Chem 226 — Problem Set #1 —
"Fundamentals of Organic Chemistry," 4th edition, John McMurry.

Chapter 1

27. How many valence electrons does each of the following atoms have?
(a) oxygen, (b) magnesium, (c) fluorine

(a) Oxygen is atomic number 8; so, neutral oxygen has 8 protons and 8 electrons. The first two electrons fill shell #1, which is the lowest energy shell and can accommodate, at most, two electrons. This leaves 6 electrons. Shell #2 can accommodate 8 electrons, so the 6 remaining ones wind up in that shell. Shell #2 is the valence shell and it contains 6 valence electrons.

(b) Magnesium is atomic number 12. We remember that shell #1 can accommodate 2 electrons, shell #2 can accommodate 8 and shell #3 can accommodate 18. We also remember that the first shell will fill before the second shell is used and that will fill before the third shell is used. So the pattern here is: Shell #1:Shell #2:Shell #3 = 2:8:2. Thus there are 2 valence electrons in the valence shell (shell #3).

(c) Fluorine is atomic number 9. The pattern here is Shell #1:Shell #2 = 2:7. So there are 7 valence electrons in shell #2.

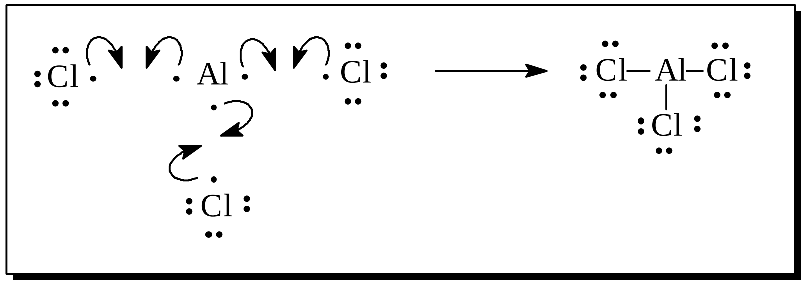
28. Give the ground-state electron configuration of the following elements. For example, carbon is $1s^2 2s^2 2p^2$.
(a) lithium, (b) sodium, (c) aluminum, (d) sulfur

To answer this question we need to know the filling (energy) order of the orbitals and Hund's rule. The order of orbitals in terms of increasing energy is 1s 2s 2p 3s 3p 4s 3d 4p 5s etc. Hund's rule says that in the case of degenerate (equal energy) orbitals the electrons don't pair up until each degenerate orbital of the set has one electron.

(a) lithium, atomic # 3: $1s^2 2s^1$, (b) sodium, atomic # 11: $1s^2 2s^2 2p^6 3s^1$,
(c) aluminum, atomic # 13: $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^0 3p_z^0$ *or* $1s^2 2s^2 2p^6 3s^2 3p^1$
(d) sulfur, atomic # 16: $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$ *or* $1s^2 2s^2 2p^6 3s^2 3p^4$

29. What are the likely formulas of the following molecules?
(a) $AlCl_?$, (b) $CF_2Cl_?$, (c) $NI_?$

(a) Aluminum has three valence electrons that it can donate or share. Chlorine has seven valence electrons. So, chlorine can accept one to get an octet or it can share one of its seven with one from another atom to have a total of 8 in its valence shell. Since the electronegativity difference between chlorine (3.0) and aluminum (1.5) is 1.5 (which is less than 1.7), these atoms will share electrons. Aluminum can share its three valence electrons; each chlorine can share one. So, three chlorines will each share one of aluminum's valence electrons. [Note that while this gives each chlorine an octet of valence electrons, aluminum winds up with only a sextet of electrons. Consequently, aluminum can act as a Lewis acid: it can accept a pair of electrons to obtain a full octet.]



$AlCl_3$ is the answer.

(b) Carbon has 4 valence electrons and fluorine and chlorine each have 7. So, following the reasoning in (a) the carbon needs to share electrons with four halogen (chlorine, fluorine) atoms. Since there are already 2 fluorines present, two chlorines are needed.
$CF_2Cl_2$ is the answer. By the way, this is Freon-12, a chlorofluorocarbon formerly used as an aerosol propellant and as a refrigerant. It's use has been banned in many countries because it destroys the ozone in the stratosphere.

(c) Iodine, like the other halogens has 7 electrons in its valence shell (You can look at the periodic table you received and get this number there.) and each iodine needs one electron to complete its octet. Nitrogen has five valence electrons (and needs three more to complete its octet). Since the electronegativity difference between nitrogen and iodine is less than 1.7, electrons will be shared. So, nitrogen can share three of its five valence electrons with the three iodines, sharing one of its valence electrons with each iodine. In this way each iodine will have an octet since each started with 7 valence electrons and now one of nitrogen's electrons is being shared with each iodine to make an eighth valence electron. Nitrogen started with 5 valence electrons and is sharing three from the iodines, making 8 in its valence shell.
$NI_3$ is the answer. By the way, $NI_3$ is a *very* shock sensitive explosive.

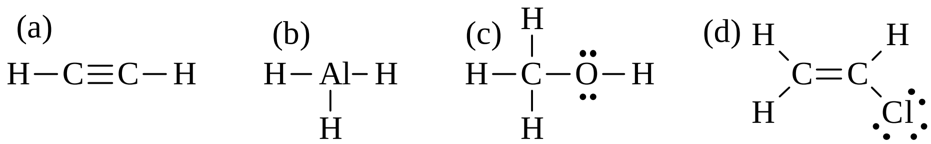
30. Identify the bonds in the following molecules as covalent, polar covalent, or ionic.
(a) $BeF_2$, (b) $SiH_4$, (c) $CBr_4$

For a bond to be ionic, the electronegativity difference between the atoms that are joined should be greater than 1.7. So, if the electronegativity difference is anywhere from 0 to about 1.7, the bond will be covalent. Strictly speaking, if the electronegativity difference is greater than 0, but less than 1.7, the bond will be polar covalent. However, as a practical matter, if the difference is less than 0.5, the bond has little polarity and can be considered nonpolar.

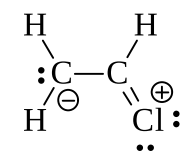
(a) $BeF_2$, $\delta EN = 2.4$, ionic. (b) $SiH_4$, $\delta EN = 0.3$, slightly polar or nonpolar covalent.
(c) $CBr_4$, $\delta EN = 0.3$, slightly polar or nonpolar covalent.

31. Write Lewis electron-dot structures for the following molecules.
(a) H-C≡C-H, (b) $AlH_3$, (c) $CH_2Cl_2$, (d) $H_2C{=}CHCl$

One needs to follow the rules for drawing Lewis structures. The answers are shown below.



It is possible to come up with a legitimate alternative Lewis structure for (d), shown in the box to the right. When one can draw two legitimate Lewis structures for the same compound we say that *resonance* exists. The concept of resonance will be discussed shortly.

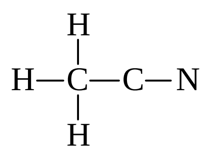


32. Write a Lewis structure for acetonitrile, $CH_3C{\equiv}N$. How many electrons does the nitrogen have in its valence shell? How many are used for bonding and how many are not used for bonding?

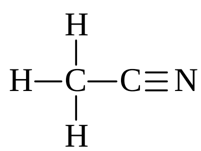
To draw the Lewis structure we start with the skeleton structure shown in the box to the right. Then we add up the number of valence electrons:

2C = 2x4 = 8
3H = 3x1 = 3
1N = 1x5 = <u>5</u>
Total = 16

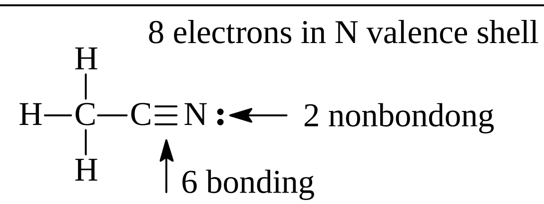
The single bonds in the skeleton structure account for 10 of these, leaving 6 for us to distribute. First we try to make more bonds – in this case we can make 2 more bonds between the N and the C to which it is attached. Now we have distributed 14 of the 16 valence electrons. The only place the remaining 2 will fit is unshared on the N.



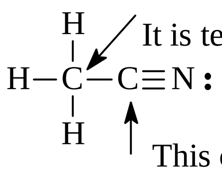
Skeleton structure: single bonds account for 10 of the 16 valence electrons.



Since in the skeleton structure the N has only 2 valence electrons and the C to which it is attached has only four, two more bonds can be accommodated between them. These two bonds comprise 4 electrons, so we have now accounted for 14 of the 16 valence electrons. The only place the remaining two valence electrons can be accommodated is unshared on the N.



33. What is the hybridization of each carbon atom in acetonitrile?



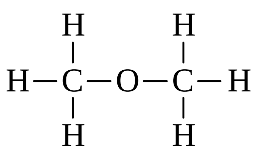
This carbon has 4 electron groups. It is tetrahedral and $sp^3$.

This carbon has 2 electron groups. It is linear and sp.

34. Fill in any unshared electrons that are missing from the following line-bond structures.

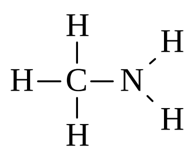
(a) $H_3C-O-CH_3$

Note: This means



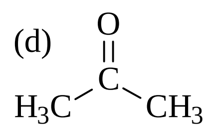
(b) $CH_3NH_2$

Note: This means

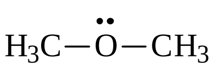


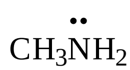
(c) $CH_2Cl_2$

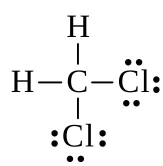
(d)

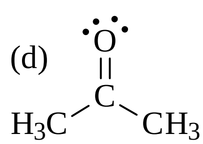


This is really another exercise in drawing Lewis structures. Follow the rules.

(a) 

(b) 

(c) 

(d) 

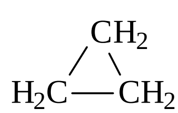
37. Convert the following molecular formulas into line-bond structures.
(a) $C_3H_8$, (b) $C_3H_7Br$ (two), (c) $C_3H_6$ (two), (d) $C_2H_6O$ (two)

(a)
$H_3C-CH_2-CH_3$

(b)
$H_3C-CHBr-CH_3$

$H_3C-CH_2-CH_2Br$

(c)
$H_2C=CH-CH_3$



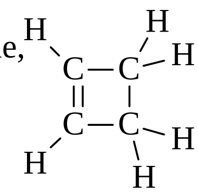
! If you got this one, give yourself a gold star.

(d)
$H_3C-CH_2-OH$

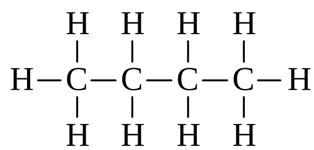
$H_3C-O-CH_3$

38. Indicate the kind of hybridization you expect for each carbon atom in the following molecules.

(a) butane, $CH_3CH_2CH_2CH_3$ (b) 1-butene, $CH_3CH_2CH{=}CH_2$

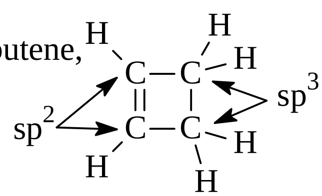
(c) Cyclobutene,  (d) 1-butene-3-yne, $H_2C{=}CH{-}C{\equiv}CH$

At this point in your chemistry career, if you need to examine molecules and they are presented in condensed form you should de-condense them. I have done this for butane so you can see what I mean. Then you need to decide how many electron *groups* surround the atom of interest: 4 means tetrahedral and $sp^3$, 3 means trigonal and $sp^2$, and 2 means linear and sp. [Remember: one *group* of electrons could be an unshared pair of electrons or a bond, whether the bond is single, double or triple.]

(a) butane,  Each carbon is $sp^3$.

(b) 1-butene, $CH_3CH_2CH{=}CH_2$

$sp^3$ $sp^2$

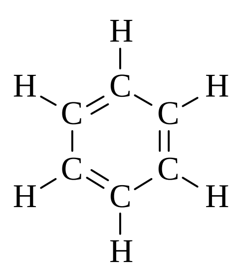
(c) Cyclobutene, 


(d) 1-butene-3-yne, $H_2C{=}CH{-}C{\equiv}CH$

$sp^2$ sp

39. What is the hybridization of each carbon atom in benzene? What shape would you expect benzene to have?

Each carbon has three electron groups around it, so each is trigonal/planar. By planar, we mean that the carbon and each of the three atoms attached to it lie in the same plane. Consequently, in this case, all of the atoms lie in the same plane.



benzene

46. Use the electronegativity table to predict which of the indicated bonds in each of the following sets is more polar.

(a) Cl–CH$_3$ Cl–Cl (b) H–CH$_3$ H–Cl (c) HO–CH$_3$ $(CH_3)_3$Si—CH$_3$

The greater the *difference* in electronegativity between the bonded atoms the greater the polarity of the bond.

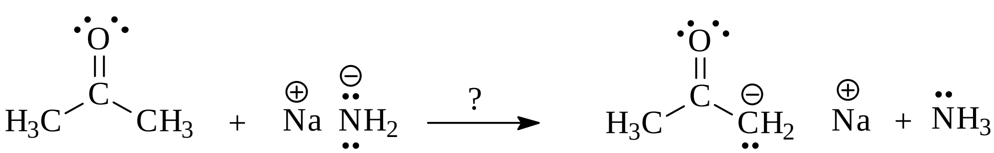
(a) $\boxed{\text{Cl–CH}_3}$ Cl–Cl (b) H–CH$_3$ $\boxed{\text{H–Cl}}$ (c) $\boxed{\text{HO–CH}_3}$ $(CH_3)_3$Si—CH$_3$

47. Indicate the direction of polarity for each bond in problem 46.

The atom that is more electronegative will develop a partial negative charge, while the other atom will develop a partial positive charge.

(a) Cl–CH$_3$ Cl–Cl (b) H–CH$_3$ H–Cl (c) HO–CH$_3$ $(CH_3)_3$Si—CH$_3$

50. Ammonia, H$_2$N-H, has a p$K_a \approx 36$ and acetone has p$K_a \approx 19$. Will the following reaction take place? Explain.



This is an acid/base equilibrium reaction. As such, we expect that the reaction will proceed in both the forward and reverse directions. So the answer to the question is yes. A better question would be, “Will a significant amount of the products that are shown actually form.” To answer this question we need to remember that the weaker acid and weaker base will be favored at equilibrium (the stronger acid and base having won the battle thereby producing the weaker acid and base). Ammonia, $NH_3$, has a $K_a \approx 10^{-36}$; acetone has a $K_a \approx 10^{-19}$. So, acetone is $10^{17}$ times more acidic than ammonia. Consequently, at equilibrium, ammonia will be favored, not acetone.

52. Which of the following substances are likely to behave as Lewis acids and which as Lewis bases?

(a) $AlBr_3$, (b) $CH_3CH_2NH_2$, (c) HF, (d) $CH_3SCH_3$

[Note that these are not full Lewis structures; unshared electrons are not shown.]

Lewis acids are electron pair acceptors. Lewis bases are electron pair donors. So, to be a Lewis acid a compound must be capable of accepting a pair of electrons and to be a Lewis base the compound must be able to donate a pair of electrons. Pretty simple. But before you proceed you must convert the molecule above into Lewis structures showing all unshared electrons. Having done that we can proceed.

(a) Aluminum's valence shell has 6 electrons, two from each of the bonds to the bromines. The aluminum does not have an unshared pair of electrons. But it would like to, to complete an octet. Therefore, the Al will act as a Lewis acid. On the other hand, the bromines each have three unshared pairs of electrons that they might donate, making them Lewis bases. It turns out (Chemistry is very much an experimental science.) that aluminum bromide is a Lewis acid; the aluminum accepts a pair of electrons. We might note in passing that halogens that are part of a molecule do not usually function as electron pair donors.

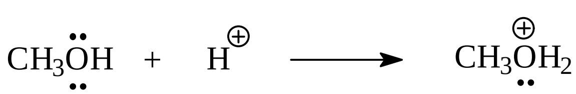
(b) Nitrogen carries an unshared pair of electrons which can be donated to another species. This is a Lewis base. Perhaps it is worth noting that hydrogens attached to carbon or nitrogen, as is the case in this compound, are usually not appreciably acidic. On the other hand, an unshared pair of electrons on an $sp^3$ nitrogen is usually basic.

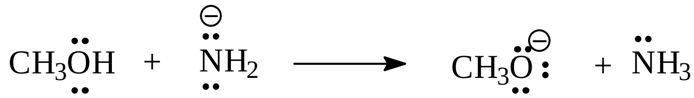
(c) This is a Bronsted-Lowry acid, being a proton donor. It is also a Lewis acid because the hydrogen can accept a pair of electrons. <u>In doing so it will depart from the fluorine leaving behind the pair of electrons that it had shared with the fluorine in the H-F bond.</u> The fluorine becomes a fluoride ion, $F^-$.

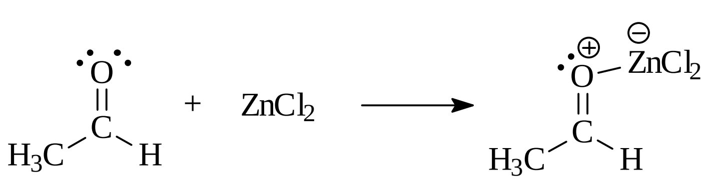
It is probably worth commenting on the underlined sentence in the preceding paragraph. When we say a Lewis acid is an electron pair acceptor we do not necessarily mean that an atom in the Lewis acid simply accepts the incoming pair of electrons and end of story. That may be the case, but very often the atom that accepts the incoming pair of electrons will have to release another pair that it already holds – most commonly, this means releasing a pair of electrons that form a bond to the atom that is accepting the new pair of electrons. That is the case here. The hydrogen would accept a pair of electrons from an electron pair donor (Lewis base) but at the same time it must release the electrons in the H-F bond.

(d) The sulfur holds two pairs of unshared electrons and can function as a Lewis base.

54. Identify the acids and bases in the following reactions.

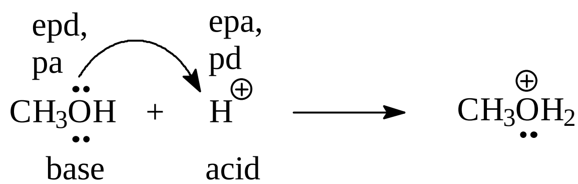
(a) 

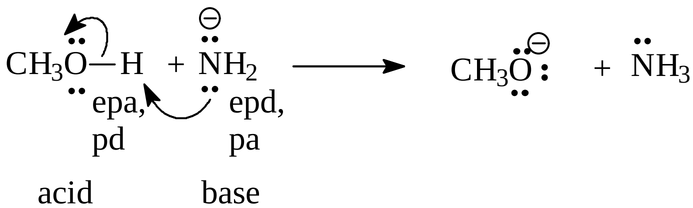
(b) 

(c) 

Bronsted-Lowry: Acids - proton donors.  Bases - proton acceptors.
Lewis:  Acids - electron pair acceptors.  Bases - electron pair donors.

electron pair donor = epd (= Lewis base)
electron pair acceptor = epa (= Lewis acid)
proton donor = pd (= Bronsted-Lowry acid)
proton acceptor = pa (= Bronsted-Lowry base)

(a)



(b)



(c)