



Course Organic Chemistry
 American University of Beirut
 Chemistry



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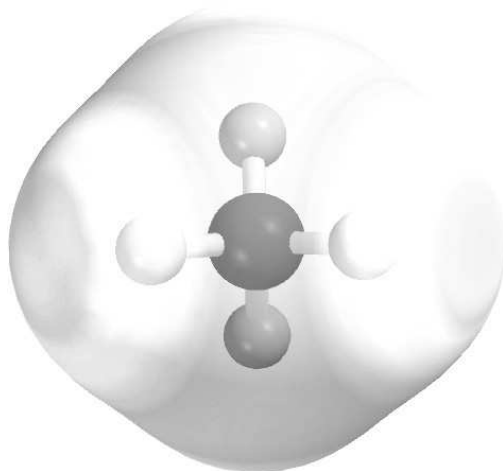
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Credits

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CHAPTER 1

Structure Determines Properties

SOLUTIONS TO TEXT PROBLEMS

1.1 The number of electrons in an element is equal to the number of protons in its nucleus and is given by its atomic number Z . For carbon, $Z = 6$. Therefore, carbon has six electrons. Of these, only the two $2s$ and two $2p$ electrons are valence electrons. The two $1s$ electrons are not valence electrons.

Silicon, like carbon, is in group 4 of the periodic table. The number of valence electrons of main-group elements is the same as the group number. Therefore, silicon has four valence electrons.

1.2 Electron configurations of elements are derived by applying the following principles:

- (a) The number of electrons in a neutral atom is equal to its atomic number Z .
- (b) The maximum number of electrons in any orbital is two.
- (c) 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.
- (d) 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	($Z = 15$)	$1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$
S	($Z = 16$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$
Cl	($Z = 17$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$
Ar	($Z = 18$)	$1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^2$

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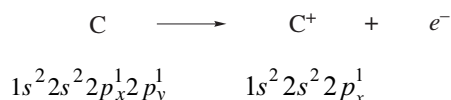
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- 1.3** A sodium atom (Na) has 11 electrons. A sodium ion (Na^+) has one less, or 10 electrons. The +2 ion that contains 10 electrons must have 12 protons in its nucleus. The element with $Z = 12$ is magnesium. Mg^{2+} is isoelectronic with Na^+ .
A -2 ion with 10 electrons must have 8 protons in its nucleus. The element with $Z = 8$ is oxygen. O^{2-} is isoelectronic with Na^+ .
- 1.4** The atomic number of chlorine is 17. The ion Cl^- has one more electron than the 17 protons in its nucleus. Therefore, Cl^- has 18 electrons. In order to have a charge of -2 , an ion that is isoelectronic with Cl^- must have 16 protons in its nucleus. The ion is S^{2-} .
- 1.5** The electron configurations of the designated ions are:

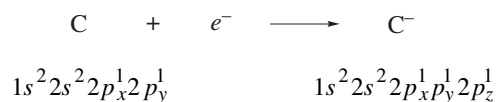
	Ion	Z	Number of Electrons in Ion	Electron Configuration of Ion
(b)	He^+	2	1	$1s^1$
(c)	H^-	1	2	$1s^2$
(d)	O^-	8	9	$1s^2 2s^2 2p^5$
(e)	F^-	9	10	$1s^2 2s^2 2p^6$
(f)	Ca^{2+}	20	18	$1s^2 2s^2 2p^6 3s^2 3p^6$

Those with a noble gas configuration are H^- , F^- , and Ca^{2+} . K^+ and Ca^{2+} are the only isoelectronic ions. Both have a total of 18 electrons.

- 1.6** A positively charged ion is formed when an electron is removed from a neutral atom. The following equation represents the ionization of carbon and the electron configurations of the neutral atom and the ion:



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

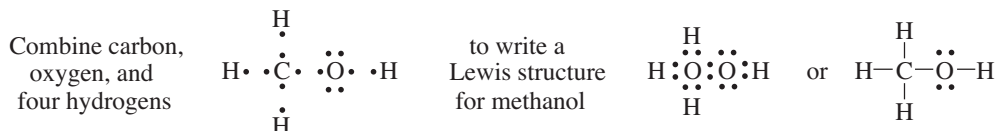


Neither C^+ nor C^- has a noble gas electron configuration.

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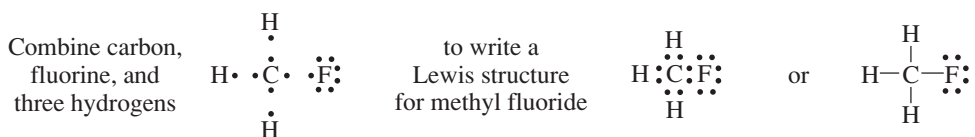
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- 1.7 (b) In order to have four bonds to carbon, CH_4O must have a carbon–oxygen bond.



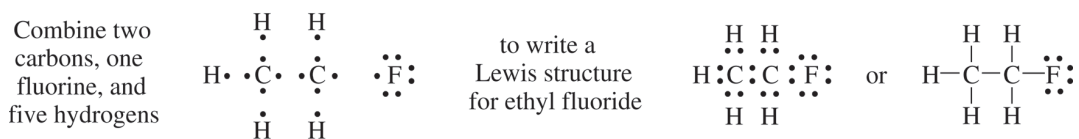
The 14 valence electrons of CH_4O are distributed among five covalent bonds and two unshared pairs of oxygen.

- (c) Three of the four bonds involving carbon are to hydrogen atoms; the fourth is to fluorine. Carbon contributes four electrons, fluorine seven, and the three hydrogens contribute one each. The total number of valence electrons in CH_3F is 14.



The 14 valence electrons of CH_3F are distributed among four covalent bonds and three unshared pairs of fluorine.

- (d) The only possible structure for $\text{C}_2\text{H}_5\text{F}$ in which each carbon has four bonds must contain a carbon–carbon bond.

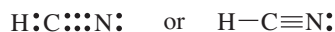


The number of valence electrons in $\text{C}_2\text{H}_5\text{F}$ is 20; eight contributed by two carbons, seven by fluorine, and a total of five by the hydrogens. These 20 valence electrons are distributed among 7 covalent bonds plus three unshared electron pairs of fluorine in $\text{C}_2\text{H}_5\text{F}$.

- 1.8 (b) Hydrogen cyanide (HCN) has 10 valence electrons; one from hydrogen, four from carbon, and five from nitrogen.



In order to satisfy the octet rule, pair the remaining unpaired electrons of carbon with those of nitrogen so as to give a triple bond in:



- 1.9 The partial positive charge of hydrogen is greatest when the atom it is attached to is most electronegative. Among the atoms to which hydrogen is bonded in the compounds CH_4 , NH_3 , H_2O , SiH_4 , and H_2S , oxygen is the most electronegative. Therefore, δ^+ is largest for hydrogen in H_2O .

Hydrogen will bear a partial negative charge when the atom to which it is bonded is less electronegative than hydrogen. The electronegativity of hydrogen is 2.1 versus 1.8 for silicon (text Table 1.3). Therefore, hydrogen bears a partial negative charge in SiH_4 .

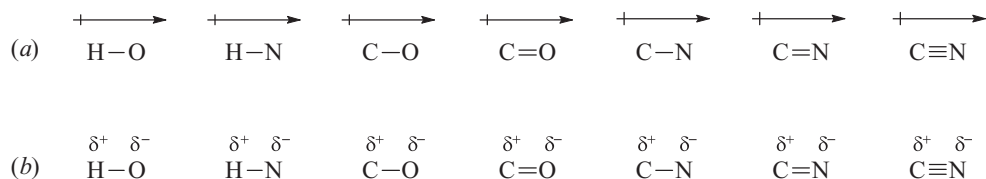
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- 1.10** The Pauling electronegativity scale (text Table 1.3) may be used to solve this problem. For instance, for the bond H—O, hydrogen is 2.1 and oxygen has a higher value of 3.5. This can be qualitatively represented two different ways as shown in the first answer in (a) and (b). The + part of the arrow indicates the electropositive atom in (a).

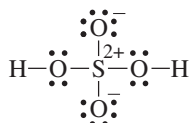
Alternatively, for (b), the δ^+ symbol indicates the electropositive atom whereas the δ^- indicates the electronegative atom.

The periodic table may also be helpful in assigning electronegativity. Electronegativity increases from left to right across a row. It decreases down a column or group. For instance, for the third entry in (a) and (b), C—O, carbon is to the left of oxygen on the periodic table; thus, carbon is less electronegative as indicated.



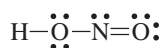
- 1.11** (b) The formal charges in sulfuric acid are calculated as follows:

	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:

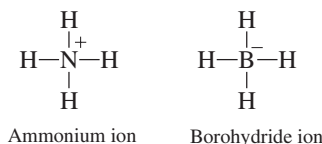
	Valence Electrons in Neutral Atom	Electron Count	Formal Charge
Hydrogen:	1	$\frac{1}{2}(2)=1$	0
Oxygen (of OH):	6	$\frac{1}{2}(4)+4=6$	0
Oxygen:	6	$\frac{1}{2}(4)+4=6$	0
Nitrogen:	5	$\frac{1}{2}(6)+2=5$	0



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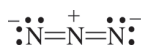
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- 1.12 The electron counts of nitrogen in ammonium ion and boron in borohydride ion are both 4 (one-half of eight electrons in covalent bonds).



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

- 1.13 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.



- 1.14 (b) First count the valence electrons in $\text{C}_3\text{H}_7\text{Cl}$.

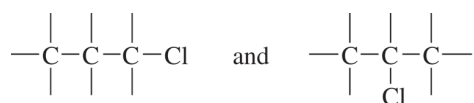
Carbon: 3 atoms \times 4 valence electrons/atom = 12 valence electrons

Hydrogen: 7 atoms \times 1 valence electron/atom = 7 valence electrons

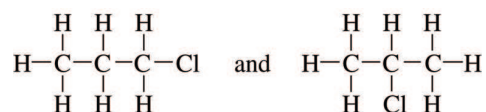
Chlorine: 1 atom \times 7 valence electrons/atom = 7 valence electrons

Total = 26 valence electrons

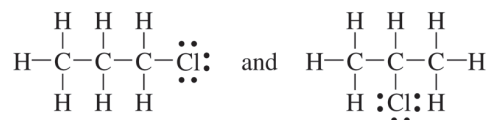
Because chlorine can be bonded only to one other atom, only two connectivities are possible.



Place one hydrogen on each of the bonds available to carbon.



Each structural formula has 10 bonds, which account for 20 electrons. Place the remaining six electrons as unshared pairs on chlorine to complete its octet.

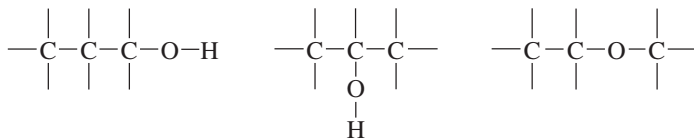


There are two constitutional isomers having the formula $\text{C}_3\text{H}_7\text{Cl}$.

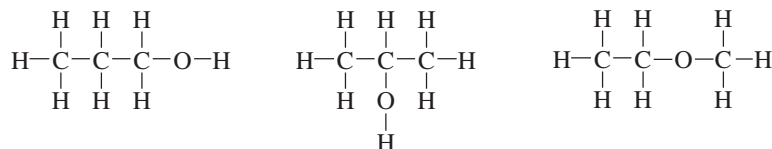
- (c) Proceed as in parts (a) and (b) of this problem.

The number of valence electrons contained in a molecular formula of $\text{C}_3\text{H}_8\text{O}$ is 26 (12 contributed by three carbons, 8 contributed by eight hydrogens, and 6 contributed by one oxygen).

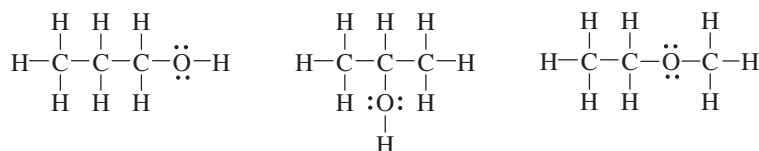
Three connectivities are possible in which carbon has four bonds. Two of these connectivities have a continuous chain of three carbons. The third has the atoms connected in the order CCOC.



Complete the number of available C—H bonds; there are seven in the first two structures, eight in the third.



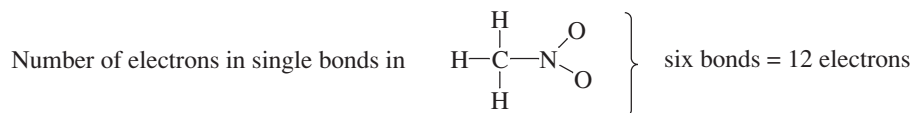
Each structural formula has 11 bonds, accounting for 22 electrons. The remaining four electrons are assigned to oxygen as two unshared pairs. The octet rule is satisfied.



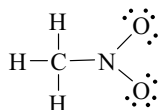
There are three constitutional isomers having the formula $\text{C}_3\text{H}_8\text{O}$.

1.15 (a) Number of valence electrons in CH_3NO_2 :

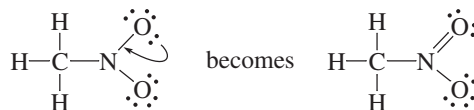
$$\left. \begin{array}{l} \text{C} = 4, \quad \text{N} = 5, \\ \text{three H} = 3, \quad \text{two O} = 12 \end{array} \right\} \text{total} = 24$$



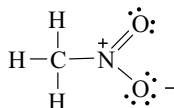
Subtracting the electrons from the single bonds from the total number of valence electrons gives a remainder of 12 electrons that need to be added. Add them in pairs, beginning with the most electronegative atom. Complete the octet of each atom before moving to the next one.



Nitrogen has only six electrons, so use one of the oxygen unshared pairs to form a double bond between nitrogen and oxygen.



Assign formal charges to give the complete Lewis structural formula.

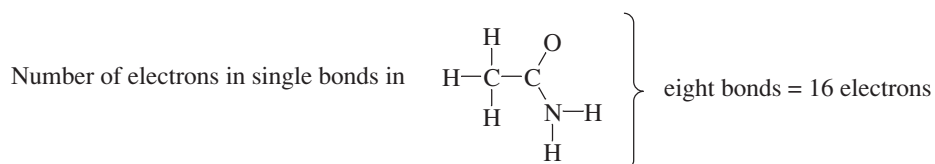


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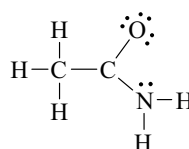
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(b) Number of valence electrons in C_2H_5NO :

$$\left. \begin{array}{l} \text{Two C} = 8, \quad \text{N} = 5, \\ \text{five H} = 5, \quad \text{O} = 6 \end{array} \right\} \text{total} = 24$$



Subtracting the electrons from the single bonds from the total number of valence electrons gives a remainder of eight electrons that need to be added. Add them in pairs, beginning with the most electronegative atom. Complete the octet of each atom before moving to the next one.

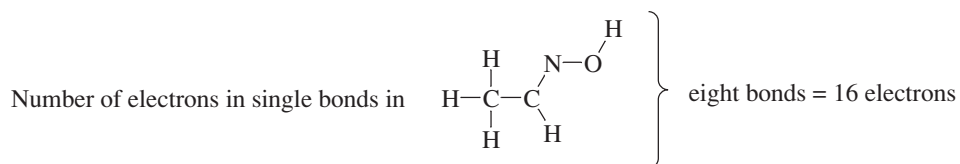


Carbon has only six electrons, so use one of the oxygen unshared pairs to form a double bond between carbon and oxygen. In this compound, there are no formal charges.



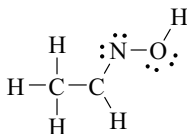
(c) Number of valence electrons in C_2H_5NO :

$$\left. \begin{array}{l} \text{Two C} = 8, \quad \text{N} = 5, \\ \text{five H} = 5, \quad \text{O} = 6 \end{array} \right\} \text{total} = 24$$



Subtracting the electrons from the single bonds from the total number of valence electrons gives a remainder of eight electrons that need to be added.

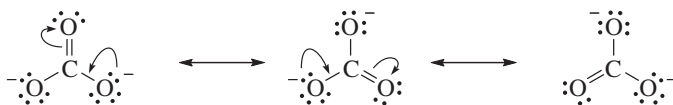
Add them in pairs, beginning with the most electronegative atom. Complete the octet of each atom before moving to the next one.



Carbon has only six electrons, so use one of the nitrogen unshared pairs to form a double bond between nitrogen and carbon. In this compound, there are no formal charges.



- 1.16** The resonance structures for carbonate are shown here. If one considers the top carbon–oxygen bond in each of the resonance structures, the left structure has a double bond whereas the other two structures have single bonds. If one considers the remaining two carbon–oxygen bonds in each structure, each has the same count: one double and two single bonds. Thus, all three carbon–oxygen bonds would be predicted to have equivalent lengths.

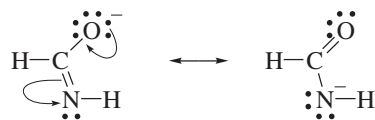


- 1.17** (b) Carbon has only six valence electrons and is positively charged in the original structural formula. Move the unshared electron pair from nitrogen to a shared position between nitrogen and carbon. The double bond becomes a triple bond.



The new structure has one more bond than the original structure so is more stable and makes a greater contribution to the resonance hybrid. The octet rule is satisfied for both carbon and nitrogen in the new Lewis structure.

- (c) Moving an unshared pair from oxygen to between carbon and oxygen converts C–O to C=O. Moving a pair of electrons to nitrogen converts C=N to C–N.



The number of bonds is the same in both the original and final structural formulas. The original structure, which has its negative charge on oxygen, is more stable than the second one, which has its negative charge on nitrogen. Oxygen is more electronegative than nitrogen and can bear a negative charge better.

- (d) Reorganizing the electrons as indicated by the curved arrows changes the electron counts and formal charges of the two oxygens.

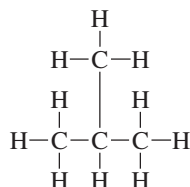


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Positively and negatively charged atoms are separated from each other in the new structure. The original structure is more stable because it has no charge separation.

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

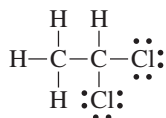


Four carbons and ten hydrogens contribute 26 valence electrons. The structure shown has 13 covalent bonds, and so all the valence electrons are accounted for. The molecule has no unshared electron pairs.

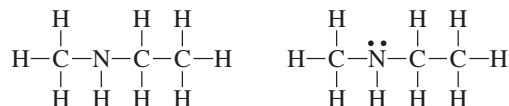
- (c) The number of valence electrons in $\text{ClCH}_2\text{CH}_2\text{Cl}$ is 26 ($2\text{Cl} = 14$; $4\text{H} = 4$; $2\text{C} = 8$). The constitution at the left shows seven covalent bonds accounting for 14 electrons. The remaining 12 electrons are divided equally between the two chlorines as unshared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



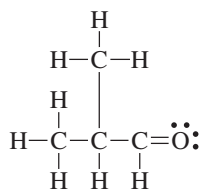
- (d) This compound has the same molecular formula as the compound in part (c) but a different structure. It is a constitutional isomer of the compound in part (c). It, too, has 26 valence electrons, and again only chlorine has unshared pairs.



- (e) The connectivity of $\text{CH}_3\text{NHCH}_2\text{CH}_3$ is shown (on the 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 (on the right).



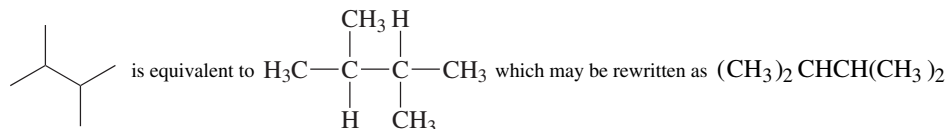
- (f) Oxygen has two unshared pairs in $(\text{CH}_3)_2\text{CHCH}=\text{O}$.



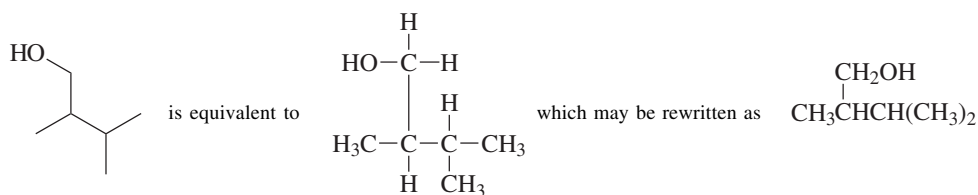
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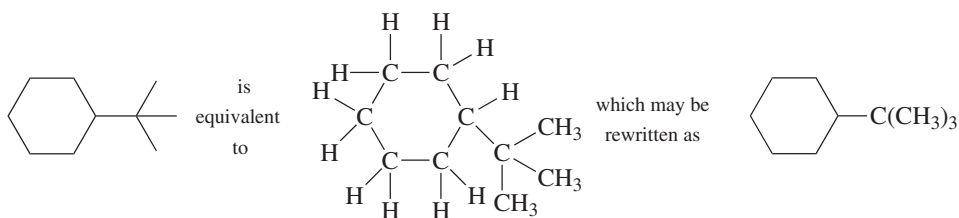
1.19 (b) This compound has a four-carbon chain to which two other carbons are attached.



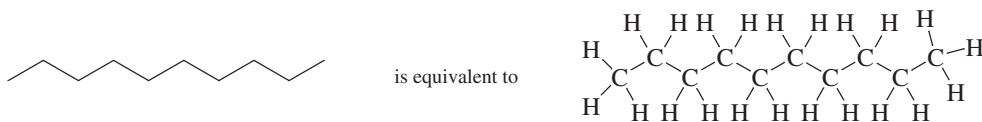
(c) The carbon skeleton is the same as that of the compound in part (b), but one of the terminal carbons bears an OH group in place of one of its hydrogens.



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



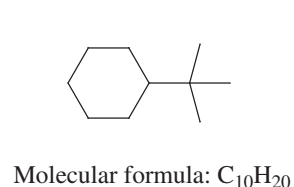
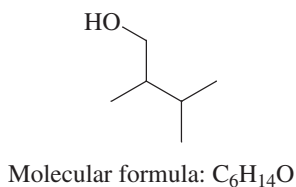
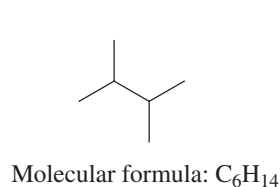
1.20 (a) Writing out the bond-line formula or carbon skeletal diagram to show all of the hydrogen and carbon atoms as shown in Problem 1.19 allows for the counting of each atom. In the case of the first molecule, the diagram



Molecular formula: $\text{C}_{10}\text{H}_{22}$

This conversion clearly shows that 10 carbon atoms and 22 hydrogen atoms are present. Thus, the formula $\text{C}_{10}\text{H}_{22}$ can be determined by counting the number of carbons and hydrogens.

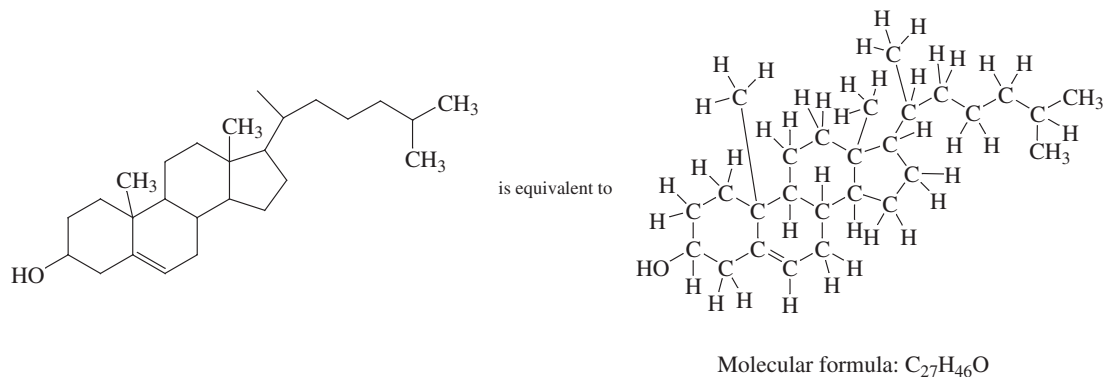
Refer to Problem 1.19 to see the expanded formulas for the remaining structures (b) through (d). By counting the individual atoms, the remaining problems are solved similarly.



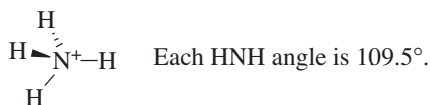
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- (b) For cholesterol, the molecular formula can be determined as before, drawing out all of the carbon, hydrogen, and oxygen atoms as shown here.



- 1.21 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° .
- 1.22 (b) Nitrogen in ammonium ion is surrounded by eight electrons in four covalent bonds. These four bonds are directed toward the corners of a tetrahedron.



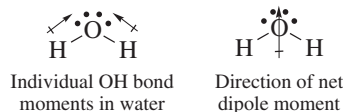
- (c) Double bonds are treated as a single unit when deducing the shape of a molecule using the VSEPR model. Thus azide ion is linear.



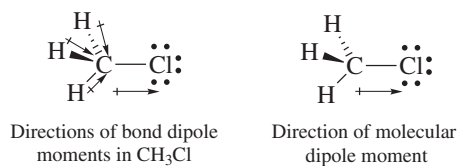
- (d) Because the double bond in carbonate ion is treated as if it were a single unit, the three sets of electrons are arranged in a trigonal planar arrangement around carbon.



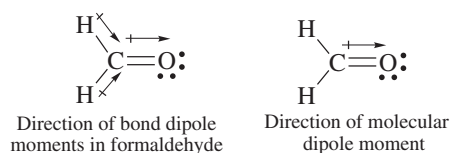
- 1.23 (b) Water is a bent molecule, and so the individual O—H bond dipole moments do not cancel. Water has a dipole moment.



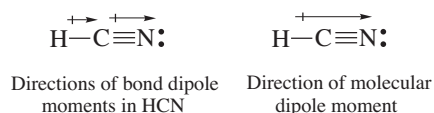
- (c) Methane, CH_4 , is perfectly tetrahedral, and so the individual (small) C—H bond dipole moments cancel. Methane has no dipole moment.
- (d) Methyl chloride has a dipole moment.



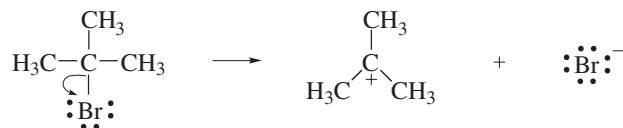
- (e) Oxygen is more electronegative than carbon and attracts electrons from it. Formaldehyde has a dipole moment.



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

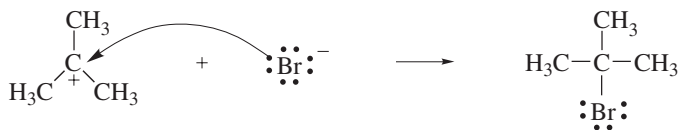


- 1.24 (b) The carbon–bromine bond breaks. The pair of electrons in that bond is retained by bromine, which becomes a bromide ion in the product. The organic product is a cation, having a formal charge of +1 on the central carbon.

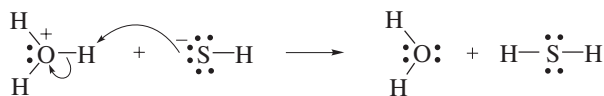


Charge is conserved. A neutral molecule dissociates to a +1 ion and a -1 ion.

- 1.25 (b) In the reverse process, an unshared pair of bromide ions becomes the pair of electrons in a C–Br bond.



- 1.26 The problem states that NaSH is converted to H_2S . Therefore, a bond must form between the sulfur of HS^- and a hydrogen of H_3O^+ . Electrons flow from the negatively charged sulfur to one of the hydrogens. The pair of electrons in the O–H bond that is broken becomes an unshared pair of oxygens.



The net charge is zero on both sides of the equation.

- 1.27 The strength of an acid can be expressed by its $\text{p}K_a$, given by the expression:

$$\text{p}K_a = -\log K_a$$

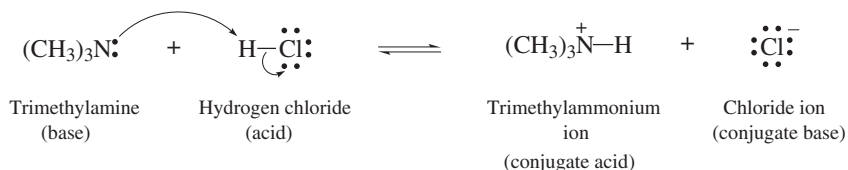
The K_a of salicylic acid is 1.06×10^{-3} ; its $\text{p}K_a$ is 2.97.

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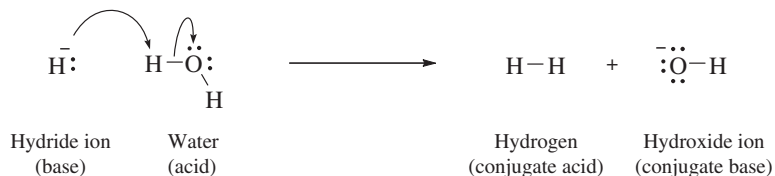
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1.28 Because the pK_a of HCN is given as 9.1, its $K_a = 10^{-9.1}$. In more conventional notation, $K_a = 8 \times 10^{-10}$.

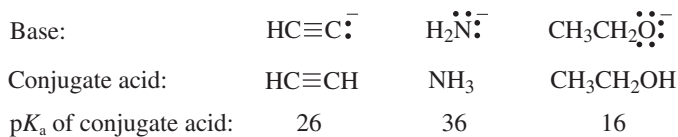
1.29 (b) In an acid–base reaction, a proton is transferred from the Brønsted acid, in this case HCl, to the Brønsted base, in this case $(\text{CH}_3)_3\text{N}$. Remember to use curved arrows to track the movement of electrons, not atoms.



1.30 Hydride ion is a strong base and will remove a proton from water. The conjugate acid of hydride ion is hydrogen (H_2).

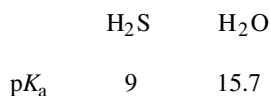


1.31 (b, c) You can determine the relative strength of two bases by comparing the pK_a 's of their respective conjugate acids. Remember that the stronger base is derived from the weaker conjugate acid.



Recall that the smaller pK_a is associated with the stronger acid. Ammonia is a weaker acid than acetylene ($\text{HC}\equiv\text{CH}$); therefore, amide ion ($\text{H}_2\ddot{\text{N}}^-$) is a stronger base than acetylide ion ($\text{HC}\equiv\text{C:}^-$). Similar reasoning leads to the conclusion that because acetylene is a weaker acid than ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), acetylide ion is a stronger base than ethoxide ion ($\text{CH}_3\text{CH}_2\ddot{\text{O}}^-$).

1.32 Bond strength weakens going down a group in the periodic table. Because sulfur lies below oxygen, the H–S bond is weaker than the H–O bond. We would expect H_2S to be a stronger acid than H_2O , and this prediction is borne out by their respective pK_a 's:



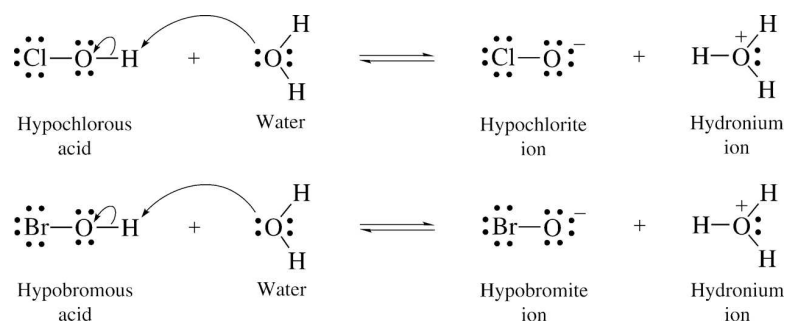
Because the stronger acid forms the weaker conjugate base, HS^- is a weaker base than HO^- .

1.33 (b) In part (a) of the problem, you determined that $(\text{CH}_3)_2\overset{+}{\text{O}}\text{H}$ is a stronger acid than $(\text{CH}_3)_3\overset{+}{\text{N}}\text{H}$.

Recalling that the weaker acid forms the stronger conjugate base, $(\text{CH}_3)_3\text{N}:$ is a stronger base than $(\text{CH}_3)_2\ddot{\text{O}}:$.

1.34 To compare the strength of bases, look up the $\text{p}K_{\text{a}}$'s of their conjugate acids. Ethanol has a $\text{p}K_{\text{a}}$ of 16; *tert*-butyl alcohol has a $\text{p}K_{\text{a}}$ of 18. Ethanol is a stronger acid than *tert*-butyl alcohol. Therefore *tert*-butoxide ion is a stronger base than ethoxide.

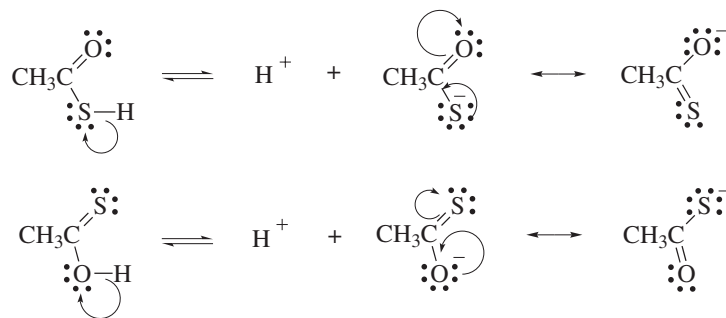
1.35 The Brønsted acid–base equilibria for the ionization of hypochlorous and hypobromous acid are



The positive character (δ^+) of the proton in HOCl is greater than the proton in HOBr because Cl is more electronegative than Br. The greater electronegativity of Cl compared to Br also stabilizes ClO^- compared to BrO^- and makes the equilibrium for the ionization of HOCl more favorable. Therefore, hypochlorous acid is a stronger acid than hypobromous acid. (This prediction is borne out by the measured $\text{p}K_{\text{a}}$'s: HOCl = 7.5; HOBr = 8.7. The trend continues with HOI, which has a $\text{p}K_{\text{a}}$ of 10.6.)

1.36 The three oxygens in nitrate ion share a total charge of -2 . The average formal charge on each oxygen atom is $-2/3 = -0.67$.

1.37 Writing the two resonance forms of each conjugate base reveals that they are equivalent.

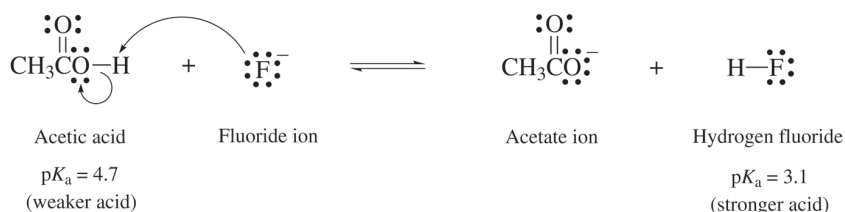


Oxygen is more electronegative than sulfur and will bear a greater share of the negative charge.

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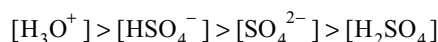
- 1.38 (b) Begin by writing the equation for the acid–base reaction between acetic acid and fluoride ion. Acetic acid will donate a proton to fluoride ion, converting acetic acid to its conjugate base (acetate ion) and fluoride ion to its conjugate acid, (hydrogen fluoride).



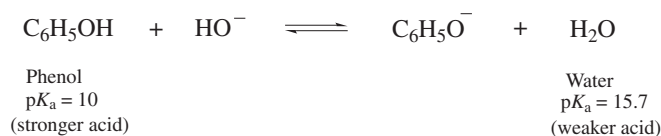
From the respective pK_a 's of the acids, you can see that the weaker acid (acetic acid) is on the left and the stronger acid (hydrogen fluoride) is on the right. Therefore, the equilibrium lies to the left. The equilibrium constant for the process is

$$K_{\text{eq}} = \frac{10^{-pK_a \text{ of acetic acid (reactant)}}}{10^{-pK_a \text{ of hydrogen fluoride (product)}}} = \frac{10^{-4.7}}{10^{-3.1}} = 10^{-1.6}$$

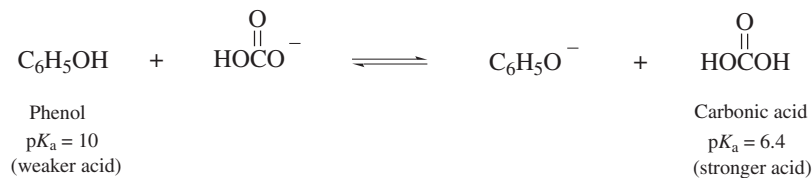
- 1.39 Sulfuric acid is a strong acid; the pK_a of the first ionization of H_2SO_4 is -4.8 . In an aqueous solution of a strong acid, the predominant acid species is H_3O^+ . Hydrogen sulfate ion is a weak acid ($pK_a = 2.0$) and will only undergo ionization to a small extent. The relative amounts of the species present will be



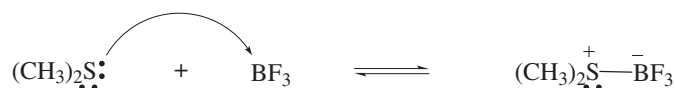
- 1.40 Comparing the pK_a 's of phenol and water reveals that, indeed, the stronger acid (phenol) is on the left in the acid–base equation and the equilibrium constant is greater than 1.



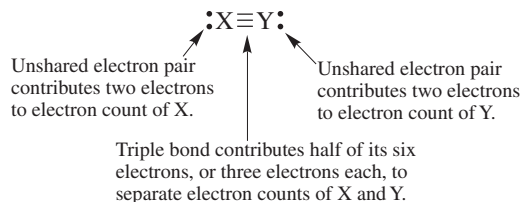
The same comparison for the reaction of phenol and hydrogen carbonate ion reveals that the stronger acid (carbonic acid) is on the right and the equilibrium constant is less than one.



- 1.41 Boron trifluoride is a Lewis acid and will accept a pair of electrons from dimethyl sulfide to form a Lewis acid–Lewis base complex.

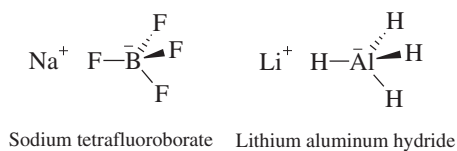


1.42 All these species are characterized by the formula $:\text{X}\equiv\text{Y}:$, and each atom has an electron count of 5.

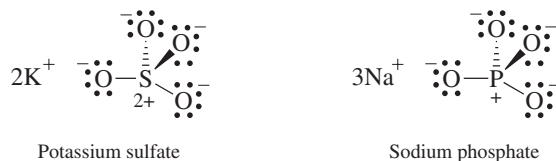


Electron count X = electron count Y = 2 + 3 = 5.

- (a) $:\text{N}\equiv\text{N}:$ A neutral nitrogen atom has five 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 four 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 one 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.
- 1.43 (a, b) The problem specifies that ionic bonding is present and that the anion is tetrahedral. The cations are the group 1 metals Na^+ and Li^+ . Both boron and aluminum are group 3 elements and, thus, have a formal charge of -1 in the tetrahedral anions BF_4^- and AlH_4^- , respectively.

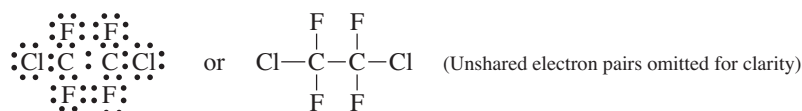


- (c, d) Both of the tetrahedral anions have 32 valence electrons. Sulfur contributes six valence electrons and phosphorus five to the anions. Each oxygen contributes six electrons. The double negative charge in sulfate contributes two more, and the triple negative charge in phosphate contributes three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

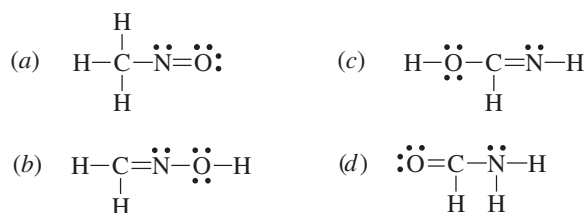


The formal charge on each oxygen in both ions is -1 . The formal charge on sulfur in sulfate is $+2$; the charge on phosphorus is $+1$. The net charge of sulfate ion is -2 ; the net charge of phosphate ion is -3 .

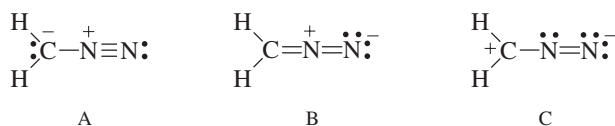
- (c) As in part (b), all of the atoms except carbon are monovalent. Because each carbon bears one chlorine, two ClCF_2 groups must be bonded together.



- 1.47 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.



- 1.48 (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 contributors of a single compound.



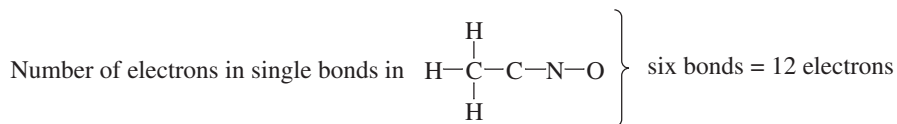
- (b) Structure A has a formal charge of -1 on carbon.
 (c) Structure C has a formal charge of $+1$ on carbon.
 (d) Structures A and B have formal charges of $+1$ on the internal nitrogen.
 (e) Structures B and C have a formal charge of -1 on the terminal nitrogen.
 (f) All resonance contributors of 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.

- 1.49 (a) Number of valence electrons in CH_3CNO (or $\text{C}_2\text{H}_3\text{NO}$):

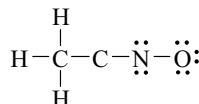
$$\left. \begin{array}{l} \text{Two C} = 8, \text{ three H} = 3, \\ \text{N} = 5, \text{ O} = 6 \end{array} \right\} \text{total} = 22$$

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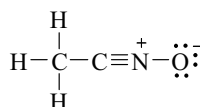
Subtracting the electrons from the single bonds from the total number of valence electrons gives a remainder of ten electrons that need to be added. Add them in pairs, beginning with the most electronegative atom. Complete the octet of each atom before moving to the next one.



One of the carbons has only four electrons, so use both of the nitrogen unshared pairs to form a triple bond between carbon and nitrogen.

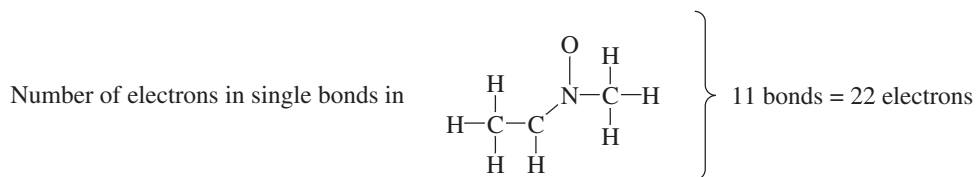


Assign formal charges to give the complete Lewis structural formula.

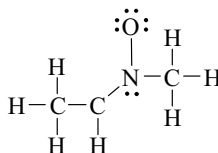


(b) Number of valence electrons in $\text{CH}_3\text{CHN}(\text{O})\text{CH}_3$ (or $\text{C}_3\text{H}_7\text{NO}$):

$$\left. \begin{array}{l} \text{Three C} = 12, \text{ seven H} = 7, \\ \text{N} = 5, \text{ O} = 6 \end{array} \right\} \text{total} = 30$$



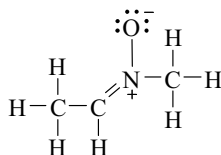
Subtracting the electrons from the single bonds from the total number of valence electrons gives a remainder of eight electrons that need to be added. Add them in pairs, beginning with the most electronegative atom. Complete the octet of each atom before moving to the next one.



One of the carbons has only six electrons, so use the nitrogen unshared pair to form a double bond between carbon and oxygen.



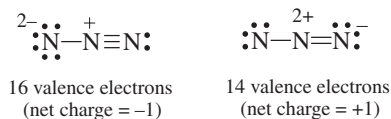
Assign formal charges to give the complete Lewis structural formula.



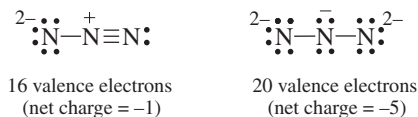
- 1.50 (a) These two structures are resonance contributors because they have the same atomic positions and the same number of electrons.



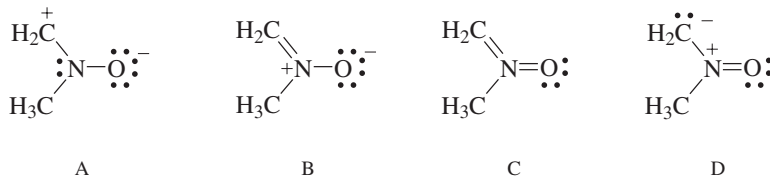
- (b) The two structures have different numbers of electrons and, therefore, cannot be resonance contributors of the same species.



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

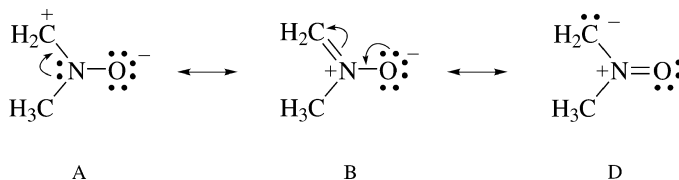


- 1.51 (a) Structure C has five covalent bonds to nitrogen (ten electrons). The octet rule limits nitrogen to a maximum of eight electrons in its valence shell.



- (b) Of the three remaining structures, B and C have four bonds and each is more stable than A, which has only three. B is more stable than D because its negative charge is on a more electronegative element (oxygen versus carbon).

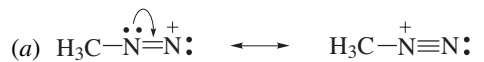
- (c) Use curved arrows to show movement of electrons among the resonance contributors.



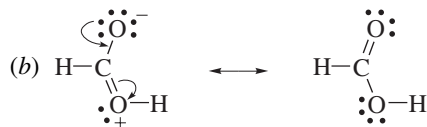
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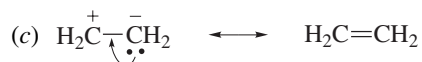
1.52 Notice that in all of the cases in which the more stable Lewis formula contains more bonds than the original one, the additional bond leads to a structure in which the octet rule is satisfied.



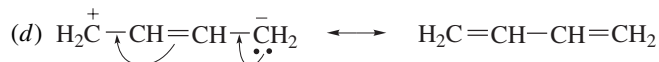
One more bond than original Lewis formula



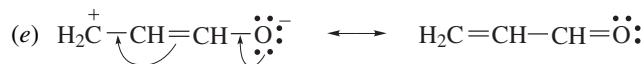
No separation of opposite charges



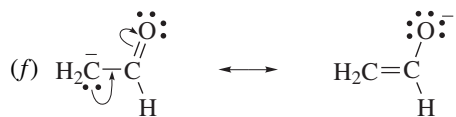
One more bond and no charge separation



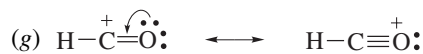
One more bond and no charge separation



One more bond and no charge separation



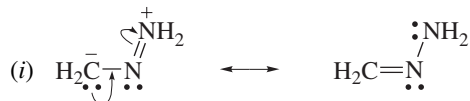
Negative charge on more electronegative element



One more bond



One more bond

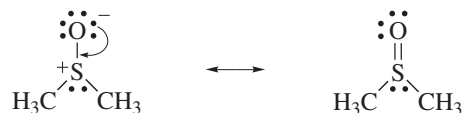


No separation of opposite charges

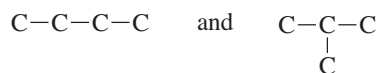
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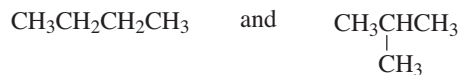
- 1.53 (a) There are 26 valence electrons in $(\text{CH}_3)_2\text{SO}$. The connectivity given corresponds to nine bonds (18 electrons). The remaining eight electrons can be placed so as to satisfy the octet rule as shown on the left:



- (b) The structural formula on the right has one more bond and lacks the charge separation of the one on the left but has ten electrons in the valence shell of sulfur.
- 1.54 (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

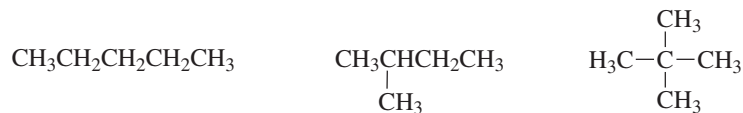


Filling in the appropriate hydrogens gives the correct structures:

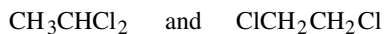


Continue with the remaining parts of the problem using the general approach outlined for part (a).

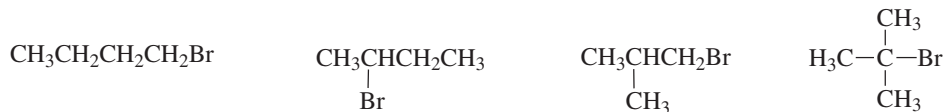
- (b) C_5H_{12}



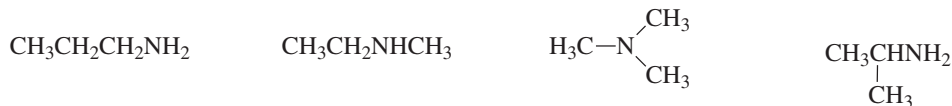
- (c) $\text{C}_2\text{H}_4\text{Cl}_2$



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



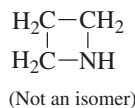
- (e) $\text{C}_3\text{H}_9\text{N}$



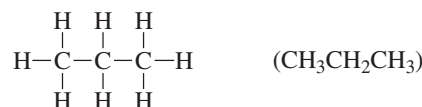
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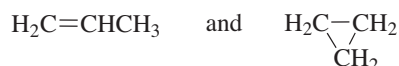
Note that when the three carbons and the nitrogen are arranged in a ring, the molecular formula based on such a structure is C_3H_7N , not C_3H_9N as required.



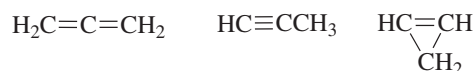
- 1.55 (a) All three carbons must be bonded together, and each one has four bonds; therefore, the molecular formula C_3H_8 uniquely corresponds to



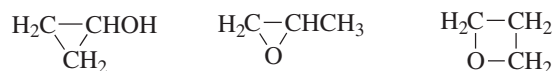
- (b) With two fewer hydrogen atoms than the preceding compound, C_3H_6 must either contain a carbon-carbon double bond or its carbons must be arranged in a ring; thus, the following structures are constitutional isomers:



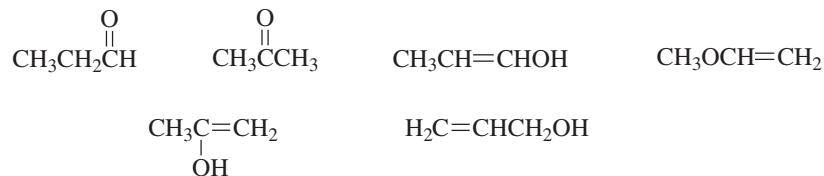
- (c) The molecular formula C_3H_4 is satisfied by the structures



- 1.56 (a) The connectivities 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.



- 1.57 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 1.3 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.

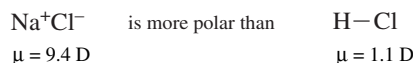


1.58 The direction of a bond dipole is governed by the electronegativity of the atoms involved. Among the halogens, the order of electronegativity is $\text{F} > \text{Cl} > \text{Br} > \text{I}$. Fluorine therefore attracts electrons away from chlorine in FCl , and chlorine attracts electrons away from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

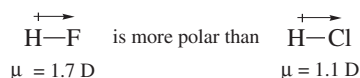


Chlorine is the positive end of the dipole in FCl and the negative end in ICl .

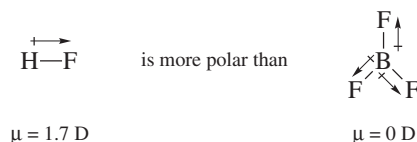
1.59 (a) Sodium chloride is ionic; it has a unit positive charge and a unit negative charge separated from each other. Hydrogen chloride has a polarized bond but is a covalent compound. Sodium chloride has a larger dipole moment. The measured values are as shown.



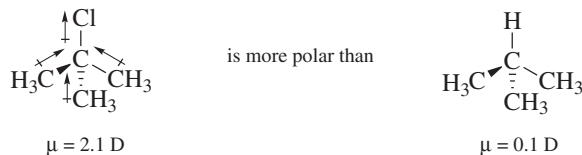
(b) Fluorine is more electronegative than chlorine, and so its bond to hydrogen is more polar, as the measured dipole moments indicate.



(c) Boron trifluoride is planar. Its individual $\text{B}-\text{F}$ bond dipoles cancel. It has no dipole moment.



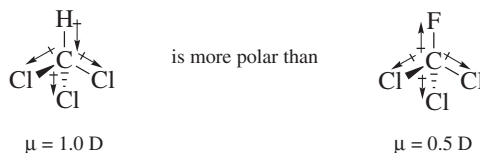
(d) A carbon–chlorine bond is strongly polar; carbon–hydrogen and carbon–carbon bonds are only weakly polar.



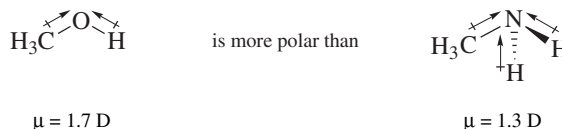
(e) A carbon–fluorine bond in CCl_3F opposes the polarizing effect of the chlorines. The carbon–hydrogen bond in CHCl_3 reinforces it. CHCl_3 therefore has a larger dipole moment.

CHAPTER 1: Structure Determines Properties

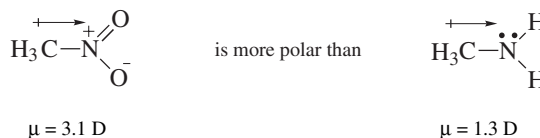
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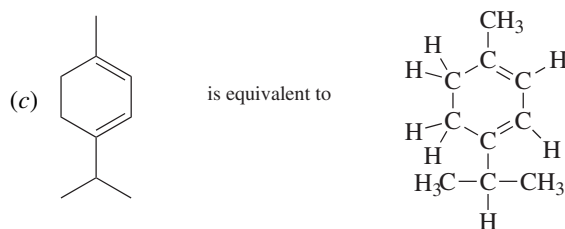
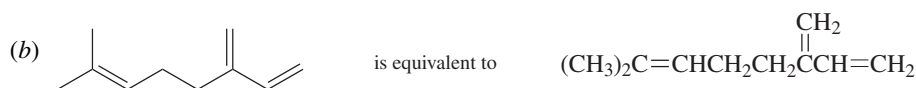
- (f) Oxygen is more electronegative than nitrogen; its bonds to carbon and hydrogen are more polar than the corresponding bonds formed by nitrogen.

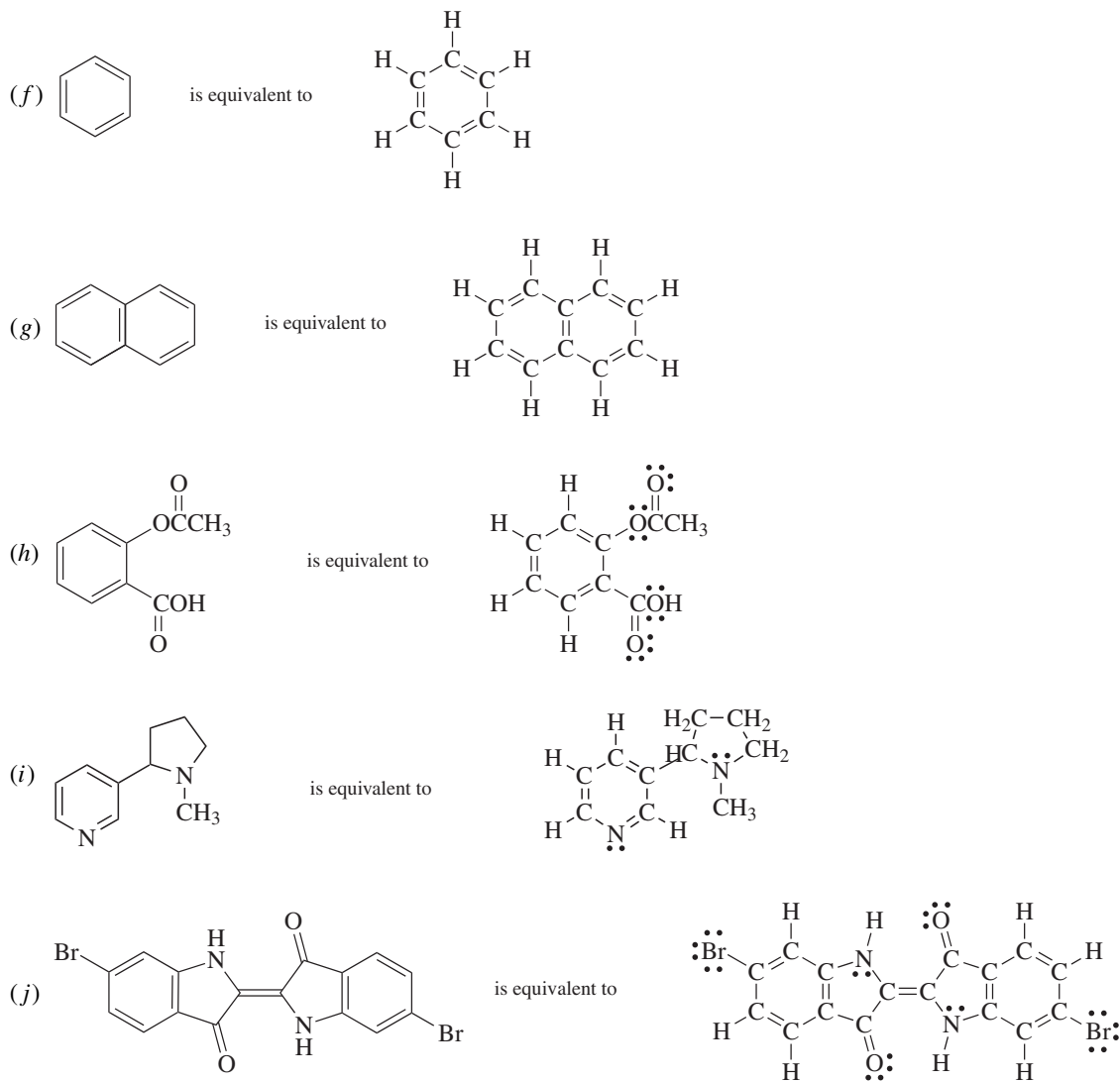


- (g) The Lewis structure for CH_3NO_2 has a formal charge of +1 on nitrogen, making it more electron-attracting than the uncharged nitrogen of CH_3NH_2 .



- 1.60** 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.



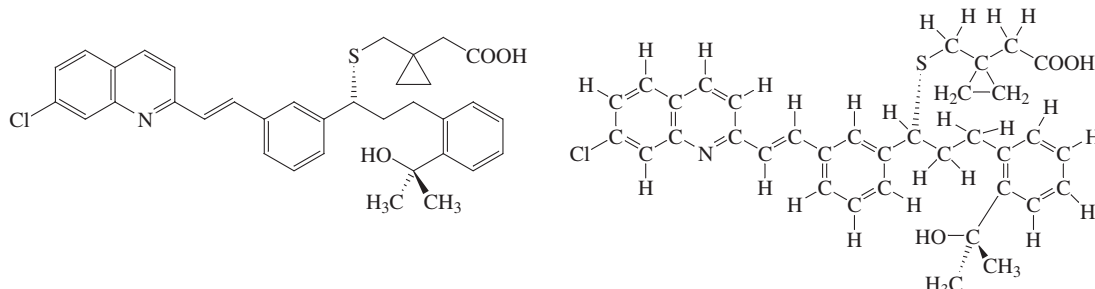
1.61 (a) C_8H_{18} (e) $C_7H_{14}O$ (i) $C_{10}H_{14}N_2$ (b) $C_{10}H_{16}$ (f) C_6H_6 (j) $C_{16}H_8Br_2N_2O_2$ (c) $C_{10}H_{16}$ (g) $C_{10}H_8$ (d) $C_7H_{16}O$ (h) $C_9H_8O_4$

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.

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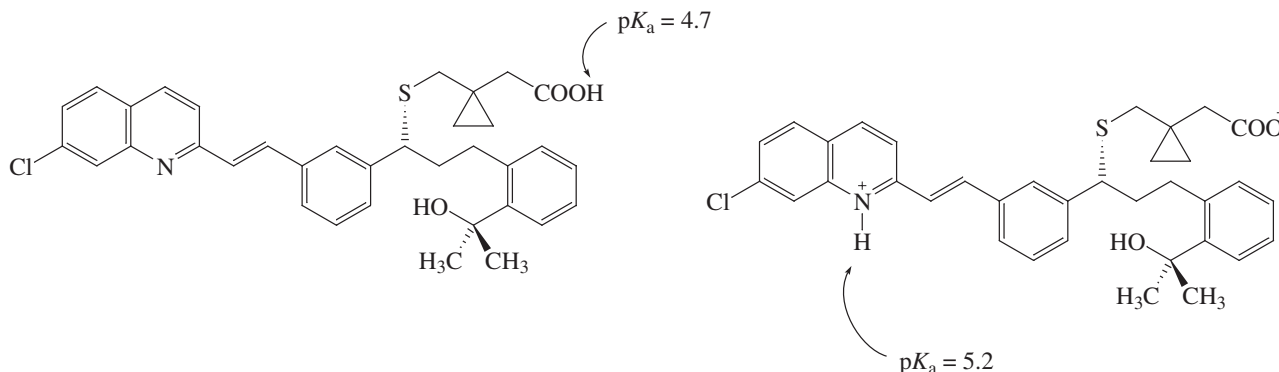
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- 1.62 (a) The molecular formula can be readily found by writing out all of the atoms that do not appear in the condensed formula. The structure on the left can be expanded to the one shown on the right.



Counting each atom gives a molecular formula for montelukast of $C_{35}H_{36}ClNO_3S$.

- (b, c, d) From Table 1.8, the pK_a of the nonzwitterionic form of montelukast can be approximated by comparing the carboxylic acid group to acetic acid ($pK_a = 4.7$). The zwitterionic form can be approximated by comparing it to the pyridinium ion ($pK_a = 5.2$). Because the carboxylic acid group is a stronger acid than the pyridinium ion, the zwitterionic structure is favored. One equivalent of NaOH will deprotonate the N-H proton of montelukast. One equivalent of HCl will protonate the carboxylate ($-COO^-$) group to give the carboxylic acid ($-COOH$).



- 1.63 (a) Because 10^{-pK_a} equals K_a , the ratio is $\frac{10^{-2}}{10^{-8}} = 10^6$. K_a for the acid with a pK_a of 2 is 1 million times larger than for the acid with a pK_a of 8.
- (b) The difference of the K_a 's between the two acids is 10,000. Since $pK_a = -\log K_a$ this corresponds to a difference in pK_a 's = $-\log(10,000) = -4$. The weaker acid has a pK_a of 5 so the stronger acid has a pK_a of $5 - 4 = 1$.
- 1.64 (a) This problem reviews the relationship between logarithms and exponential numbers. We need to determine K_a , given pK_a . The equation that relates the two is

$$pK_a = -\log_{10} K_a$$

Therefore

$$\begin{aligned} K_a &= 10^{-pK_a} \\ &= 10^{-3.48} \\ &= 3.3 \times 10^{-4} \end{aligned}$$

(b) As described in part (a), $K_a = 10^{-\text{p}K_a}$; therefore, K_a for vitamin C is given by the expression

$$\begin{aligned} K_a &= 10^{-4.17} \\ &= 6.7 \times 10^{-5} \end{aligned}$$

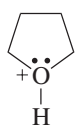
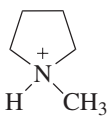
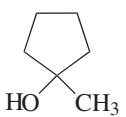
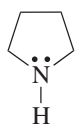
(c) Similarly, $K_a = 1.8 \times 10^{-4}$ for formic acid ($\text{p}K_a$ 3.75).

(d) $K_a = 6.5 \times 10^{-2}$ for oxalic acid ($\text{p}K_a$ 1.19).

In ranking the acids in order of decreasing acidity, remember that the larger the equilibrium constant K_a , the stronger the acid; and the lower the $\text{p}K_a$ value, the stronger the acid.

Acid	K_a	$\text{p}K_a$
Oxalic (strongest)	6.5×10^{-2}	1.19
Aspirin	3.3×10^{-4}	3.48
Formic acid	1.8×10^{-4}	3.75
Vitamin C (weakest)	6.7×10^{-5}	4.17

1.65 By comparison with examples found in Table 1.8, the relative acidities of these four compounds and species can be determined. The two cations are more acidic than the neutral compounds, and because oxygen is more electronegative than nitrogen, the oxygen cation is more acidic than the nitrogen cation. Likewise, the neutral compound containing oxygen is more acidic than the one containing nitrogen.

Most acidic		comparable in acidity to	H_3O^+	$\text{p}K_a = -1.7$
		comparable in acidity to	$(\text{CH}_3)_2\text{NH}_2^+$	$\text{p}K_a = 10.7$
		comparable in acidity to	$(\text{CH}_3)_3\text{COH}$	$\text{p}K_a = 18$
Least acidic		comparable in acidity to	$[(\text{CH}_3)_2\text{CH}]_2\text{NH}$	$\text{p}K_a = 36$

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1.66 As in the previous problem, the species given in the problem can be compared with examples in Table 1.8. The best way to determine the basicity of an anion is to consider the acidity of its conjugate acid, remembering that the weaker the acid the stronger the conjugate base.

Most basic	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{C}^-$	is the conjugate base of	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$	$\text{p}K_{\text{a}} = 26$
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\ddot{\text{O}}^-$	is the conjugate base of	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	$\text{p}K_{\text{a}} = 16$
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\ddot{\text{S}}^-$	is the conjugate base of	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$	$\text{p}K_{\text{a}} = 10.7$
Least basic	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\ddot{\text{O}})_2^-$	is the conjugate base of	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{OH})_2$	$\text{p}K_{\text{a}} = 4.7$

1.67 In each case, the more basic solution will be the one that contains the stronger base. Only the anions need be considered; sodium ion is a spectator ion and can be ignored. Remember that the stronger base is the one with the weaker conjugate acid.

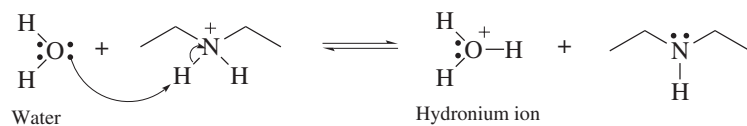
- (a) HCN ($\text{p}K_{\text{a}} = 9.1$) is a weaker acid than HF ($\text{p}K_{\text{a}} = 3.1$), and a solution of CN^- (from NaCN) will be more basic than a solution of F^- (from NaF).
- (b) Carbonic acid ($\text{p}K_{\text{a}} = 6.4$) is a weaker acid than acetic acid ($\text{p}K_{\text{a}} = 4.7$). A solution of sodium carbonate will be more basic than a solution of sodium acetate.
- (c) Methanethiol (CH_3SH , $\text{p}K_{\text{a}} = 10.7$) is the conjugate acid of methanethiolate ion. Methanethiol is a weaker acid than sulfuric acid ($\text{p}K_{\text{a}} = -4.8$), and a solution of sodium methanethiolate will be more basic than a solution of sodium sulfate.

- 1.68** (a) Comparing two atoms as we go down a group in the periodic table, the bond to hydrogen becomes weaker and acid strength increases. Thus, $(\text{CH}_3)_3\text{P}^+\text{H}$ is a stronger acid than $(\text{CH}_3)_3\text{N}^+\text{H}$.
- (b) The weaker acid forms the stronger conjugate base, so $(\text{CH}_3)_3\text{N}^\bullet$ is a stronger base than $(\text{CH}_3)_3\text{P}^\bullet$.

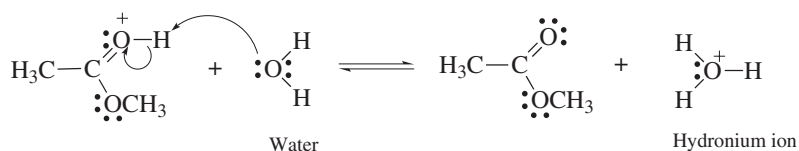
1.69 (a) Water will remove the proton from HCN in a Brønsted acid–base reaction.



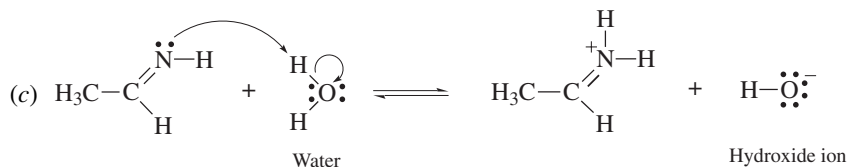
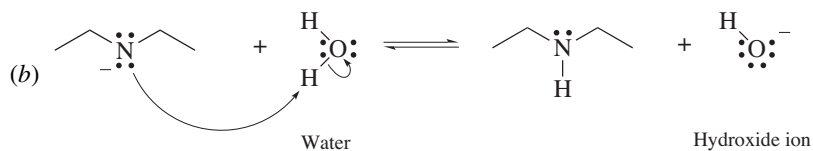
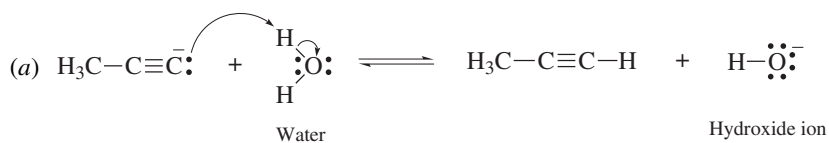
(b) Water uses one of its unshared electron pairs to remove a proton from nitrogen.



(c) The proton on the positively charged oxygen is the one that is transferred to water.



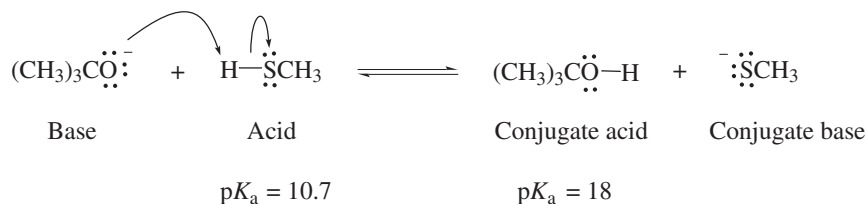
1.70 Water can act as both a base, as in the previous problem, or as an acid as in this problem. Water donates one of its protons and forms hydroxide ion in each case. Remember to use curved arrows to track electron movement, not the movement of atoms.



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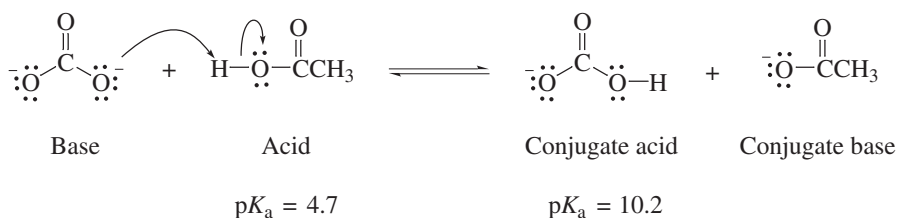
1.71 (a)



The equilibrium constant can be calculated from the ratio of the two K_a 's of the acids in the preceding equation. The K_a 's can be obtained from the pK_a 's in Table 1.8 by rearranging the equation $pK_a = -\log K_a$ to $K_a = 10^{-pK_a}$. Taking the ratio of the acid and conjugate acid K_a 's gives the equilibrium constant K_{eq} :

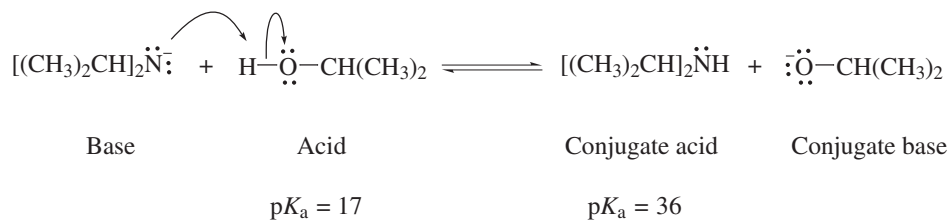
$$K_{\text{eq}} = \frac{K_a(\text{acid})}{K_a(\text{conjugate acid})} = \frac{10^{-10.7}}{10^{-18}} = 10^{7.3} = 2 \times 10^7$$

(b)



$$K_{\text{eq}} = \frac{K_a(\text{acid})}{K_a(\text{conjugate acid})} = \frac{10^{-4.7}}{10^{-10.2}} = 10^{5.5} = 3.2 \times 10^5$$

(c)



$$K_{\text{eq}} = \frac{K_a(\text{acid})}{K_a(\text{conjugate acid})} = \frac{10^{-17}}{10^{-36}} = 1 \times 10^{19}$$

- 1.72 (a) The acid on the left is acetylene. Amide ion is the base, which abstracts a proton from acetylene. Their pK_a 's are shown in the equation.



Acetylene is a stronger acid than ammonia. The equilibrium lies to the right. The equilibrium constant is

$$K_{\text{eq}} = \frac{10^{-pK_a} \text{ of reactant acid}}{10^{-pK_a} \text{ of product acid}}$$

$$K_{\text{eq}} = \frac{10^{-26}}{10^{-36}} = 10^{10}$$

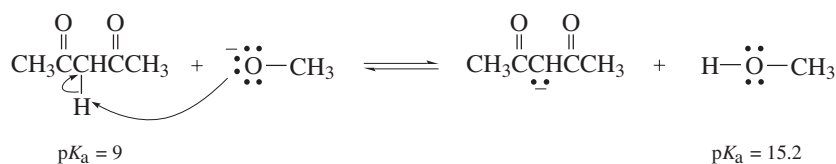
- (b) Contrast this part of the problem with part (a). Methoxide ion is a much weaker base than the amide ion of part (a).



Here, the weaker acid is on the left. The equilibrium lies to the left. The equilibrium constant is more than 10^{20} times smaller than that of part (a):

$$K_{\text{eq}} = \frac{10^{-26}}{10^{-15.2}} = 10^{-10.8} = 1.6 \times 10^{-11}$$

- (c) Table 1.8 tells us that the most acidic protons in the reactant (2,4-pentanedione) are those in the CH_2 group.



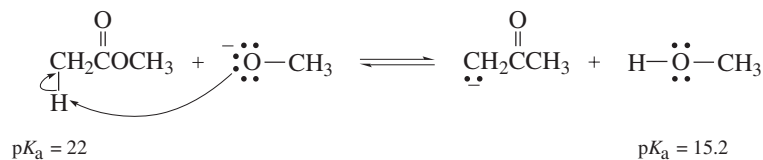
2,4-Pentanedione is a stronger acid than methanol. The equilibrium lies to the right and the equilibrium constant is:

$$K_{\text{eq}} = \frac{10^{-9}}{10^{-15.2}} = 10^{5.2} = 1.6 \times 10^5$$

- (d) The acidic proton in part (c) was part of a CH_2 flanked by two $\text{C}=\text{O}$ groups. In methyl butanoate (given in Table 1.8), the CH_2 is flanked by only one $\text{C}=\text{O}$ group and is far less acidic.

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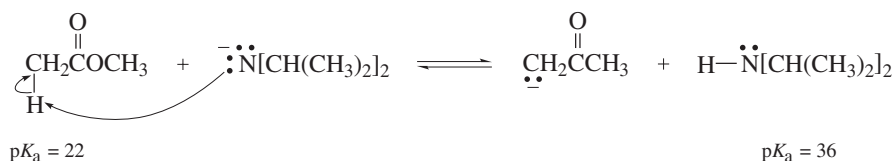
33



The stronger acid is on the right. Therefore, the equilibrium lies to the left and the equilibrium constant is

$$K_{\text{eq}} = \frac{10^{-22}}{10^{-15.2}} = 10^{-6.8} = 1.6 \times 10^{-7}$$

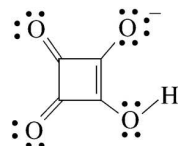
- (e) As in part (d), methyl butanoate is the reactant acid. The base in this case is far stronger than the base in part (d), however.



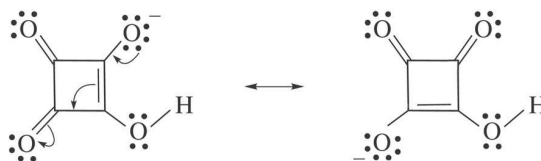
The stronger acid is on the left. The equilibrium lies far to the right.

$$K_{\text{eq}} = \frac{10^{-22}}{10^{-36}} = 10^{14}$$

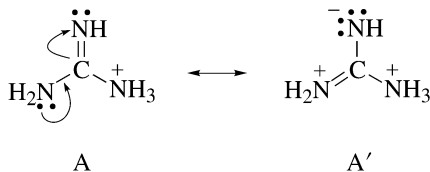
- 1.73 The conjugate base of squaric acid has the structure



Move electron pairs as indicated, beginning at the negatively charged oxygen.

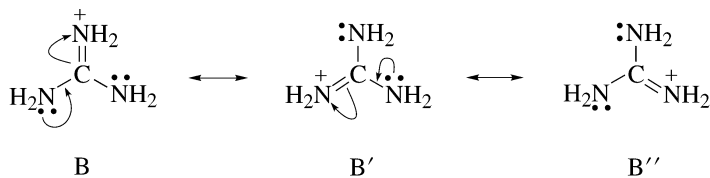


- 1.74 In structure A, the only contributing structure that can be written that satisfies the octet rule is A:



Contributing structure A' is less stable than A because it has more charge separation than A.

In structure B, electron delocalization disperses the charge without increasing charge separation. All three resonance forms are equally stable.



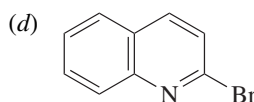
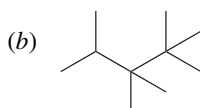
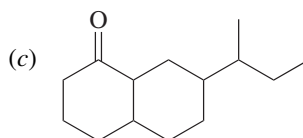
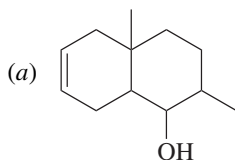
Structure B is stabilized by electron delocalization more than A.

ANSWERS TO INTERPRETIVE PROBLEMS

1.75 D; 1.76 B; 1.77 A; 1.78 C; 1.79 A

SELF-TEST

- Write the electron configuration for each of the following:
 - Phosphorus
 - Sulfide ion in Na_2S
- Determine the formal charge of each atom and the net charge for each of the following species:
 - $\text{:}\ddot{\text{N}}=\text{C}=\ddot{\text{S}}\text{:}$
 - $\text{:O}\equiv\text{N}-\ddot{\text{O}}\text{:}$
 - $\begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\ | \\ \text{HC}=\text{NH}_2 \end{array}$
- Write a second Lewis structure that satisfies the octet rule for each of the species in Problem 2, and determine the formal charge of each atom. Which of the Lewis structures for each species in this and Problem 2 is more stable?
- Write a correct Lewis structure for each of the following. Be sure to show explicitly any unshared pairs of electrons.
 - Methylamine, CH_3NH_2
 - Acetaldehyde, $\text{C}_2\text{H}_4\text{O}$ (The connectivity is CCO; all the hydrogens are connected to carbon.)
- What is the molecular formula of each of the structures shown? Clearly draw any unshared electron pairs that are present.



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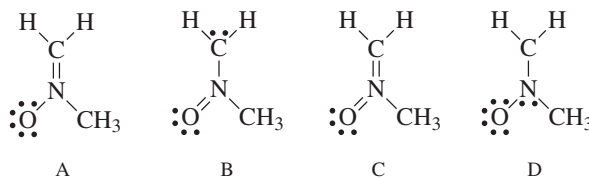
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6. Write the products of the acid–base reaction that follows; and identify the acid, base, conjugate acid, and conjugate base. What is the value of the equilibrium constant, K_{eq} ? The approximate $\text{p}K_{\text{a}}$ of NH_3 is 36; that of $\text{CH}_3\text{CH}_2\text{OH}$ is 16.



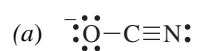
Show all unshared electron pairs and formal charges, and use curved arrows to track electron movement.

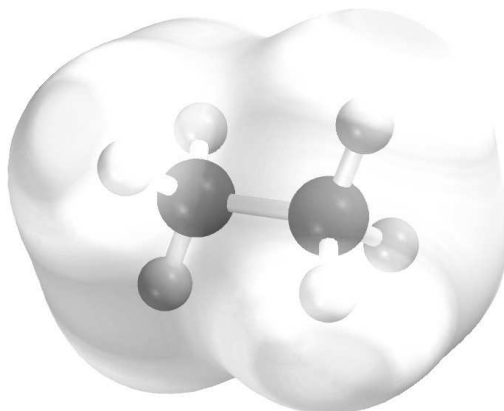
7. Account for the fact that all three sulfur–oxygen bonds in SO_3 are the same by drawing the appropriate Lewis structure(s).
8. The cyanate ion contains 16 valence electrons, and its three atoms are connected in the order OCN. Write the most stable Lewis structure for this species, and assign a formal charge to each atom. What is the net charge of the ion?
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?
10. Assign the shape of each of the following as either linear or bent.
- (a) CO_2 (b) NO_2^+ (c) NO_2^-
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?

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.
13. Draw a second resonance contributor for each of the species shown. Be sure to show all unshared electron pairs, and indicate the formal charge (if any) on each atom. Is the first or the second structure more stable?



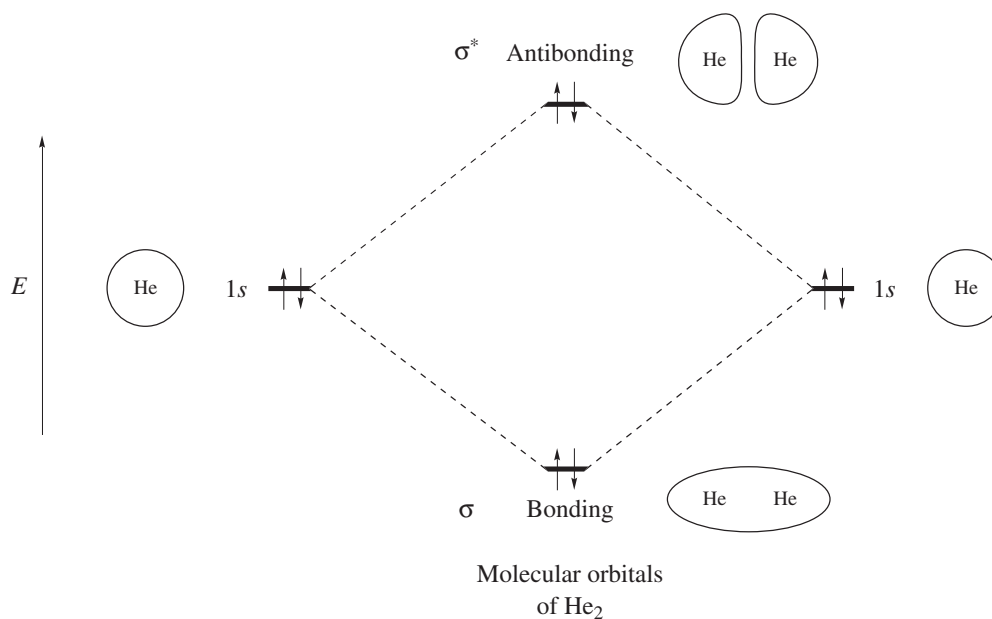


CHAPTER 2

Alkanes and Cycloalkanes: Introduction to Hydrocarbons

SOLUTIONS TO TEXT PROBLEMS

- 2.1 (a) A $1s$ orbital from one helium atom is combined with that of a second helium atom to give two new molecular orbitals—one bonding and one antibonding—as shown in the diagram. Because each helium $1s$ atomic orbital has two electrons, two electrons are placed in each of the new molecular orbitals as shown. Although not part of the requested answer, the orbital shapes are also included in the diagram.

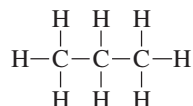


- (b) As shown in the preceding diagram, diatomic helium would have electrons in antibonding orbitals, which is destabilizing. The energy required to place the two electrons in the antibonding orbital offsets the gain in bonding energy from the two electrons in the bonding orbital.

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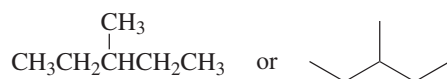
CHAPTER 2: Alkanes and Cycloalkanes: Introduction to Hydrocarbons

- 2.2 A carbon atom is sp^3 -hybridized when it is directly bonded to four atoms. Each of the three carbons of propane is bonded to four atoms, either carbon or hydrogen:

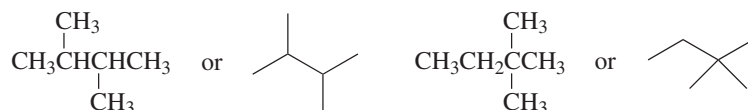


Each carbon–carbon σ bond arises from overlap of two half-filled sp^3 hybrid orbitals, one from each carbon atom. The eight carbon–hydrogen bonds are sp^3 - $1s$ σ bonds.

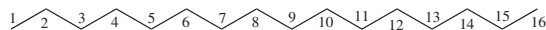
- 2.3 An unbranched alkane (n -alkane) of 28 carbons has 26 methylene (CH_2) groups flanked by a methyl (CH_3) group at each end. The condensed formula is $\text{CH}_3(\text{CH}_2)_{26}\text{CH}_3$.
- 2.4 The alkane represented by the bond-line formula has 11 carbons. The general formula for an alkane is $\text{C}_n\text{H}_{2n+2}$, and thus there are 24 hydrogens. The molecular formula is $\text{C}_{11}\text{H}_{24}$; the condensed structural formula is $\text{CH}_3(\text{CH}_2)_9\text{CH}_3$.
- 2.5 In addition to $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ and $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_3$, there are three more isomers. One has a five-carbon chain with a one-carbon (methyl) branch:



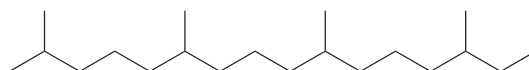
The remaining two isomers have two methyl branches on a four-carbon chain.



- 2.6 (b) Octacosane is not listed in Table 2.2, but its structure can be deduced from its systematic name. The suffix *-cosane* pertains to alkanes that contain 20–29 carbons in their longest continuous chain. The prefix *octa-* means “eight.” *Octacosane* is therefore the unbranched alkane having 28 carbon atoms. It is $\text{CH}_3(\text{CH}_2)_{26}\text{CH}_3$.
- (c) The alkane in Problem 2.4 has an unbranched chain of 11 carbon atoms and is named *undecane*.
- 2.7 The ending *-hexadecane* reveals that the longest continuous carbon chain has 16 carbon atoms.



There are four methyl groups (represented by *tetramethyl-*), and they are located at carbons 2, 6, 10, and 14.



2,6,10,14-Tetramethylhexadecane
(phytane)

CHAPTER 2: Alkanes and Cycloalkanes: Introduction to Hydrocarbons

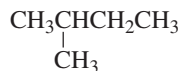
39

- 2.8 (b) The systematic name of the unbranched C_5H_{12} isomer is *pentane* (Table 2.2).



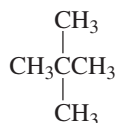
IUPAC name: **pentane**

A second isomer, $(CH_3)_2CHCH_2CH_3$, has four carbons in the longest continuous chain and so is named as a derivative of butane. Because it has a methyl group at C-2, it is *2-methylbutane*.



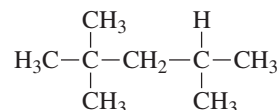
IUPAC name: **2-methylbutane**

The remaining isomer, $(CH_3)_4C$, has three carbons in its longest continuous chain and so is named as a derivative of propane. There are two methyl groups at C-2, and so it is a 2,2-dimethyl derivative of propane.

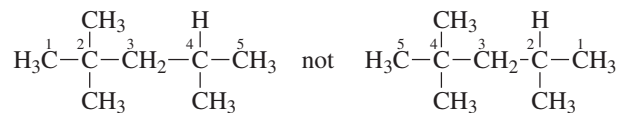


IUPAC name: **2,2-dimethylpropane**

- (c) First write out the structure in more detail, and identify the longest continuous carbon chain.

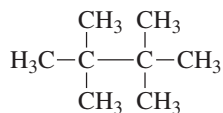


There are five carbon atoms in the longest chain, and so the compound is named as a derivative of pentane. This five-carbon chain has three methyl substituents attached to it, making it a trimethyl derivative of pentane. Number the chain in the direction that gives the lowest numbers to the substituents at the first point of difference.



2,2,4-Trimethylpentane (correct) 2,4,4-Trimethylpentane (incorrect)

- (d) The longest continuous chain in $(CH_3)_3CC(CH_3)_3$ contains four carbon atoms.

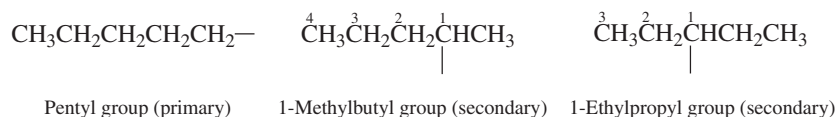


The compound is named as a tetramethyl derivative of butane; it is *2,2,3,3-tetramethylbutane*.

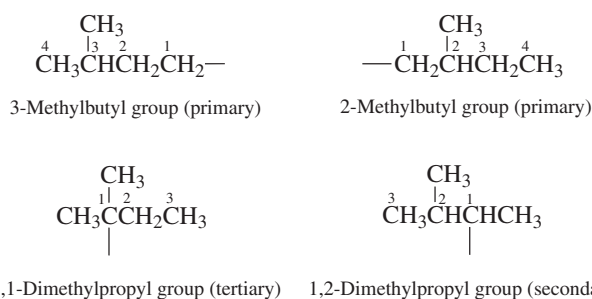
40

CHAPTER 2: Alkanes and Cycloalkanes: Introduction to Hydrocarbons

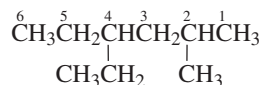
- 2.9 There are three C_5H_{11} alkyl groups with unbranched carbon chains. One is primary, and two are secondary. The IUPAC name of each group is given beneath the structure. Remember to number the alkyl groups from the potential point of attachment.



Four alkyl groups are derived from $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$. Two are primary, one is secondary, and one is tertiary.

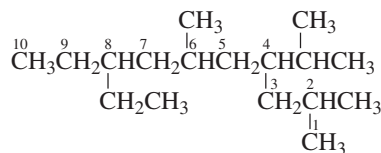


- 2.10 (b) Begin by writing the structure in more detail, showing each of the groups written in parentheses. The compound is named as a derivative of hexane, because it has six carbons in its longest continuous chain.



The chain is numbered so as to give the lowest number to the substituent that appears closest to the end of the chain. In this case, it is numbered right to left so that the substituents are located at C-2 and C-4 rather than at C-3 and C-5. In alphabetical order, the groups are ethyl and methyl; they are listed in alphabetical order in the name. The compound is *4-ethyl-2-methylhexane*.

- (c) The longest continuous chain is shown in the structure; it contains ten carbon atoms. The structure also shows the numbering scheme that gives the lowest number to the substituent nearest the end of the chain.

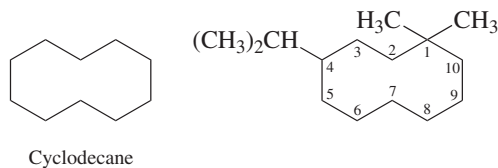


In alphabetical order, the substituents are ethyl (at C-8), isopropyl (at C-4), and two methyl groups (at C-2 and C-6). The alkane is *8-ethyl-4-isopropyl-2,6-dimethyldecane*. The systematic name for the isopropyl group (1-methylethyl) may also be used, and the name becomes *8-ethyl-2,6-dimethyl-4-(1-methylethyl)decane*. Notice in both names that the “di” prefix is ignored when alphabetizing.

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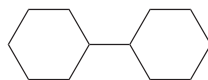
41

- 2.11 (b) There are ten carbon atoms in the ring in this cycloalkane; thus, it is named as a derivative of cyclodecane.



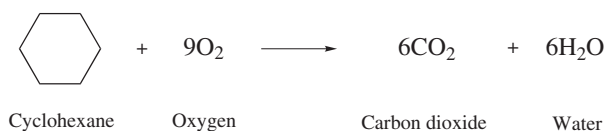
The numbering pattern of the ring is chosen so as to give the lowest number to the substituent at the first point of difference between them. Thus, the carbon bearing two methyl groups is C-1, and the ring is numbered counterclockwise, placing the isopropyl group on C-4 (numbering clockwise would place the isopropyl on C-8). Listing the substituent groups in alphabetical order, the correct name is *4-isopropyl-1,1-dimethylcyclodecane*. Alternatively, the systematic name for isopropyl (1-methylethyl) could be used, and the name would become *1,1-dimethyl-4-(1-methylethyl)cyclodecane*.

- (c) When two cycloalkyl groups are attached by a single bond, the compound is named as a cycloalkyl-substituted cycloalkane. This compound is *cyclohexylcyclohexane*.



- 2.12 The alkane that has the most carbons (nonane) has the highest boiling point (151°C). Among the others, all of which have eight carbons, the unbranched isomer (octane) has the highest boiling point (126°C) and the most branched one (2,2,3,3-tetramethylbutane) the lowest (106°C). The remaining alkane, 2-methylheptane, boils at 116°C.

- 2.13 All hydrocarbons burn in air to give carbon dioxide and water. To balance the equation for the combustion of cyclohexane (C₆H₁₂), first balance the carbons and the hydrogens on the right side. Then balance the oxygens on the left side.



- 2.14 (b) Icosane (Table 2.2) is C₂₀H₄₂. It has four more methylene (CH₂) groups than hexadecane, the last unbranched alkane in Table 2.3. Its calculated heat of combustion is therefore (4 × 653 kJ/mol) higher.

$$\begin{aligned}
 \text{Heat of combustion of icosane} &= \text{heat of combustion of hexadecane} + (4 \times 653 \text{ kJ/mol}) \\
 &= 10,701 \text{ kJ/mol} + 2612 \text{ kJ/mol} \\
 &= 13,313 \text{ kJ/mol}
 \end{aligned}$$

- 2.15 Two factors that influence the heats of combustion of alkanes are, in order of decreasing importance, (1) the number of carbon atoms and (2) the extent of chain branching. Pentane, 2-methylbutane, and 2,2-dimethylpropane are all C₅H₁₂; hexane is C₆H₁₄. Hexane has the largest heat of combustion. Branching leads to a lower heat of combustion; 2,2-dimethylpropane is the most branched and has the lowest heat of combustion.

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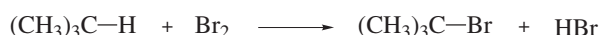
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Hexane	$\text{CH}_3(\text{CH}_2)_4\text{CH}_3$	Heat of combustion 4163 kJ/mol (995.0 kcal/mol)
Pentane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Heat of combustion 3536 kJ/mol (845.3 kcal/mol)
2-Methylbutane	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_3$	Heat of combustion 3529 kJ/mol (843.4 kcal/mol)
2,2-Dimethylpropane	$(\text{CH}_3)_4\text{C}$	Heat of combustion 3514 kJ/mol (839.9 kcal/mol)

2.16 In the first reaction, a carbon–oxygen bond is replaced by a carbon–chlorine bond.

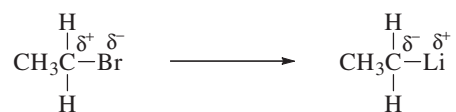


Both oxygen and chlorine are more electronegative than carbon, so the oxidation number of carbon does not change in this reaction. In the second reaction, a carbon–hydrogen bond is replaced by a carbon–bromine bond.



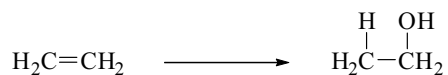
Bromine is more electronegative than carbon; hydrogen is less electronegative. The oxidation number of carbon has increased, and carbon has been oxidized. Reduction of bromine has also occurred; the oxidation number of bromine in Br_2 is 0; in HBr it is -1 .

2.17 (b) The CH_3 carbon is unchanged in this reaction; however, the carbon of CH_2Br is bonded to the electronegative Br making the carbon partially positive whereas the carbon of CH_2Li is bonded to an electropositive Li making the carbon partially negative. The change from a partially positive carbon to a partially negative carbon is considered a reduction. Thus, a reducing reagent is required for this reaction.



(c) This reaction can be considered as an addition of a proton (H^+) to the left carbon and an addition of a hydroxide (HO^-) to the right carbon. The left carbon is thus reduced and the right carbon is oxidized, resulting in no net oxidation.

Alternatively, hydrogen is slightly more electropositive than carbon and oxygen is more electronegative than carbon. Using this method, one carbon is more electronegative and one more electropositive, relative to the starting material. Neither an oxidation reagent nor reducing reagent is required.

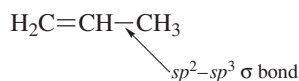


(d) An oxygen has been added to the molecule such that each carbon contains a new bond to oxygen. Each carbon has been oxidized, so an oxidizing reagent is required for this reaction.

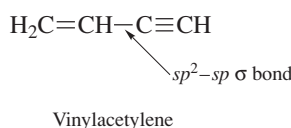
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- 2.18 The carbons of the double bond are both sp^2 -hybridized. The carbon of the methyl group is sp^3 -hybridized. The bond indicated with the arrow is formed by overlap of an sp^2 and an sp^3 hybrid orbital. It is a σ bond, as are all single bonds.

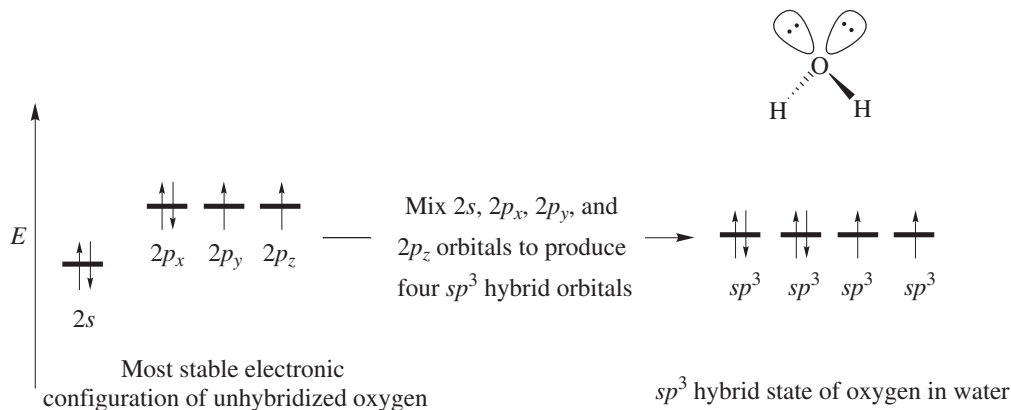


- 2.19 The carbons of the double bond are both sp^2 -hybridized. The carbons of the triple bond are sp -hybridized. The σ bond indicated with the arrow is formed by overlap of an sp^2 and an sp hybrid orbital.



There is a total of seven σ bonds in vinylacetylene: three sp^2-1s C—H bonds, one $sp-1s$ C—H bond, one sp^2-sp^2 C—C bond (the σ component of the double bond), one $sp-sp$ C—C bond (the σ component of the triple bond), and the sp^2-sp C—C bond described earlier. In addition, there are three π bonds: one in the double bond and two in the triple bond.

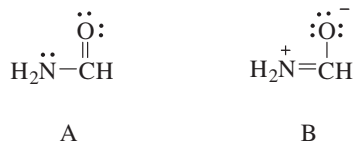
- 2.20 Oxygen in water has a total of four groups, two hydrogen atoms and two lone electron pairs. This leads to the prediction of an sp^3 -hybridized oxygen. The mixing of the $2s$ and the three $2p$ orbitals gives the four hybridized sp^3 orbitals shown here. In the H_2O molecule, the two sp^3 orbitals containing the lone electron pairs are aligned with the plane of the paper, whereas the other two sp^3 hybrid orbitals (not shown) are aligned with the wedge-and-dash bonds.



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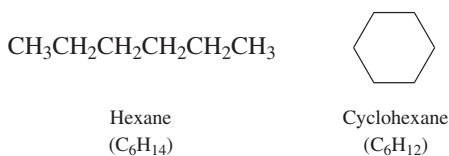
- 2.21 Of the two Lewis structures, the electron distribution in structure B is more consistent with the observed planar geometry of formamide than A.



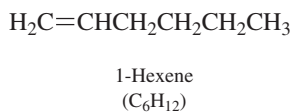
In B, both nitrogen and carbon are sp^2 -hybridized, and the double bond connecting them has a σ component and a π component. All six atoms of B lie in the same plane. In A, nitrogen has three bonded electron pairs and an unshared pair. Maximum separation of these four electron pairs suggests a pyramidal geometry at nitrogen and a nonplanar structure for formamide.

- 2.22 Each ring decreases the number of hydrogens in the general molecular formula of the hydrocarbon by two.

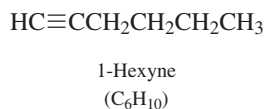
- (a) Cycloalkanes have the general formula C_nH_{2n} . Compare hexane (C_6H_{14}) with cyclohexane (C_6H_{12}), for example:



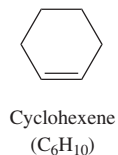
- (b) The general formula of an alkene has two fewer hydrogens than that of an alkane and is C_nH_{2n} . A typical example is 1-hexene (C_6H_{12}):



- (c) A triple bond decreases the general molecular formula by four hydrogens; the general molecular formula of an alkyne is C_nH_{2n-2} . An example is 1-hexyne (C_6H_{10}).



- (d) A compound that has both a ring and a double bond would have the general molecular formula C_nH_{2n-2} . Cyclohexene is an example:



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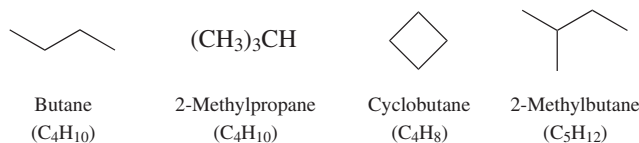
45

2.23 A hydrocarbon with a molecular formula C_5H_8 fits the general formula C_nH_{2n-2} . Therefore, the compound must have two rings, two double bonds, one double bond and one ring, or one triple bond.

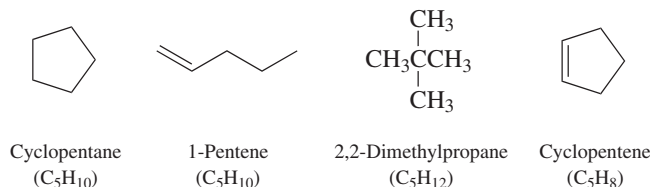
(a) The hydrocarbon cannot be a cycloalkane because a cycloalkane with five carbon atoms would have the formula C_5H_{10} .

(b-d) Each of the remaining possibilities (one ring and one double bond, two double bonds, and one triple bond) are plausible for a formula C_5H_8 .

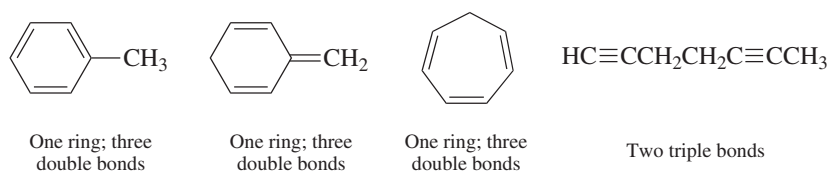
2.24 (a) Isomers are different compounds that have the same molecular formula. Butane and 2-methylpropane both have the molecular formula C_4H_{10} and are isomers. The molecular formula of cyclobutane is C_4H_8 and that of 2-methylbutane is C_5H_{12} .



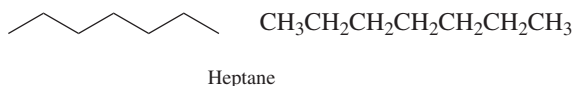
(b) The general molecular formula for a compound with either a ring or a double bond is C_nH_{2n} . Cyclopentane and 1-pentene are isomers; the molecular formula of both compounds is C_5H_{10} .



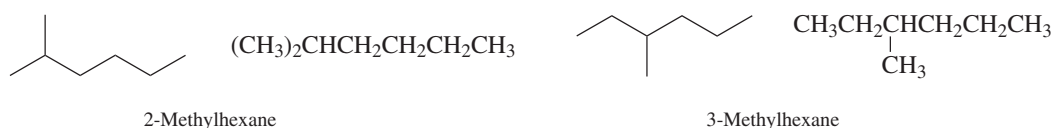
(c) Any combination of four rings or double bonds will give a compound with the general molecular formula C_nH_{2n-6} . A compound with two triple bonds will also have the same molecular formula. All four compounds shown are isomers because they all have the molecular formula C_7H_8 .



2.25 It is best to approach problems of this type systematically. Because the problem requires all the isomers of C_7H_{16} to be written, begin with the unbranched isomer heptane.



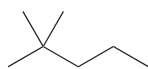
Two isomers have six carbons in their longest continuous chain. One bears a methyl substituent at C-2, the other a methyl substituent at C-3.



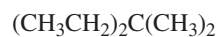
Now consider all the isomers that have two methyl groups as substituents on a five-carbon continuous chain.

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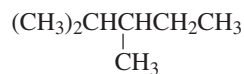
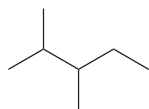
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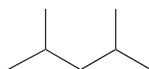
2,2-Dimethylpentane



3,3-Dimethylpentane

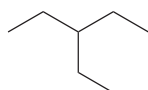


2,3-Dimethylpentane



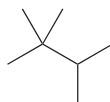
2,4-Dimethylpentane

There is one isomer characterized by an ethyl substituent on a five-carbon chain:



3-Ethylpentane

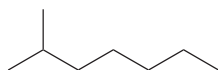
The remaining isomer has three methyl substituents attached to a four-carbon chain.



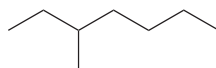
2,2,3-Trimethylbutane

2.26 In the course of doing this problem, you will write and name the 17 alkanes that, in addition to octane, $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$, comprise the 18 constitutional isomers of C_8H_{18} .

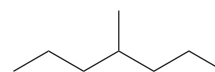
(a) The easiest way to attack this part of the exercise is to draw a bond-line depiction of heptane and add a methyl branch to the various positions.



2-Methylheptane



3-Methylheptane



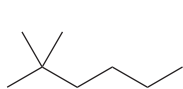
4-Methylheptane

Other structures bearing a continuous chain of seven carbons would be duplicates of these isomers rather than unique isomers. “5-Methylheptane,” for example, is an incorrect name for 3-methylheptane, and “6-methylheptane” is an incorrect name for 2-methylheptane.

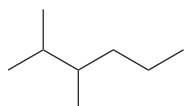
CHAPTER 2: Alkanes and Cycloalkanes: Introduction to Hydrocarbons

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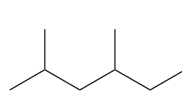
- (b) Six of the isomers named as derivatives of hexane contain two methyl branches on a continuous chain of six carbons.



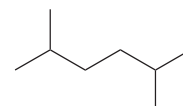
2,2-Dimethylhexane



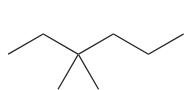
2,3-Dimethylhexane



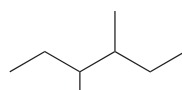
2,4-Dimethylhexane



2,5-Dimethylhexane

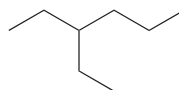


3,3-Dimethylhexane



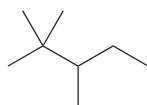
3,4-Dimethylhexane

One isomer bears an ethyl substituent:

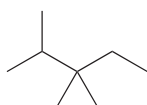


3-Ethylhexane

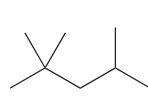
- (c) Four isomers are trimethyl-substituted derivatives of pentane:



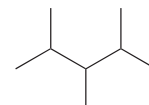
2,2,3-Trimethylpentane



2,3,3-Trimethylpentane

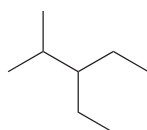


2,2,4-Trimethylpentane

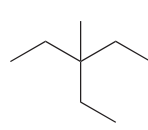


2,3,4-Trimethylpentane

Two bear an ethyl group and a methyl group on a continuous chain of five carbons:



3-Ethyl-2-methylpentane



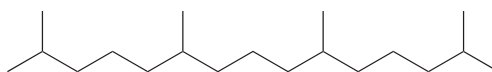
3-Ethyl-3-methylpentane

- (d) Only one isomer is named as a derivative of butane:



2,2,3,3-Tetramethylbutane

- 2.27** The IUPAC name for pristane reveals that the longest chain contains 15 carbon atoms (as indicated by *-pentadecane*). The chain is substituted with four methyl groups at the positions indicated in the name.



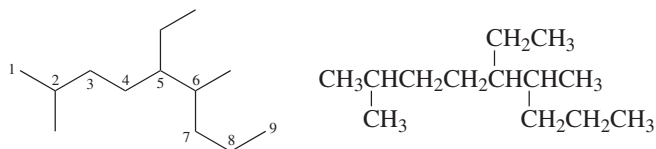
Pristane
(2,6,10,14-tetramethylpentadecane)

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2.28 (a) The alkane contains 13 carbons. Because all alkanes have the molecular formula C_nH_{2n+2} , the molecular formula must be $C_{13}H_{28}$.

(b) The longest continuous chain is indicated and numbered as shown.



In alphabetical order, the substituents are ethyl (at C-5), methyl (at C-2), and methyl (at C-6). The IUPAC name is *5-ethyl-2,6-dimethylnonane*.

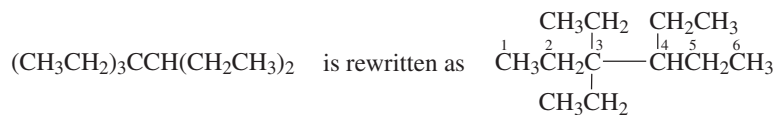
(c) Fill in the hydrogens in the alkane to identify the various kinds of groups present. There are five *methyl* (CH_3) groups, five *methylene* (CH_2) groups, and three *methine* (CH) groups in the molecule.

(d) A primary carbon is attached to one other carbon. There are five primary carbons (the carbons of the five CH_3 groups). A secondary carbon is attached to two other carbons, and there are five of these (the carbons of the five CH_2 groups). A tertiary carbon is attached to three other carbons, and there are three of these (the carbons of the three methine groups). A quaternary carbon is attached to four other carbons. None of the carbons is a quaternary carbon.

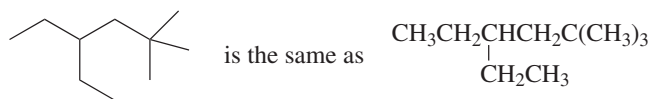
2.29 (a) This compound is an unbranched alkane with 27 carbons. Table 2.2 in the text indicates that alkanes with 20–29 carbons have names ending in *-cosane*. Thus, we add the prefix *hepta-* (“seven”) to *cosane* to name the alkane $\text{CH}_3(\text{CH}_2)_{25}\text{CH}_3$ as *heptacosane*.

(b) The alkane $(\text{CH}_3)_2\text{CHCH}_2(\text{CH}_2)_{14}\text{CH}_3$ has 18 carbons in its longest continuous chain. It is named as a derivative of *octadecane*. There is a single substituent, a methyl group at C-2. The compound is *2-methyloctadecane*.

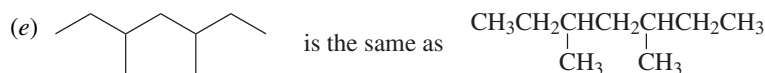
(c) Write the structure out in more detail to reveal that it is *3,3,4-triethylhexane*.



(d) Each line of a bond-line formula represents a bond between two carbon atoms. Hydrogens are added so that the number of bonds to each carbon atom totals four.



The IUPAC name is *4-ethyl-2,2-dimethylhexane*.

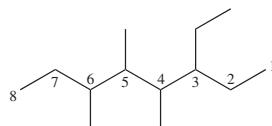


The IUPAC name is *3,5-dimethylheptane*.

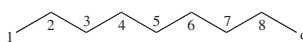
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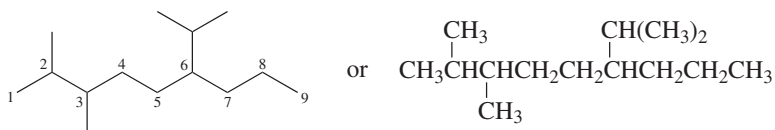
- (f) Number the chain in the direction shown to give *3-ethyl-4,5,6-trimethyloctane*. When numbered in the opposite direction, the locants are also 3, 4, 5, and 6. In the case of ties, however, choose the direction that gives the lower number to the substituent that appears first in the name. "Ethyl" precedes "methyl" alphabetically.



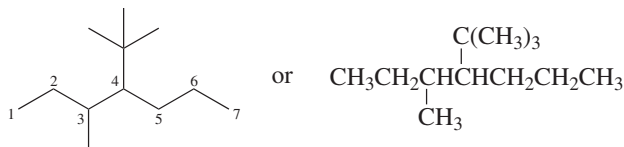
- 2.30 (a) The longest continuous chain contains nine carbon atoms. Begin the problem by writing and numbering the carbon skeleton of nonane.



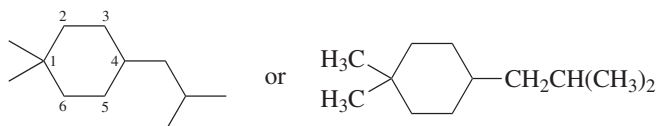
Now add two methyl groups (one to C-2 and the other to C-3) and an isopropyl group (to C-6) to give a structural formula for 6-isopropyl-2,3-dimethylnonane.



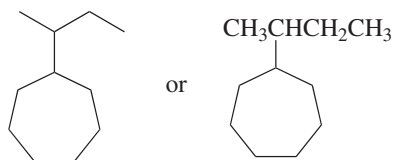
- (b) To the carbon skeleton of heptane (seven carbons) add a *tert*-butyl group to C-4 and a methyl group to C-3 to give *4-tert-butyl-3-methylheptane*.



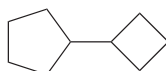
- (c) An isobutyl group is $\text{—CH}_2\text{CH}(\text{CH}_3)_2$. The structure of 4-isobutyl-1,1-dimethylcyclohexane is as shown.



- (d) A *sec*-butyl group is $\text{CH}_3\text{CHCH}_2\text{CH}_3$. *sec*-Butylcycloheptane has a *sec*-butyl group on a seven-membered ring.



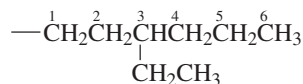
- (e) A cyclobutyl group is a substituent on a five-membered ring in cyclobutylcyclopentane.



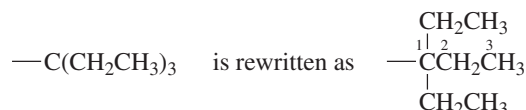
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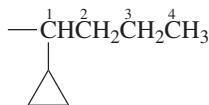
- 2.31 (a) The group $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2-$ is an unbranched alkyl group with 12 carbons. It is a *dodecyl group*. The carbon at the point of attachment is directly attached to only one other carbon. It is a primary alkyl group.
- (b) The longest continuous chain from the point of attachment is six carbons; it is a hexyl group bearing an ethyl substituent at C-3. The group is a *3-ethylhexyl group*. It is a primary alkyl group.



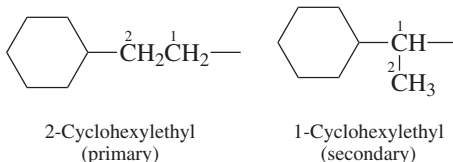
- (c) By writing the structural formula of this alkyl group in more detail, we see that the longest continuous chain from the point of attachment contains three carbons. It is a *1,1-diethylpropyl group*. Because the carbon at the point of attachment is directly bonded to three other carbons, it is a tertiary alkyl group.



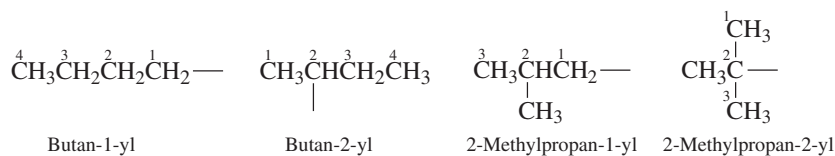
- (d) This group contains four carbons in its longest continuous chain. It is named as a butyl group with a cyclopropyl substituent at C-1. It is a *1-cyclopropylbutyl group* and is a secondary alkyl group.



- (e, f) A two-carbon group that bears a cyclohexyl substituent is a *cyclohexylethyl group*. Number from the potential point of attachment when assigning a locant to the cyclohexyl group.

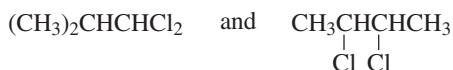


- 2.32 The C_4H_9 alkyl groups are named according to the 2004 IUPAC recommendations as follows:



- 2.33 (a) Methylene groups are $\text{---CH}_2\text{---}$. $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ is therefore the $\text{C}_4\text{H}_8\text{Cl}_2$ isomer in which all the carbons belong to methylene groups.

- (b) The $\text{C}_4\text{H}_8\text{Cl}_2$ isomers that lack methylene groups are



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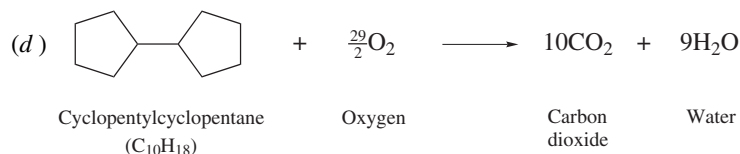
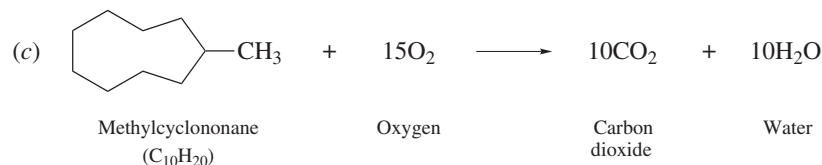
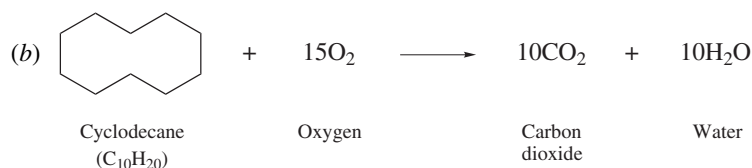
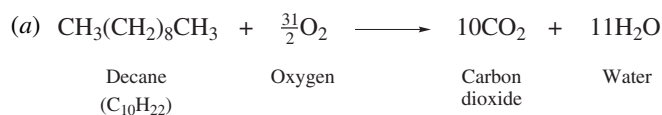
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- 2.34 Because it is an alkane, the sex attractant of the tiger moth has a molecular formula of C_nH_{2n+2} . The number of carbons and hydrogens may be calculated from its molecular weight.

$$\begin{aligned} (\text{Atomic weight of carbon})n + (\text{atomic weight of hydrogen})(2n + 2) &= 254 \\ 12n + 1(2n + 2) &= 254 \\ 14n &= 252 \\ n &= 18 \end{aligned}$$

The molecular formula of the alkane is $C_{18}H_{38}$. In the problem, the sex attractant is stated as a 2-methyl-branched alkane. It is therefore 2-methylheptadecane, $(CH_3)_2CHCH_2(CH_2)_{13}CH_3$.

- 2.35 When any hydrocarbon is burned in air, the products of combustion are carbon dioxide and water.



- 2.36 To determine the quantity of heat evolved per unit mass of material, divide the heat of combustion by the molecular weight.

Methane Heat of combustion = 890 kJ/mol (212.8 kcal/mol)
Molecular weight = 16.0 g/mol
Heat evolved per gram = 55.6 kJ/g (13.3 kcal/g)

Butane Heat of combustion = 2876 kJ/mol (687.4 kcal/mol)
Molecular weight = 58.0 g/mol
Heat evolved per gram = 49.6 kJ/g (11.8 kcal/g)

When equal masses of methane and butane are compared, methane evolves more heat when it is burned. Equal volumes of gases contain an equal number of moles, so that when equal volumes of methane and butane are compared, the one with the greater heat of combustion in kilojoules (or kilocalories) per mole gives off more heat. Butane evolves more heat when it is burned than does an equal volume of methane.

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2.37 When comparing heats of combustion of alkanes, two factors are important:

1. The heats of combustion of alkanes increase as the number of carbon atoms increases.
 2. An unbranched alkane has a greater heat of combustion than a branched isomer.
- (a) In the group hexane, heptane, and octane, three unbranched alkanes are being compared. Octane (C_8H_{18}) has the most carbons and has the greatest heat of combustion. Hexane (C_6H_{14}) has the fewest carbons and the lowest heat of combustion. The measured values in this group are as follows:

Hexane	Heat of combustion 4163 kJ/mol (995.0 kcal/mol)
Heptane	Heat of combustion 4817 kJ/mol (1151.3 kcal/mol)
Octane	Heat of combustion 5471 kJ/mol (1307.5 kcal/mol)

- (b) 2-Methylpropane has fewer carbons than either pentane or 2-methylbutane and so is the member of the group with the lowest heat of combustion. 2-Methylbutane is a 2-methyl-branched isomer of pentane and so has a lower heat of combustion. Pentane has the highest heat of combustion among these compounds.

2-Methylpropane	$(CH_3)_3CH$	Heat of combustion 2868 kJ/mol (685.4 kcal/mol)
2-Methylbutane	$(CH_3)_2CHCH_2CH_3$	Heat of combustion 3529 kJ/mol (843.4 kcal/mol)
Pentane	$CH_3CH_2CH_2CH_2CH_3$	Heat of combustion 3536 kJ/mol (845.3 kcal/mol)

- (c) 2-Methylbutane and 2,2-dimethylpropane each have fewer carbons than 2-methylpentane, which therefore has the greatest heat of combustion. 2,2-Dimethylpropane is more highly branched than 2-methylbutane; 2,2-dimethylpropane has the lowest heat of combustion.

2,2-Dimethylpropane	$(CH_3)_4C$	Heat of combustion 3514 kJ/mol (839.9 kcal/mol)
2-Methylbutane	$(CH_3)_2CHCH_2CH_3$	Heat of combustion 3529 kJ/mol (843.4 kcal/mol)
2-Methylpentane	$CH_3CH_2CH_2CH_2CH_3$	Heat of combustion 4157 kJ/mol (993.6 kcal/mol)

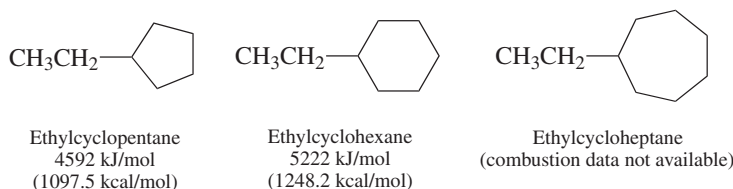
- (d) Chain branching has a small effect on heat of combustion; the number of carbons has a much larger effect. The alkane with the most carbons in this group is 3,3-dimethylpentane; it has the greatest heat of combustion. Pentane has the fewest carbons in this group and has the smallest heat of combustion.

Pentane	$CH_3CH_2CH_2CH_2CH_3$	Heat of combustion 3527 kJ/mol (845.3 kcal/mol)
3-Methylpentane	$(CH_3CH_2)_2CHCH_3$	Heat of combustion 4159 kJ/mol (994.1 kcal/mol)
3,3-Dimethylpentane	$(CH_3CH_2)_2C(CH_3)_2$	Heat of combustion 4804 kJ/mol (1148.3 kcal/mol)

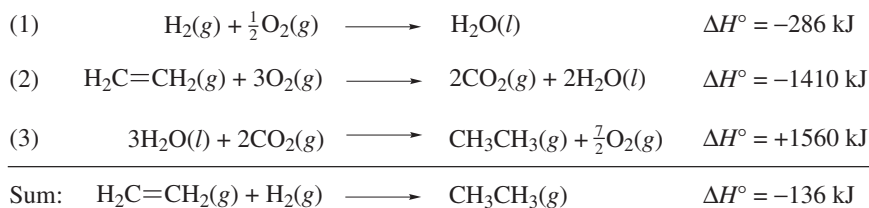
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- (e) In this series, the heat of combustion increases with increasing number of carbons. Ethylcyclopentane has the lowest heat of combustion; ethylcycloheptane has the greatest.

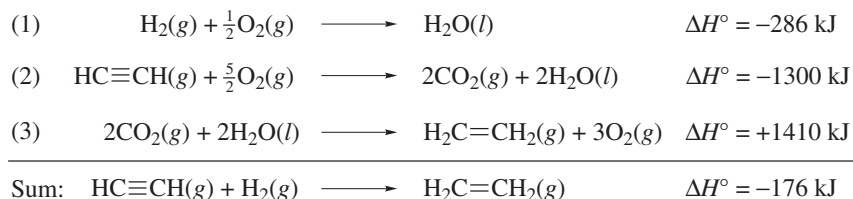


- 2.38 (a) The equation for the hydrogenation of ethylene is given by the sum of the following three reactions:



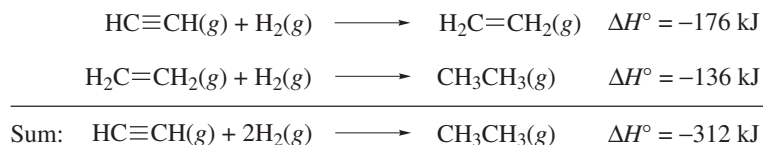
Equations (1) and (2) are the combustion of hydrogen and ethylene, respectively, and ΔH° values for these reactions are given in the statement of the problem. Equation (3) is the reverse of the combustion of ethane, and its value of ΔH° is the negative of the heat of combustion of ethane.

- (b) Again, we need to collect equations of reactions for which the ΔH° values are known.



Equations (1) and (2) are the combustion of hydrogen and acetylene, respectively. Equation (3) is the reverse of the combustion of ethylene, and its value of ΔH° is the negative of the heat of combustion of ethylene.

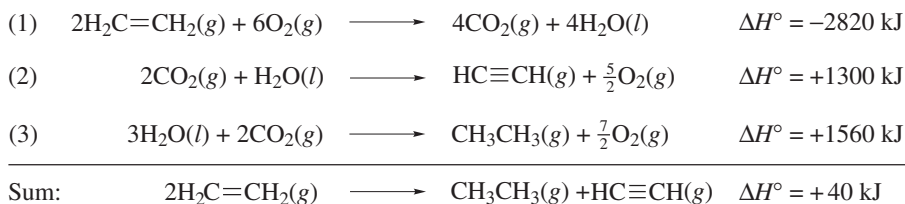
The value of ΔH° for the hydrogenation of acetylene to ethane is equal to the sum of the two reactions just calculated:



- (c) We use the equations for the combustion of ethane, ethylene, and acetylene as shown.

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The value of ΔH° for reaction (1) is twice that for the combustion of ethylene because 2 moles of ethylene are involved.

2.39 Greater stability is *not* the reason branched isomers have lower boiling points. Branching affects boiling point because of the effect on a molecule's shape. A branched isomer is more spherical and has a smaller surface than an unbranched isomer. The smaller surface area results in fewer induced-dipole/induced-dipole intermolecular attractions and, thus, a lower boiling point.

Branched isomers are more stable because of stronger intramolecular van der Waals forces. Although the trends in boiling point and stability are parallel, there is not a cause and effect relationship between them. One trend is not the reason for the other.

2.40 Branched alkanes actually give off less heat, not more, on combustion. Branched isomers of an alkane are more stable than unbranched ones. A compound that is more stable has a lower heat of combustion and will give off less heat than a less stable isomer.

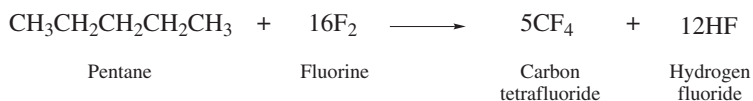
2.41 (a) In the reaction



bonds between carbon and an atom more electronegative than itself (chlorine) are replaced by bonds between carbon and an atom less electronegative than itself (silicon). Carbon is reduced; silicon is oxidized.

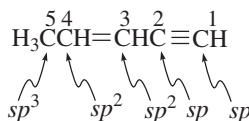
(b) Silicon has a tetrahedral shape in $(\text{CH}_3)_2\text{SiCl}_2$. This shape is best described by the sp^3 -hybridization bonding model. Silicon is in the third row of the periodic table so the principal quantum number, n , equals 3.

2.42 (a) The reaction between pentane and fluorine can be described by the equation



(b) Each carbon of pentane becomes bonded to four fluorines in the reaction shown. Fluorine is more electronegative than carbon, and each carbon atom has become oxidized.

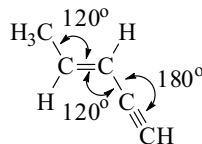
2.43 Carbon-1 is bonded to two atoms: one hydrogen and one carbon (C-2). It also has two π bonds to carbon-2. Carbon-2 is similarly bonded to two atoms: C-1 and C-3. It has two π bonds to carbon-1. Carbon-3 is bonded to three atoms: two carbons (C-2 and C-4) and one hydrogen. It has one π bond to carbon-4. Carbon-4 is similarly bonded to three atoms: two carbons (C-3 and C-5) and one hydrogen. It has one π bond to carbon-3. Carbon-5 is bonded to four atoms: three hydrogens and one carbon (C-4). It does not have any π bonds.



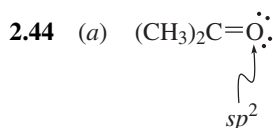
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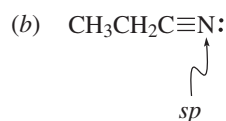
Drawing each hybrid carbon showing all of the C–C–C bonds gives the following structure.



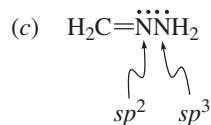
The sp^2 -hybridized carbons have a trigonal planar geometry; sp -hybridized carbons have a linear geometry. Note that all of these atoms (with the exception of some hydrogen atoms on the methyl (CH_3) substituent) are in the plane of the paper.



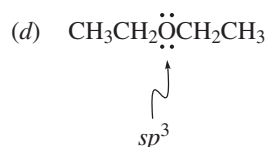
One π bond to oxygen indicates sp^2 -hybridization.



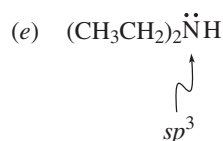
Two π bonds to nitrogen: sp -hybridization.



For the left nitrogen, one π bond indicates sp^2 -hybridization. The nitrogen on the right has no π bonds; thus, it must be sp^3 -hybridized.



The oxygen atom has no π bonds: sp^3 -hybridization.

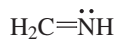


The nitrogen has no π bonds: sp^3 -hybridization.

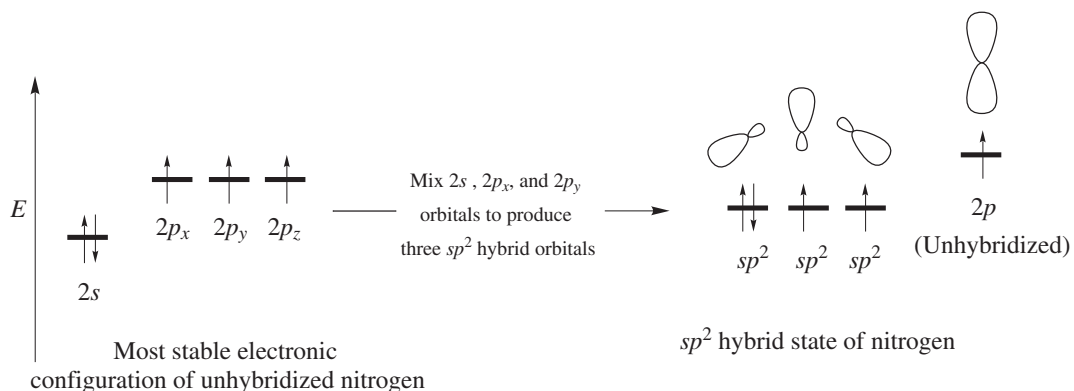
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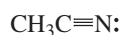
2.45



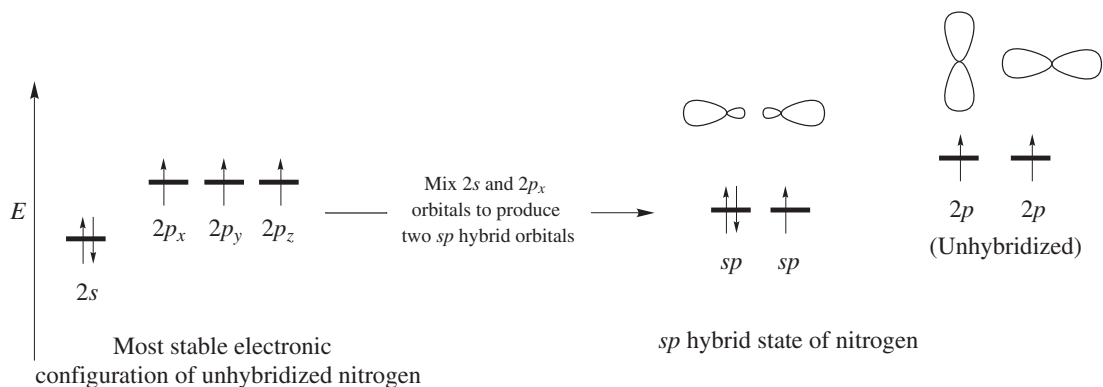
The nitrogen has one π bond to carbon, so it is sp^2 -hybridized.



The three sp^2 hybrid orbitals are in the same plane, and the large lobes are oriented at 120° bond angles to each other. The $2p$ orbital is oriented perpendicular to the plane of the sp^2 hybrid orbitals.



The nitrogen has two π bonds to carbon, so it is sp -hybridized.



The large lobes of the two sp hybrid orbitals are oriented at 180° angles to each other. The $2p$ orbitals are oriented at 90° to each other and are in the same plane. The sp hybrid orbitals are aligned perpendicular to the unhybridized $2p$ orbitals.

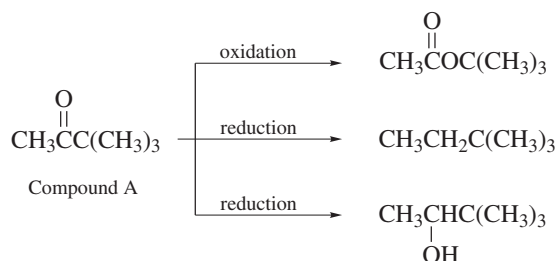
2.46 Two atoms appear in their elemental state: Na on the left and H_2 on the right. The oxidation state of an atom in its elemental state is 0. Assign an oxidation state of +1 to the hydrogen in the OH group of $\text{CH}_3\text{CH}_2\text{OH}$. H goes from +1 on the left to 0 on the right; it is reduced. Na goes from 0 on the left to +1 on the right; it is oxidized.



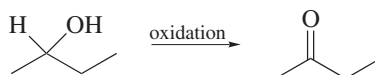
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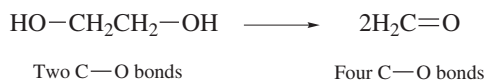
- 2.47 (a, b) An oxidizing agent is required when the reaction to be carried out is an oxidation. Carbon is oxidized when the oxygen content of the molecule has increased, as in the top reaction. A reducing agent brings about a reduction. Reduction occurs when the hydrogen content of the molecule increases or the oxygen content (or bonds to oxygen) decreases, or both. The second and third reactions are reductions.



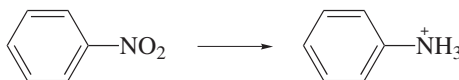
- 2.48 (a) The hydrogen content increases in going from $\text{CH}_3\text{C}\equiv\text{CH}$ to $\text{CH}_3\text{CH}=\text{CH}_2$. The organic compound $\text{CH}_3\text{C}\equiv\text{CH}$ is *reduced*.
- (b) *Oxidation* occurs because a C—O bond has replaced a C—H bond in going from starting material to product.



- (c) There are two carbon–oxygen bonds in the starting material and four carbon–oxygen bonds in the products. *Oxidation* occurs.

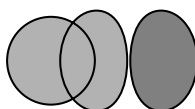


- (d) Although the oxidation state of carbon is unchanged in the process



overall, *reduction* of the organic compound has occurred. Its hydrogen content has increased and its oxygen content has decreased. Nitrogen is reduced.

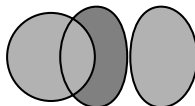
- 2.49 A bonding interaction exists when two orbitals overlap “in phase” with each other, that is, when the algebraic signs of their wave functions are the same in the region of overlap. The following orbital is a bonding orbital. It involves overlap of an *s* orbital with the lobe of a *p* orbital of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



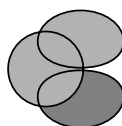
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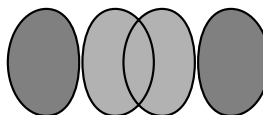
On the other hand, the overlap of an s orbital with the lobe of a p orbital of opposite sign is antibonding.



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.



- 2.50 The end-to-end overlap of two p orbitals corresponds to a σ bond as the overlap is symmetrical along the internuclear axis. The side-to-side overlap of two parallel p orbitals gives rise to a bond.

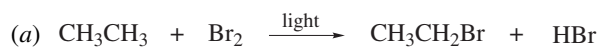


ANSWERS TO INTERPRETIVE PROBLEMS

2.51 C; 2.52 B; 2.53 C; 2.54 C

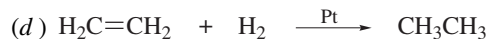
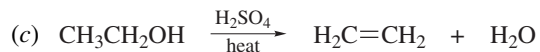
SELF-TEST

- Write the structure of each of the four-carbon alkyl groups. Give the common name and the systematic name for each.
- How many σ bonds are present in each of the following?
 - Nonane
 - Cyclononane
- Classify each of the following reactions according to whether the organic substrate is oxidized, reduced, or neither.

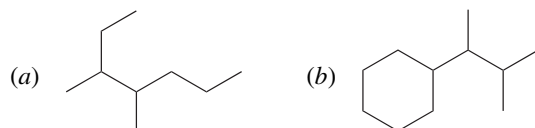


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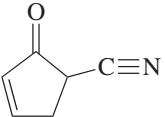
4. (a) Write a structural formula for 3-isopropyl-2,4-dimethylpentane.
 (b) How many methyl groups are there in this compound? How many isopropyl groups?
5. Give the IUPAC name for each of the following substances:



6. The compounds in each part of the previous question contain _____ primary carbon(s), _____ secondary carbon(s), and _____ tertiary carbon(s).
7. Using the method outlined in text Section 2.13, give an IUPAC name for each of the following alkyl groups, and classify each one as primary, secondary, or tertiary.
- (a) $(\text{CH}_3)_2\text{CHCH}_2\text{CHCH}_3$ (b) $(\text{CH}_3\text{CH}_2)_3\text{C}-$ (c) $(\text{CH}_3\text{CH}_2)_3\text{CCH}_2-$
8. Write a balanced chemical equation for the complete combustion of 2,3-dimethylpentane.
9. Write structural formulas and give the names of all the constitutional isomers of C_5H_{10} that contain a ring.
10. Each of the following names is incorrect. Give the correct name for each compound.
- (a) 2,3-Diethylhexane (c) 2,3-Dimethyl-3-propylpentane
- (b) (2-Ethylpropyl)cyclohexane
11. Which C_8H_{18} isomer
- (a) Has the highest boiling point?
 (b) Has the lowest boiling point?
 (c) Has the greatest number of tertiary carbons?
 (d) Has only primary and quaternary carbons?
12. Draw the constitutional isomers of C_7H_{16} that have five carbons in their longest chain, and give an IUPAC name for each of them.

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13. Given the following heats of combustion (in kilojoules per mole) for the homologous series of unbranched alkanes: hexane (4163), heptane (4817), octane (5471), nonane (6125), estimate the heat of combustion (in kilojoules per mole) for **pentadecane**.
14. How many σ and π bonds are present in each of the following?
- (a) $\text{CH}_3\text{CH}=\text{CHCH}_3$
- (c) 
- (b) $\text{HC}\equiv\text{CCH}_2\text{CH}_3$
- (d) 
15. Give the hybridization of each carbon atom in the preceding problem.