CHAPTER 8

BONDING: GENERAL CONCEPTS

Questions

15. a. This diagram represents a polar covalent bond as in HCl. In a polar covalent bond, there is an electron rich region (indicated by the red color) and an electron poor region (indicated by the blue color). In HCl, the more electronegative Cl atom (on the red side of the diagram) has a slightly greater ability to attract the bonding electrons than does H (on the blue side of the diagram), which in turn produces a dipole moment.

    b. This diagram represents an ionic bond as in NaCl. Here, the electronegativity differences between the Na and Cl are so great that the valence electron of sodium is transferred to the chlorine atom. This results in the formation of a cation, an anion, and an ionic bond.

    c. This diagram represents a pure covalent bond as in H_2. Both atoms attract the bonding electrons equally, so there is no bond dipole formed. This is illustrated in the electrostatic potential diagram as the various red and blue colors are equally distributed about the molecule. The diagram shows no one region that is red nor one region that is blue (there is no specific partial negative end and no specific partial positive end), so the molecule is nonpolar.

16. In F_2 the bonding is pure covalent, with the bonding electrons shared equally between the two fluorine atoms. In HF, there is also a shared pair of bonding electrons, but the shared pair is drawn more closely to the fluorine atom. This is called a polar covalent bond as opposed to the pure covalent bond in F_2.

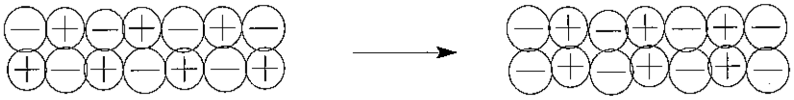
17. Of the compounds listed, P_2O_5 is the only compound containing only covalent bonds. $(NH_4)_2SO_4$, $Ca_3(PO_4)_2$, K_2O, and KCl are all compounds composed of ions, so they exhibit ionic bonding. The polyatomic ions in $(NH_4)_2SO_4$ are NH_4^+ and SO_4^{2-}. Covalent bonds exist between the N and H atoms in NH_4^+ and between the S and O atoms in SO_4^{2-}. Therefore, $(NH_4)_2SO_4$ contains both ionic and covalent bonds. The same is true for $Ca_3(PO_4)_2$. The bonding is ionic between the Ca^{2+} and PO_4^{3-} ions and covalent between the P and O atoms in PO_4^{3-}. Therefore, $(NH_4)_2SO_4$ and $Ca_3(PO_4)_2$ are the compounds with both ionic and covalent bonds.

18. Ionic solids are held together by strong electrostatic forces that are omnidirectional.

    i. For electrical conductivity, charged species must be free to move. In ionic solids, the charged ions are held rigidly in place. Once the forces are disrupted (melting or dissolution), the ions can move about (conduct).

    ii. Melting and boiling disrupts the attractions of the ions for each other. Because these electrostatic forces are strong, it will take a lot of energy (high temperature) to accomplish this.

iii. If we try to bend a piece of material, the ions must slide across each other. For an ionic solid the following might happen:



strong attraction strong repulsion

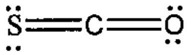
Just as the layers begin to slide, there will be very strong repulsions causing the solid to snap across a fairly clean plane.

iv. Polar molecules are attracted to ions and can break up the lattice.

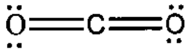
These properties and their correlation to chemical forces will be discussed in detail in Chapters 10 and 11.

19. Electronegativity increases left to right across the periodic table and decreases from top to bottom. Hydrogen has an electronegativity value between B and C in the second row and identical to P in the third row. Going further down the periodic table, H has an electronegativity value between As and Se (row 4) and identical to Te (row 5). It is important to know where hydrogen fits into the electronegativity trend, especially for rows 2 and 3. If you know where H fits into the trend, then you can predict bond dipole directions for nonmetals bonded to hydrogen.

20. Linear structure (180° bond angle)

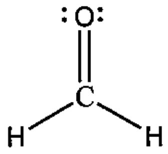


Polar; bond dipoles do not cancel.

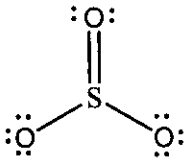


Nonpolar; bond dipoles cancel.

Trigonal planar structure (120° bond angle)



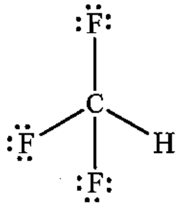
Polar; bond dipoles do not cancel.



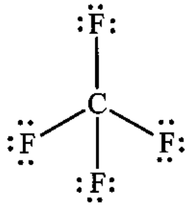
+ 2 other resonance structures

Nonpolar; bond dipoles cancel.

Tetrahedral structure (109.5° bond angles)



Polar; bond dipoles do not cancel.



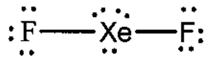
Nonpolar; bond dipoles cancel.

21. For ions, concentrate on the number of protons and the number of electrons present. The species whose nucleus holds the electrons most tightly will be smallest. For example, anions are larger than the neutral atom. The anion has more electrons held by the same number of protons in the nucleus. These electrons will not be held as tightly, resulting in a bigger size for the anion as compared to the neutral atom. For isoelectronic ions, the same number of electrons are held by different numbers of protons in the various ions. The ion with the most protons holds the electrons tightest and is smallest in size.

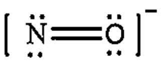
22. Two other factors that must be considered are the ionization energy needed to produce more positively charged ions and the electron affinity needed to produce more negatively charged ions. The favorable lattice energy more than compensates for the unfavorable ionization energy of the metal and for the unfavorable electron affinity of the nonmetal as long as electrons are added to or removed from the valence shell. Once the valence shell is empty, the ionization energy required to remove the next (inner-core) electron is extremely unfavorable; the same is true for electron affinity when an electron is added to a higher *n* shell. These two quantities are so unfavorable after the valence shell is complete that they overshadow the favorable lattice energy, and the higher charged ionic compounds do not form.

23. Fossil fuels contain a lot of carbon and hydrogen atoms. Combustion of fossil fuels (reaction with O_2) produces CO_2 and H_2O. Both these compounds have very strong bonds. Because stronger product bonds are formed than reactant bonds broken, combustion reactions are very exothermic.

24. Statements a and c are true. For statement a, XeF_2 has 22 valence electrons, and it is impossible to satisfy the octet rule for all atoms with this number of electrons. The best Lewis structure is:

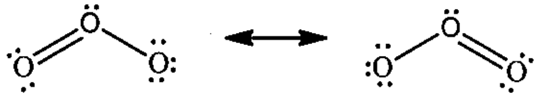


For statement c, NO^+ has 10 valence electrons, whereas NO^- has 12 valence electrons. The Lewis structures are:



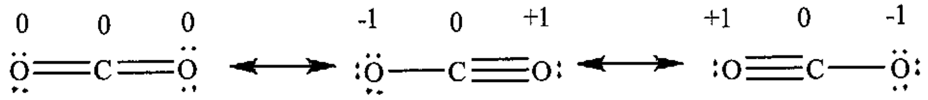
Because a triple bond is stronger than a double bond, NO^+ has a stronger bond.

For statement b, SF_4 has five electron pairs around the sulfur in the best Lewis structure; it is an exception to the octet rule. Because OF_4 has the same number of valence electrons as SF_4, OF_4 would also have to be an exception to the octet rule. However, row 2 elements such as O never have more than 8 electrons around them, so OF_4 does not exist. For statement d, two resonance structures can be drawn for ozone:



When resonance structures can be drawn, the actual bond lengths and strengths are all equal to each other. Even though each Lewis structure implies the two O–O bonds are different, this is not the case in real life. In real life, both of the O–O bonds are equivalent. When resonance structures can be drawn, you can think of the bonding as an average of all of the resonance structures.

25. CO_2, 4 + 2(6) = 16 valence electrons



The formal charges are shown above the atoms in the three Lewis structures. The best Lewis structure for CO_2 from a formal charge standpoint is the first structure having each oxygen double bonded to carbon. This structure has a formal charge of zero on all atoms (which is preferred). The other two resonance structures have nonzero formal charges on the oxygens, making them less reasonable. For CO_2, we usually ignore the last two resonance structures and think of the first structure as the true Lewis structure for CO_2.

26. Only statement c is true. The bond dipoles in CF_4 and KrF_4 are arranged in a manner that they all cancel each other out, making them nonpolar molecules (CF_4 has a tetrahedral molecular structure, whereas KrF_4 has a square planar molecular structure). In SeF_4, the bond dipoles in this see-saw molecule do not cancel each other out, so SeF_4 is polar. For statement a, all the molecules have either a trigonal planar geometry or a trigonal bipyramid geometry, both of which have 120° bond angles. However, $XeCl_2$ has three lone pairs and two bonded chlorine atoms around it. $XeCl_2$ has a linear molecular structure with a 180° bond angle. With three lone pairs, we no longer have a 120° bond angle in $XeCl_2$. For statement b, SO_2 has a V-shaped molecular structure with a bond angle of about 120°. CS_2 is linear with a 180° bond angle, and SCl_2 is V-shaped but with an approximate 109.5° bond angle. The three compounds do not have the same bond angle. For statement d, central atoms adopt a geometry to minimize electron repulsions, not maximize them.

Exercises

Chemical Bonds and Electronegativity

27. Using the periodic table, the general trend for electronegativity is:

(1) Increase as we go from left to right across a period

(2) Decrease as we go down a group

Using these trends, the expected orders are:

a. $C < N < O$ b. $Se < S < Cl$ c. $Sn < Ge < Si$ d. $Tl < Ge < S$

28. a. $Rb < K < Na$ b. $Ga < B < O$ c. $Br < Cl < F$ d. $S < O < F$

29. The most polar bond will have the greatest difference in electronegativity between the two atoms. From positions in the periodic table, we would predict:

a. Ge–F b. P–Cl c. S–F d. Ti–Cl

30. a. Sn–H b. Tl–Br c. Si–O d. O–F

31. The general trends in electronegativity used in Exercises 27 and 29 are only rules of thumb. In this exercise, we use experimental values of electronegativities and can begin to see several exceptions. The order of EN from Figure 8.3 is:

a. C (2.5) < N (3.0) < O (3.5) same as predicted
b. Se (2.4) < S (2.5) < Cl (3.0) same
c. Si = Ge = Sn (1.8) different
d. Tl (1.8) = Ge (1.8) < S (2.5) different

Most polar bonds using actual EN values:

a. Si–F and Ge–F have equal polarity (Ge–F predicted).

b. P–Cl (same as predicted)

c. S–F (same as predicted)

d. Ti–Cl (same as predicted)

32. The order of EN from Figure 8.3 is:

a. Rb (0.8) = K (0.8) < Na (0.9), different

b. Ga (1.6) < B (2.0) < O (3.5), same

c. Br (2.8) < Cl (3.0) < F (4.0), same

d. S (2.5) < O (3.5) < F (4.0), same

Most polar bonds using actual EN values:

a. C–H most polar (Sn–H predicted)

b. Al–Br most polar (Tl–Br predicted).

c. Si–O (same as predicted).

d. Each bond has the same polarity, but the bond dipoles point in opposite directions. Oxygen is the positive end in the O–F bond dipole, and oxygen is the negative end in the O–Cl bond dipole (O–F predicted).

33. Use the electronegativity trend to predict the partial negative end and the partial positive end of the bond dipole (if there is one). To do this, you need to remember that H has electronegativity between B and C and identical to P. Answers b, d, and e are incorrect. For d (Br_2), the bond between two Br atoms will be a pure covalent bond, where there is equal sharing of the bonding electrons, and no dipole moment exists. For b and e, the bond polarities are reversed. In Cl–I, the more electronegative Cl atom will be the partial negative end of the bond dipole, with I having the partial positive end. In O–P, the more electronegative oxygen will be the partial negative end of the bond dipole, with P having the partial positive end. In the following, we used arrows to indicate the bond dipole. The arrow always points to the partial negative end of a bond dipole (which always is the most electronegative atom in the bond).

$$\overset{\longleftarrow}{\mathrm{Cl{-}\!{-}I}} \qquad \overset{\longleftarrow}{\mathrm{O{-}\!{-}P}}$$

34. See Exercise 33 for a discussion on bond dipoles. We will use arrows to indicate the bond dipoles. The arrow always points to the partial negative end of the bond dipole, which will always be to the more electronegative atom. The tail of the arrow indicates the partial positive end of the bond dipole.

a. $\overrightarrow{\mathrm{C{-}O}}$

b. P–H is a pure covalent (nonpolar) bond because P and H have identical electronegativities.

c. $\overrightarrow{\mathrm{H{-}Cl}}$

d. $\overleftarrow{\mathrm{Br{-}Te}}$

e. $\overrightarrow{\mathrm{Se{-}S}}$ The actual electronegativity difference between Se and S is so small that this bond is probably best characterized as a pure covalent bond having no bond dipole.

35. Bonding between a metal and a nonmetal is generally ionic. Bonding between two nonmetals is covalent, and in general, the bonding between two different nonmetals is usually polar covalent. When two different nonmetals have very similar electronegativities, the bonding is pure covalent or just covalent.

a. ionic b. covalent c. polar covalent

d. ionic e. polar covalent f. covalent

36. The possible ionic bonds that can form are between the metal Cs and the nonmetals P, O, and H. These ionic compounds are Cs_3P, Cs_2O, and CsH. The bonding between the various nonmetals will be covalent. P_4, O_2, and H_2 are all pure covalent (or just covalent) with equal sharing of the bonding electrons. P–H will also be a covalent bond because P and H have identical electronegativities. The other possible covalent bonds that can form will all be polar covalent because the nonmetals involved in the bonds all have intermediate differences in electronegativities. The possible polar covalent bonds are P–O and O–H.

Note: The bonding among cesium atoms is called metallic. This type of bonding between metals will be discussed in Chapter 10.

37. Electronegativity values increase from left to right across the periodic table. The order of electronegativities for the atoms from smallest to largest electronegativity will be $H = P < C < N < O < F$. The most polar bond will be F–H since it will have the largest difference in electronegativities, and the least polar bond will be P–H since it will have the smallest difference in electronegativities ($\Delta EN = 0$). The order of the bonds in decreasing polarity will be F–H > O–H > N–H > C–H > P–H.

38. Ionic character is proportional to the difference in electronegativity values between the two elements forming the bond. Using the trend in electronegativity, the order will be:

Br–Br < N–O < C–F < Ca–O < K–F

least ionic character ... most ionic character

Note that Br–Br, N–O, and C–F bonds are all covalent bonds since the elements are all nonmetals. The Ca–O and K–F bonds are ionic, as is generally the case when a metal forms a bond with a nonmetal.

39. A permanent dipole moment exists in a molecule if the molecule has one specific area with a partial negative end (a red end in an electrostatic potential diagram) and a different specific region with a partial positive end (a blue end in an electrostatic potential diagram). If the blue and red colors are equally distributed in the electrostatic potential diagrams, then no permanent dipole exists.

a. Has a permanent dipole. b. Has no permanent dipole.

c. Has no permanent dipole. d. Has a permanent dipole.

e. Has no permanent dipole. f. Has no permanent dipole.

40. a. H_2O; both H_2O and NH_3 have permanent dipole moments in part due to the polar O–H and N–H bonds. But because oxygen is more electronegative than nitrogen, one would expect H_2O to have a slightly greater dipole moment. This diagram has the more intense red color on one end and the more intense blue color at the other end indicating a larger dipole moment.

b. NH_3; this diagram is for a polar molecule, but the colors are not as intense as the diagram in part a. Hence, this diagram is for a molecule which is not as polar as H_2O. Since N is less electronegative than O, NH_3 will not be as polar as H_2O.

c. CH_4; this diagram has no one specific red region and has four blue regions arranged symmetrically about the molecule. This diagram is for a molecule which has no dipole moment. This is only true for CH_4. The C–H bonds are at best, slightly polar because carbon and hydrogen have similar electronegativity values. In addition, the slightly polar C–H bond dipoles are arranged about carbon so that they cancel each other out, making CH_4 a nonpolar molecule. See Example 8.2.

Ions and Ionic Compounds

41. Al^{3+}: $[He]2s^22p^6$; Ba^{2+}: $[Kr]5s^24d^{10}5p^6$; Se^{2-}: $[Ar]4s^23d^{10}4p^6$; I^-: $[Kr]5s^24d^{10}5p^6$

42. Te^{2-}: $[Kr]5s^24d^{10}5p^6$; Cl^-: $[Ne]3s^23p^6$; Sr^{2+}: $[Ar]4s^23d^{10}4p^6$; Li^+: $1s^2$

43. a. Li^+ and N^{3-} are the expected ions. The formula of the compound would be Li_3N (lithium nitride).

b. Ga^{3+} and O^{2-}; Ga_2O_3, gallium(III) oxide or gallium oxide

c. Rb^+ and Cl^-; RbCl, rubidium chloride d. Ba^{2+} and S^{2-}; BaS, barium sulfide

44. a. Al^{3+} and Cl^-; $AlCl_3$, aluminum chloride b. Na^+ and O^{2-}; Na_2O, sodium oxide

c. Sr^{2+} and F^-; SrF_2, strontium fluoride d. Ca^{2+} and S^{2-}; CaS, calcium sulfide

45. a. Mg^{2+}: $1s^22s^22p^6$; K^+: $1s^22s^22p^63s^23p^6$; Al^{3+}: $1s^22s^22p^6$

b. N^{3-}, O^{2-}, and F^-: $1s^22s^22p^6$; Te^{2-}: $[Kr]5s^24d^{10}5p^6$

46. a. Sr^{2+}: $[Ar]4s^23d^{10}4p^6$; Cs^+: $[Kr]5s^24d^{10}5p^6$; In^+: $[Kr]5s^24d^{10}$; Pb^{2+}: $[Xe]6s^24f^{14}5d^{10}$

b. P^{3-} and S^{2-}: $[Ne]3s^23p^6$; Br^-: $[Ar]4s^23d^{10}4p^6$

47. a. Sc^{3+}: [Ar] b. Te^{2-}: [Xe] c. Ce^{4+}: [Xe] and Ti^{4+}: [Ar] d. Ba^{2+}: [Xe]

All these ions have the noble gas electron configuration shown in brackets.

48. a. Cs_2S is composed of Cs^+ and S^{2-}. Cs^+ has the same electron configuration as Xe, and S^{2-} has the same configuration as Ar.

b. SrF_2; Sr^{2+} has the Kr electron configuration, and F^- has the Ne configuration.

c. Ca_3N_2; Ca^{2+} has the Ar electron configuration, and N^{3-} has the Ne configuration.

d. $AlBr_3$; Al^{3+} has the Ne electron configuration, and Br^- has the Kr configuration.

49. a. Na^+ has 10 electrons. F^-, O^{2-}, and N^{3-} are some possible anions also having 10 electrons.

b. Ca^{2+} has 18 electrons. Cl^-, S^{2-}, and P^{3-} also have 18 electrons.

c. Al^{3+} has 10 electrons. F^-, O^{2-}, and N^{3-} also have 10 electrons.

d. Rb^+ has 36 electrons. Br^-, Se^{2-}, and As^{3-} also have 36 electrons.

50. a. Ne has 10 electrons. AlN, MgF_2, and Na_2O are some possible ionic compounds where each ion has 10 electrons.

b. CaS, K_3P, and KCl are some examples where each ion is isoelectronic with Ar; i.e., each ion has 18 electrons.

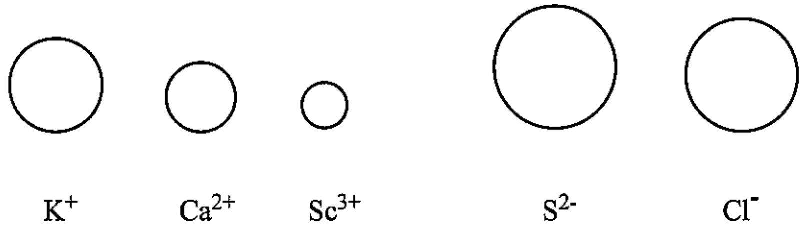
c. Each ion in Sr_3As_2, $SrBr_2$, and Rb_2Se is isoelectronic with Kr.

d. Each ion in BaTe and CsI is isoelectronic with Xe.

51. Neon has 10 electrons; there are many possible ions with 10 electrons. Some are N^{3-}, O^{2-}, F^-, Na^+, Mg^{2+}, and Al^{3+}. In terms of size, the ion with the most protons will hold the electrons the tightest and will be the smallest. The largest ion will be the ion with the fewest protons. The size trend is:

$Al^{3+} < Mg^{2+} < Na^+ < F^- < O^{2-} < N^{3-}$
smallest largest

52. All these ions have 18 e^-; the smallest ion (Sc^{3+}) has the most protons attracting the 18 e^-, and the largest ion has the fewest protons (S^{2-}). The order in terms of increasing size is $Sc^{3+} < Ca^{2+} < K^+ < Cl^- < S^{2-}$. In terms of the atom size indicated in the question:



53. a. $Cu > Cu^+ > Cu^{2+}$ b. $Pt^{2+} > Pd^{2+} > Ni^{2+}$ c. $O^{2-} > O^- > O$

d. $La^{3+} > Eu^{3+} > Gd^{3+} > Yb^{3+}$ e. $Te^{2-} > I^- > Cs^+ > Ba^{2+} > La^{3+}$

For answer a, as electrons are removed from an atom, size decreases. Answers b and d follow the radius trend. For answer c, as electrons are added to an atom, size increases. Answer e follows the trend for an isoelectronic series; i.e., the smallest ion has the most protons.

54. a. $V > V^{2+} > V^{3+} > V^{5+}$ b. $Cs^+ > Rb^+ > K^+ > Na^+$ c. $Te^{2-} > I^- > Cs^+ > Ba^{2+}$

d. $P^{3-} > P^{2-} > P^- > P$ e. $Te^{2-} > Se^{2-} > S^{2-} > O^{2-}$

55. Lattice energy is proportional to $-Q_1Q_2/r$, where Q is the charge of the ions and r is the distance between the centers of the ions. The more negative the lattice energy, the more stable the ionic compound. So greater charged ions as well as smaller sized ions lead to more negative lattice energy values and more stable ionic compounds.

a. NaCl; Na^+ is smaller than K^+.

b. LiF; F^- is smaller than Cl^-.

c. MgO; O^{2-} has a greater charge than OH^-.

d. $Fe(OH)_3$; Fe^{3+} has a greater charge than Fe^{2+}.

e. Na_2O; O^{2-} has a greater charge than Cl^-.

f. MgO; both ions are smaller in MgO.

56. a. LiF; Li^+ is smaller than Cs^+.

b. NaBr; Br^- is smaller than I^-.

c. BaO; O^{2-} has a greater charge than Cl^-.

d. $CaSO_4$; Ca^{2+} has a greater charge than Na^+.

e. K_2O; O^{2-} has a greater charge than F^-.

f. Li_2O; both ions are smaller in Li_2O.

57.

$$\begin{array}{rl}
K(s) \rightarrow K(g) & \Delta H = 90.\text{ kJ (sublimation)} \\
K(g) \rightarrow K^+(g) + e^- & \Delta H = 419\text{ kJ (ionization energy)} \\
1/2\ Cl_2(g) \rightarrow Cl(g) & \Delta H = 239/2\text{ kJ (bond energy)} \\
Cl(g) + e^- \rightarrow Cl^-(g) & \Delta H = -349\text{ kJ (electron affinity)} \\
K^+(g) + Cl^-(g) \rightarrow KCl(s) & \Delta H = -690.\text{ kJ (lattice energy)} \\
\hline
K(s) + 1/2\ Cl_2(g) \rightarrow KCl(s) & \Delta H_f^\circ = -411\text{ kJ/mol}
\end{array}$$

58.

$$\begin{array}{rll}
Mg(s) \rightarrow Mg(g) & \Delta H = 150.\ kJ & \text{(sublimation)} \\
Mg(g) \rightarrow Mg^+(g) + e^- & \Delta H = 735\ kJ & (IE_1) \\
Mg^+(g) \rightarrow Mg^{2+}(g) + e^- & \Delta H = 1445\ kJ & (IE_2) \\
F_2(g) \rightarrow 2\ F(g) & \Delta H = 154\ kJ & (BE) \\
2\ F(g) + 2\ e^- \rightarrow 2\ F^-(g) & \Delta H = 2(-328)\ kJ & (EA) \\
Mg^{2+}(g) + 2\ F^-(g) \rightarrow MgF_2(s) & \Delta H = -2913\ kJ & (LE) \\
\hline
Mg(s) + F_2(g) \rightarrow MgF_2(s) & \Delta H_f^\circ = -1085\ kJ/mol &
\end{array}$$

59. From the data given, it takes less energy to produce $Mg^+(g) + O^-(g)$ than to produce $Mg^{2+}(g) + O^{2-}(g)$. However, the lattice energy for $Mg^{2+}O^{2-}$ will be much more exothermic than that for Mg^+O^- due to the greater charges in $Mg^{2+}O^{2-}$. The favorable lattice energy term dominates, and $Mg^{2+}O^{2-}$ forms.

60.

$$\begin{array}{rl}
Na(g) \rightarrow Na^+(g) + e^- & \Delta H = IE = 495\ kJ\ \text{(Table 7.5)} \\
F(g) + e^- \rightarrow F^-(g) & \Delta H = EA = -327.8\ kJ\ \text{(Table 7.7)} \\
\hline
Na(g) + F(g) \rightarrow Na^+(g) + F^-(g) & \Delta H = 167\ kJ
\end{array}$$

The described process is endothermic. What we haven't accounted for is the extremely favorable lattice energy. Here, the lattice energy is a large negative (exothermic) value, making the overall formation of NaF a favorable exothermic process.

61. Use Figure 8.11 as a template for this problem.

$$\begin{array}{rl}
Li(s) \rightarrow Li(g) & \Delta H_{sub} = ? \\
Li(g) \rightarrow Li^+(g) + e^- & \Delta H = 520.\ kJ \\
1/2\ I_2(g) \rightarrow I(g) & \Delta H = 151/2\ kJ \\
I(g) + e^- \rightarrow I^-(g) & \Delta H = -295\ kJ \\
Li^+(g) + I^-(g) \rightarrow LiI(s) & \Delta H = -753\ kJ \\
\hline
Li(s) + 1/2\ I_2(g) \rightarrow LiI(s) & \Delta H = -292\ kJ
\end{array}$$

$\Delta H_{sub} + 520. + 151/2 - 295 - 753 = -292$, $\Delta H_{sub} = 161\ kJ$

62. Let us look at the complete cycle for Na_2S.

$$\begin{array}{rl}
2\ Na(s) \rightarrow 2\ Na(g) & 2\Delta H_{sub,\ Na} = 2(109)\ kJ \\
2\ Na(g) \rightarrow 2\ Na^+(g) + 2\ e^- & 2IE = 2(495)\ kJ \\
S(s) \rightarrow S(g) & \Delta H_{sub,\ S} = 277\ kJ \\
S(g) + e^- \rightarrow S^-(g) & EA_1 = -200.\ kJ \\
S^-(g) + e^- \rightarrow S^{2-}(g) & EA_2 = ? \\
2\ Na^+(g) + S^{2-}(g) \rightarrow Na_2S(s) & LE = -2203\ kJ \\
\hline
2\ Na(s) + S(s) \rightarrow Na_2S(s) & \Delta H_f^\circ = -365\ kJ
\end{array}$$

$\Delta H_f^\circ = 2\Delta H_{sub,\ Na} + 2IE + \Delta H_{sub,\ S} + EA_1 + EA_2 + LE$, $-365 = -918 + EA_2$, $EA_2 = 553\ kJ$

For each salt: $\Delta H_f^\circ = 2\Delta H_{sub, M} + 2IE + 277 - 200. + LE + EA_2$

K_2S: $-381 = 2(90.) + 2(419) + 277 - 200. - 2052 + EA_2$, $EA_2 = 576$ kJ

Rb_2S: $-361 = 2(82) + 2(409) + 277 - 200. - 1949 + EA_2$, $EA_2 = 529$ kJ

Cs_2S: $-360. = 2(78) + 2(382) + 277 - 200. - 1850. + EA_2$, $EA_2 = 493$ kJ

We get values from 493 to 576 kJ.

The mean value is: $\frac{553 + 576 + 529 + 493}{4} = 538$ kJ. We can represent the results as $EA_2 = 540 \pm 50$ kJ.

63. Ca^{2+} has a greater charge than Na^+, and Se^{2-} is smaller than Te^{2-}. The effect of charge on the lattice energy is greater than the effect of size. We expect the trend from most exothermic lattice energy to least exothermic to be:

$$\underset{(-2862)}{CaSe} > \underset{(-2721)}{CaTe} > \underset{(-2130)}{Na_2Se} > \underset{(-2095)}{Na_2Te}$$

This is what we observe.

64. Lattice energy is proportional to the charge of the cation times the charge of the anion Q_1Q_2.

Compound	Q_1Q_2	Lattice Energy
$FeCl_2$	$(+2)(-1) = -2$	−2631 kJ/mol
$FeCl_3$	$(+3)(-1) = -3$	−5359 kJ/mol
Fe_2O_3	$(+3)(-2) = -6$	−14,744 kJ/mol

Bond Energies

65. a. $H{-}H + Cl{-}Cl \longrightarrow 2\,H{-}Cl$

Bonds broken:

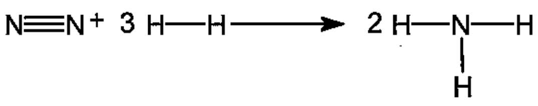
1 H–H (432 kJ/mol)
1 Cl–Cl (239 kJ/mol)

Bonds formed:

2 H–Cl (427 kJ/mol)

$\Delta H = \Sigma D_{broken} - \Sigma D_{formed}$, $\Delta H = 432 \text{ kJ} + 239 \text{ kJ} - 2(427) \text{ kJ} = -183$ kJ

b.



$N{\equiv}N + 3\,H{-}H \longrightarrow 2\,H{-}\underset{\displaystyle H}{\underset{|}{N}}{-}H$

Bonds broken:

1 N≡N (941 kJ/mol)
3 H–H (432 kJ/mol)

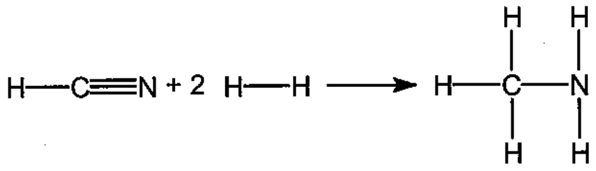
Bonds formed:

6 N–H (391 kJ/mol)

$\Delta H = 941 \text{ kJ} + 3(432) \text{ kJ} - 6(391) \text{ kJ} = -109$ kJ

66. Sometimes some of the bonds remain the same between reactants and products. To save time, only break and form bonds that are involved in the reaction.

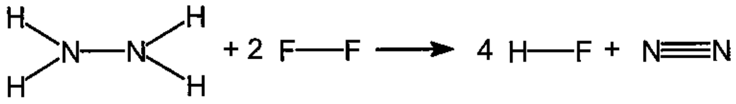
a.



Bonds broken:	Bonds formed:
1 C≡N (891 kJ/mol)	1 C–N (305 kJ/mol)
2 H–H (432 kJ/mol)	2 C–H (413 kJ/mol)
	2 N–H (391 kJ/mol)

$\Delta H = 891 \text{ kJ} + 2(432 \text{ kJ}) - [305 \text{ kJ} + 2(413 \text{ kJ}) + 2(391 \text{ kJ})] = -158 \text{ kJ}$

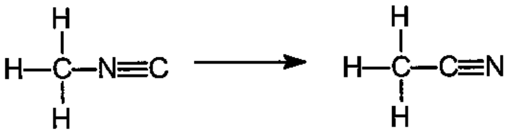
b.



Bonds broken:	Bonds formed:
1 N–N (160. kJ/mol)	4 H–F (565 kJ/mol)
4 N–H (391 kJ/mol)	1 N ≡ N (941 kJ/mol)
2 F–F (154 kJ/mol)	

$\Delta H = 160. \text{ kJ} + 4(391 \text{ kJ}) + 2(154 \text{ kJ}) - [4(565 \text{ kJ}) + 941 \text{ kJ}] = -1169 \text{ kJ}$

67.

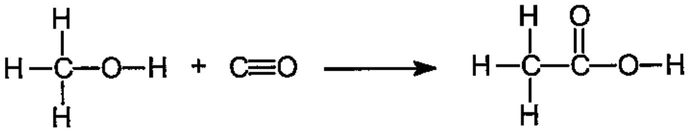


Bonds broken: 1 C–N (305 kJ/mol) Bonds formed: 1 C–C (347 kJ/mol)

$\Delta H = \Sigma D_{\text{broken}} - \Sigma D_{\text{formed}}$, $\Delta H = 305 - 347 = -42 \text{ kJ}$

Note: Sometimes some of the bonds remain the same between reactants and products. To save time, only break and form bonds that are involved in the reaction.

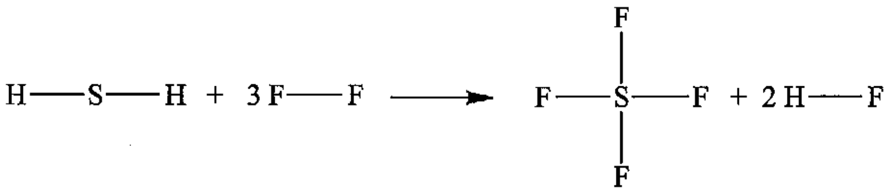
68.



Bonds broken:	Bonds formed:
1 C≡O (1072 kJ/mol)	1 C–C (347 kJ/mol)
1 C–O (358 kJ/mol)	1 C=O (745 kJ/mol)
	1 C–O (358 kJ/mol)

$\Delta H = 1072 + 358 - [347 + 745 + 358] = -20.$ kJ

69.

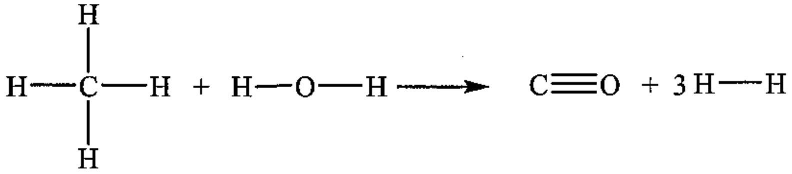


$$\mathrm{H{-}S{-}H} + 3\,\mathrm{F{-}F} \longrightarrow \mathrm{F{-}\underset{\displaystyle F}{\overset{\displaystyle F}{S}}{-}F} + 2\,\mathrm{H{-}F}$$

Bonds broken:	Bonds formed:
2 S–H (347 kJ/mol)	4 S–F (327 kJ/mol)
3 F–F (154 kJ/mol)	2 H–F (565 kJ/mol)

$\Delta H = 2(347) + 3(154) - [4(327) + 2(565)] = -1282$ kJ

70.



$$\mathrm{H{-}\underset{\displaystyle H}{\overset{\displaystyle H}{C}}{-}H} + \mathrm{H{-}O{-}H} \longrightarrow \mathrm{C{\equiv}O} + 3\,\mathrm{H{-}H}$$

Bonds broken:	Bonds formed:
4 C–H (413 kJ/mol)	1 C≡O (1072 kJ/mol)
2 O–H (467 kJ/mol)	3 H–H (432 kJ/mol)

$\Delta H = 4(413) + 2(467) - [1072 + 3(432)] = 218$ kJ

71. H–C≡C–H + 5/2 O=O → 2 O=C=O + H–O–H

Bonds broken:	Bonds formed:
2 C–H (413 kJ/mol)	2 × 2 C=O (799 kJ/mol)
1 C≡C (839 kJ/mol)	2 O–H (467 kJ/mol)
5/2 O=O (495 kJ/mol)	

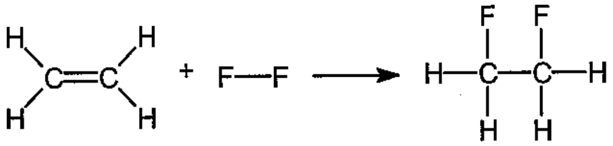
$\Delta H = 2(413\text{ kJ}) + 839\text{ kJ} + 5/2\,(495\text{ kJ}) - [4(799\text{ kJ}) + 2(467\text{ kJ})] = -1228$ kJ

72. $CH_4 + 2\,O{=}O \rightarrow O{=}C{=}O + 2\,H{-}O{-}H$

Bonds broken:	Bonds formed:
4 C–H (413 kJ/mol)	2 C=O (799 kJ/mol)
2 O=O (495 kJ/mol)	2 × 2 O–H (467 kJ/mol)

$\Delta H = 4(413\text{ kJ}) + 2(495\text{ kJ}) - [2(799\text{ kJ}) + 4(467\text{ kJ})] = -824\text{ kJ}$

73.



ΔH = -549 kJ

Bonds broken:	Bonds formed:
1 C=C (614 kJ/mol)	1 C–C (347 kJ/mol)
1 F–F (154 kJ/mol)	2 C–F (D_{CF} = C–F bond energy)

$\Delta H = -549\text{ kJ} = 614\text{ kJ} + 154\text{ kJ} - [347\text{ kJ} + 2D_{CF}]$, $2D_{CF} = 970.$, $D_{CF} = 485\text{ kJ/mol}$

74. Let x = bond energy for A_2, so $2x$ = bond energy for AB.

$\Delta H = -285\text{ kJ} = x + 432\text{ kJ} - [2(2x)]$, $3x = 717$, $x = 239\text{ kJ/mol}$

The bond energy for A_2 is 239 kJ/mol.

75. a. $\Delta H^\circ = 2\Delta H^\circ_{f,\,HCl} = 2\text{ mol}(-92\text{ kJ/mol}) = -184\text{ kJ}$ (–183 kJ from bond energies)

b. $\Delta H^\circ = 2\Delta H^\circ_{f,\,NH_3} = 2\text{ mol}(-46\text{ kJ/mol}) = -92\text{ kJ}$ (–109 kJ from bond energies)

Comparing the values for each reaction, bond energies seem to give a reasonably good estimate for the enthalpy change of a reaction. The estimate is especially good for gas phase reactions.

76. $CH_3OH(g) + CO(g) \rightarrow CH_3COOH(l)$ $\Delta H^\circ = -484\text{ kJ} - [(-201\text{ kJ}) + (-110.5\text{ kJ})] = -173\text{ kJ}$

Using bond energies, ΔH = –20. kJ. For this reaction, bond energies give a much poorer estimate for ΔH as compared with gas-phase reactions (see Exercise 75). The major reason for the large discrepancy is that not all species are gases in Exercise 68. Bond energies do not account for the energy changes that occur when liquids and solids form instead of gases. These energy changes are due to intermolecular forces and will be discussed in Chapter 10.

77. a. Using SF_4 data: $SF_4(g) \rightarrow S(g) + 4\,F(g)$

$$\Delta H^\circ = 4D_{SF} = 278.8 + 4\,(79.0) - (-775) = 1370.\text{ kJ}$$

$$D_{SF} = \frac{1370.\text{ kJ}}{4\text{ mol SF bonds}} = 342.5\text{ kJ/mol} = \text{S–F bond energy}$$

Using SF_6 data: $SF_6(g) \rightarrow S(g) + 6\,F(g)$

$$\Delta H° = 6D_{SF} = 278.8 + 6\,(79.0) - (-1209) = 1962\text{ kJ}$$

$$D_{SF} = \frac{1962\text{ kJ}}{6\text{ mol}} = 327.0\text{ kJ/mol} = \text{S–F bond energy}$$

b. The S–F bond energy in Table 8.4 is 327 kJ/mol. The value in the table was based on the S–F bond in SF_6.

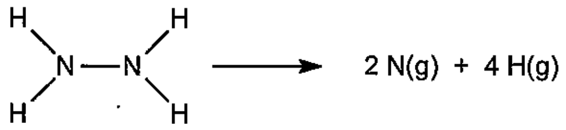
c. S(g) and F(g) are not the most stable forms of the elements at 25°C and 1 atm. The most stable forms are $S_8(s)$ and $F_2(g)$; $\Delta H^\circ_f = 0$ for these two species.

78. $NH_3(g) \rightarrow N(g) + 3\,H(g)$ $\Delta H° = 3D_{NH} = 472.7 + 3(216.0) - (-46.1) = 1166.8\text{ kJ}$

$$D_{NH} = \frac{1166.8\text{ kJ}}{3\text{ mol NH bonds}} = 388.93\text{ kJ/mol} \approx 389\text{ kJ/mol}$$

D_{calc} = 389 kJ/mol as compared with 391 kJ/mol in Table 8.4. There is good agreement.

79.



$\Delta H = D_{N\text{–}N} + 4D_{N\text{–}H} = D_{N\text{–}N} + 4(388.9)$

$$\Delta H° = 2\Delta H^\circ_{f,\,N} + 4\Delta H^\circ_{f,\,H} - \Delta H^\circ_{f,\,N_2H_4} = 2(472.7\text{ kJ}) + 4(216.0\text{ kJ}) - 95.4\text{ kJ}$$

$$\Delta H° = 1714.0\text{ kJ} = D_{N\text{–}N} + 4(388.9)$$

$D_{N\text{–}N}$ = 158.4 kJ/mol (versus 160. kJ/mol in Table 8.4)

80. $1/2\,N_2(g) + 1/2\,O_2(g) \rightarrow NO(g)$ $\Delta H = 90.\text{ kJ}$

Bonds broken:	Bonds formed:
1/2 N≡N (941 kJ/mol)	1 NO (D_{NO} = NO bond energy)
1/2 O=O (495 kJ/mol)	

$\Delta H = 90.\text{ kJ} = 1/2(941) + 1/2(495) - (D_{NO})$, $D_{NO} = 628\text{ kJ/mol}$

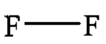
From this data, the calculated NO bond energy is 628 kJ/mol.

Lewis Structures and Resonance

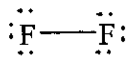
81. Drawing Lewis structures is mostly trial and error. However, the first two steps are always the same. These steps are (1) count the valence electrons available in the molecule/ion, and (2) attach all atoms to each other with single bonds (called the skeletal structure). Unless noted otherwise, the atom listed first is assumed to be the atom in the middle, called the central atom, and all other atoms in the formula are attached to this atom. The most notable exceptions to the rule are formulas that begin with H, e.g., H_2O, H_2CO, etc. Hydrogen can never be a central atom since this would require H to have more than two electrons. In these compounds, the atom listed second is assumed to be the central atom.

After counting valence electrons and drawing the skeletal structure, the rest is trial and error. We place the remaining electrons around the various atoms in an attempt to satisfy the octet rule (or duet rule for H). Keep in mind that practice makes perfect. After practicing, you can (and will) become very adept at drawing Lewis structures.

a. F_2 has 2(7) = 14 valence electrons.

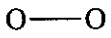


Skeletal structure

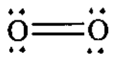


Lewis structure

b. O_2 has 2(6) = 12 valence electrons.

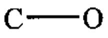


Skeletal structure

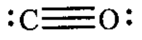


Lewis structure

c. CO has 4 + 6 = 10 valence electrons.

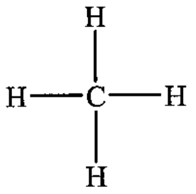


Skeletal structure

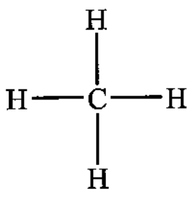


Lewis structure

d. CH_4 has 4 + 4(1) = 8 valence electrons.

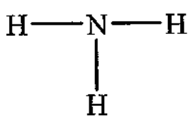


Skeletal structure

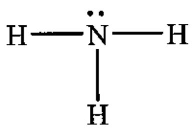


Lewis structure

e. NH_3 has 5 + 3(1) = 8 valence electrons.

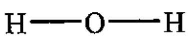


Skeletal structure

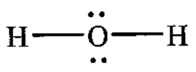


Lewis structure

f. H_2O has 2(1) + 6 = 8 valence electrons.



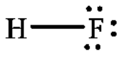
Skeletal structure



Lewis structure

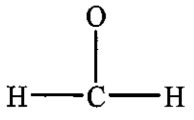
g. HF has 1 + 7 = 8 valence electrons.

Skeletal structure

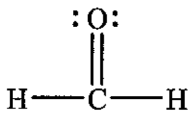


Lewis structure

82. a. H_2CO has 2(1) + 4 + 6 = 12 valence electrons.

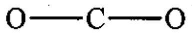


Skeletal structure

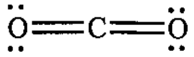


Lewis structure

b. CO_2 has 4 + 2(6) = 16 valence electrons.

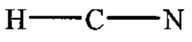


Skeletal structure

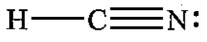


Lewis structure

c. HCN has 1 + 4 + 5 = 10 valence electrons.



Skeletal structure

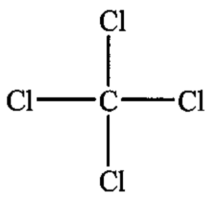


Lewis structure

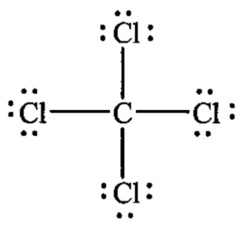
83. Drawing Lewis structures is mostly trial and error. However, the first two steps are always the same. These steps are (1) count the valence electrons available in the molecule/ion, and (2) attach all atoms to each other with single bonds (called the skeletal structure). Unless noted otherwise, the atom listed first is assumed to be the atom in the middle, called the central atom, and all other atoms in the formula are attached to this atom. The most notable exceptions to the rule are formulas that begin with H, e.g., H_2O, H_2CO, etc. Hydrogen can never be a central atom since this would require H to have more than two electrons. In these compounds, the atom listed second is assumed to be the central atom.

After counting valence electrons and drawing the skeletal structure, the rest is trial and error. We place the remaining electrons around the various atoms in an attempt to satisfy the octet rule (or duet rule for H).

a. CCl_4 has 4 + 4(7) = 32 valence electrons.

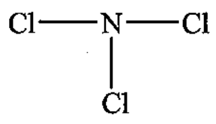


Skeletal structure

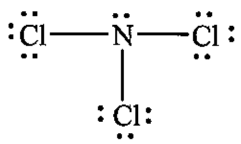


Lewis structure

b. NCl_3 has 5 + 3(7) = 26 valence electrons.

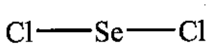


Skeletal structure

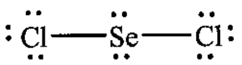


Lewis structure

c. $SeCl_2$ has 6 + 2(7) = 20 valence electrons.

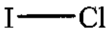


Skeletal structure

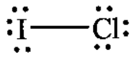


Lewis structure

d. ICl has 7 + 7 = 14 valence electrons.

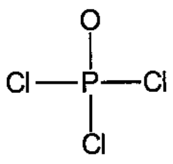


Skeletal structure

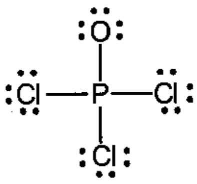


Lewis structure

84. a. $POCl_3$ has 5 + 6 + 3(7) = 32 valence electrons.



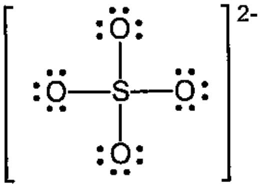
Skeletal structure



Lewis structure

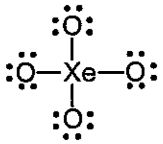
Note: This structure uses all 32 e^- while satisfying the octet rule for all atoms. This is a valid Lewis structure.

SO_4^{2-} has 6 + 4(6) + 2 = 32 valence electrons.

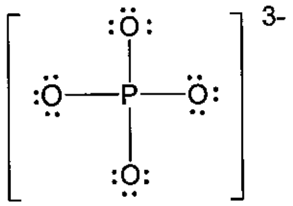


Note: A negatively charged ion will have additional electrons to those that come from the valence shell of the atoms. The magnitude of the negative charge indicates the number of extra electrons to add in.

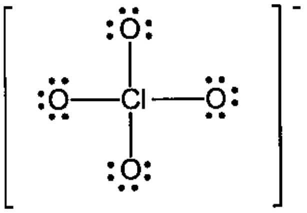
XeO_4, 8 + 4(6) = 32 e^-



PO_4^{3-}, 5 + 4(6) + 3 = 32 e^-

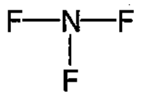


ClO_4^- has 7 + 4(6) + 1 = 32 valence electrons

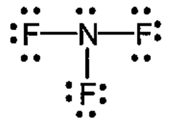


Note: All of these species have the same number of atoms and the same number of valence electrons. They also have the same Lewis structure.

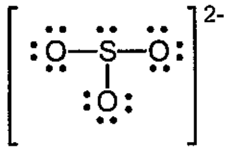
b. NF_3 has 5 + 3(7) = 26 valence electrons. SO_3^{2-}, 6 + 3(6) + 2 = 26 e^-



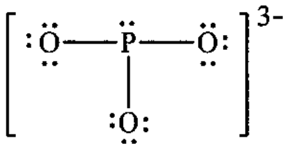
Skeletal structure



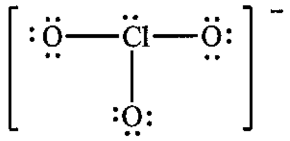
Lewis structure



PO_3^{3-}, 5 + 3(6) + 3 = 26 e^-

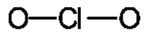


ClO_3^-, 7 + 3(6) + 1 = 26 e^-

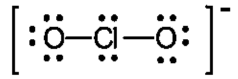


Note: Species with the same number of atoms and valence electrons have similar Lewis structures.

c. ClO_2^- has 7 + 2(6) + 1 = 20 valence

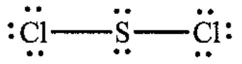


Skeletal structure

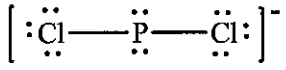


Lewis structure

SCl_2, 6 + 2(7) = 20 e^-



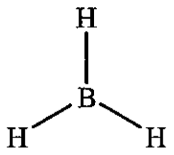
PCl_2^-, 5 + 2(7) + 1 = 20 e^-



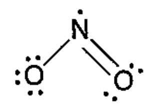
Note: Species with the same number of atoms and valence electrons have similar Lewis structures.

d. Molecules ions that have the same number of valence electrons and the same number of atoms will have similar Lewis structures.

85. BeH_2, 2 + 2(1) = 4 valence electrons BH_3, 3 + 3(1) = 6 valence electrons

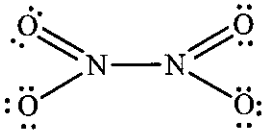


86. a. NO_2, 5 + 2(6) = 17 e^-



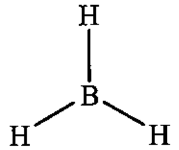
Plus others

N_2O_4, 2(5) + 4(6) = 34 e^-

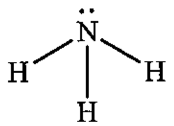


Plus other resonance structures

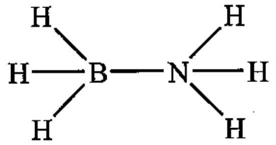
b. BH_3, 3 + 3(1) = 6 e^-



NH_3, 5 + 3(1) = 8 e^-

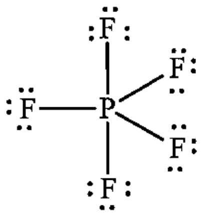


BH_3NH_3, 6 + 8 = 14 e^-

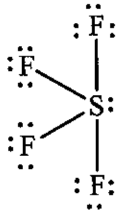


In reaction a, NO_2 has an odd number of electrons, so it is impossible to satisfy the octet rule. By dimerizing to form N_2O_4, the odd electron on two NO_2 molecules can pair up, giving a species whose Lewis structure can satisfy the octet rule. In general, odd-electron species are very reactive. In reaction b, BH_3 is electron-deficient. Boron has only six electrons around it. By forming BH_3NH_3, the boron atom satisfies the octet rule by accepting a lone pair of electrons from NH_3 to form a fourth bond.

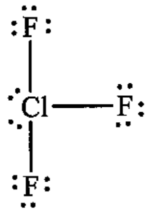
87. PF_5, 5 +5(7) = 40 valence electrons



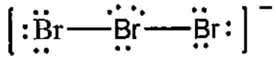
SF_4, 6 + 4(7) = 34 e^-



ClF_3, 7 + 3(7) = 28 e^-



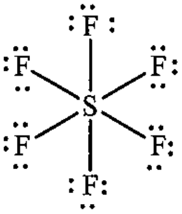
Br_3^-, 3(7) + 1 = 22 e^-



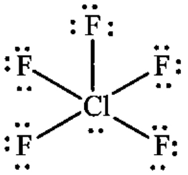
Row 3 and heavier nonmetals can have more than 8 electrons around them when they have to. Row 3 and heavier elements have empty d orbitals that are close in energy to valence s and p orbitals. These empty d orbitals can accept extra electrons.

For example, P in PF_5 has its five valence electrons in the 3s and 3p orbitals. These s and p orbitals have room for three more electrons, and if it has to, P can use the empty 3d orbitals for any electrons above 8.

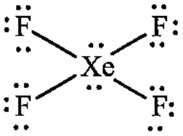
88. SF_6, $6 + 6(7) = 48\ e^-$



ClF_5, $7 + 5(7) = 42\ e^-$

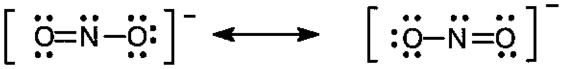


XeF_4, $8 + 4(7) = 36\ e^-$



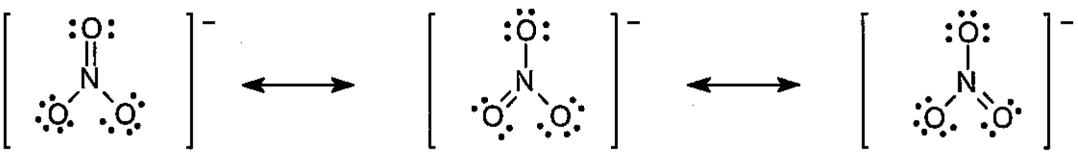
89. a. NO_2^- has $5 + 2(6) + 1 = 18$ valence electrons. The skeletal structure is O–N–O.

To get an octet about the nitrogen and only use 18 e^-, we must form a double bond to one of the oxygen atoms.

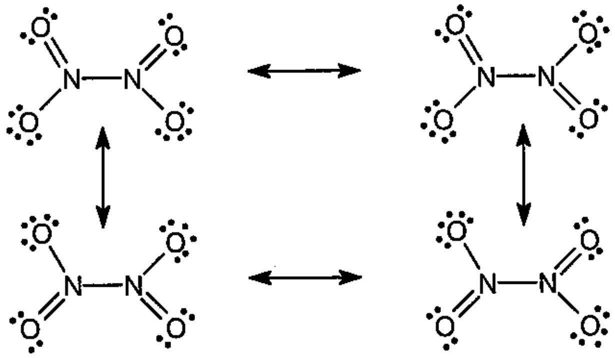


Because there is no reason to have the double bond to a particular oxygen atom, we can draw two resonance structures. Each Lewis structure uses the correct number of electrons and satisfies the octet rule, so each is a valid Lewis structure. Resonance structures occur when you have multiple bonds that can be in various positions. We say the actual structure is an average of these two resonance structures.

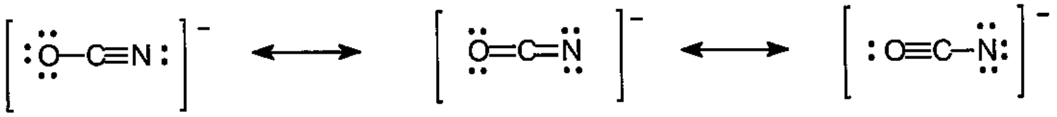
NO_3^- has $5 + 3(6) + 1 = 24$ valence electrons. We can draw three resonance structures for NO_3^-, with the double bond rotating among the three oxygen atoms.



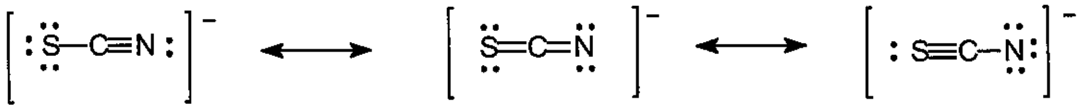
N_2O_4 has 2(5) + 4(6) = 34 valence electrons. We can draw four resonance structures for N_2O_4.



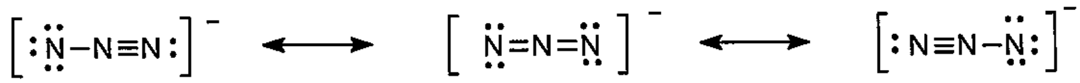
b. OCN^- has 6 + 4 + 5 + 1 = 16 valence electrons. We can draw three resonance structures for OCN^-.



SCN^- has 6 + 4 + 5 + 1 = 16 valence electrons. Three resonance structures can be drawn.



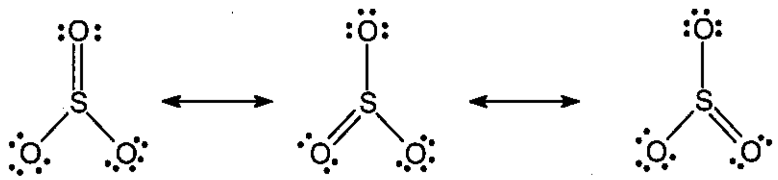
N_3^- has 3(5) + 1 = 16 valence electrons. As with OCN^- and SCN^-, three different resonance structures can be drawn.



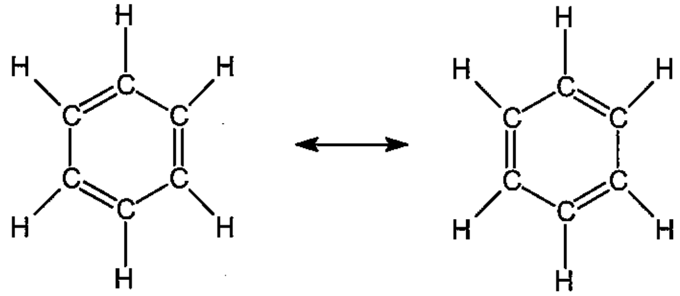
90. Ozone: O_3 has 3(6) = 18 valence electrons.

Sulfur dioxide: SO_2 has 6 + 2(6) = 18 valence electrons.

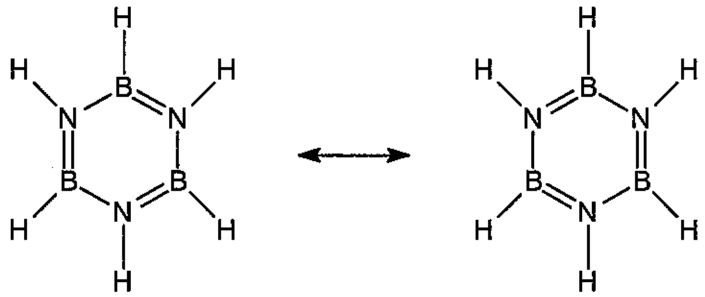
Sulfur trioxide: SO_3 has 6 + 3(6) = 24 valence electrons.



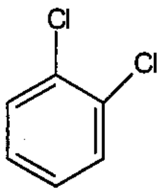
91. Benzene has 6(4) + 6(1) = 30 valence electrons. Two resonance structures can be drawn for benzene. The actual structure of benzene is an average of these two resonance structures; i.e., all carbon-carbon bonds are equivalent with a bond length and bond strength somewhere between a single and a double bond.

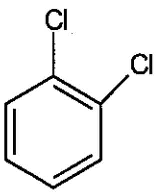


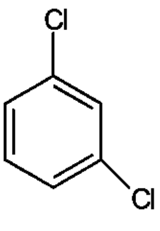
92. Borazine ($B_3N_3H_6$) has 3(3) + 3(5) + 6(1) = 30 valence electrons. The possible resonance structures are similar to those of benzene in Exercise 91.



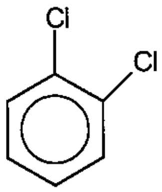
93. We will use a hexagon to represent the six-member carbon ring, and we will omit the four hydrogen atoms and the three lone pairs of electrons on each chlorine. If no resonance existed, we could draw four different molecules:

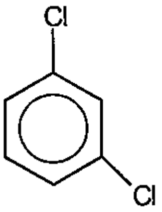


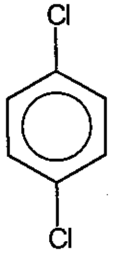




If the double bonds in the benzene ring exhibit resonance, then we can draw only three different dichlorobenzenes. The circle in the hexagon represents the delocalization of the three double bonds in the benzene ring (see Exercise 91).

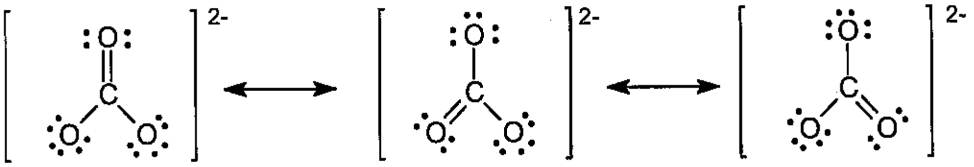






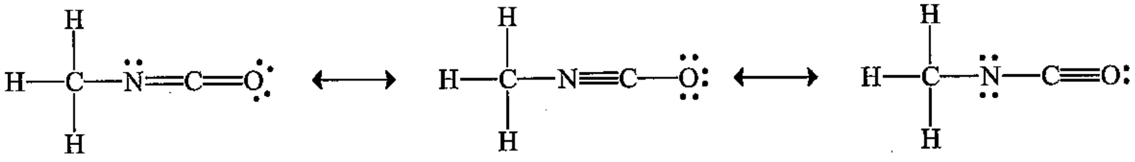
With resonance, all carbon-carbon bonds are equivalent. We can't distinguish between a single and double bond between adjacent carbons that have a chlorine attached. That only three isomers are observed supports the concept of resonance.

94. CO_3^{2-} has 4 + 3(6) + 2 = 24 valence electrons.

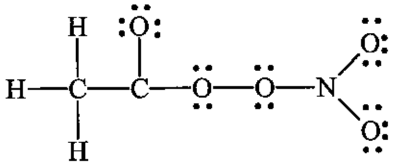


Three resonance structures can be drawn for CO_3^{2-}. The actual structure for CO_3^{2-} is an average of these three resonance structures. That is, the three C–O bond lengths are all equivalent, with a length somewhere between a single and a double bond. The actual bond length of 136 pm is consistent with this resonance view of CO_3^{2-}.

95. CH_3NCO has 4 + 3(1) + 5 + 4 + 6 = 22 valence electrons. Three resonance structures can be drawn for methyl isocyanate.

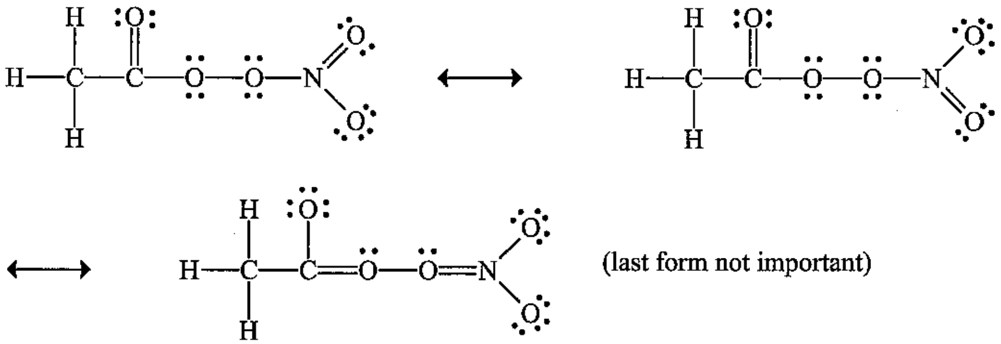


96. PAN ($H_3C_2NO_5$) has 3(1) + 2(4) + 5 + 5(6) = 46 valence electrons.



This is the skeletal structure with complete octets about oxygen atoms (46 electrons used).

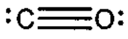
This structure has used all 46 electrons, but there are only six electrons around one of the carbon atoms and the nitrogen atom. Two unshared pairs must become shared; i.e., we must form double bonds. The three possible resonance structures for PAN are:



(last form not important)

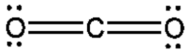
97. The Lewis structures for the various species are:

CO (10 e^-):



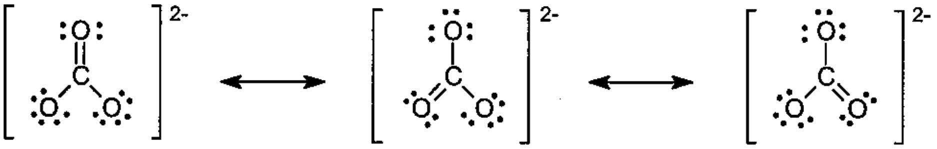
Triple bond between C and O.

CO_2 (16 e^-):



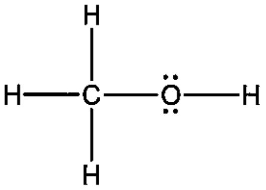
Double bond between C and O.

CO_3^{2-} (24 e^-):



Average of 1 1/3 bond between C and O in CO_3^{2-}.

CH_3OH (14 e^-):



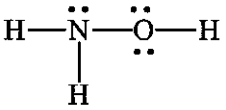
Single bond between C and O.

As the number of bonds increases between two atoms, bond strength increases, and bond length decreases. With this in mind, then:

Longest → shortest C – O bond: $CH_3OH > CO_3^{2-} > CO_2 > CO$

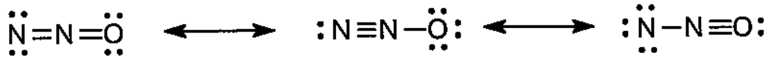
Weakest → strongest C – O bond: $CH_3OH < CO_3^{2-} < CO_2 < CO$

98. H_2NOH (14 e^-)



Single bond between N and O

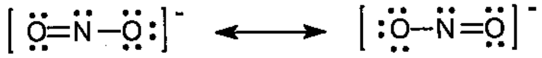
N_2O (16 e^-):



Average of a double bond between N and O

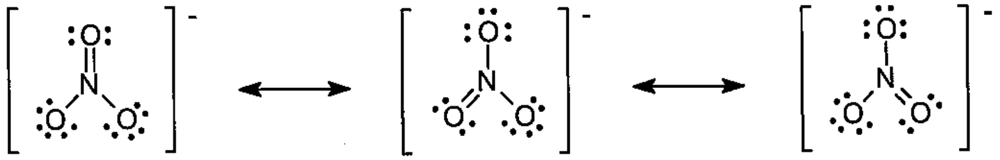
NO^+ (10 e^-): $[:N\equiv O:]^+$ Triple bond between N and O

NO_2^- (18 e^-):



Average of 1 1/2 bond between N and O

NO_3^- (24 e^-):



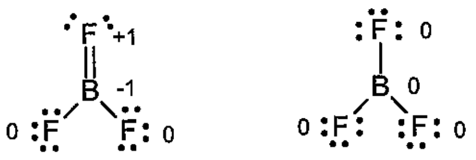
Average of 1 1/3 bond between N and O

From the Lewis structures, the order from shortest → longest N–O bond is:

$NO^+ < N_2O < NO_2^- < NO_3^- < H_2NOH$

Formal Charge

99. BF_3 has 3 + 3(7) = 24 valence electrons. The two Lewis structures to consider are:



The formal charges for the various atoms are assigned in the Lewis structures. Formal charge = number of valence electrons on free atom – number of lone pair electrons on atoms – 1/2 (number of shared electrons of atom). For B in the first Lewis structure, formal charge (FC) = 3 – 0 – 1/2(8) = –1. For F in the first structure with the double bond, FC = 7 – 4 – 1/2(4) = +1. The others all have a formal charge equal to zero [FC = 7 – 6 – 1/2(2) = 0].

The first Lewis structure obeys the octet rule but has a +1 formal charge on the most electronegative element there is, fluorine, and a negative formal charge on a much less electronegative element, boron. This is just the opposite of what we expect: negative formal charge on F and positive formal charge on B. The other Lewis structure does not obey the octet rule for B but has a zero formal charge on each element in BF_3. Because structures generally want to minimize formal charge, then BF_3 with only single bonds is best from a formal charge point of view.

100. :C≡O: Carbon: FC = 4 – 2 – 1/2(6) = –1; oxygen: FC = 6 – 2 – 1/2(6) = +1

Electronegativity predicts the opposite polarization. The two opposing effects seem to partially cancel to give a much less polar molecule than expected.

101. See Exercise 84 for the Lewis structures of $POCl_3$, SO_4^{2-}, ClO_4^- and PO_4^{3-}. All these compounds/ions have similar Lewis structures to those of SO_2Cl_2 and XeO_4 shown below. Formal charge = [number of valence electrons on free atom] – [number of lone pair electrons on atom + 1/2(number of shared electrons of atom)].

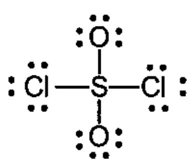
a. $POCl_3$: P, FC = 5 – 1/2(8) = +1

b. SO_4^{2-}: S, FC = 6 – 1/2(8) = +2

c. ClO_4^-: Cl, FC = 7 – 1/2(8) = +3

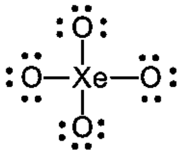
d. PO_4^{3-}: P, FC = 5 – 1/2(8) = +1

e. SO_2Cl_2, 6 + 2(6) + 2(7) = 32 e^-



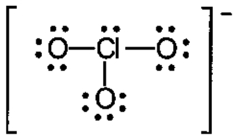
S, FC = 6 – 1/2(8) = +2

f. XeO_4, 8 + 4(6) = 32 e^-



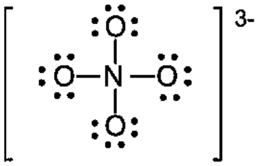
Xe, FC = 8 – 1/2(8) = +4

g. ClO_3^-, 7 + 3(6) + 1 = 26 e^-



Cl, FC = 7 – 2 – 1/2(6) = +2

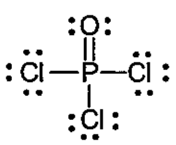
h. NO_4^{3-}, 5 + 4(6) + 3 = 32 e^-



N, FC = 5 – 1/2(8) = +1

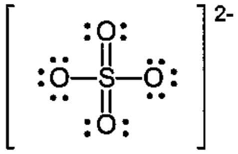
102. For SO_4^{2-}, ClO_4^-, PO_4^{3-} and ClO_3^-, only one of the possible resonance structures is drawn.

a. Must have five bonds to P to minimize formal charge of P. The best choice is to form a double bond to O since this will give O a formal charge of zero, and single bonds to Cl for the same reason.



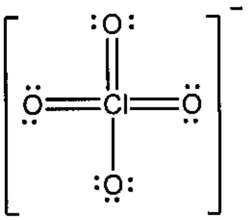
P, FC = 0

b. Must form six bonds to S to minimize formal charge of S.



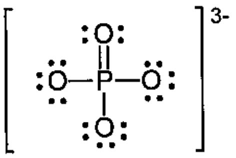
S, FC = 0

c. Must form seven bonds to Cl to minimize formal charge.



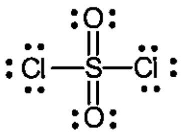
Cl, FC = O

d. Must form five bonds to P to minimize formal charge.



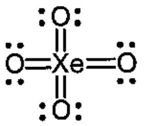
P, FC = 0

e.



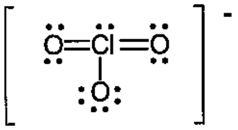
S, FC = 0
Cl, FC = 0
O, FC = 0

f.



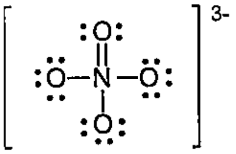
Xe, FC = 0

g.



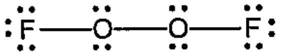
Cl, FC = 0

h. We can't. The following structure has a zero formal charge for N:



but N does not expand its octet. We wouldn't expect this resonance form to exist.

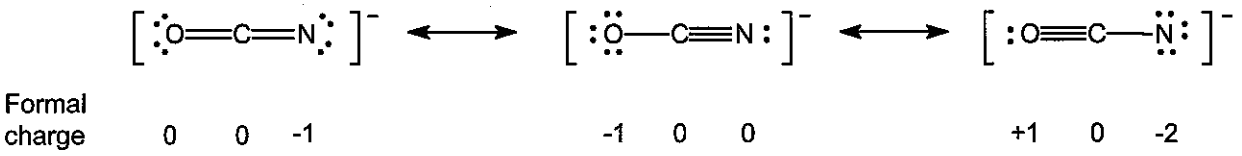
103. O_2F_2 has 2(6) + 2(7) = 26 valence e^-. The formal charge and oxidation number (state) of each atom is below the Lewis structure of O_2F_2.



Formal Charge	0	0	0	0
Oxid. Number	-1	+1	+1	-1

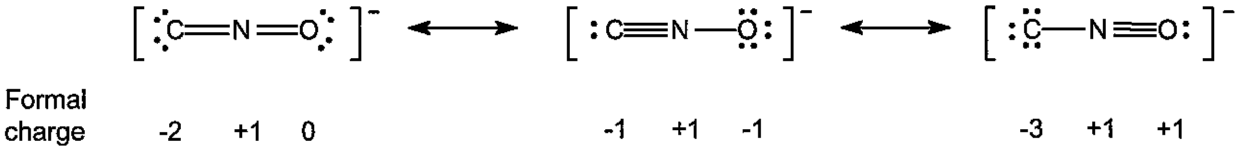
Oxidation states are more useful when accounting for the reactivity of O_2F_2. We are forced to assign +1 as the oxidation state for oxygen due to the bonding to fluorine. Oxygen is very electronegative, and +1 is not a stable oxidation state for this element.

104. OCN^- has 6 + 4 + 5 + 1 = 16 valence electrons.



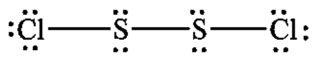
Only the first two resonance structures should be important. The third places a positive formal charge on the most electronegative atom in the ion and a –2 formal charge on N.

CNO^- will also have 16 valence electrons.

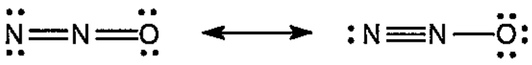


All the resonance structures for fulminate (CNO^-) involve greater formal charges than in cyanate (OCN^-), making fulminate more reactive (less stable).

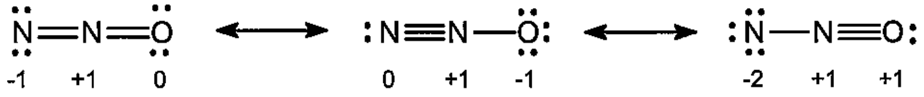
105. SCl, 6 + 7 = 13; the formula could be SCl (13 valence electrons), S_2Cl_2 (26 valence electrons), S_3Cl_3 (39 valence electrons), etc. For a formal charge of zero on S, we will need each sulfur in the Lewis structure to have two bonds to it and two lone pairs [FC = 6 – 4 – 1/2(4) = 0]. Cl will need one bond and three lone pairs for a formal charge of zero [FC = 7 – 6 – 1/2(2) = 0]. Since chlorine wants only one bond to it, it will not be a central atom here. With this in mind, only S_2Cl_2 can have a Lewis structure with a formal charge of zero on all atoms. The structure is:



106. The nitrogen-nitrogen bond length of 112 pm is between a double (120 pm) and a triple (110 pm) bond. The nitrogen-oxygen bond length of 119 pm is between a single (147 pm) and a double bond (115 pm). The third resonance structure shown below doesn't appear to be as important as the other two since there is no evidence from bond lengths for a nitrogen-oxygen triple bond or a nitrogen-nitrogen single bond as in the third resonance form. We can adequately describe the structure of N_2O using the resonance forms:



Assigning formal charges for all three resonance forms:



For:

$(\,\underset{\cdot\cdot}{\ddot{\mathrm{N}}}=\,)$, FC = 5 - 4 - 1/2(4) = -1

$(=\mathrm{N}=)$, FC = 5 - 1/2(8) = +1 , Same for $(\equiv\mathrm{N}-)$ and $(-\mathrm{N}\equiv)$

$(:\underset{\cdot\cdot}{\ddot{\mathrm{N}}}-)$, FC = 5 - 6 - 1/2(2) = -2 ; $(:\mathrm{N}\equiv)$, FC = 5 - 2 - 1/2(6) = 0

$(=\underset{\cdot\cdot}{\ddot{\mathrm{O}}})$, FC = 6 - 4 - 1/2(4) = 0; $(-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:)$, FC = 6 - 6 - 1/2(2) = -1

$(\equiv\mathrm{O}:)$, FC = 6 - 2 - 1/2(6) = +1

We should eliminate N–N≡O because it has a formal charge of +1 on the most electronegative element (O). This is consistent with the observation that the N–N bond is between a double and triple bond and that the N–O bond is between a single and double bond.

107. For formal charge values of zero:

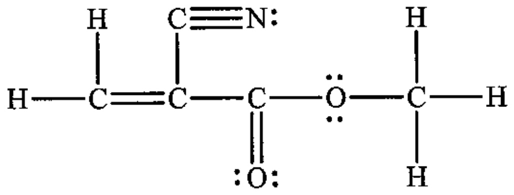
(1) each carbon in the structure has 4 bonding pairs of electrons and no lone pairs;

(2) each N has 3 bonding pairs of electrons and 1 lone pair of electrons;

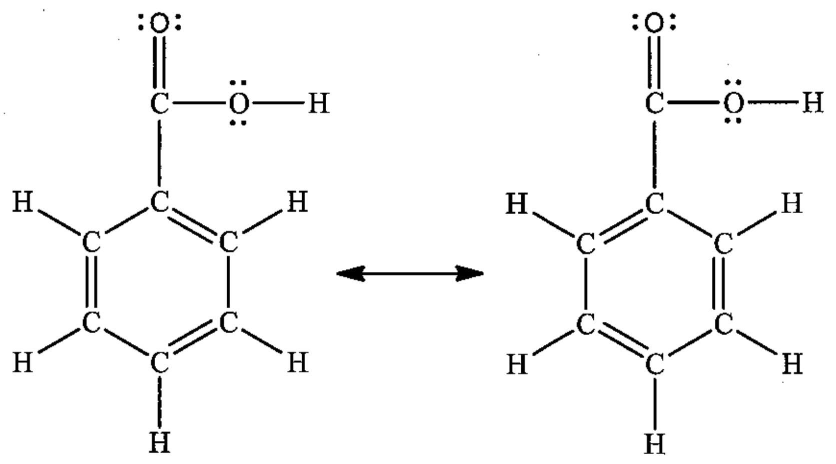
(3) each O has 2 bonding pairs of electrons and 2 lone pairs of electrons;

(4) each H is attached by only a single bond (1 bonding pair of electrons).

Following these guidelines, the Lewis structure is:



108. For a formal charge of zero, carbon atoms in the structure will all satisfy the octet rule by forming four bonds (with no lone pairs). Oxygen atoms have a formal charge of zero by forming two bonds and having two lone pairs of electrons. Hydrogen atoms have a formal charge of zero by forming a single bond (with no lone pairs). Following these guidelines, two resonance structures can be drawn for benzoic acid (see next page).



Molecular Structure and Polarity

109. The first step always is to draw a valid Lewis structure when predicting molecular structure. When resonance is possible, only one of the possible resonance structures is necessary to predict the correct structure because all resonance structures give the same structure. The Lewis structures are in Exercises 83 and 89. The structures and bond angles for each follow.

83: a. CCl_4: tetrahedral, 109.5° b. NCl_3: trigonal pyramid, <109.5°

c. $SeCl_2$: V-shaped or bent, <109.5° d. ICl: linear, but there is no bond angle present

Note: NCl_3 and $SeCl_2$ both have lone pairs of electrons on the central atom that result in bond angles that are something less than predicted from a tetrahedral arrangement (109.5°). However, we cannot predict the exact number. For the solutions manual, we will insert a less than sign to indicate this phenomenon. For bond angles equal to 120°, the lone pair phenomenon isn't as significant as compared to smaller bond angles. For these molecules, for example, NO_2^-, we will insert an approximate sign in front of the 120° to note that there may be a slight distortion from the VSEPR predicted bond angle.

89: a. NO_2^-: V-shaped, ≈120°; NO_3^-: trigonal planar, 120°

N_2O_4: trigonal planar, 120° about both N atoms

b. OCN^-, SCN^-, and N_3^- are all linear with 180° bond angles.

110. See Exercises 84 and 90 for the Lewis structures.

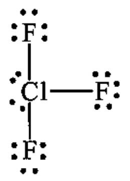
84: a. All are tetrahedral; 109.5°

b. All are trigonal pyramid; <109.5°

c. All are V-shaped; <109.5°

90: O_3 and SO_2 are V-shaped (or bent) with a bond angle ≈120°. SO_3 is trigonal planar with 120° bond angles.

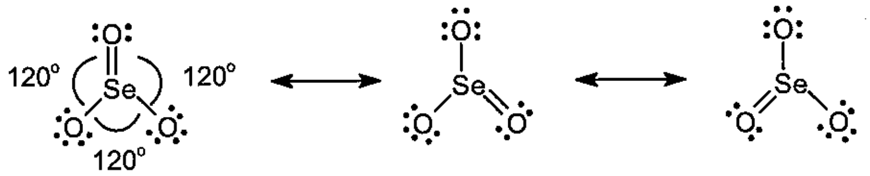
111. From the Lewis structures (see Exercise 87), Br_3^- would have a linear molecular structure, ClF_3 would have a T-shaped molecular structure, and SF_4 would have a see-saw molecular structure. For example, consider ClF_3 (28 valence electrons):



The central Cl atom is surrounded by five electron pairs, which requires a trigonal bipyramid geometry. Since there are three bonded atoms and two lone pairs of electrons about Cl, we describe the molecular structure of ClF_3 as T-shaped with predicted bond angles of about 90°. The actual bond angles will be slightly less than 90° due to the stronger repulsive effect of the lone-pair electrons as compared to the bonding electrons.

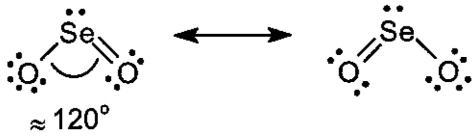
112. From the Lewis structures (see Exercise 88), XeF_4 would have a square planar molecular structure, and ClF_5 would have a square pyramid molecular structure.

113. a. SeO_3, $6 + 3(6) = 24\ e^-$



SeO_3 has a trigonal planar molecular structure with all bond angles equal to 120°. Note that any one of the resonance structures could be used to predict molecular structure and bond angles.

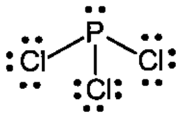
b. SeO_2, $6 + 2(6) = 18\ e^-$



SeO_2 has a V-shaped molecular structure. We would expect the bond angle to be approximately 120° as expected for trigonal planar geometry.

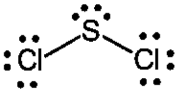
Note: Both SeO_3 and SeO_2 structures have three effective pairs of electrons about the central atom. All of the structures are based on a trigonal planar geometry, but only SeO_3 is described as having a trigonal planar structure. Molecular structure always describes the relative positions of the atoms.

114. a. PCl_3 has $5 + 3(7) = 26$ valence electrons.



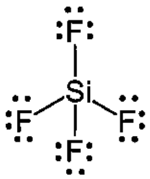
Trigonal pyramid; all angles are <109.5°.

b. SCl_2 has $6 + 2(7) = 20$ valence electrons.



V-shaped; angle is <109.5°.

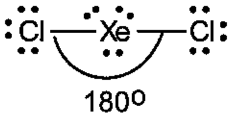
c. SiF_4 has 4 + 4(7) = 32 valence electrons.



Tetrahedral; all angles are 109.5°.

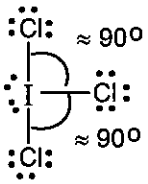
Note: In PCl_3, SCl_2, and SiF_4, there are four pairs of electrons about the central atom in each case in this exercise. All of the structures are based on a tetrahedral geometry, but only SiF_4 has a tetrahedral structure. We consider only the relative positions of the atoms when describing the molecular structure.

115. a. $XeCl_2$ has 8 + 2(7) = 22 valence electrons.



There are five pairs of electrons about the central Xe atom. The structure will be based on a trigonal bipyramid geometry. The most stable arrangement of the atoms in $XeCl_2$ is a linear molecular structure with a 180° bond angle.

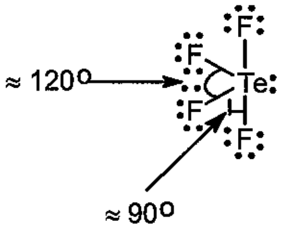
b. ICl_3 has 7 + 3(7) = 28 valence electrons.



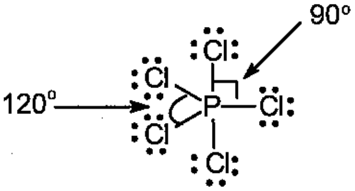
T-shaped; the ClICl angles are ≈90°. Since the lone pairs will take up more space, the ClICl bond angles will probably be slightly less than 90°.

c. TeF_4 has 6 + 4(7) = 34 valence electrons.

d. PCl_5 has 5 + 5(7) = 40 valence electrons.



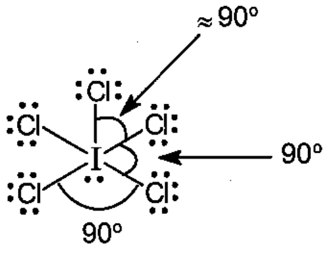
See-saw or teeter-totter or distorted tetrahedron



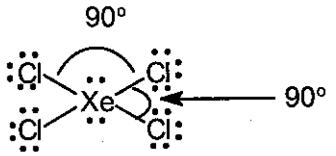
Trigonal bipyramid

All the species in this exercise have five pairs of electrons around the central atom. All the structures are based on a trigonal bipyramid geometry, but only in PCl_5 are all the pairs, bonding pairs. Thus PCl_5 is the only one for which we describe the molecular structure as trigonal bipyramid. Still, we had to begin with the trigonal bipyramid geometry to get to the structures (and bond angles) of the others.

116. a. $ICl_5, 7 + 5(7) = 42\ e^-$ b. $XeCl_4, 8 + 4(7) = 36\ e^-$

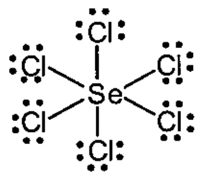


Square pyramid, ≈90° bond angles



Square planar, 90° bond angles

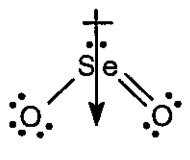
c. $SeCl_6$ has $6 + 6(7) = 48$ valence electrons.



Octahedral, 90° bond angles

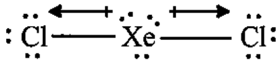
Note: All these species have six pairs of electrons around the central atom. All three structures are based on the octahedron, but only $SeCl_6$ has an octahedral molecular structure.

117. SeO_3 and SeO_2 both have polar bonds, but only SeO_2 has a dipole moment. The three bond dipoles from the three polar Se–O bonds in SeO_3 will all cancel when summed together. Hence SeO_3 is nonpolar since the overall molecule has no resulting dipole moment. In SeO_2, the two Se–O bond dipoles do not cancel when summed together; hence SeO_2 has a net dipole moment (is polar). Since O is more electronegative than Se, the negative end of the dipole moment is between the two O atoms, and the positive end is around the Se atom. The arrow in the following illustration represents the overall dipole moment in SeO_2. Note that to predict polarity for SeO_2, either of the two resonance structures can be used.



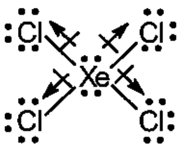
118. All have polar bonds; in SiF_4, the individual bond dipoles cancel when summed together, and in PCl_3 and SCl_2, the individual bond dipoles do not cancel. Therefore, SiF_4 has no net dipole moment (is nonpolar), and PCl_3 and SCl_2 have net dipole moments (are polar). For PCl_3, the negative end of the dipole moment is between the more electronegative chlorine atoms, and the positive end is around P. For SCl_2, the negative end is between the more electronegative Cl atoms, and the positive end of the dipole moment is around S.

119. All have polar bonds, but only TeF_4 and ICl_3 have dipole moments. The bond dipoles from the five P–Cl bonds in PCl_5 cancel each other when summed together, so PCl_5 has no net dipole moment. The bond dipoles in $XeCl_2$ also cancel:



Because the bond dipoles from the two Xe–Cl bonds are equal in magnitude but point in opposite directions, they cancel each other, and $XeCl_2$ has no net dipole moment (is nonpolar). For TeF_4 and ICl_3, the arrangement of these molecules is such that the individual bond dipoles do *not* all cancel, so each has an overall net dipole moment (is polar).

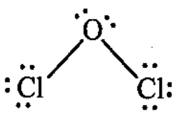
120. All have polar bonds, but only ICl_5 has an overall net dipole moment. The six bond dipoles in $SeCl_6$ all cancel each other, so $SeCl_6$ has no net dipole moment. The same is true for $XeCl_4$:

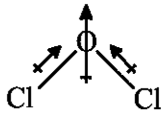


When the four bond dipoles are added together, they all cancel each other, resulting in $XeCl_4$ having no overall dipole moment (is nonpolar). ICl_5 has a structure in which the individual bond dipoles do *not* all cancel, hence ICl_5 has a dipole moment (is polar)

121. Molecules that have an overall dipole moment are called polar molecules, and molecules that do not have an overall dipole moment are called nonpolar molecules.

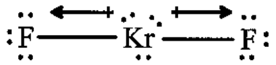
a. OCl_2, $6 + 2(7) = 20\ e^-$





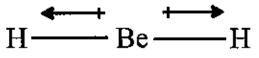
V-shaped, polar; OCl_2 is polar because the two O–Cl bond dipoles don't cancel each other. The resulting dipole moment is shown in the drawing.

KrF_2, $8 + 2(7) = 22\ e^-$



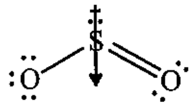
Linear, nonpolar; the molecule is nonpolar because the two Kr–F bond dipoles cancel each other.

BeH_2, $2 + 2(1) = 4\ e^-$



Linear, nonpolar; Be–H bond dipoles are equal and point in opposite directions. They cancel each other. BeH_2 is nonpolar.

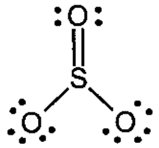
SO_2, $6 + 2(6) = 18\ e^-$



V-shaped, polar; the S–O bond dipoles do not cancel, so SO_2 is polar (has a net dipole moment). Only one resonance structure is shown.

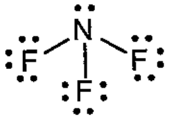
Note: All four species contain three atoms. They have different structures because the number of lone pairs of electrons around the central atom are different in each case.

b. SO_3, $6 + 3(6) = 24\ e^-$



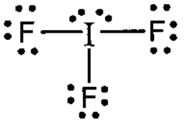
Trigonal planar, nonpolar; bond dipoles cancel. Only one resonance structure is shown.

NF_3, $5 + 3(7) = 26\ e^-$



Trigonal pyramid, polar; bond dipoles do not cancel.

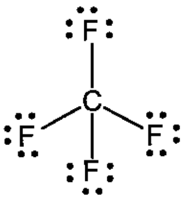
IF_3 has $7 + 3(7) = 28$ valence electrons.



T-shaped, polar; bond dipoles do not cancel.

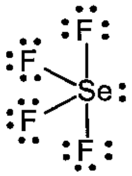
Note: Each molecule has the same number of atoms but different structures because of differing numbers of lone pairs around each central atom.

c. CF_4, $4 + 4(7) = 32\ e^-$



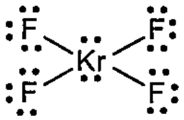
Tetrahedral, nonpolar; bond dipoles cancel.

SeF_4, $6 + 4(7) = 34\ e^-$



See-saw, polar; bond dipoles do not cancel.

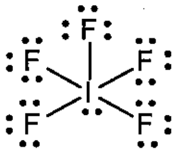
KrF_4, 8 + 4(7) = 36 valence electrons



Square planar, nonpolar; bond dipoles cancel.

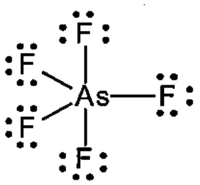
Note: Again, each molecule has the same number of atoms but different structures because of differing numbers of lone pairs around the central atom.

d. IF_5, $7 + 5(7) = 42\ e^-$



Square pyramid, polar; bond dipoles do not cancel.

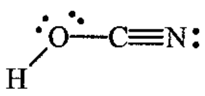
AsF_5, $5 + 5(7) = 40\ e^-$



Trigonal bipyramid, nonpolar; bond dipoles cancel.

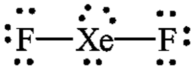
Note: Yet again, the molecules have the same number of atoms but different structures because of the presence of differing numbers of lone pairs.

122. a.



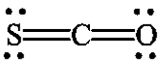
Polar; the bond dipoles do not cancel.

c.



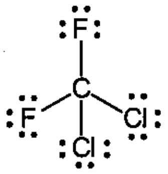
Nonpolar; the two Xe–F bond dipoles cancel each other.

b.



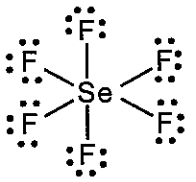
Polar; the C–O bond is a more polar bond than the C–S bond, so the two bond dipoles do not cancel each other.

d.



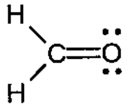
Polar; all the bond dipoles are not equivalent, and they don't cancel each other.

e.



Nonpolar; the six Se–F bond dipoles cancel each other.

f.



Polar; the bond dipoles are not equivalent, and they don't cancel

123. EO_3^- is the formula of the ion. The Lewis structure has 26 valence electrons. Let x = number of valence electrons of element E.

$$26 = x + 3(6) + 1, \quad x = 7 \text{ valence electrons}$$

Element E is a halogen because halogens have seven valence electrons. Some possible identities are F, Cl, Br, and I. The EO_3^- ion has a trigonal pyramid molecular structure with bond angles of less than 109.5° (<109.5°).

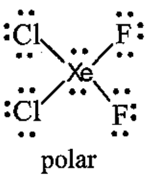
124. The formula is EF_2O^{2-}, and the Lewis structure has 28 valence electrons.

$$28 = x + 2(7) + 6 + 2, \quad x = 6 \text{ valence electrons for element E}$$

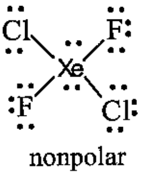
Element E must belong to the Group 6A elements since E has six valence electrons. E must also be a row 3 or heavier element since this ion has more than eight electrons around the central E atom (row 2 elements never have more than eight electrons around them). Some possible identities for E are S, Se, and Te. The ion has a T-shaped molecular structure with bond angles of ≈90°.

125. All these molecules have polar bonds that are symmetrically arranged about the central atoms. In each molecule, the individual bond dipoles cancel each other out to give no net overall dipole moment. All these molecules are nonpolar even though they all contain polar bonds.

126. XeF_2Cl_2, $8 + 2(7) + 2(7) = 36\ e^-$



polar



nonpolar

The two possible structures for XeF_2Cl_2 are above. In the first structure, the F atoms are 90° apart from each other, and the Cl atoms are also 90° apart. The individual bond dipoles would not cancel in this molecule, so this molecule is polar. In the second possible structure, the F atoms are 180° apart, as are the Cl atoms. Here, the bond dipoles are symmetrically arranged so they do cancel each other out, and this molecule is nonpolar. Therefore, measurement of the dipole moment would differentiate between the two compounds. These are different compounds and not resonance structures.

Additional Exercises

127\. a. Radius: $N^+ < N < N^-$; IE: $N^- < N < N^+$

N^+ has the fewest electrons held by the seven protons in the nucleus, whereas N^- has the most electrons held by the seven protons. The seven protons in the nucleus will hold the electrons most tightly in N^+ and least tightly in N^-. Therefore, N^+ has the smallest radius with the largest ionization energy (IE), and N^- is the largest species with the smallest IE.

b. Radius: $Cl^+ < Cl < Se < Se^-$; IE: $Se^- < Se < Cl < Cl^+$

The general trends tell us that Cl has a smaller radius than Se and a larger IE than Se. Cl^+, with fewer electron-electron repulsions than Cl, will be smaller than Cl and have a larger IE. Se^-, with more electron-electron repulsions than Se, will be larger than Se and have a smaller IE.

c. Radius: $Sr^{2+} < Rb^+ < Br^-$; IE: $Br^- < Rb^+ < Sr^{2+}$

These ions are isoelectronic. The species with the most protons (Sr^{2+}) will hold the electrons most tightly and will have the smallest radius and largest IE. The ion with the fewest protons (Br^-) will hold the electrons least tightly and will have the largest radius and smallest IE.

128\. a. $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ b. $NH_4^+(g) + Br^-(g) \rightarrow NH_4Br(s)$

c. $Mg^{2+}(g) + S^{2-}(g) \rightarrow MgS(s)$ d. $O_2(g) \rightarrow 2\ O(g)$

129\. a.

$$\begin{array}{rl}
HF(g) \rightarrow H(g) + F(g) & \Delta H = 565\ kJ \\
H(g) \rightarrow H^+(g) + e^- & \Delta H = 1312\ kJ \\
F(g) + e^- \rightarrow F^-(g) & \Delta H = -327.8\ kJ \\
\hline
HF(g) \rightarrow H^+(g) + F^-(g) & \Delta H = 1549\ kJ
\end{array}$$

b.

$$\begin{array}{rl}
HCl(g) \rightarrow H(g) + Cl(g) & \Delta H = 427\ kJ \\
H(g) \rightarrow H^+(g) + e^- & \Delta H = 1312\ kJ \\
Cl(g) + e^- \rightarrow Cl^-(g) & \Delta H = -348.7\ kJ \\
\hline
HCl(g) \rightarrow H^+(g) + Cl^-(g) & \Delta H = 1390.\ kJ
\end{array}$$

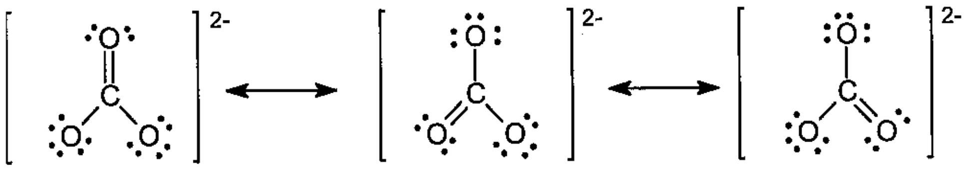
c.

$$\begin{array}{rl}
HI(g) \rightarrow H(g) + I(g) & \Delta H = 295\ kJ \\
H(g) \rightarrow H^+(g) + e^- & \Delta H = 1312\ kJ \\
I(g) + e^- \rightarrow I^-(g) & \Delta H = -295.2\ kJ \\
\hline
HI(g) \rightarrow H^+(g) + I^-(g) & \Delta H = 1312\ kJ
\end{array}$$

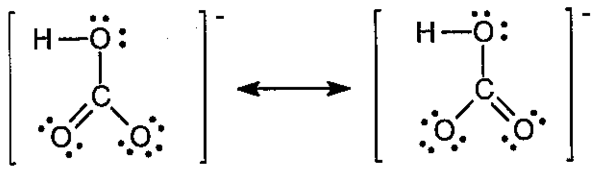
d.

$$\begin{array}{rl}
H_2O(g) \rightarrow OH(g) + H(g) & \Delta H = 467\ kJ \\
H(g) \rightarrow H^+(g) + e^- & \Delta H = 1312\ kJ \\
OH(g) + e^- \rightarrow OH^-(g) & \Delta H = -180.\ kJ \\
\hline
H_2O(g) \rightarrow H^+(g) + OH^-(g) & \Delta H = 1599\ kJ
\end{array}$$

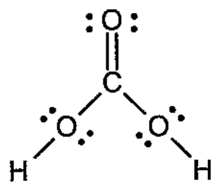
130. CO_3^{2-} has 4 + 3(6) + 2 = 24 valence electrons.



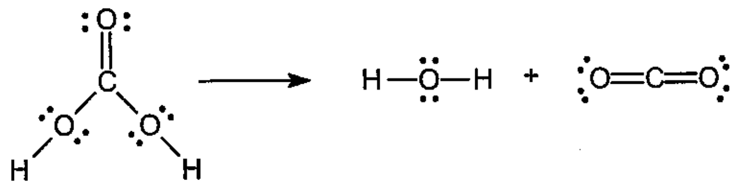
HCO_3^- has 1 + 4 + 3(6) + 1 = 24 valence electrons.



H_2CO_3 has 2(1) + 4 + 3(6) = 24 valence electrons.



The Lewis structures for the reactants and products are:



Bonds broken:	Bonds formed:
2 C–O (358 kJ/mol)	1 C=O (799 kJ/mol)
1 O–H (467 kJ/mol)	1 O–H (467 kJ/mol)

ΔH = 2(358) + 467 – [799 + 467] = –83 kJ; the carbon-oxygen double bond is stronger than two carbon-oxygen single bonds; hence CO_2 and H_2O are more stable than H_2CO_3.

131. The stable species are:

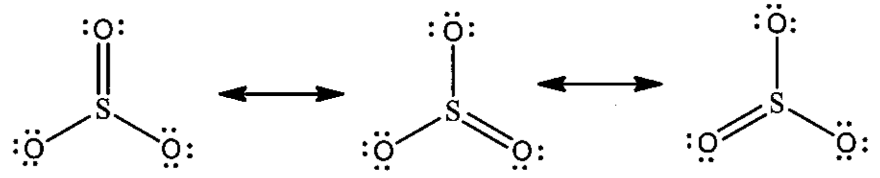
a. NaBr: In $NaBr_2$, the sodium ion would have a 2+ charge, assuming that each bromine has a 1– charge. Sodium doesn't form stable Na^{2+} ionic compounds.

b. ClO_4^-: ClO_4 has 31 valence electrons, so it is impossible to satisfy the octet rule for all atoms in ClO_4. The extra electron from the 1– charge in ClO_4^- allows for complete octets for all atoms.

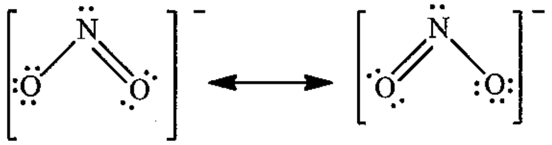
c. XeO_4: We can't draw a Lewis structure that obeys the octet rule for SO_4 (30 electrons), unlike XeO_4 (32 electrons).

d. SeF_4: Both compounds require the central atom to expand its octet. O is too small and doesn't have low-energy d orbitals to expand its octet (which is true for all row 2 elements).

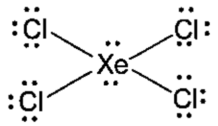
132. a. All have 24 valence electrons and the same number of atoms in the formula. All have the same resonance Lewis structures; the structures are all trigonal planar with 120° bond angles. The Lewis structures for NO_3^- and CO_3^{2-} will be the same as the three SO_3 Lewis structures shown below.

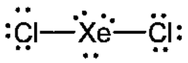


b. All have 18 valence electrons and the same number of atoms. All have the same resonance Lewis structures; the molecular structures are all V-shaped with ≈120° bond angles. O_3 and SO_2 have the same two Lewis structures as is shown for NO_2^-.



133. a. $XeCl_4$, $8 + 4(7) = 36\ e^-$ $XeCl_2$, $8 + 2(7) = 22\ e^-$



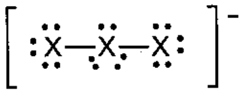


Square planar, 90°, nonpolar Linear, 180°, nonpolar

Both compounds have a central Xe atom with lone pairs and terminal Cl atoms, and both compounds do not satisfy the octet rule. In addition, both are nonpolar because the Xe–Cl bond dipoles and lone pairs around Xe are arranged in such a manner that they cancel each other out. The last item in common is that both have 180° bond angles. Although we haven't emphasized this, the bond angles between the Cl atoms on the diagonal in $XeCl_4$ are 180° apart from each other.

b. All of these are polar covalent compounds. The bond dipoles do not cancel out each other when summed together. The reason the bond dipoles are not symmetrically arranged in these compounds is that they all have at least one lone pair of electrons on the central atom, which disrupts the symmetry. Note that there are molecules that have lone pairs and are nonpolar, e.g., $XeCl_4$ and $XeCl_2$ in the preceding problem. A lone pair on a central atom does not guarantee a polar molecule.

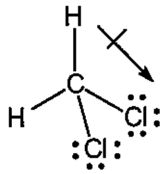
134. The general structure of the trihalide ions is:



Bromine and iodine are large enough and have low-energy, empty d orbitals to accommodate the expanded octet. Fluorine is small, and its valence shell contains only 2s and 2p orbitals (four orbitals) and cannot expand its octet. The lowest-energy d orbitals in F are 3d; they are too high in energy compared with 2s and 2p to be used in bonding.

135. Yes, each structure has the same number of effective pairs around the central atom, giving the same predicted molecular structure for each compound/ion. (A multiple bond is counted as a single group of electrons.)

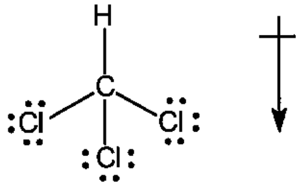
136. a.



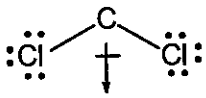
The C–H bonds are assumed nonpolar since the electronegativities of C and H are about equal.

$\overset{\delta+}{\text{C}}\text{–}\overset{\delta-}{\text{Cl}}$ is the charge distribution for each C–Cl bond. In CH_2Cl_2, the two individual C–Cl bond dipoles add together to give an overall dipole moment for the molecule. The overall dipole will point from C (positive end) to the midpoint of the two Cl atoms (negative end).

In $CHCl_3$, the C–H bond is essentially nonpolar. The three C–Cl bond dipoles in $CHCl_3$ add together to give an overall dipole moment for the molecule. The overall dipole will have the negative end at the midpoint of the three chlorines and the positive end around the carbon.

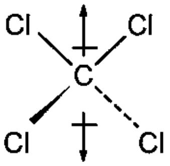


CCl_4 is nonpolar. CCl_4 is a tetrahedral molecule where all four C–Cl bond dipoles cancel when added together. Let's consider just the C and two of the Cl atoms. There will be a net dipole pointing in the direction of the middle of the two Cl atoms.



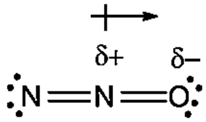
There will be an equal and opposite dipole arising from the other two Cl atoms.

Combining:



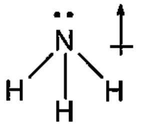
The two dipoles cancel, and CCl_4 is nonpolar.

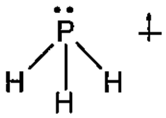
b. CO_2 is nonpolar. CO_2 is a linear molecule with two equivalence bond dipoles that cancel. N_2O, which is also a linear molecule, is polar because the nonequivalent bond dipoles do not cancel.



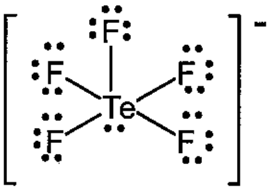
c. NH_3 is polar. The 3 N–H bond dipoles add together to give a net dipole in the direction of the lone pair. We would predict PH_3 to be nonpolar on the basis of electronegativitity, i.e., P–H bonds are nonpolar. However, the presence of the lone pair makes the PH_3 molecule slightly polar. The net dipole is in the direction of the lone pair and has a magnitude about one third that of the NH_3 dipole.

δ− δ+
N − H





137. TeF_5^- has 6 + 5(7) + 1 = 42 valence electrons.



The lone pair of electrons around Te exerts a stronger repulsion than the bonding pairs of electrons. This pushes the four square-planar F atoms away from the lone pair and reduces the bond angles between the axial F atom and the square-planar F atoms.

138. $C \equiv O$ (1072 kJ/mol); $N \equiv N$ (941 kJ/mol); CO is polar, whereas N_2 is nonpolar. This may lead to a great reactivity for the CO bond.

ChemWork Problems

The answers to the problems 139-146 (or a variation to these problems) are found in OWL. These problems are also assignable in OWL.

Challenge Problems

147. a. There are two attractions of the form $\frac{(+1)(-1)}{r}$, where $r = 1 \times 10^{-10}$ m = 0.1 nm.

$$V = 2 \times (2.31 \times 10^{-19}\ \text{J nm})\left[\frac{(+1)(-1)}{0.1\ \text{nm}}\right] = -4.62 \times 10^{-18}\ \text{J} = -5 \times 10^{-18}\ \text{J}$$

b. There are four attractions of +1 and −1 charges at a distance of 0.1 nm from each other. The two negative charges and the two positive charges repel each other across the diagonal of the square. This is at a distance of $\sqrt{2} \times 0.1$ nm.

$$V = 4 \times (2.31 \times 10^{-19})\left[\frac{(+1)(-1)}{0.1}\right] + 2.31 \times 10^{-19}\left[\frac{(+1)(+1)}{\sqrt{2}\,(0.1)}\right] + 2.31 \times 10^{-19}\left[\frac{(-1)(-1)}{\sqrt{2}\,(0.1)}\right]$$

$$V = -9.24 \times 10^{-18}\ \text{J} + 1.63 \times 10^{-18}\ \text{J} + 1.63 \times 10^{-18}\ \text{J} = -5.98 \times 10^{-18}\ \text{J} = -6 \times 10^{-18}\ \text{J}$$

Note: There is a greater net attraction in arrangement b than in a.

148.

	(IE − EA)	(IE − EA)/502	EN (text)	2006/502 = 4.0
F	2006 kJ/mol	4.0	4.0	
Cl	1604 kJ/mol	3.2	3.0	
Br	1463 kJ/mol	2.9	2.8	
I	1302 kJ/mol	2.6	2.5	

The values calculated from ionization energies and electron affinities show the same trend as (and agree fairly closely) with the values given in the text.

149. The reaction is:

$$1/2\ I_2(g) + 1/2\ Cl_2(g) \rightarrow ICl(g) \qquad \Delta H_f^\circ = ?$$

Using Hess's law:

$1/2\ I_2(s) \rightarrow 1/2\ I_2(g)$	$\Delta H = 1/2(62\ \text{kJ})$	(Appendix 4)
$1/2\ I_2(g) \rightarrow I(g)$	$\Delta H = 1/2(149\ \text{kJ})$	(Table 8.4)
$1/2\ Cl_2(g) \rightarrow Cl(g)$	$\Delta H = 1/2(239\ \text{kJ})$	(Table 8.4)
$I(g) + Cl(g) \rightarrow ICl(g)$	$\Delta H = -208\ \text{kJ}$	(Table 8.4)
$1/2\ I_2(s) + 1/2\ Cl_2(g) \rightarrow ICl(g)$	$\Delta H = 17\ \text{kJ}$ so $\Delta H_f^\circ = 17$ kJ/mol	

150.

$$\begin{array}{rcll}
2\,Li^+(g) + 2\,Cl^-(g) & \rightarrow & 2\,LiCl(s) & \Delta H = 2(-829\text{ kJ}) \\
2\,Li(g) & \rightarrow & 2\,Li^+(g) + 2\,e^- & \Delta H = 2(520.\text{ kJ}) \\
2\,Li(s) & \rightarrow & 2\,Li(g) & \Delta H = 2(166\text{ kJ}) \\
2\,HCl(g) & \rightarrow & 2\,H(g) + 2\,Cl(g) & \Delta H = 2(427\text{ kJ}) \\
2\,Cl(g) + 2\,e^- & \rightarrow & 2\,Cl^-(g) & \Delta H = 2(-349\text{ kJ}) \\
2\,H(g) & \rightarrow & H_2(g) & \Delta H = -(432\text{ kJ}) \\
\hline
2\,Li(s) + 2\,HCl(g) & \rightarrow & 2\,LiCl(s) + H_2(g) & \Delta H = -562\text{ kJ}
\end{array}$$

151. See Figure 8.11 to see the data supporting MgO as an ionic compound. Note that the lattice energy is large enough to overcome all of the other processes (removing two electrons from Mg, etc.). The bond energy for O_2 (247 kJ/mol) and electron affinity (737 kJ/mol) are the same when making CO. However, ionizing carbon to form a C^{2+} ion must be too large. See Figure 7.32 to see that the first ionization energy for carbon is about 350 kJ/mol greater than the first ionization energy for magnesium. If all other numbers were equal, the overall energy change would be down to ~250 kJ/mol (see Figure 8.11). It is not unreasonable to assume that the second ionization energy for carbon is more than 250 kJ/mol greater than the second ionization energy of magnesium. This would result in a positive ΔH value for the formation of CO as an ionic compound. One wouldn't expect CO to be ionic if the energetics were unfavorable.

152. a. (1) Removing an electron from the metal: ionization energy, positive ($\Delta H > 0$)

(2) Adding an electron to the nonmetal: electron affinity, often negative ($\Delta H < 0$)

(3) Allowing the metal cation and nonmetal anion to come together: lattice energy, negative ($\Delta H < 0$)

b. Often the sign of the sum of the first two processes is positive (or unfavorable). This is especially true due to the fact that we must also vaporize the metal and often break a bond on a diatomic gas. For example, the ionization energy for Na is +495 kJ/mol, and the electron affinity for F is −328 kJ/mol. Overall, the energy change is +167 kJ/mol (unfavorable).

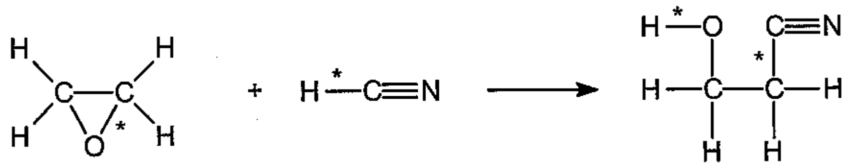
c. For an ionic compound to form, the sum must be negative (exothermic).

d. The lattice energy must be favorable enough to overcome the endothermic process of forming the ions; i.e., the lattice energy must be a large negative quantity.

e. While Na_2Cl (or $NaCl_2$) would have a greater lattice energy than NaCl, the energy to make a Cl^{2-} ion (or Na^{2+} ion) must be larger (more unfavorable) than what would be gained by the larger lattice energy. The same argument can be made for MgO compared to MgO_2 or Mg_2O. The energy to make the ions is too unfavorable or the lattice energy is not favorable enough, and the compounds do not form.

153. As the halogen atoms get larger, it becomes more difficult to fit three halogen atoms around the small nitrogen atom, and the NX_3 molecule becomes less stable.

154. a. I.



Bonds broken (*):

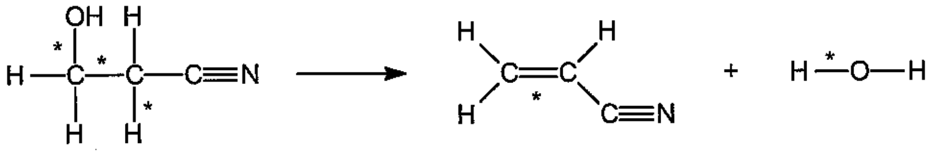
1 C–O (358 kJ)
1 C–H (413 kJ)

Bonds formed (*):

1 O–H (467 kJ)
1 C–C (347 kJ)

$\Delta H_I = 358 \text{ kJ} + 413 \text{ kJ} - (467 \text{ kJ} + 347 \text{ kJ}) = -43 \text{ kJ}$

II.



Bonds broken (*):

1 C–O (358 kJ/mol)
1 C–H (413 kJ/mol)
1 C–C (347 kJ/mol)

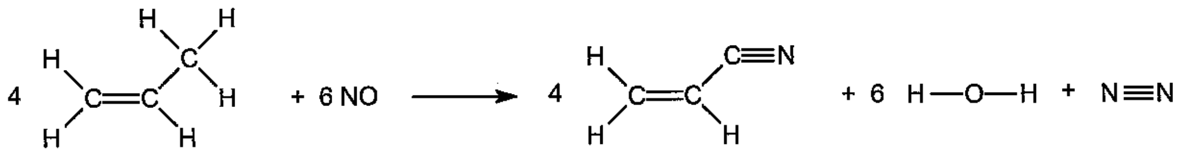
Bonds formed (*):

1 H–O (467 kJ/mol)
1 C=C (614 kJ/mol)

$\Delta H_{II} = 358 \text{ kJ} + 413 \text{ kJ} + 347 \text{ kJ} - [467 \text{ kJ} + 614 \text{ kJ}] = +37 \text{ kJ}$

$\Delta H_{\text{overall}} = \Delta H_I + \Delta H_{II} = -43 \text{ kJ} + 37 \text{ kJ} = -6 \text{ kJ}$

b.



Bonds broken:

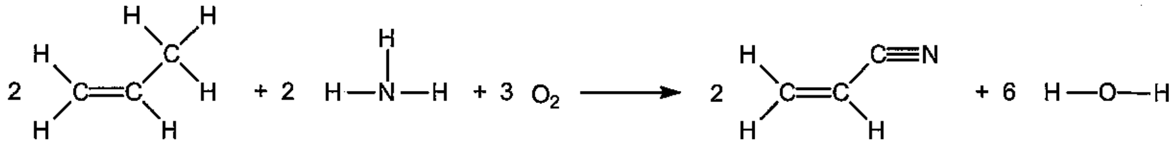
4 × 3 C–H (413 kJ/mol)
6 N=O (630. kJ/mol)

Bonds formed:

4 C≡N (891 kJ/mol)
6 × 2 H–O (467 kJ/mol)
1 N≡N (941 kJ/mol)

$\Delta H = 12(413) + 6(630.) - [4(891) + 12(467) + 941] = -1373 \text{ kJ}$

c.



Bonds broken:

- 2 × 3 C–H (413 kJ/mol)
- 2 × 3 N–H (391 kJ/mol)
- 3 O=O (495 kJ/mol)

Bonds formed:

- 2 C≡N (891 kJ/mol)
- 6 × 2 O–H (467 kJ/mol)

$$\Delta H = 6(413) + 6(391) + 3(495) - [2(891) + 12(467)] = -1077 \text{ kJ}$$

d. Because both reactions are highly exothermic, the high temperature is not needed to provide energy. It must be necessary for some other reason. The reason is to increase the speed of the reaction. This is discussed in Chapter 12 on kinetics.

155. a. i. $C_6H_6N_{12}O_{12} \rightarrow 6\ CO + 6\ N_2 + 3\ H_2O + 3/2\ O_2$

The NO_2 groups are assumed to have one N–O single bond and one N=O double bond, and each carbon atom has one C–H single bond. We must break and form all bonds.

Bonds broken:

- 3 C–C (347 kJ/mol)
- 6 C–H (413 kJ/mol)
- 12 C–N (305 kJ/mol)
- 6 N–N (160. kJ/mol)
- 6 N–O (201 kJ/mol)
- 6 N=O (607 kJ/mol)

ΣD_{broken} = 12,987 kJ

Bonds formed:

- 6 C≡O (1072 kJ/mol)
- 6 N≡N (941 kJ/mol)
- 6 H–O (467 kJ/mol)
- 3/2 O=O (495 kJ/mol)

ΣD_{formed} = 15,623 kJ

$$\Delta H = \Sigma D_{\text{broken}} - \Sigma D_{\text{formed}} = 12{,}987 \text{ kJ} - 15{,}623 \text{ kJ} = -2636 \text{ kJ}$$

ii. $C_6H_6N_{12}O_{12} \rightarrow 3\ CO + 3\ CO_2 + 6\ N_2 + 3\ H_2O$

Note: The bonds broken will be the same for all three reactions.

Bonds formed:

- 3 C≡O (1072 kJ/mol)
- 6 C=O (799 kJ/mol)
- 6 N≡N (941 kJ/mol)
- 6 H–O (467 kJ/mol)

ΣD_{formed} = 16,458 kJ

$$\Delta H = 12{,}987 \text{ kJ} - 16{,}458 \text{ kJ} = -3471 \text{ kJ}$$

iii. $C_6H_6N_{12}O_{12} \rightarrow 6\ CO_2 + 6\ N_2 + 3\ H_2$

Bonds formed:

12 C=O (799 kJ/mol)
6 N≡N (941 kJ/mol)
3 H–H (432 kJ/mol)
$\Sigma D_{formed} = 16{,}530.$ kJ

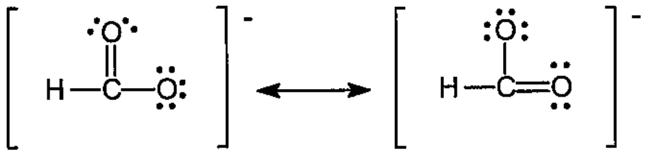
$\Delta H = 12{,}987\text{ kJ} - 16{,}530.\text{ kJ} = -3543\text{ kJ}$

b. Reaction iii yields the most energy per mole of CL-20, so it will yield the most energy per kilogram.

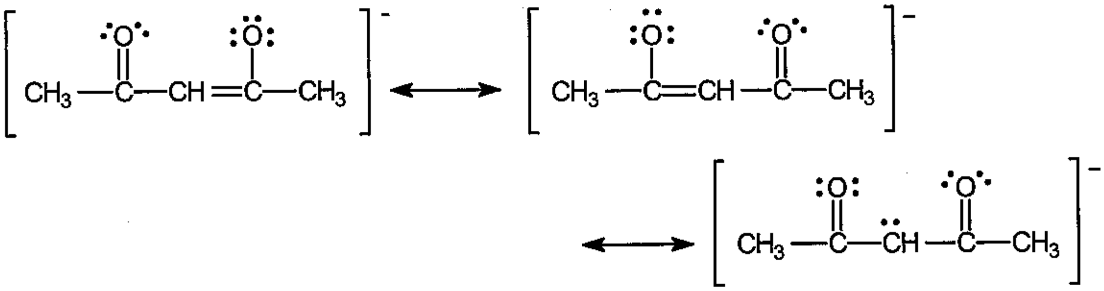
$$\frac{-3543\text{ kJ}}{\text{mol}} \times \frac{1\text{ mol}}{438.23\text{ g}} \times \frac{1000\text{ g}}{\text{kg}} = -8085\text{ kJ/kg}$$

156. We can draw resonance forms for the anion after the loss of H^+, we can argue that the extra stability of the anion causes the proton to be more readily lost, i.e., makes the compound a better acid.

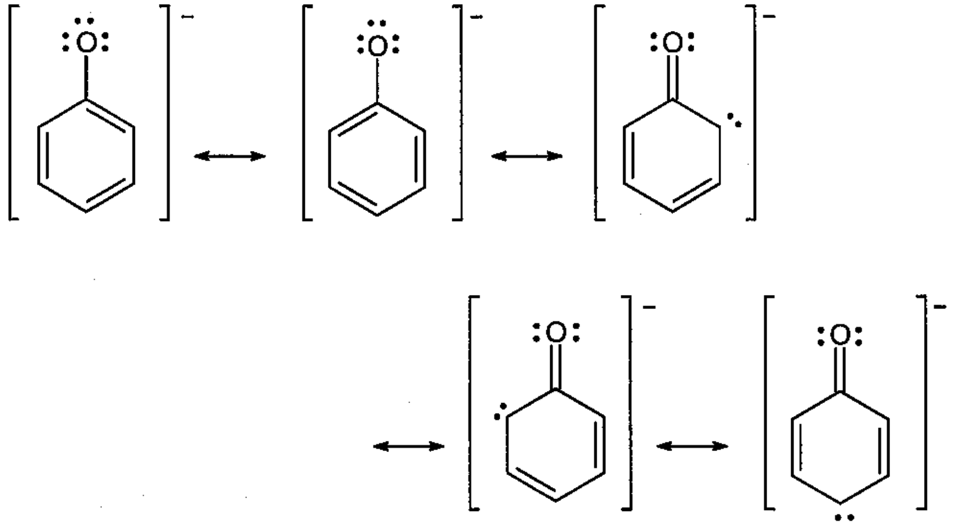
a.



b.

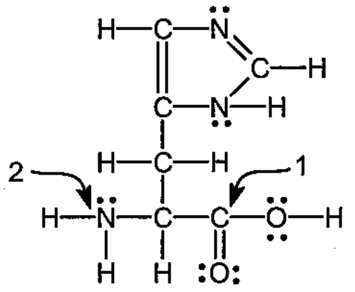


c.



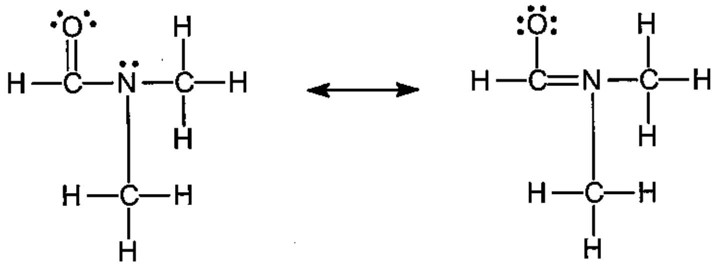
In all three cases, extra resonance forms can be drawn for the anion that are not possible when the H^+ is present, which leads to enhanced stability.

157. For carbon atoms to have a formal charge of zero, each C atom must satisfy the octet rule by forming four bonds (with no lone pairs). For nitrogen atoms to have a formal charge of zero, each N atom must satisfy the octet rule by forming three bonds and have one lone pair of electrons. For oxygen atoms to have a formal charge of zero, each O atom must satisfy the octet rule by forming two bonds and have two lone pairs of electrons. With these bonding requirements in mind, then the Lewis structure of histidine, where all atoms have a formal charge of zero, is:

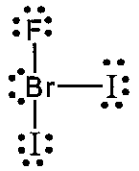


We would expect 120° bond angles about the carbon atom labeled 1 and ≈109.5° bond angles about the nitrogen atom labeled 2. The nitrogen bond angles should be slightly smaller than 109.5° due to the lone pair of electrons on nitrogen.

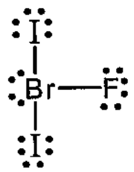
158. This molecule has 30 valence electrons. The only C–N bond that can possibly have a double-bond character is the N bound to the C with O attached. Double bonds to the other two C–N bonds would require carbon in each case to have 10 valence electrons (which carbon never does). The resonance structures are:



159. a. BrFI$_2$, 7 +7 + 2(7) = 28 e$^-$; two possible structures exist with Br as the central atom; each has a T-shaped molecular structure.

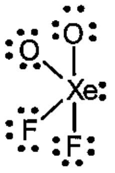


90° bond angles between I atoms

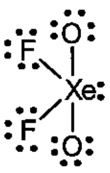


180° bond angles between I atoms

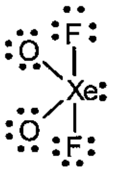
b. XeO$_2$F$_2$, 8 + 2(6) + 2(7) = 34 e$^-$; three possible structures exist with Xe as the central atom; each has a see-saw molecular structure.



90° bond angle between O atoms

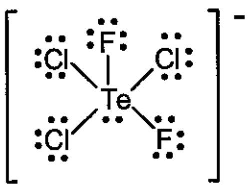


180° bond angle between O atoms

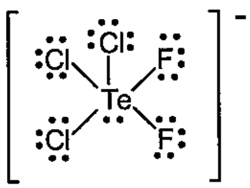


120° bond angle between O atoms

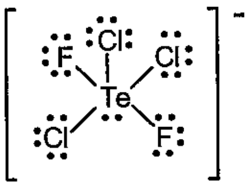
c. TeF$_2$Cl$_3^-$; 6 + 2(7) + 3(7) + 1 = 42 e$^-$; three possible structures exist with Te as the central atom; each has a square pyramid molecular structure.



One F is 180° from the lone pair.

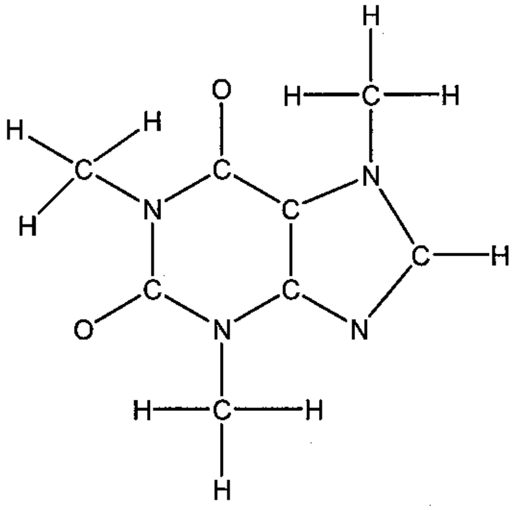


Both F atoms are 90° from the lone pair and 90° from each other.



Both F atoms are 90° from the lone pair and 180° from each other.

160. The skeletal structure of caffeine is:



For a formal charge of zero on all atoms, the bonding requirements are:

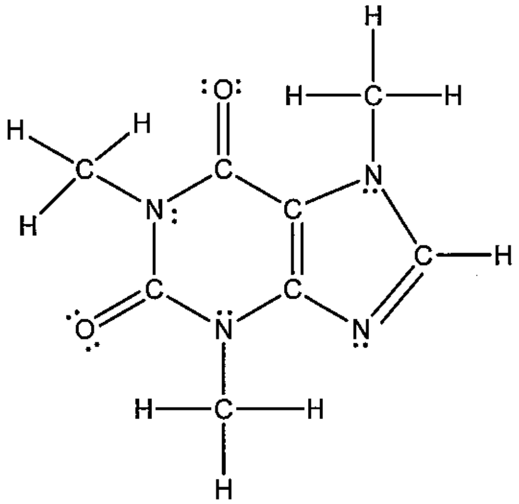
(1) four bonds and no lone pairs for each carbon atom;

(2) three bonds and one lone pair for each nitrogen atom;

(3) two bonds and two lone pairs for each oxygen atom;

(4) one bond and no lone pairs for each hydrogen atom.

Following these guidelines gives a Lewis structure that has a formal charge of zero for all the atoms in the molecule. The Lewis structure is:



Integrative Problems

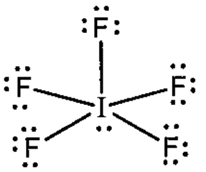
161. Assuming 100.00 g of compound: $42.81 \text{ g F} = \dfrac{1 \text{ mol X}}{19.00 \text{ g F}} = 2.253 \text{ mol F}$

The number of moles of X in XF_5 is: $2.53 \text{ mol F} \times \dfrac{1 \text{ mol X}}{5 \text{ mol F}} = 0.4506 \text{ mol X}$

This number of moles of X has a mass of 57.19 g (= 100.00 g – 42.81 g). The molar mass of X is:

$\dfrac{57.19 \text{ g X}}{0.4506 \text{ mol X}} = 126.9$ g/mol; this is element I and the compound is IF_5.

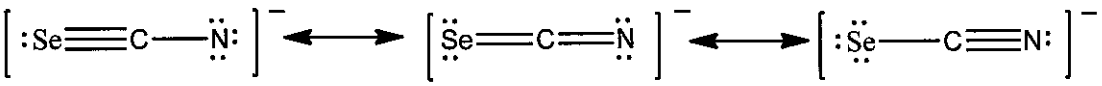
IF_5, $7 + 5(7) = 42\ e^-$



The molecular structure is square pyramid.

162. If X^{2-} has a configuration of $[Ar]4s^2 3d^{10} 4p^6$, then X must have a configuration with two fewer electrons, $[Ar]4s^2 3d^{10} 4p^4$. This is element Se.

$SeCN^-$, $6 + 4 + 5 + 1 = 16\ e^-$



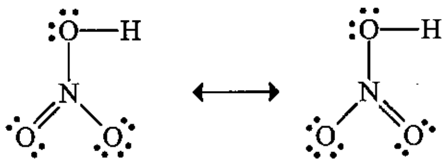
163. The elements are identified by their electron configurations:

$[Ar]4s^1 3d^5$ = Cr; $[Ne]3s^2 3p^3$ = P; $[Ar]4s^2 3d^{10} 4p^3$ = As; $[Ne]3s^2 3p^5$ = Cl

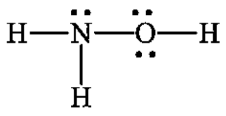
Following the electronegativity trend, the order is Cr < As < P < Cl.

Marathon Problem

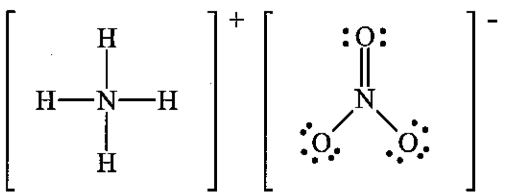
164. Compound A: This compound is a strong acid (part g). HNO_3 is a strong acid and is available in concentrated solutions of 16 *M* (part c). The highest possible oxidation state of nitrogen is +5, and in HNO_3, the oxidation state of nitrogen is +5 (part b). Therefore, compound A is most likely HNO_3. The Lewis structures for HNO_3 are:



Compound B: This compound is basic (part g) and has one nitrogen (part b). The formal charge of zero (part b) tells us that there are three bonds to the nitrogen and that the nitrogen has one lone pair. Assuming compound B is monobasic, then the data in part g tell us that the molar mass of B is 33.0 g/mol (21.98 mL of 1.000 *M* HCl = 0.02198 mol HCl; thus there are 0.02198 mol of B; 0.726 g/0.02198 mol = 33.0 g/mol). Because this number is rather small, it limits the possibilities. That is, there is one nitrogen, and the remainder of the atoms are O and H. Since the molar mass of B is 33.0 g/mol, then only one O oxygen atom can be present. The N and O atoms have a combined molar mass of 30.0 g/mol; the rest is made up of hydrogens (3 H atoms), giving the formula NH_3O. From the list of K_b values for weak bases in Appendix 5 of the text, compound B is most likely NH_2OH. The Lewis structure is:



Compound C: From parts a and f and assuming compound A is HNO_3 , then compound C contains the nitrate ion, NO_3^-. Because part b tells us that there are two nitrogens, the other ion needs to have one N atom and some H atoms. In addition, compound C must be a weak acid (part g), which must be due to the other ion since NO_3^- has no acidic properties. Also, the nitrogen atom in the other ion must have an oxidation state of -3 (part b) and a formal charge of +1. The ammonium ion fits the data. Thus compound C is most likely NH_4NO_3. A Lewis structure is:



Note: Two more resonance structures can be drawn for NO_3^-.

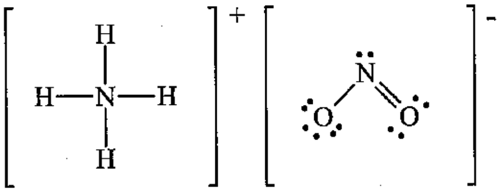
Compound D: From part f, this compound has one less oxygen atom than compound C; thus NH_4NO_2 is a likely formula. Data from part e confirm this. Assuming 100.0 g of compound, we have:

43.7 g N × 1 mol/14.01 g = 3.12 mol N
50.0 g O × 1 mol/16.00 g = 3.12 mol O
6.3 g H × 1 mol/1.008 g = 6.25 mol H

There is a 1 : 1 : 2 mole ratio among N to O to H. The empirical formula is NOH_2, which has an empirical formula mass of 32.0 g/mol.

$$\text{Molar mass} = \frac{dRT}{P} = \frac{2.86\text{ g/L}(0.08206\text{ L atm/K}\bullet\text{mol})(273\text{ K})}{1.00\text{ atm}} = 64.1\text{ g/mol}$$

For a correct molar mass, the molecular formula of compound D is $N_2O_2H_4$ or NH_4NO_2. A Lewis structure is:



Note: One more resonance structure for NO_2^- can be drawn.

<u>Compound E:</u> A basic solution (part g) that is commercially available at 15 *M* (part c) is ammonium hydroxide (NH_4OH). This is also consistent with the information given in parts b and d. The Lewis structure for NH_4OH is: