

CHAPTER 1

CHEMICAL BONDING

SOLUTIONS TO TEXT PROBLEMS

- 1.1 The element carbon has atomic number 6, and so it has a total of six electrons. Two of these electrons are in the $1s$ level. The four electrons in the $2s$ and $2p$ levels (the valence shell) are the valence electrons. Carbon has four valence electrons.
- 1.2 Electron configurations of elements are derived by applying the following principles:
- The number of electrons in a neutral atom is equal to its atomic number Z .
 - The maximum number of electrons in any orbital is 2.
 - Electrons are added to orbitals in order of increasing energy, filling the $1s$ orbital before any electrons occupy the $2s$ level. The $2s$ orbital is filled before any of the $2p$ orbitals, and the $3s$ orbital is filled before any of the $3p$ orbitals.
 - All the $2p$ orbitals ($2p_x$, $2p_y$, $2p_z$) are of equal energy, and each is singly occupied before any is doubly occupied. The same holds for the $3p$ orbitals.

With this as background, the electron configuration of the third-row elements is derived as follows [$2p^6 = 2p_x^2 2p_y^2 2p_z^2$]:

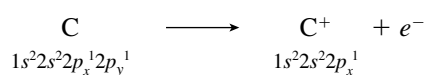
Na ($Z = 11$)	$1s^2 2s^2 2p^6 3s^1$
Mg ($Z = 12$)	$1s^2 2s^2 2p^6 3s^2$
Al ($Z = 13$)	$1s^2 2s^2 2p^6 3s^2 3p_x^1$
Si ($Z = 14$)	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1$
P ($Z = 15$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$
S ($Z = 16$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$
Cl ($Z = 17$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^2$
Ar ($Z = 18$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^2$

1.3 The electron configurations of the designated ions are:

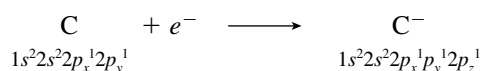
Ion	Z	Number of Electrons in Ion	Electron Configuration of Ion
(b) He ⁺	2	1	1s ¹
(c) H ⁻	1	2	1s ²
(d) O ⁻	8	9	1s ² 2s ² 2p _x ² 2p _y ² 2p _z ¹
(e) F ⁻	9	10	1s ² 2s ² 2p ⁶
(f) Ca ²⁺	20	18	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶

Those with a noble gas configuration are H⁻, F⁻, and Ca²⁺.

1.4 A positively charged ion is formed when an electron is removed from a neutral atom. The equation representing the ionization of carbon and the electron configurations of the neutral atom and the ion is:



A negatively charged carbon is formed when an electron is added to a carbon atom. The additional electron enters the 2p_z orbital.



Neither C⁺ nor C⁻ has a noble gas electron configuration.

1.5 Hydrogen has one valence electron, and fluorine has seven. The covalent bond in hydrogen fluoride arises by sharing the single electron of hydrogen with the unpaired electron of fluorine.

Combine H· and ·F: to give the Lewis structure for hydrogen fluoride H:F:

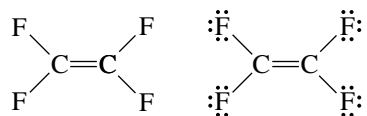
1.6 We are told that C₂H₆ has a carbon–carbon bond.

Thus, we combine two ·C· and six H· to write the Lewis structure of ethane

$$\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}:\text{C}:\text{C}:\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$$

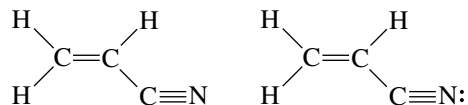
There are a total of 14 valence electrons distributed as shown. Each carbon is surrounded by eight electrons.

1.7 (b) Each carbon contributes four valence electrons, and each fluorine contributes seven. Thus, C₂F₄ has 36 valence electrons. The octet rule is satisfied for carbon only if the two carbons are attached by a double bond and there are two fluorines on each carbon. The pattern of connections shown (below left) accounts for 12 electrons. The remaining 24 electrons are divided equally (six each) among the four fluorines. The complete Lewis structure is shown at right below.



(c) Since the problem states that the atoms in C₃H₃N are connected in the order CCCN and all hydrogens are bonded to carbon, the order of attachments can only be as shown (below left) so as to have four bonds to each carbon. Three carbons contribute 12 valence electrons, three hydrogens contribute 3, and nitrogen contributes 5, for a total of 20 valence electrons. The nine

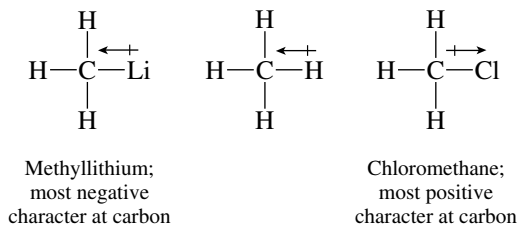
bonds indicated in the partial structure account for 18 electrons. Since the octet rule is satisfied for carbon, add the remaining two electrons as an unshared pair on nitrogen (below right).



- 1.8 The degree of positive or negative character at carbon depends on the difference in electronegativity between the carbon and the atoms to which it is attached. From Table 1.2, we find the electronegativity values for the atoms contained in the molecules given in the problem are:

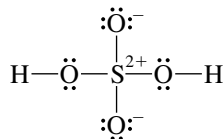
Li	1.0
H	2.1
C	2.5
Cl	3.0

Thus, carbon is more electronegative than hydrogen and lithium, but less electronegative than chlorine. When bonded to carbon, hydrogen and lithium bear a partial positive charge, and carbon bears a partial negative charge. Conversely, when chlorine is bonded to carbon, it bears a partial negative charge, and carbon becomes partially positive. In this group of compounds, lithium is the least electronegative element, chlorine the most electronegative.



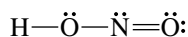
- 1.9 (b) The formal charges in sulfuric acid are calculated as follows:

	Valence Electrons in Neutral Atom	Electron Count	Formal Charge
Hydrogen:	1	$\frac{1}{2}(2) = 1$	0
Oxygen (of OH):	6	$\frac{1}{2}(4) + 4 = 6$	0
Oxygen:	6	$\frac{1}{2}(2) + 6 = 7$	-1
Sulfur:	6	$\frac{1}{2}(8) + 0 = 4$	+2

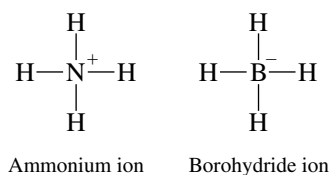


- (c) The formal charges in nitrous acid are calculated as follows:

	Valence Electrons in Neutral Atom	Electron Count	Formal Charge
Hydrogen:	1	$\frac{1}{2}(2) = 1$	0
Oxygen (of OH):	6	$\frac{1}{2}(4) + 4 = 6$	0
Oxygen:	6	$\frac{1}{2}(4) + 4 = 6$	0
Nitrogen:	5	$\frac{1}{2}(6) + 2 = 5$	0

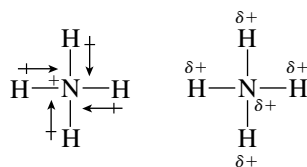


- 1.10 The electron counts of nitrogen in ammonium ion and boron in borohydride ion are both 4 (one half of 8 electrons in covalent bonds).

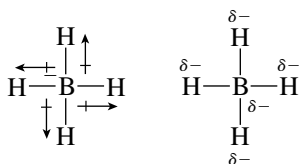


Since a neutral nitrogen has 5 electrons in its valence shell, an electron count of 4 gives it a formal charge of +1. A neutral boron has 3 valence electrons, and so an electron count of 4 in borohydride ion corresponds to a formal charge of -1.

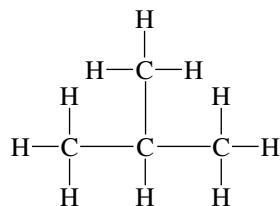
- 1.11 As shown in the text in Table 1.2, nitrogen is more electronegative than hydrogen and will draw the electrons in N—H bonds toward itself. Nitrogen with a formal charge of +1 is even more electronegative than a neutral nitrogen.



Boron (electronegativity = 2.0) is, on the other hand, slightly less electronegative than hydrogen (electronegativity = 2.1). Boron with a formal charge of -1 is less electronegative than a neutral boron. The electron density in the B—H bonds of BH_4^- is therefore drawn toward hydrogen and away from boron.

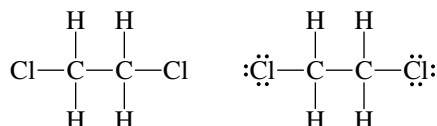


- 1.12 (b) The compound $(\text{CH}_3)_3\text{CH}$ has a central carbon to which are attached three CH_3 groups and a hydrogen.

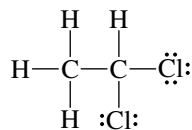


Four carbons and 10 hydrogens contribute 26 valence electrons. The structure shown has 13 covalent bonds, and so all the valence electrons are accounted for. The molecule has no unshared electron pairs.

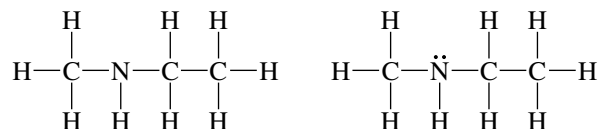
- (c) The number of valence electrons in $\text{ClCH}_2\text{CH}_2\text{Cl}$ is 26 ($2\text{Cl} = 14$; $4\text{H} = 4$; $2\text{C} = 8$). The constitution at the left below shows seven covalent bonds accounting for 14 electrons. The remaining 12 electrons are divided equally between the two chlorines as unshared electron pairs. The octet rule is satisfied for both carbon and chlorine in the structure at the right below.



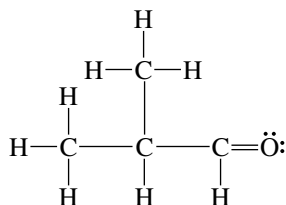
- (d) This compound has the same molecular formula as the compound in part (c), but a different structure. It, too, has 26 valence electrons, and again only chlorine has unshared pairs.



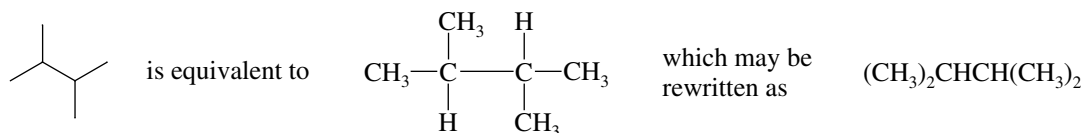
- (e) The constitution of $\text{CH}_3\text{NHCH}_2\text{CH}_3$ is shown (below left). There are 26 valence electrons, and 24 of them are accounted for by the covalent bonds in the structural formula. The remaining two electrons complete the octet of nitrogen as an unshared pair (below right).



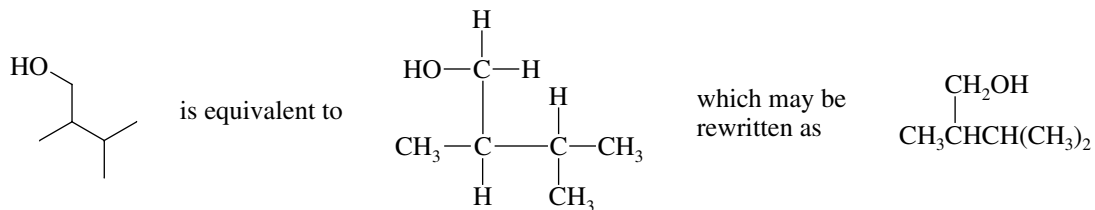
- (f) Oxygen has two unshared pairs in $(\text{CH}_3)_2\text{CHCH}=\text{O}$.



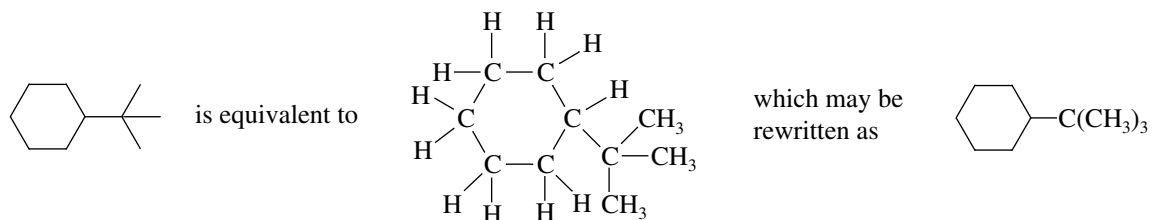
- 1.13** (b) This compound has a four-carbon chain to which are appended two other carbons.



- (c) The carbon skeleton is the same as that of the compound in part (b), but one of the terminal carbons bears an OH group in place of one of its hydrogens.

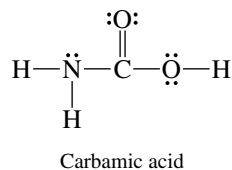


- (d) The compound is a six-membered ring that bears a $-\text{C}(\text{CH}_3)_3$ substituent.

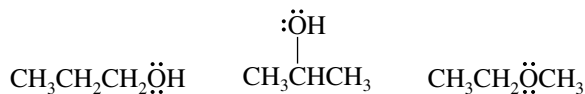


- 1.14** The problem specifies that nitrogen and both oxygens of carbamic acid are bonded to carbon and one of the carbon–oxygen bonds is a double bond. Since a neutral carbon is associated with four

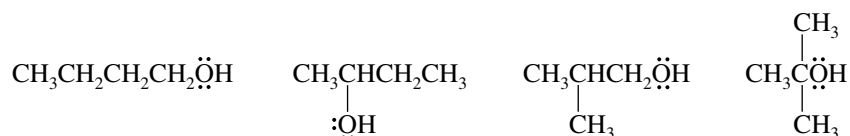
bonds, a neutral nitrogen three (plus one unshared electron pair), and a neutral oxygen two (plus two unshared electron pairs), this gives the Lewis structure shown.



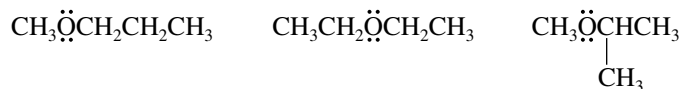
- 1.15 (b) There are three constitutional isomers of $\text{C}_3\text{H}_8\text{O}$:



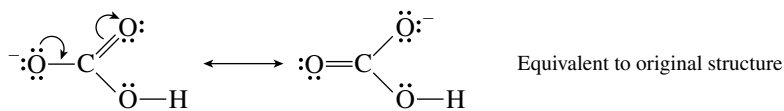
- (c) Four isomers of $\text{C}_4\text{H}_{10}\text{O}$ have —OH groups:



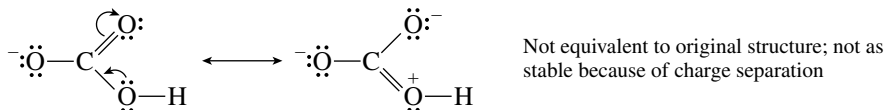
Three isomers have C—O—C units:



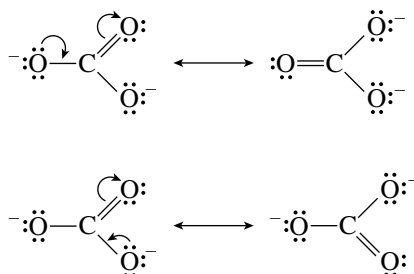
- 1.16 (b) Move electrons from the negatively charged oxygen, as shown by the curved arrows.



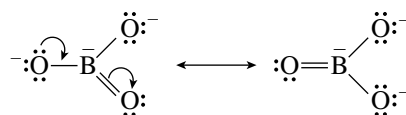
The resonance interaction shown for bicarbonate ion is more important than an alternative one involving delocalization of lone-pair electrons in the OH group.



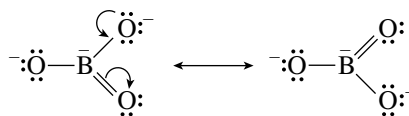
- (c) All three oxygens are equivalent in carbonate ion. Either negatively charged oxygen can serve as the donor atom.



(d) Resonance in borate ion is exactly analogous to that in carbonate.

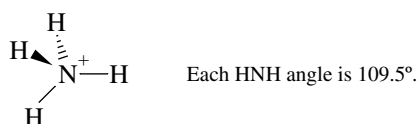


and



1.17 There are four B—H bonds in BH_4^- . The four electron pairs surround boron in a tetrahedral orientation. The H—B—H angles are 109.5° .

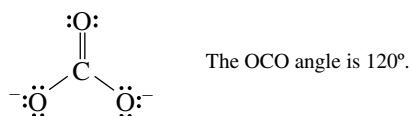
1.18 (b) Nitrogen in ammonium ion is surrounded by 8 electrons in four covalent bonds. These four bonds are directed toward the corners of a tetrahedron.



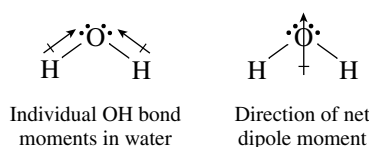
(c) Double bonds are treated as a single unit when deducing the shape of a molecule using the VSEPR model. Thus azide ion is linear.



(d) Since the double bond in carbonate ion is treated as if it were a single unit, the three sets of electrons are arranged in a trigonal planar arrangement around carbon.

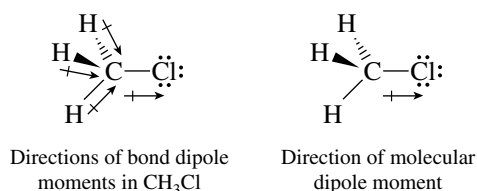


1.19 (b) Water is a bent molecule, and so the individual O—H bond dipole moments do not cancel. Water has a dipole moment.

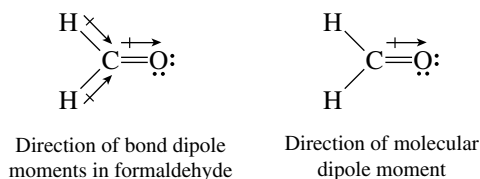


(c) Methane, CH_4 , is perfectly tetrahedral, and so the individual (small) C—H bond dipole moments cancel. Methane has no dipole moment.

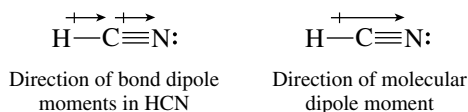
(d) Methyl chloride has a dipole moment.



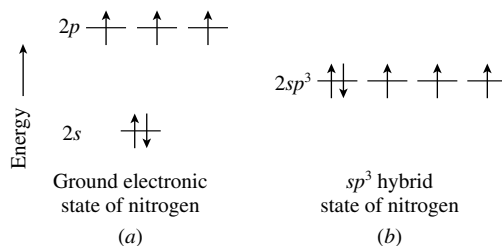
- (e) Oxygen is more electronegative than carbon and attracts electrons from it. Formaldehyde has a dipole moment.



- (f) Nitrogen is more electronegative than carbon. Hydrogen cyanide has a dipole moment.

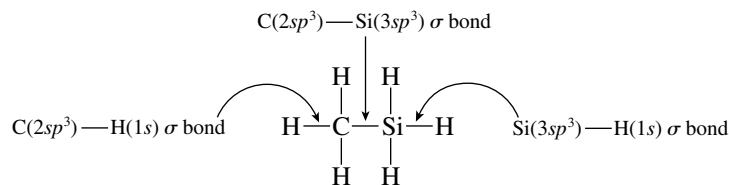


- 1.20** The orbital diagram for sp^3 -hybridized nitrogen is the same as for sp^3 -hybridized carbon, except nitrogen has one more electron.



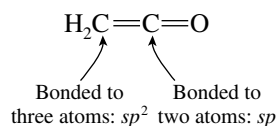
The unshared electron pair in ammonia ($:\text{NH}_3$) occupies an sp^3 -hybridized orbital of nitrogen. Each $\text{N}-\text{H}$ bond corresponds to overlap of a half-filled sp^3 hybrid orbital of nitrogen and a $1s$ orbital of hydrogen.

- 1.21** Silicon lies below carbon in the periodic table, and it is reasonable to assume that both carbon and silicon are sp^3 -hybridized in H_3CSiH_3 . The $\text{C}-\text{Si}$ bond and all of the $\text{C}-\text{H}$ and $\text{Si}-\text{H}$ bonds are σ bonds.

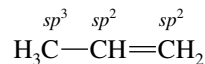


The principal quantum number of the carbon orbitals that are hybridized is 2; the principal quantum number for the silicon orbitals is 3.

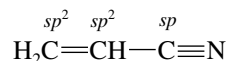
- 1.22** (b) Carbon in formaldehyde ($\text{H}_2\text{C}=\text{O}$) is directly bonded to three other atoms (two hydrogens and one oxygen). It is sp^2 -hybridized.
 (c) Ketene has two carbons in different hybridization states. One is sp^2 -hybridized; the other is sp -hybridized.



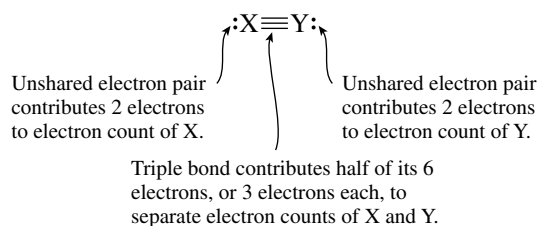
- (d) One of the carbons in propene is sp^3 -hybridized. The carbons of the double bond are sp^2 -hybridized.



- (e) The carbons of the CH_3 groups in acetone $[(\text{CH}_3)_2\text{C}=\text{O}]$ are sp^3 -hybridized. The $\text{C}=\text{O}$ carbon is sp^2 -hybridized.
 (f) The carbons in acrylonitrile are hybridized as shown:



- 1.23** All these species are characterized by the formula $:\text{X}\equiv\text{Y}:$, and each atom has an electron count of 5.

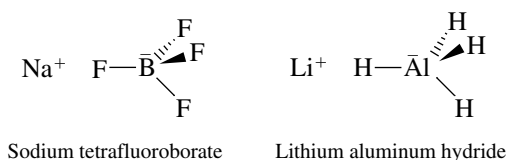


$$\text{Electron count X} = \text{electron count Y} = 2 + 3 = 5$$

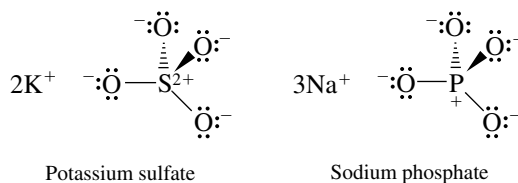
- (a) $:\text{N}\equiv\text{N}:$ A neutral nitrogen atom has 5 valence electrons: therefore, each atom is electrically neutral in molecular nitrogen.
- (b) $:\text{C}\equiv\text{N}:$ Nitrogen, as before, is electrically neutral. A neutral carbon has 4 valence electrons, and so carbon in this species, with an electron count of 5, has a unit negative charge. The species is cyanide anion; its net charge is -1 .
- (c) $:\text{C}\equiv\text{C}:$ There are two negatively charged carbon atoms in this species. It is a dianion; its net charge is -2 .
- (d) $:\text{N}\equiv\text{O}:$ Here again is a species with a neutral nitrogen atom. Oxygen, with an electron count of 5, has 1 less electron in its valence shell than a neutral oxygen atom. Oxygen has a formal charge of $+1$; the net charge is $+1$.
- (e) $:\text{C}\equiv\text{O}:$ Carbon has a formal charge of -1 ; oxygen has a formal charge of $+1$. Carbon monoxide is a neutral molecule.
- 1.24** All these species are of the type $:\ddot{\text{Y}}=\text{X}=\ddot{\text{Y}}:$. Atom X has an electron count of 4, corresponding to half of the 8 shared electrons in its four covalent bonds. Each atom Y has an electron count of 6; 4 unshared electrons plus half of the 4 electrons in the double bond of each Y to X.
- (a) $:\ddot{\text{O}}=\text{C}=\ddot{\text{O}}:$ Oxygen, with an electron count of 6, and carbon, with an electron count of 4, both correspond to the respective neutral atoms in the number of electrons they “own.” Carbon dioxide is a neutral molecule, and neither carbon nor oxygen has a formal charge in this Lewis structure.
- (b) $:\ddot{\text{N}}=\text{N}=\ddot{\text{N}}:$ The two terminal nitrogens each have an electron count (6) that is one more than a neutral atom and thus each has a formal charge of -1 . The central N has an electron count (4) that is one less than a neutral nitrogen; it has a formal charge of $+1$. The net charge on the species is $(-1 + 1 - 1)$, or -1 .
- (c) $:\ddot{\text{O}}=\text{N}=\ddot{\text{O}}:$ As in part (b), the central nitrogen has a formal charge of $+1$. As in part (a), each oxygen is electrically neutral. The net charge is $+1$.

- 1.25** (a, b) The problem specifies that ionic bonding is present and that the anion is tetrahedral. The cations are the group I metals Na^+ and Li^+ . Both boron and aluminum are group III

elements, and thus have a formal charge of -1 in the tetrahedral anions BF_4^- and AlH_4^- respectively.

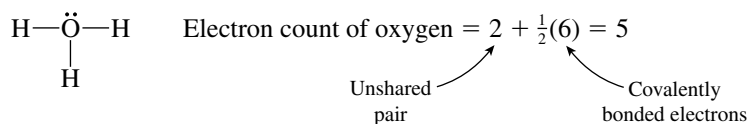


- (c, d) Both of the tetrahedral anions have 32 valence electrons. Sulfur contributes 6 valence electrons and phosphorus 5 to the anions. Each oxygen contributes 6 electrons. The double negative charge in sulfate contributes 2 more, and the triple negative charge in phosphate contributes 3 more.



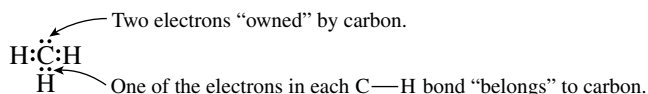
The formal charge on each oxygen in both ions is -1 . The formal charge on sulfur in sulfate is $+2$; the charge on phosphorus is $+1$. The net charge of sulfate ion is -2 ; the net charge of phosphate ion is -3 .

- 1.26 (a) Each hydrogen has a formal charge of 0, as is always the case when hydrogen is covalently bonded to one substituent. Oxygen has an electron count of 5.



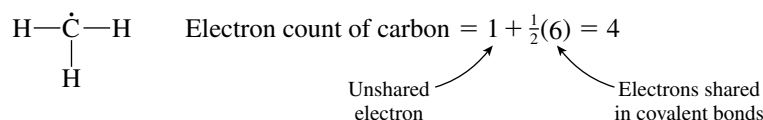
A neutral oxygen atom has 6 valence electrons; therefore, oxygen in this species has a formal charge of $+1$. The species as a whole has a unit positive charge. It is the hydronium ion, H_3O^+ .

- (b) The electron count of carbon is 5; there are 2 electrons in an unshared pair, and 3 electrons are counted as carbon's share of the three covalent bonds to hydrogen.



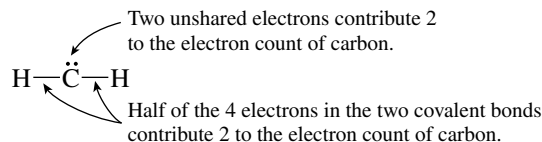
An electron count of 5 is one more than that for a neutral carbon atom. The formal charge on carbon is -1 , as is the net charge on this species.

- (c) This species has 1 less electron than that of part (b). None of the atoms bears a formal charge. The species is neutral.

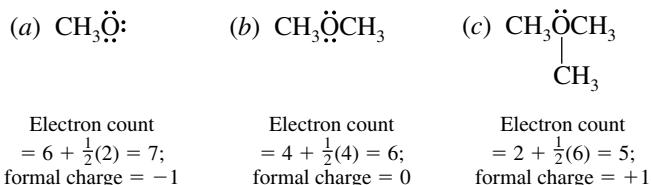


- (d) The formal charge of carbon in this species is $+1$. Its only electrons are those in its three covalent bonds to hydrogen, and so its electron count is 3. This corresponds to 1 less electron than in a neutral carbon atom, giving it a unit positive charge.

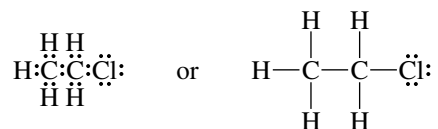
- (e) In this species the electron count of carbon is 4, or, exactly as in part (c), that of a neutral carbon atom. Its formal charge is 0, and the species is neutral.



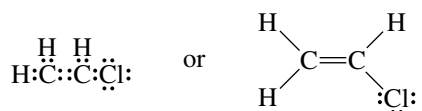
- 1.27 Oxygen is surrounded by a complete octet of electrons in each structure but has a different “electron count” in each one because the proportion of shared to unshared pairs is different.



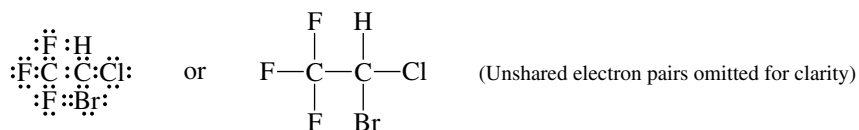
- 1.28 (a) Each carbon has 4 valence electrons, each hydrogen 1, and chlorine has 7. Hydrogen and chlorine each can form only one bond, and so the only stable structure must have a carbon–carbon bond. Of the 20 valence electrons, 14 are present in the seven covalent bonds and 6 reside in the three unshared electron pairs of chlorine.



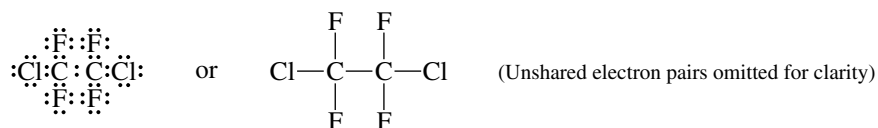
- (b) As in part (a) the single chlorine as well as all of the hydrogens must be connected to carbon. There are 18 valence electrons in $\text{C}_2\text{H}_3\text{Cl}$, and the framework of five single bonds accounts for only 10 electrons. Six of the remaining 8 are used to complete the octet of chlorine as three unshared pairs, and the last 2 are used to form a carbon–carbon double bond.



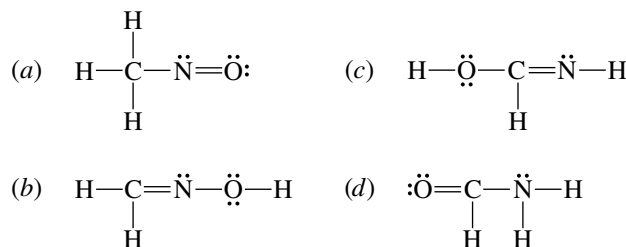
- (c) All of the atoms except carbon (H, Br, Cl, and F) are monovalent; therefore, they can only be bonded to carbon. The problem states that all three fluorines are bonded to the same carbon, and so one of the carbons is present as a CF_3 group. The other carbon must be present as a CHBrCl group. Connect these groups together to give the structure of haloethane.



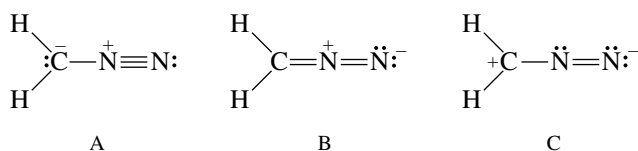
- (d) As in part (c) all of the atoms except carbon are monovalent. Since each carbon bears one chlorine, two ClCF_2 groups must be bonded together.



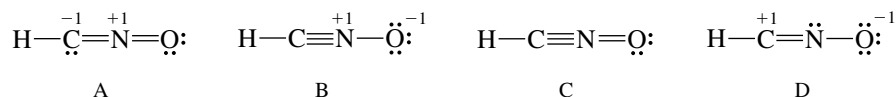
- 1.29 Place hydrogens on the given atoms so that carbon has four bonds, nitrogen three, and oxygen two. Place unshared electron pairs on nitrogen and oxygen so that nitrogen has an electron count of 5 and oxygen has an electron count of 6. These electron counts satisfy the octet rule when nitrogen has three bonds and oxygen two.



- 1.30 (a) Species A, B, and C have the same molecular formula, the same atomic positions, and the same number of electrons. They differ only in the arrangement of their electrons. They are therefore resonance forms of a single compound.

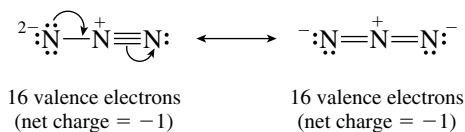


- (b) Structure A has a formal charge of -1 on carbon.
 (c) Structure C has a formal charge of $+1$ on carbon.
 (d) Structures A and B have formal charges of $+1$ on the internal nitrogen.
 (e) Structures B and C have a formal charge of -1 on the terminal nitrogen.
 (f) All resonance forms of a particular species must have the same net charge. In this case, the net charge on A, B, and C is 0.
 (g) Both A and B have the same number of covalent bonds, but the negative charge is on a more electronegative atom in B (nitrogen) than it is in A (carbon). Structure B is more stable.
 (h) Structure B is more stable than structure C. Structure B has one more covalent bond, all of its atoms have octets of electrons, and it has a lesser degree of charge separation than C. The carbon in structure C does not have an octet of electrons.
 (i) The CNN unit is linear in A and B, but bent in C according to VSEPR. This is an example of how VSEPR can fail when comparing resonance structures.
- 1.31 The structures given and their calculated formal charges are:

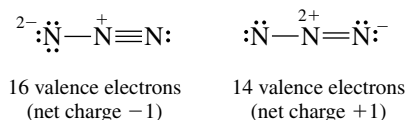


- (a) Structure D contains a positively charged carbon.
 (b) Structures A and B contain a positively charged nitrogen.
 (c) None of the structures contain a positively charged oxygen.
 (d) Structure A contains a negatively charged carbon.
 (e) None of the structures contain a negatively charged nitrogen.
 (f) Structures B and D contain a negatively charged oxygen.
 (g) All the structures are electrically neutral.
 (h) Structure B is the most stable. All the atoms except hydrogen have octets of electrons, and the negative charge resides on the most electronegative element (oxygen).
 (i) Structure C is the least stable. Nitrogen has five bonds (10 electrons), which violates the octet rule.

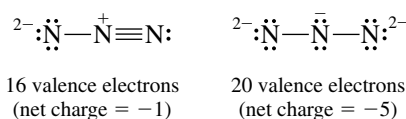
- 1.32 (a) These two structures are resonance forms since they have the same atomic positions and the same number of electrons.



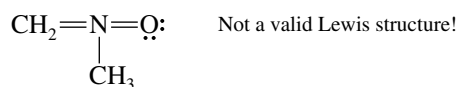
- (b) The two structures have different numbers of electrons and, therefore, can't be resonance forms of each other.



- (c) These two structures have different numbers of electrons; they are not resonance forms.

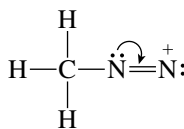


- 1.33 Structure C has 10 electrons surrounding nitrogen, but the octet rule limits nitrogen to 8 electrons. Structure C is incorrect.

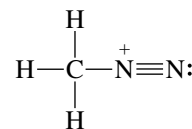


- 1.34 (a) The terminal nitrogen has only 6 electrons; therefore, use the unshared pair of the adjacent nitrogen to form another covalent bond.

By moving electrons of the nitrogen lone pair as shown by the arrow

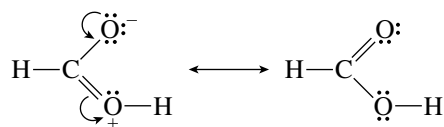


a structure that has octets about both nitrogen atoms is obtained.

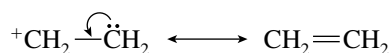


In general, move electrons from sites of high electron density toward sites of low electron density. Notice that the location of formal charge has changed, but the net charge on the species remains the same.

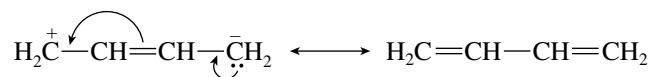
- (b) The dipolar Lewis structure given can be transformed to one that has no charge separation by moving electron pairs as shown:



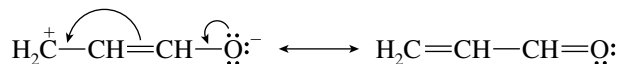
- (c) Move electrons toward the positive charge. Sharing the lone pair gives an additional covalent bond and avoids the separation of opposite charges.



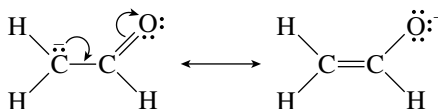
- (d) Octets of electrons at all the carbon atoms can be produced by moving the electrons toward the site of positive charge.



- (e) As in part (d), move the electron pairs toward the carbon atom that has only 6 electrons.



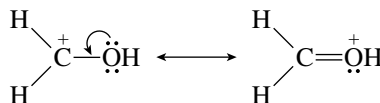
- (f) The negative charge can be placed on the most electronegative atom (oxygen) in this molecule by moving electrons as indicated.



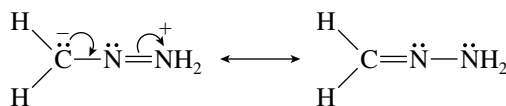
- (g) Octets of electrons are present around both carbon and oxygen if an oxygen unshared electron pair is moved toward the positively charged carbon to give an additional covalent bond.



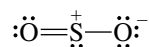
- (h) This exercise is similar to part (g); move electrons from oxygen to carbon so as to produce an additional bond and satisfy the octet rule for both carbon and oxygen.



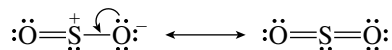
- (i) By moving electrons from the site of negative charge toward the positive charge, a structure that has no charge separation is generated.



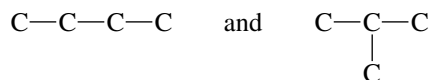
- 1.35** (a) Sulfur is in the same group of the periodic table as oxygen (group VI A) and, like oxygen, has 6 valence electrons. Sulfur dioxide, therefore, has 18 valence electrons. A Lewis structure in which sulfur and both oxygens have complete octets of electrons is:



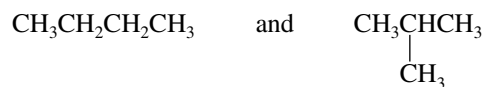
- (b) Move an electron pair from the singly bonded oxygen in part (a) to generate a second double bond. The resulting Lewis structure has 10 valence electrons around sulfur. It is a valid Lewis structure because sulfur can expand its valence shell beyond 8 electrons by using its 3d orbitals.



- 1.36** (a) To generate constitutionally isomeric structures having the molecular formula C_4H_{10} , you need to consider the various ways in which four carbon atoms can be bonded together. These are

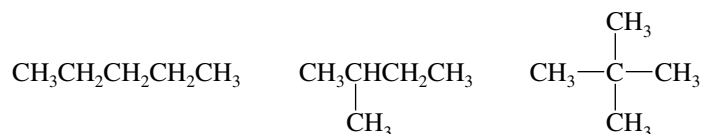


Filling in the appropriate hydrogens gives the correct structures:

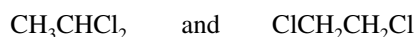


Continue with the remaining parts of the problem using the general approach outlined for part (a).

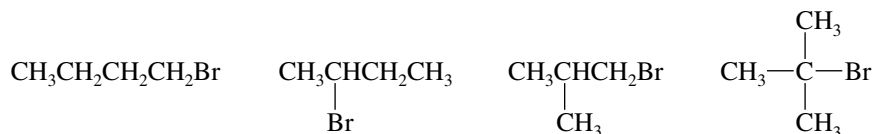
(b) C_5H_{12}



(c) $\text{C}_2\text{H}_4\text{Cl}_2$



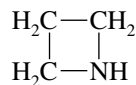
(d) $\text{C}_4\text{H}_9\text{Br}$



(e) $\text{C}_3\text{H}_9\text{N}$

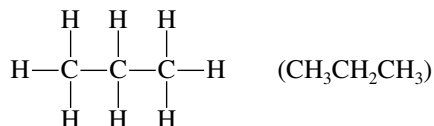


Note that when the three carbons and the nitrogen are arranged in a ring, the molecular formula based on such a structure is $\text{C}_3\text{H}_7\text{N}$, not $\text{C}_3\text{H}_9\text{N}$ as required.

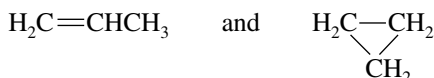


(not an isomer)

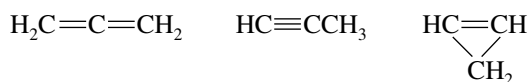
- 1.37 (a) All three carbons must be bonded together, and each one has four bonds; therefore, the molecular formula C_3H_8 uniquely corresponds to:



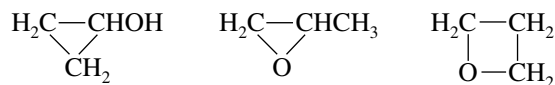
- (b) With two fewer hydrogen atoms than the preceding compound, either C_3H_6 must contain a carbon-carbon double bond or its carbons must be arranged in a ring; thus the following structures are constitutional isomers:



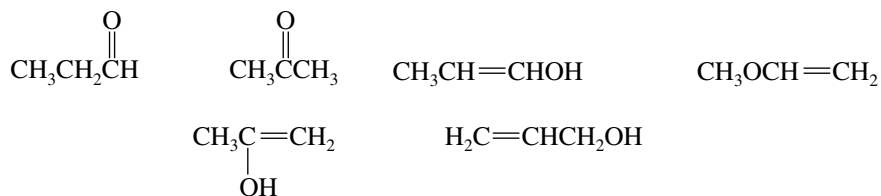
- (c) The molecular formula C_3H_4 is satisfied by the structures



- 1.38 (a) The only atomic arrangements of C_3H_6O that contain only single bonds must have a ring as part of their structure.



- (b) Structures corresponding to C_3H_6O are possible in noncyclic compounds if they contain a carbon-carbon or carbon-oxygen double bond.



- 1.39 The direction of a bond dipole is governed by the electronegativity of the atoms it connects. In each of the parts to this problem, the more electronegative atom is partially negative and the less electronegative atom is partially positive. Electronegativities of the elements are given in Table 1.2 of the text.

- (a) Chlorine is more electronegative than hydrogen.



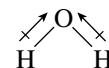
- (b) Chlorine is more electronegative than iodine.



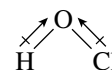
- (c) Iodine is more electronegative than hydrogen.



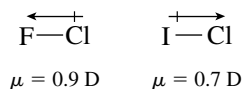
- (d) Oxygen is more electronegative than hydrogen.



- (e) Oxygen is more electronegative than either hydrogen or chlorine.

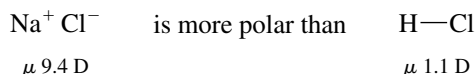


- 1.40 The direction of a bond dipole is governed by the electronegativity of the atoms involved. Among the halogens the order of electronegativity is $F > Cl > Br > I$. Fluorine therefore attracts electrons away from chlorine in FCl , and chlorine attracts electrons away from iodine in ICl .

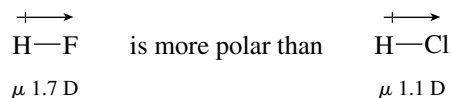


Chlorine is the positive end of the dipole in FCl and the negative end in ICl .

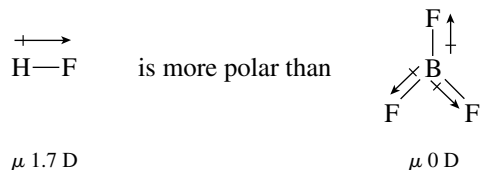
- 1.41 (a) Sodium chloride is ionic; it has a unit positive charge and a unit negative charge separated from each other. Hydrogen chloride has a polarized bond but is a covalent compound. Sodium chloride has a larger dipole moment. The measured values are as shown.



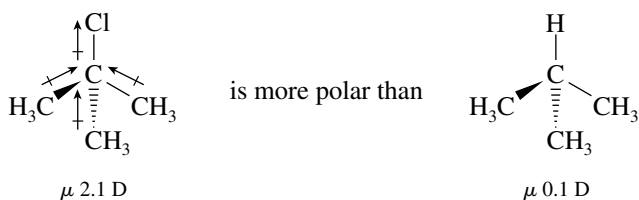
- (b) Fluorine is more electronegative than chlorine, and so its bond to hydrogen is more polar, as the measured dipole moments indicate.



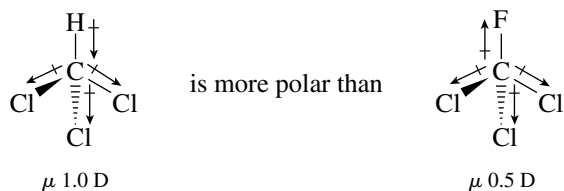
- (c) Boron trifluoride is planar. Its individual B—F bond dipoles cancel. It has no dipole moment.



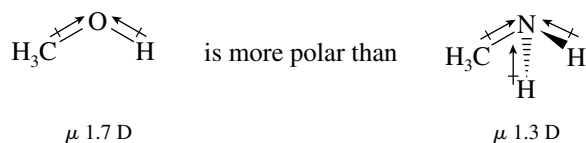
- (d) A carbon–chlorine bond is strongly polar; carbon–hydrogen and carbon–carbon bonds are only weakly polar.



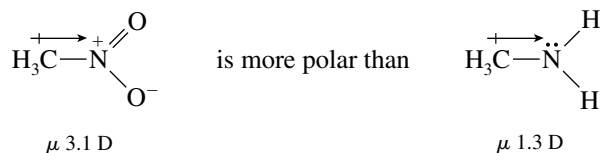
- (e) A carbon–fluorine bond in CCl_3F opposes the polarizing effect of the chlorines. The carbon–hydrogen bond in CHCl_3 reinforces it. CHCl_3 therefore has a larger dipole moment.



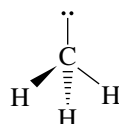
- (f) Oxygen is more electronegative than nitrogen; its bonds to carbon and hydrogen are more polar than the corresponding bonds formed by nitrogen.



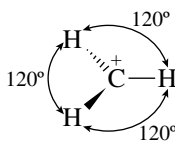
- (g) The Lewis structure for CH_3NO_2 has a formal charge of +1 on nitrogen, making it more electron-attracting than the uncharged nitrogen of CH_3NH_2 .



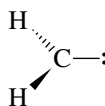
- 1.42** (a) There are four electron pairs around carbon in $\text{:}\bar{\text{C}}\text{H}_3$; they are arranged in a tetrahedral fashion. The atoms of this species are in a trigonal pyramidal arrangement.



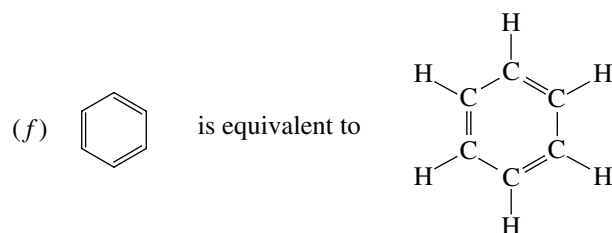
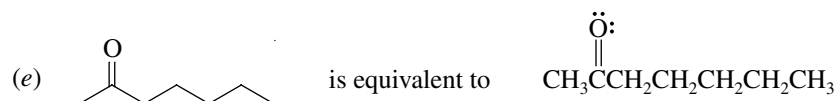
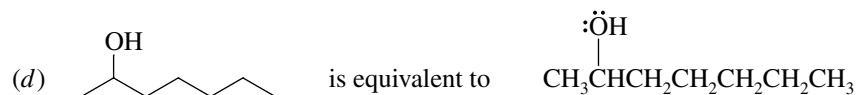
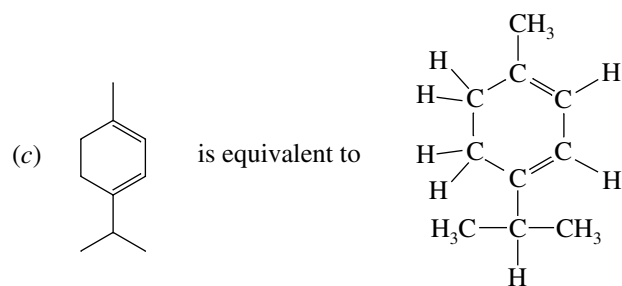
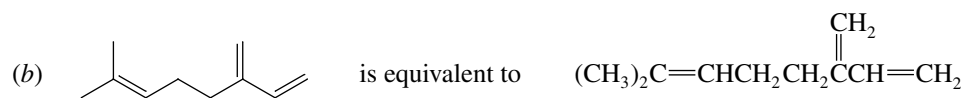
- (b) Only three electron pairs are present in $\overset{+}{\text{C}}\text{H}_3$, and so it is trigonal planar.

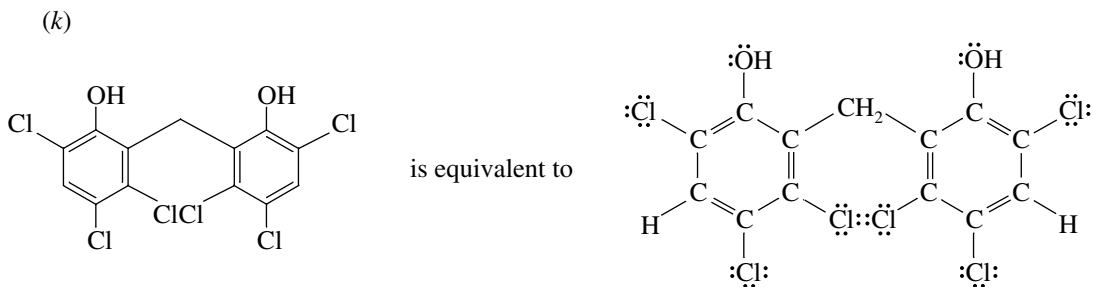
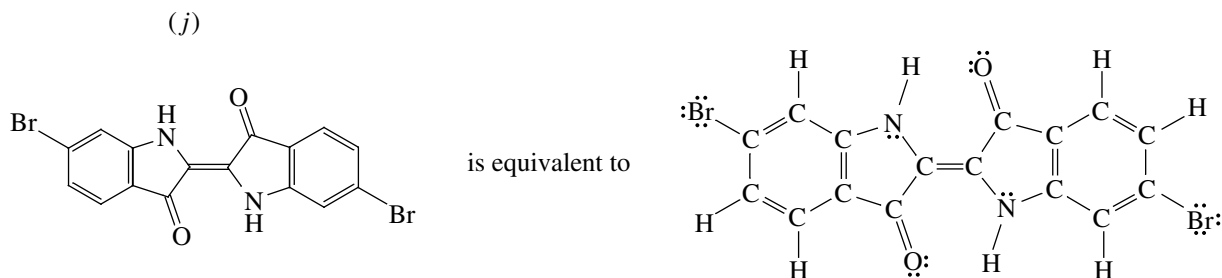
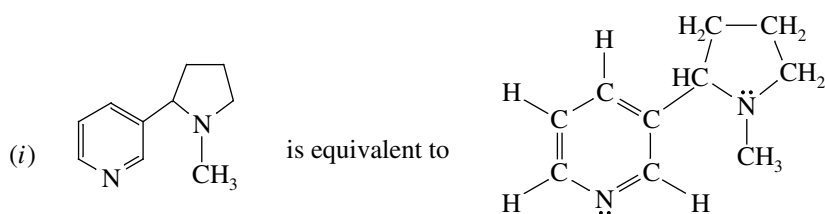
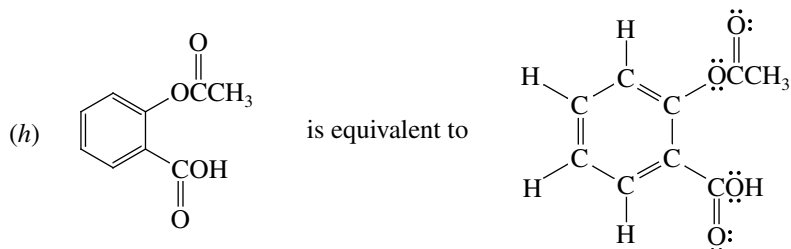
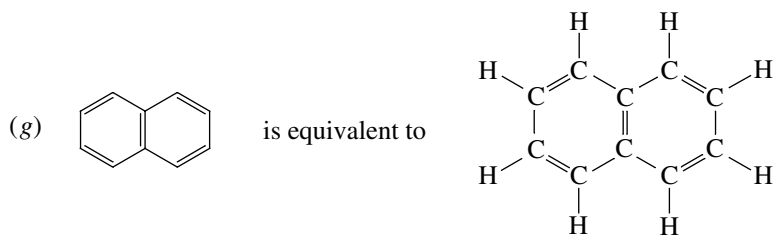


- (c) As in part (b), there are three electron pairs. When these electron pairs are arranged in a plane, the atoms in :CH_2 are not collinear. The atoms of this species are arranged in a bent structure according to VSEPR considerations.



- 1.43** The structures, written in a form that indicates hydrogens and unshared electrons, are as shown. Remember: A neutral carbon has four bonds, a neutral nitrogen has three bonds plus one unshared electron pair, and a neutral oxygen has two bonds plus two unshared electron pairs. Halogen substituents have one bond and three unshared electron pairs.

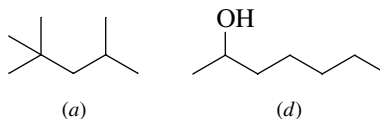




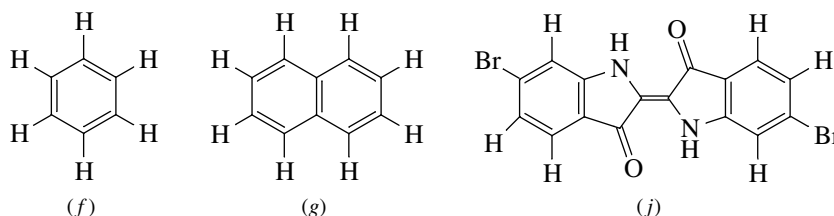
- 1.44 (a) C_8H_{18} (g) $C_{10}H_8$
 (b) $C_{10}H_{16}$ (h) $C_9H_8O_4$
 (c) $C_{10}H_{16}$ (i) $C_{10}H_{14}N_2$
 (d) $C_7H_{16}O$ (j) $C_{16}H_8Br_2N_2O_2$
 (e) $C_7H_{14}O$ (k) $C_{13}H_6Cl_6O_2$
 (f) C_6H_6

Isomers are different compounds that have the same molecular formula. Two of these compounds, (b) and (c), have the same molecular formula and are isomers of each other.

- 1.45 (a) Carbon is sp^3 -hybridized when it is directly bonded to four other atoms. Compounds (a) and (d) in Problem 1.43 are the only ones in which *all* of the carbons are sp^3 -hybridized.



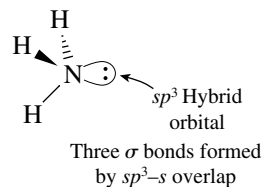
- (b) Carbon is sp^2 -hybridized when it is directly bonded to three other atoms. Compounds (f), (g), and (j) in Problem 1.43 have only sp^2 -hybridized carbons.



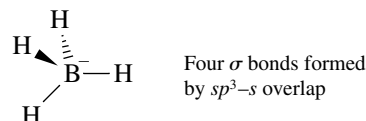
None of the compounds in Problem 1.43 contain an sp -hybridized carbon.

- 1.46 The problem specifies that the second-row element is sp^3 -hybridized in each of the compounds. Any unshared electron pairs therefore occupy sp^3 -hybridized orbitals, and bonded pairs are located in σ orbitals.

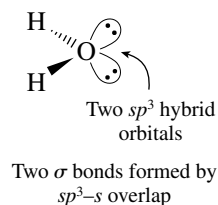
- (a) Ammonia



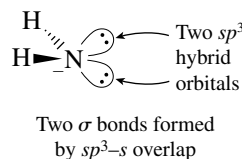
- (e) Borohydride anion



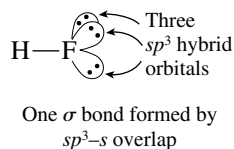
- (b) Water



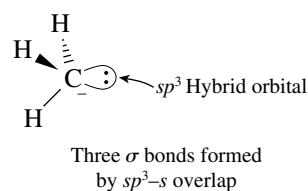
- (f) Amide anion



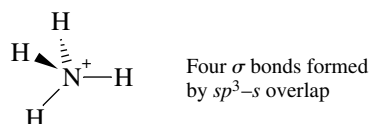
- (c) Hydrogen fluoride



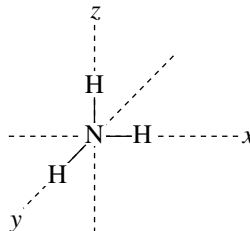
- (g) Methyl anion



- (d) Ammonium ion



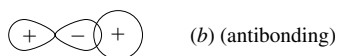
- 1.47 (a) The electron configuration of N is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$. If the half-filled $2p_x$, $2p_y$, and $2p_z$ orbitals are involved in bonding to H, then the unshared pair would correspond to the two electrons in the $2s$ orbital.
- (b) The three p orbitals $2p_x$, $2p_y$, and $2p_z$ have their axes at right angles to one another. The H—N—H angles would therefore be 90° .



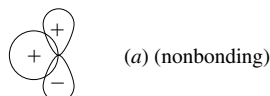
- 1.48 A bonding interaction exists when two orbitals overlap “in phase” with each other, that is, when the algebraic signs of their wave functions are the same in the region of overlap. The following orbital is a bonding orbital. It involves overlap of an s orbital with the lobe of a p orbital of the same sign.



On the other hand, the overlap of an s orbital with the lobe of a p orbital of opposite sign is antibonding.



Overlap in the manner shown next is nonbonding. Both the positive lobe and the negative lobe of the p orbital overlap with the spherically symmetrical s orbital. The bonding overlap between the s orbital and one lobe of the p orbital is exactly canceled by an antibonding interaction between the s orbital and the lobe of opposite sign.



- 1.49–1.55 Solutions to molecular modeling exercises are not provided in this *Study Guide and Solutions Manual*. You should use *Learning By Modeling* for these exercises.

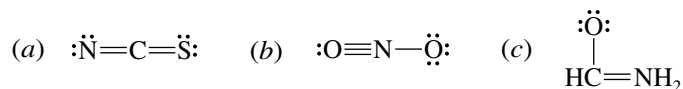
SELF-TEST

PART A

A-1. Write the electronic configuration for each of the following:

- (a) Phosphorus (b) Sulfide ion in Na_2S

A-2. Determine the formal charge of each atom and the net charge for each of the following species:

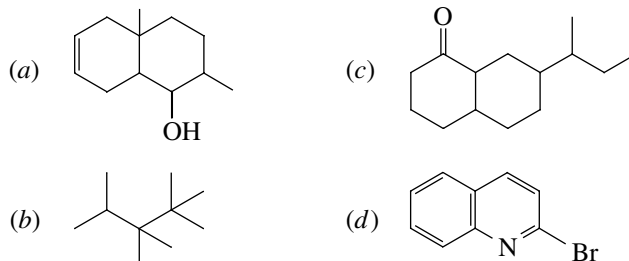


A-3. Write a second Lewis structure that satisfies the octet rule for each of the species in Problem A-2, and determine the formal charge of each atom. Which of the Lewis structures for each species in this and Problem A-2 is more stable?

A-4. Write a correct Lewis structure for each of the following. Be sure to show explicitly any unshared pairs of electrons.

- (a) Methylamine, CH_3NH_2
 (b) Acetaldehyde, $\text{C}_2\text{H}_4\text{O}$ (the atomic order is CCO; all the hydrogens are connected to carbon.)

A-5. What is the molecular formula of each of the structures shown? Clearly draw any unshared electron pairs that are present.



A-6. Which compound in Problem A-5 has

- (a) Only sp^3 -hybridized carbons
 (b) Only sp^2 -hybridized carbons
 (c) A single sp^2 -hybridized carbon atom

A-7. Account for the fact that all three sulfur–oxygen bonds in SO_3 are the same by drawing the appropriate Lewis structure(s).

A-8. The cyanate ion contains 16 valence electrons, and its three atoms are arranged in the order OCN. Write the most stable Lewis structure for this species, and assign a formal charge to each atom. What is the net charge of the ion?

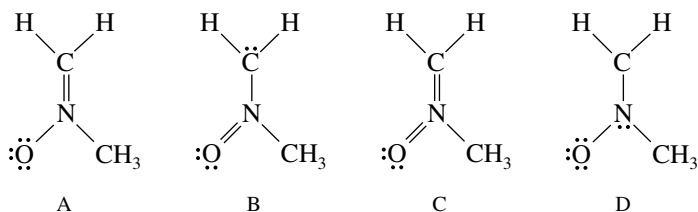
A-9. Using the VSEPR method,

- (a) Describe the geometry at each carbon atom and the oxygen atom in the following molecule: $\text{CH}_3\text{OCH}=\text{CHCH}_3$.
 (b) Deduce the shape of NCl_3 , and draw a three-dimensional representation of the molecule. Is NCl_3 polar?

A-10. Assign the shape of each of the following as either linear or bent.

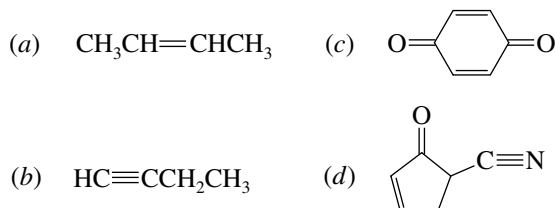
- (a) CO_2 (b) NO_2^+ (c) NO_2^-

A-11. Consider structures A, B, C, and D:



- (a) Which structure (or structures) contains a positively charged carbon?
 (b) Which structure (or structures) contains a positively charged nitrogen?
 (c) Which structure (or structures) contains a positively charged oxygen?
 (d) Which structure (or structures) contains a negatively charged carbon?
 (e) Which structure (or structures) contains a negatively charged nitrogen?
 (f) Which structure (or structures) contains a negatively charged oxygen?
 (g) Which structure is the most stable?
 (h) Which structure is the least stable?

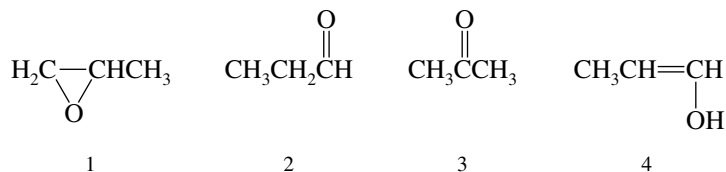
- A-12.** Given the following information, write a Lewis structure for urea, $\text{CH}_4\text{N}_2\text{O}$. The oxygen atom and both nitrogen atoms are bonded to carbon, there is a carbon–oxygen double bond, and none of the atoms bears a formal charge. Be sure to include all unshared electron pairs.
- A-13.** How many σ and π bonds are present in each of the following?



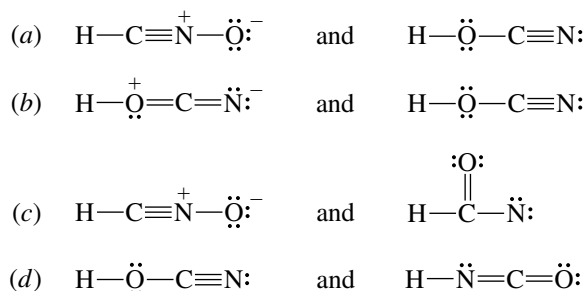
- A-14.** Give the hybridization of each carbon atom in the preceding problem.

PART B

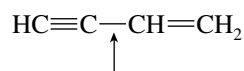
- B-1.** Which one of the following is most likely to have ionic bonds?
 (a) HCl (b) Na_2O (c) N_2O (d) NCl_3
- B-2.** Which of the following is *not* an electronic configuration for an atom in its ground state?
 (a) $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ (c) $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$
 (b) $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^0$ (d) $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$
- B-3.** The formal charge on phosphorus in $(\text{CH}_3)_4\text{P}$ is
 (a) 0 (b) -1 (c) +1 (d) +2
- B-4.** Which of the following is an isomer of compound 1?



- (a) 2 (c) 2 and 3
 (b) 4 (d) All are isomers.
- B-5.** In which of the following is oxygen the positive end of the bond dipole?
 (a) $\text{O}-\text{F}$ (b) $\text{O}-\text{N}$ (c) $\text{O}-\text{S}$ (d) $\text{O}-\text{H}$
- B-6.** What two structural formulas are resonance forms of one another?

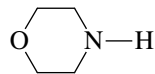


B-7. The bond identified (with the arrow) in the following structure is best described as:



- (a) $2sp-2sp^2 \sigma$ (c) $2sp^2-2sp^3 \sigma$ (e) $2p-2p \sigma$
 (b) $2p-2p \pi$ (d) $2sp^2-2sp^2 \sigma$

B-8. The total number of *unshared pairs* of electrons in the molecule



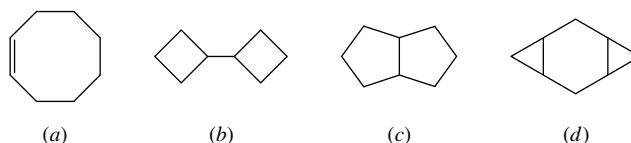
is

- (a) 0 (b) 1 (c) 2 (d) 3

B-9. Which of the following contains a triple bond?

- (a) SO_2 (b) HCN (c) C_2H_4 (d) NH_3

B-10. Which one of the compounds shown is *not* an isomer of the other three?



B-11. Which one of the following is the most stable Lewis structure? The answer must be correct in terms of bonds, unshared pairs of electrons, and formal charges.

- (a) $:\ddot{\text{O}}=\text{N}=\text{CH}_2$ (c) $:\ddot{\text{O}}=\ddot{\text{N}}-\overset{\ominus}{\text{C}}\text{H}_2$ (e) $:\ddot{\text{O}}-\overset{\ominus}{\text{N}}-\overset{\oplus}{\text{C}}\text{H}_2$
 (b) $^-\ddot{\text{O}}-\ddot{\text{N}}=\text{CH}_2$ (d) $:\ddot{\text{O}}=\overset{\ominus}{\text{N}}=\text{CH}_2$

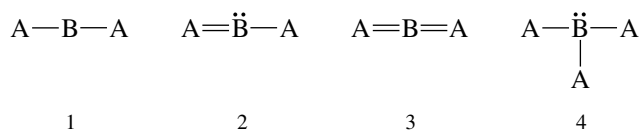
B-12. Repeat the previous question for the following Lewis structures.

- (a) $:\overset{\ominus}{\text{N}}-\overset{\oplus}{\text{N}}-\overset{\oplus}{\text{C}}\text{H}_2$ (c) $:\overset{\ominus}{\text{N}}=\overset{\oplus}{\text{N}}-\overset{\ominus}{\text{C}}\text{H}_2$ (e) $^-\overset{\oplus}{\text{N}}=\overset{\oplus}{\text{N}}=\text{CH}_2$
 (b) $:\overset{\ominus}{\text{N}}-\overset{\oplus}{\text{N}}=\text{CH}_2$ (d) $:\text{N}\equiv\overset{\oplus}{\text{N}}-\text{CH}_2$

B-13. Which of the following molecules would you expect to be *nonpolar*?

1. CH_2F_2 2. CO_2 3. CF_4 4. CH_3OCH_3
 (a) 1 and 2 (b) 1 and 3 (c) 1 and 4 (d) 2 and 3 (e) 2, 3, and 4

The remaining two questions refer to the hypothetical compounds:



B-14. Which substance(s) is (are) linear?

- (a) 1 only (b) 1 and 3 (c) 1 and 2 (d) 3 only

B-15. Assuming A is more electronegative than B, which substance(s) is (are) polar?

- (a) 1 and 3 (b) 2 only (c) 4 only (d) 2 and 4