronegative than silicon, but fluorine is the most electronegative element, so the molecule will be polar (fluorine side negative).

(d) The Lewis structure is:



The ion has a **trigonal pyramidal** geometry (AB₃E).

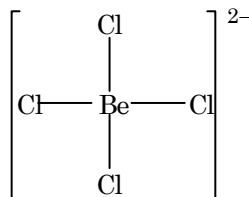
(e) The Lewis structure is:



The molecule will be tetrahedral (AB₄) but still **polar**. The negative end of the dipole moment will be on the side with the two bromine atoms; the positive end will be on the hydrogen side.

10.72 Only ICl_2^- and CdBr_2 will be linear. The rest are bent.

10.73 The Lewis structure is shown below.



The molecule is of the AB₄ type and should therefore be **tetrahedral**. The hybridization of the Be atom should be sp^3 .

10.74 (a)

Strategy: The steps for determining the hybridization of the central atom in a molecule are:

draw Lewis Structure of the molecule	→	use VSEPR to determine the electron pair arrangement surrounding the central atom (Table 10.1 of the text)	→	use Table 10.4 of the text to determine the hybridization state of the central atom
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Solution:

The geometry around each nitrogen is identical. To complete an octet of electrons around N, you must add a lone pair of electrons. Count the number of electron pairs around N. There are three electron pairs around each N.

Since there are three electron pairs around N, the electron-pair arrangement that minimizes electron-pair repulsion is trigonal planar.

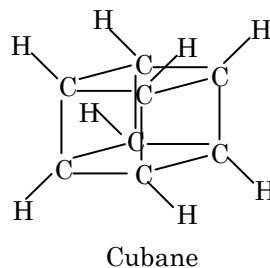
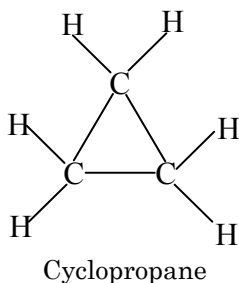
We conclude that each N is sp^2 hybridized because it has the electron arrangement of three sp^2 hybrid orbitals.

(b)

Strategy: Keep in mind that the dipole moment of a molecule depends on both the difference in electronegativities of the elements present and its geometry. A molecule can have polar bonds (if the bonded atoms have different electronegativities), but it may not possess a dipole moment if it has a highly symmetrical geometry.

Solution: An N–F bond is polar because F is more electronegative than N. The **structure on the right** has a **dipole moment** because the two N–F bond moments do not cancel each other out and so the molecule has a net dipole moment. On the other hand, the two N–F bond moments in the left-hand structure cancel. The sum or resultant dipole moment will be *zero*.

10.75 (a) The structures for cyclopropane and cubane are



(b) The C–C–C bond in cyclopropane is 60° and in cubane is 90° . Both are smaller than the 109.5° expected for sp^3 hybridized carbon. Consequently, there is considerable strain on the molecules.

(c) They would be more difficult to make than an sp^3 hybridized carbon in an unconstrained (that is, not in a small ring) system in which the carbons can adopt bond angles closer to 109.5° .

10.76 In 1,2-dichloroethane, the two C atoms are joined by a sigma bond. Rotation about a sigma bond does not destroy the bond, and the bond is therefore free (or relatively free) to rotate. Thus, all angles are permitted and the molecule is nonpolar because the C–Cl bond moments cancel each other because of the averaging effect brought about by rotation. In *cis*-dichloroethylene the two C–Cl bonds are locked in position. The π bond between the C atoms prevents rotation (in order to rotate, the π bond must be broken, using an energy source such as light or heat). Therefore, there is no rotation about the C=C in *cis*-dichloroethylene, and the molecule is polar.

10.77 The analysis in Problem 10.39 shows the allene molecule to be polar (why?). Consider the overlap of the $2p$ orbitals on each carbon atom.



The geometric planes containing the CHCl groups at each end of the molecule are mutually perpendicular. This is because the two carbon-carbon double bonds must use different $2p$ orbitals on the middle carbon, and these two $2p$ orbitals are perpendicular. This means that the two chlorine atoms can be considered to be on one side of the molecule and the two hydrogen atoms on the other. **The molecule has a dipole moment.** Draw the end-on view if you aren't convinced.

10.78 C has no d orbitals but Si does ($3d$). Thus, H_2O molecules can add to Si in hydrolysis (valence-shell expansion).

10.79 B_2 is $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_y})^1(\pi_{2p_z})^1$. It is **paramagnetic**.

10.80 The **carbons** are in sp^2 hybridization states. The **nitrogens** are in the sp^3 hybridization state, except for the **ring nitrogen double-bonded to a carbon** that is sp^2 hybridized. The oxygen atom is sp^2 hybridized.

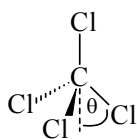
10.81 In Problem 9.105, we see that F_2 has a bond enthalpy of 156.9 kJ/mol, whereas F_2^- has a bond enthalpy of 114 kJ/mol (calculate in Problem 9.105). Referring to Table 10.5, we see that F_2^- has an extra electron in $\sigma_{2p_x}^*$. Therefore, it only has a bond order of $\frac{1}{2}$ (compared with a bond order of one for F_2).

10.82 $1 D = 3.336 \times 10^{-30} C \cdot m$

electronic charge (e) = $1.6022 \times 10^{-19} C$

$$\frac{\mu}{ed} \times 100\% = \frac{1.92 \cancel{D} \times \frac{3.336 \times 10^{-30} \cancel{C \cdot m}}{1 \cancel{D}}}{(1.6022 \times 10^{-19} \cancel{C}) \times (91.7 \times 10^{-12} \cancel{m})} \times 100\% = \mathbf{43.6\%}$$
 ionic character

10.83 CCl_4 can be represented by:



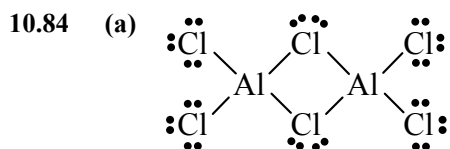
Let ρ be a C–Cl bond moment. Thus,

$$\rho = 3\rho \cos \theta$$

$$\cos \theta = \frac{1}{3}$$

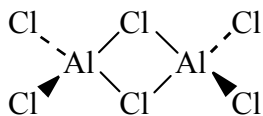
$$\theta = 70.5^\circ$$

$$\text{Tetrahedral angle} = 180^\circ - 70.5^\circ = \mathbf{109.5^\circ}$$



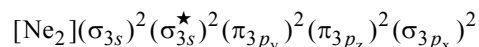
(b) The hybridization of Al in $AlCl_3$ is sp^2 . The molecule is trigonal planar. The hybridization of Al in Al_2Cl_6 is sp^3 .

(c) The geometry about each Al atom is tetrahedral.



(d) The molecules are nonpolar; they **do not possess a dipole moment**.

- 10.85 (a)** Looking at the electronic configuration for N_2 shown in Table 10.5 of the text, we write the electronic configuration for P_2 .

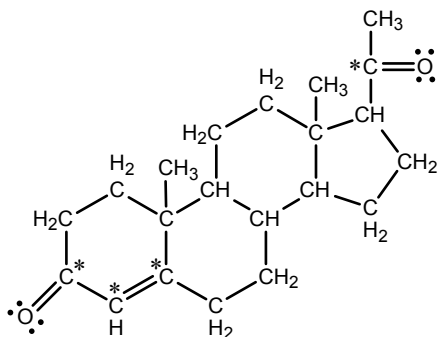


- (b)** Past the Ne_2 core configuration, there are 8 bonding electrons and 2 antibonding electrons. The bond order is:

$$\text{bond order} = \frac{1}{2}(8 - 2) = 3$$

- (c)** All the electrons in the electronic configuration are paired. P_2 is **diamagnetic**.

- 10.86** The complete structure of progesterone is shown below.



The **four carbons** marked with an **asterisk** are sp^2 hybridized. The **remaining carbons** are sp^3 hybridized.

- 10.87** The **second and third vibrational motions** are responsible for CO_2 to behave as a greenhouse gas. CO_2 is a nonpolar molecule. The second and third vibrational motions, create a changing dipole moment. The first vibration, a symmetric stretch, does *not* create a dipole moment. Since CO , NO_2 , and N_2O are all polar molecules, they will also act as greenhouse gases.

- 10.88 (a)** A σ bond is formed by orbitals overlapping end-to-end. Rotation will not break this end-to-end overlap. A π bond is formed by the sideways overlapping of orbitals. The two 90° rotations (180° total) will break and then reform the π bond, thereby converting *cis*-dichloroethylene to *trans*-dichloroethylene.
- (b)** The π bond is weaker because of the lesser extent of sideways orbital overlap, compared to the end-to-end overlap in a sigma bond.
- (c)** The bond enthalpy is given in the unit, kJ/mol. To find the longest wavelength of light needed to bring about the conversion from *cis* to *trans*, we need the energy to break a π bond in a single molecule. We convert from kJ/mol to J/molecule.

$$\frac{270 \text{ kJ}}{1 \cancel{\text{mol}}} \times \frac{1 \cancel{\text{mol}}}{6.022 \times 10^{23} \text{ molecules}} = 4.48 \times 10^{-22} \text{ kJ/molecule} = 4.48 \times 10^{-19} \text{ J/molecule}$$

Now that we have the energy needed to cause the conversion from *cis* to *trans* in one molecule, we can calculate the wavelength from this energy.

$$E = \frac{hc}{\lambda}$$

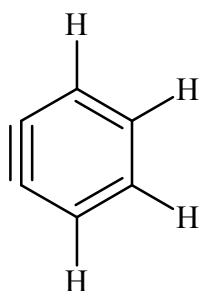
$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{4.48 \times 10^{-19} \text{ J}}$$

$$\lambda = 4.44 \times 10^{-7} \text{ m} = 444 \text{ nm}$$

10.89 In each case, we examine the molecular orbital that is occupied by the valence electrons of the molecule to see if it is a bonding or antibonding molecular orbital. If the electron is in a bonding molecular orbital, it is more stable than an electron in an atomic orbital ($1s$ or $2p$ atomic orbital) and thus will have a higher ionization energy compared to the lone atom. On the other hand, if the electron is in an antibonding molecular orbital, it is less stable than an electron in an atomic orbital ($1s$ or $2p$ atomic orbital) and thus will have a lower ionization energy compared to the lone atom. Refer to Table 10.5 of the text.

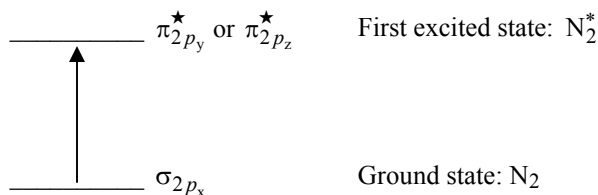
- (a) H_2 (b) N_2 (c) O (d) F

10.90



The normal bond angle for a hexagon is 60° . However, the triple bond requires an angle of 180° (linear) and therefore there is a great deal of strain in the molecule. Consequently, the molecule is very reactive (breaking the bond to relieve the strain).

10.91 (a) From Table 10.5 of the text:

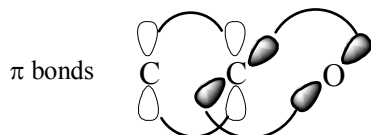
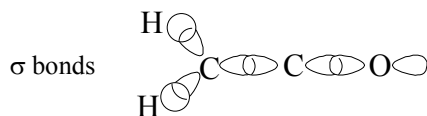
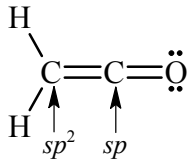


- (b) The bond order for N_2 is 3. The bond order for N_2^* is $\frac{1}{2}(5 - 1) = 2$. N_2^* should have a longer bond length than N_2 .
- (c) N_2^* is **diamagnetic**. Electrons do not change their spins during transitions.

(d)
$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{470 \times 10^{-9} \text{ m}} = 4.23 \times 10^{-19} \text{ J}$$

10.92 The Lewis structure shows 4 pairs of electrons on the two oxygen atoms. From Table 10.5 of the text, we see that these 8 valence electrons are placed in the σ_{2p_x} , π_{2p_y} , π_{2p_z} , $\pi_{2p_y}^*$, and $\pi_{2p_z}^*$ orbitals. For all the electrons to be paired, energy is needed to flip the spin in one of the antibonding molecular orbitals ($\pi_{2p_y}^*$ or $\pi_{2p_z}^*$). According to Hund's rule, this arrangement is less stable than the ground-state configuration shown in Table 10.5, and hence the Lewis structure shown actually corresponds to an excited state of the oxygen molecule.

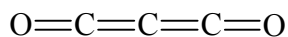
10.93



10.94 (a) Although the O atoms are sp^3 hybridized, they are locked in a planar structure by the benzene rings. The molecule is symmetrical and therefore **does not possess a dipole moment**.

(b) **20 σ bonds and 6 π bonds.**

10.95 The skeletal structure of carbon suboxide is:



The C=O bond moments on each end of the molecule are equal and opposite and will cancel. Carbon suboxide is linear (the C atoms are all sp hybridized) and does **not possess a dipole moment**.

10.96 (a) and (c) possess dipole moments. ClF_2^+ has a bent geometry and IF_4^+ has a distorted tetrahedron or see-saw geometry. Draw correct Lewis structures to determine the polarity. ClF_2^- has a linear geometry and IF_4^- has a square planar geometry. Both of these molecules have no net dipole moment.