CHAPTER 13

BONDING: GENERAL CONCEPTS

Chemical Bonds and Electronegativity

11.   Electronegativity is the ability of an atom in a molecule to attract electrons to itself. Electronegativity is a bonding term. Electron affinity is the energy change when an electron is added to a substance. Electron affinity deals with isolated atoms in the gas phase.

A covalent bond is a sharing of electron pair(s) in a bond between two atoms. An ionic bond is a complete transfer of electrons from one atom to another to form ions. The electrostatic attraction of the oppositely charged ions is the ionic bond.

A pure covalent bond is an equal sharing of shared electron pair(s) in a bond. A polar covalent bond is an unequal sharing.

Ionic bonds form when there is a large difference in electronegativity between the two atoms bonding together. This usually occurs when a metal with a small electronegativity is bonded to a nonmetal having a large electronegativity. A pure covalent bond forms between atoms having identical or nearly identical eletronegativities. A polar covalent bond forms when there is an intermediate electronegativity difference. In general, nonmetals bond together by forming covalent bonds, either pure covalent or polar covalent.

Ionic bonds form due to the strong electrostatic attraction between two oppositely charged ions. Covalent bonds form because the shared electrons in the bond are attracted to two different nuclei, unlike the isolated atoms where electrons are only attracted to one nuclei. The attraction to another nuclei overrides the added electron-electron repulsions.

12.   a.   There are two attractions of the form $\dfrac{(+1)(-1)}{r}$, 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 4 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.

13.   Using the periodic table, we expect the general trend for electronegativity to be:

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

   2. Decrease as we go down a group

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

   d. $Tl < Ge < S$ e. $Rb < K < Na$ f. $Ga < B < O$

14.   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   e. Sn–H   f. Tl–Br

15.   The general trends in electronegativity used in Exercises 13.13 and 13.14 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 using Figure 13.3 is:

   a. $C\ (2.6) < N\ (3.0) < O\ (3.4)$ same as predicted

   b. $Se\ (2.6) = S\ (2.6) < Cl\ (3.2)$ different

   c. $Si\ (1.9) < Ge\ (2.0) = Sn\ (2.0)$ different   d. $Tl\ (2.0) = Ge\ (2.0) < S\ (2.6)$ different

   e. $Rb\ (0.8) = K\ (0.8) < Na\ (0.9)$ different   f. $Ga\ (1.8) < B\ (2.0) < O\ (3.4)$ same

   Most polar bonds using actual EN values:

   a. Si–F (Ge–F predicted)   b. P–Cl (same as predicted)

   c. S–F (same as predicted)   d. Ti–Cl (same as predicted)

   e. C–H (Sn–H predicted)   f. Al–Br (Tl–Br predicted)

16.   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.

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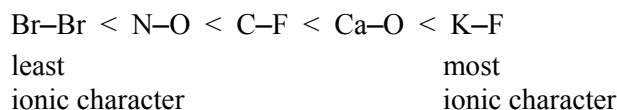
Note that Br–Br, N–O and C–F bonds are all covalent bonds since the elements are all non-metals. The Ca–O and K–F bonds are ionic, as is generally the case when a metal forms a bond with a nonmetal.

18.   (IE – EA)   (IE – EA)/502   EN (text) $2006/502 = 4.0$

F   2006 kJ/mol   4.0   4.0
Cl   1604   3.2   3.2
Br   1463   2.9   3.0
I   1302   2.6   2.7

The values calculated from IE and EA show the same trend as (and agree fairly closely) with the values given in the text.

Ionic Compounds

19.   Anions are larger than the neutral atom, and cations are smaller than the neutral atom. For anions, the added electrons increase the electron-electron repulsions. To counteract this, the size of the electron cloud increases, placing the electrons further apart from one another. For cations, as electrons are removed, there are fewer electron-electron repulsions, and the electron cloud can be pulled closer to the nucleus.

Isoelectronic: same number of electrons. Two variables, the number of protons and the number of electrons, determine the size of an ion. Keeping the number of electrons constant, we only have to consider the number of protons to predict trends in size. The ion with the most protons attracts the same number of electrons most strongly, resulting in a smaller size.

20.   All of 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:


K⁺   Ca²⁺   Sc³⁺   S²⁻   Cl⁻
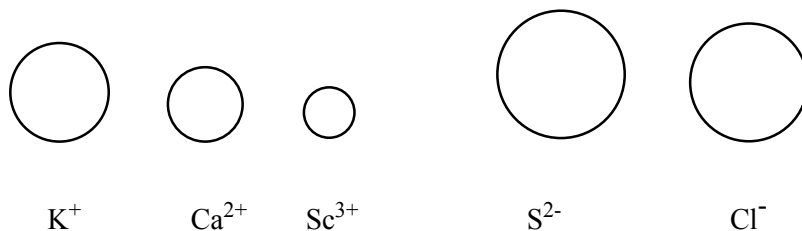
21.   a. $Cu > Cu^+ > Cu^{2+}$ b. $Pt^{2+} > Pd^{2+} > Ni^{2+}$ c. $O^{2-} > O^- > O$

       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.
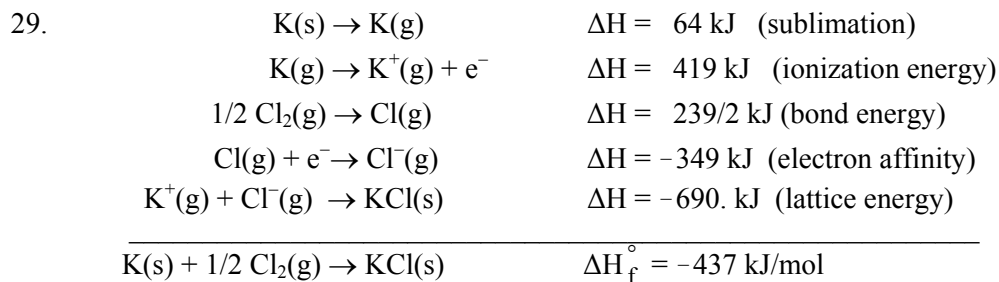
22.   a. Mg^{2+}: $1s^2 2s^2 2p^6$ Sn^{2+}: $[Kr]5s^2 4d^{10}$

            K^+: $1s^2 2s^2 2p^6 3s^2 3p^6$ Al^{3+}: $1s^2 2s^2 2p^6$

            Tl^+: $[Xe]6s^2 4f^{14} 5d^{10}$ As^{3+}: $[Ar]4s^2 3d^{10}$

       b. N^{3-}, O^{2-} and F^-: $1s^2 2s^2 2p^6$ Te^{2-}: $[Kr]5s^2 4d^{10} 5p^6$

       c. Be^{2+}: $1s^2$ Rb^+: $[Ar]4s^2 3d^{10} 4p^6$

            Ba^{2+}: $[Kr]5s^2 4d^{10} 5p^6$ Se^{2-}: $[Ar]4s^2 3d^{10} 4p^6$

            I^-: $[Kr]5s^2 4d^{10} 5p^6$

23.   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.

24.   a. Sc^{3+} b. Te^{2-} c. Ce^{4+} and Ti^{4+} d. Ba^{2+}

       All of these have the number of electrons of a noble gas.

25. Se^{2-}, Br^-, Rb^+, Sr^{2+}, Y^{3+}, and Zr^{4+} are some ions that are isoelectronic with Kr (36 electrons). In terms of size, the ion with the most protons will hold the electrons tightest and will be the smallest. The size trend is:

            $Zr^{4+} < Y^{3+} < Sr^{2+} < Rb^+ < Br^- < Se^{2-}$
            smallest   largest

26.   Lattice energy is proportional to $Q_1 Q_2 / r$, where Q is the charge of the ions and r is the distance between the ions. In general, charge effects on lattice energy are greater than size effects.

       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^+.
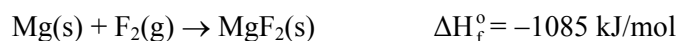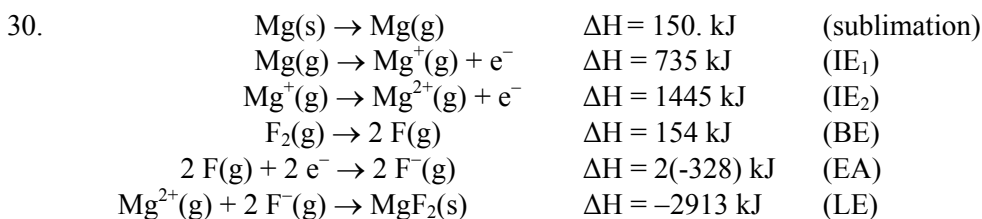
e. K_2O; O^{2-} has a greater charge than F^-.   f. Li_2O; The ions are smaller in Li_2O.

27.   a. Al^{3+} and S^{2-} are the expected ions. The formula of the compound would be Al_2S_3 (aluminum sulfide).

         b. K^+ and N^{3-}; K_3N, potassium nitride

         c. Mg^{2+} and Cl^-; $MgCl_2$, magnesium chloride

         d. Cs^+ and Br^-; CsBr, cesium bromide

28.   Ionic solids can be characterized as being held together by strong omnidirectional forces.

         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. If the 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 atoms/ions must slide across each other. For an ionic solid, the following might happen:

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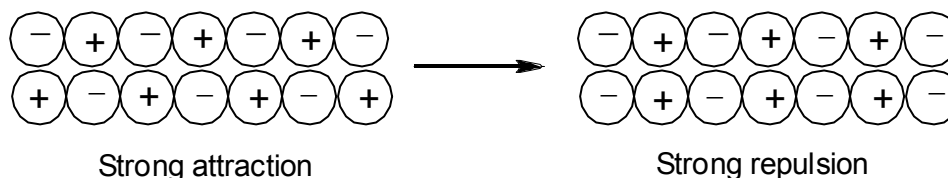
         Just as the layers begin to slide, there will be very strong repulsions causing the solid to snap across a fairly clean plane.

These properties and their correlation to chemical forces will be discussed in detail in Chapter 16.

29. $K(s) \rightarrow K(g)$ $\Delta H =$ 64 kJ (sublimation)
                          $K(g) \rightarrow K^+(g) + e^-$ $\Delta H =$ 419 kJ   (ionization energy)
                      $1/2\ Cl_2(g) \rightarrow Cl(g)$ $\Delta H =$ 239/2 kJ (bond energy)
                       $Cl(g) + e^- \rightarrow Cl^-(g)$ $\Delta H = -349$ kJ (electron affinity)
                $K^+(g) + Cl^-(g)\ \rightarrow KCl(s)$ $\Delta H = -690.$ kJ (lattice energy)
                      _____

                $K(s) + 1/2\ Cl_2(g) \rightarrow KCl(s)$ $\Delta H^{\circ}_f = -437$ kJ/mol

30. $Mg(s) \rightarrow Mg(g)$ $\Delta H = 150. \text{ kJ}$ (sublimation)
                           $Mg(g) \rightarrow Mg^+(g) + e^-$ $\Delta H = 735 \text{ kJ}$ (IE_1)
                          $Mg^+(g) \rightarrow Mg^{2+}(g) + e^-$ $\Delta H = 1445 \text{ kJ}$ (IE_2)
                           $F_2(g) \rightarrow 2 \text{ F}(g)$ $\Delta H = 154 \text{ kJ}$ (BE)
                    $2 \text{ F}(g) + 2 \text{ e}^- \rightarrow 2 \text{ F}^-(g)$ $\Delta H = 2(-328) \text{ kJ}$ (EA)
           $Mg^{2+}(g) + 2 \text{ F}^-(g) \rightarrow MgF_2(s)$ $\Delta H = -2913 \text{ kJ}$ (LE)
   _____

              $Mg(s) + F_2(g) \rightarrow MgF_2(s)$ $\Delta H_f^o = -1085 \text{ kJ/mol}$

31.   Use Figure 13.11 as a template for this problem.

                    $Li(s) \rightarrow Li(g)$ $\Delta H_{sub} = ?$
                    $Li(g) \rightarrow Li^+(g) + e^-$ $\Delta H = 520. \text{ kJ}$
                    $1/2 \text{ I}_2(g) \rightarrow \text{ I}(g)$ $\Delta H = 151/2 \text{ kJ}$
                    $I(g) + e^- \rightarrow I^-(g)$ $\Delta H = -295 \text{ kJ}$
              $Li^+(g) + I^-(g) \rightarrow LiI(s)$ $\Delta H = -753 \text{ kJ}$
        _____

        $Li(s) + 1/2 \text{ I}_2(g) \rightarrow LiI(s)$ $\Delta H = -272 \text{ kJ}$
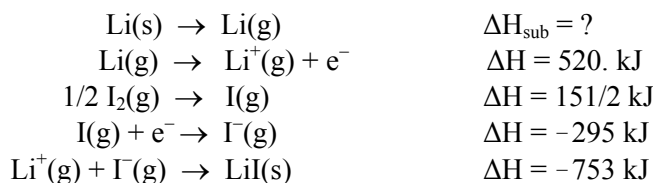
        $\Delta H_{sub} + 520. + 151/2 - 295 - 753 = -272, \ \Delta H_{sub} = 181 \text{ kJ}$

32.   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 full, the
        ionization energy required to remove another 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.

33.   a.   From the data given, less energy is required 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 for Mg^+O^- (due to the greater charges in $Mg^{2+}O^{2-}$). The favorable lattice energy
             term will dominate and $Mg^{2+}O^{2-}$ forms.

        b. Mg^+ and O^- both have unpaired electrons. In Mg^{2+} and O^{2-} there are no unpaired
             electrons. Hence Mg^+O^- would be paramagnetic; $Mg^{2+}O^{2-}$ would be diamagnetic.
             Paramagnetism can be detected by measuring the mass of a sample in the presence and
             absence of a magnetic field. The apparent mass of a paramagnetic substance will be
             larger in a magnetic field because of the force between the unpaired electrons and the
             field.

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

$$2\ Na(s) \rightarrow 2\ Na(g) \qquad\qquad 2\Delta H_{sub,\ Na} = 2(109)\ kJ$$
$$2\ Na(g) \rightarrow 2\ Na^+(g) + 2\ e^- \qquad 2IE = 2(495)\ kJ$$
$$S(s) \rightarrow S(g) \qquad\qquad\qquad \Delta H_{sub,\ S} = 277\ kJ$$
$$S(g) + e^- \rightarrow S^-(g) \qquad\qquad EA_1 = {-200.}\ kJ$$
$$S^-(g) + e^- \rightarrow S^{2-}(g) \qquad\quad EA_2 = ?$$
$$2\ Na^+(g) + S^{2-}(g) \rightarrow Na_2S(s) \qquad LE = {-2203}\ kJ$$

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$$2\ Na(s) + S(s) \rightarrow Na_2S(s) \qquad\qquad \Delta H_f^\circ = {-365}\ kJ$$
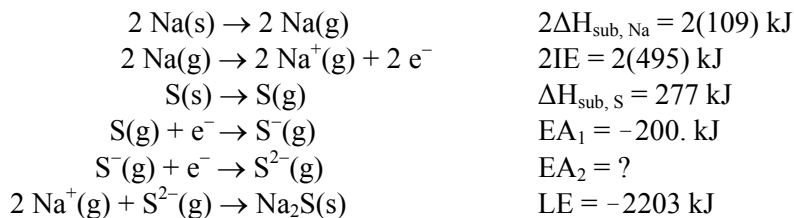
$\Delta H_f^\circ = 2\Delta H_{sub,\ Na} + 2IE + \Delta H_{sub,\ S} + EA_1 + EA_2 + LE,\ \ -365 = -918 + EA_2,\ \ EA_2 = 553\ kJ$

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

35. 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 to least exothermic to be:

     $CaSe\ >\ CaTe\ >\ Na_2Se\ >\ Na_2Te$
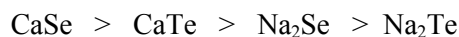
     $(-2862)\quad (-2721)\quad (-2130)\quad (-2095\ kJ/mol)$ This is what we observe.

36.   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
$FeCl_3$	$(+3)(-1) = -3$	-5339 kJ/mol
Fe_2O_3	$(+3)(-2) = -6$	$-14,744$ kJ/mol

Bond Energies

37.   a. $H{-\!\!-\!\!-}H\ +\ Cl{-\!\!-\!\!-}Cl\ \longrightarrow\ 2\ H{-}Cl$

Bonds broken: Bonds formed:

    1 H–H (432 kJ/mol)   2 H–Cl (427 kJ/mol)
    1 Cl–Cl (239 kJ/mol)

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

b.   N≡N + 3 H—H ⟶ 2 H—N—H
                             |
                             H
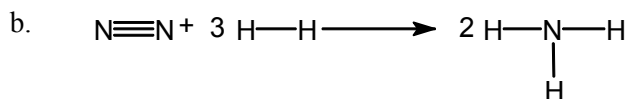
Bonds broken: Bonds formed:

    1 N ≡ N (941 kJ/mol)   6 N–H (391 kJ/mol)
    3 H–H (432 kJ/mol)

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

c.   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.

                                       H   H
                                       | |
    H—C≡N + 2 H—H ⟶ H—C—N
                                       | |
                                       H   H

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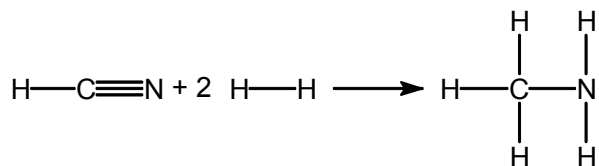
    1 C≡N (891 kJ/mol)   1 C–N (305 kJ/mol)
    2 H–H (432 kJ/mol)   2 C–H (413 kJ/mol)
                                        2 N–H (391 kJ/mol)

$\Delta H = 891$ kJ $+ 2(432$ kJ$) - [305$ kJ $+ 2(413$ kJ$) + 2(391$ kJ$)] = -158$ kJ
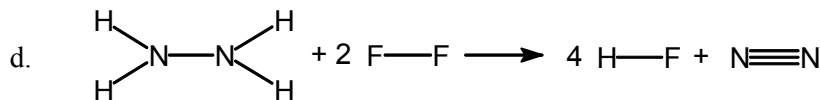
d.   H\   /H
           N—N   + 2 F—F ⟶ 4 H—F + N≡N
    H/   \H

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)

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

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

b. $\Delta H = 2\Delta H^o_{f, NH_3} = 2$ mol(-46 kJ/mol) = −92 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.

39.
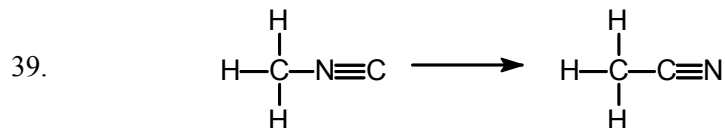
Bonds broken: 1 C−N (305 kJ/mol)   Bonds formed: 1 C−C (347 kJ/mol)

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

40.

Bonds broken: Bonds formed:

5 C−H (413 kJ/mol)   2 × 2 C=O (799 kJ/mol)
1 C−C (347 kJ/mol)   3 × 2 O−H (467 kJ/mol)
1 C−O (358 kJ/mol)
1 O−H (467 kJ/mol)
3 O=O (495 kJ/mol)

$\Delta H = 5(413$ kJ$) + 347$ kJ $+ 358$ kJ $+ 467$ kJ $+ 3(495$ kJ$) - [4(799$ kJ$) + 6(467$ kJ$)] = -1276$ kJ
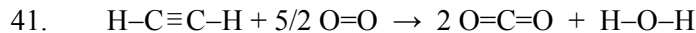
41.   H−C≡C−H + 5/2 O=O → 2 O=C=O + H−O−H

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)

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

42.   Let $x =$ bond energy for A_2, and then $2x =$ bond energy for AB.

$\Delta H = -285$ kJ $= x + 432$ kJ $- [2(2x)]$, $3x = 717$, $x = 239$ kJ/mol = bond energy for A_2

43.
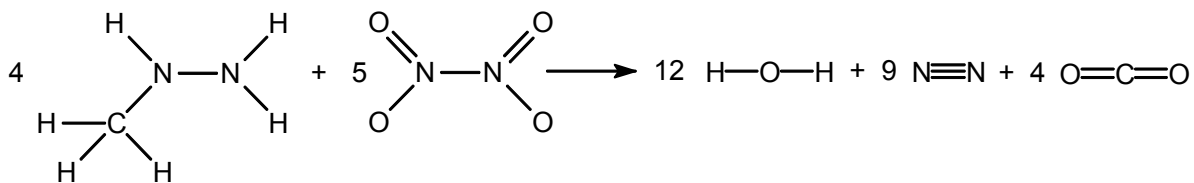
Bonds broken:

9 N–N (160. kJ/mol)
4 N–C (305 kJ/mol)
12 C–H (413 kJ/mol)
12 N–H (391 kJ/mol)
10 N=O (607 kJ/mol)
10 N–O   (201 kJ/mol)

Bonds formed:

24 O–H (467 kJ/mol)
9 N≡N (941 kJ/mol)
8 C=O (799 kJ/mol)

$\Delta H = 9(160.) + 4(305) + 12(413) + 12(391) + 10(607) + 10(201)$

$- [24(467) + 9(941) + 8(799)]$

$\Delta H = 20,388 \text{ kJ} - 26,069 \text{ kJ} = -5681 \text{ kJ}$

44.   a.   I.
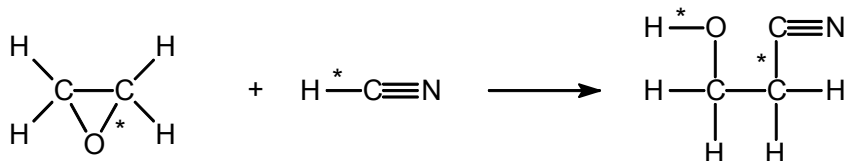
Bonds broken (*):

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.
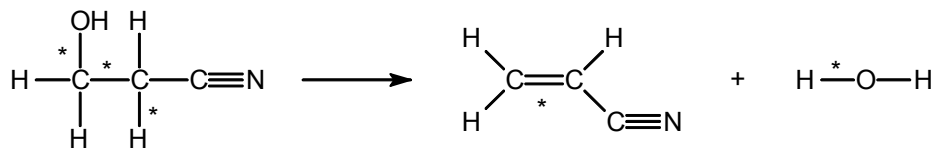
Bonds broken (*):   Bonds formed (*):

    1 C–O (358 kJ/mol)   1 H–O (467 kJ/mol)
    1 C–H (413 kJ/mol)   1 C=C (614 kJ/mol)
    1 C–C (347 kJ/mol)

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

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

b.
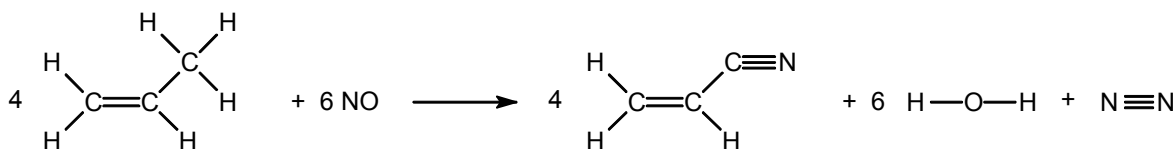
Bonds broken: Bonds formed:

    4 × 3 C–H (413 kJ/mol)   4 C≡N (891 kJ/mol)

    6 N=O (630. 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.
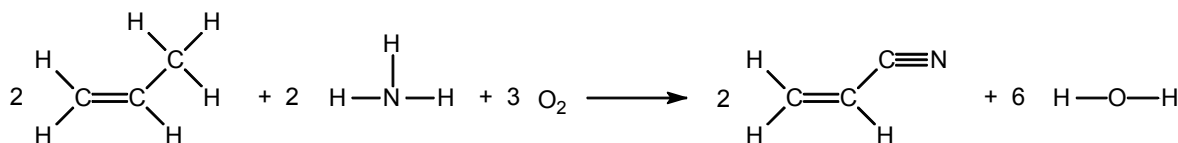
Bonds broken: Bonds formed:

    2 × 3 C–H (413 kJ/mol)   2 C≡N (891 kJ/mol)
    2 × 3 N–H (391 kJ/mol)   6 × 2 O–H (467 kJ/mol)
    3 O=O (495 kJ/mol)

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

45.   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 will be discussed in Chapter 15 on kinetics.

46.

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)
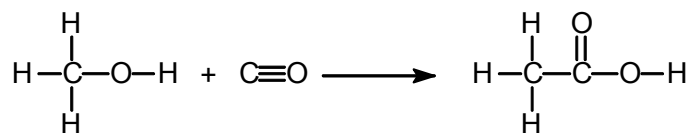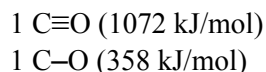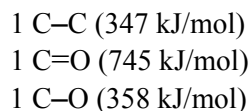
$\Delta H = 1072 + 358 - (347 + 745 + 358) = -20. \ kJ$

$CH_3OH(g) + CO(g) \rightarrow CH_3COOH(l)$ $\Delta H° = -484 \ kJ - [(-201 \ kJ) + (-110.5 \ kJ)] = -173 \ kJ$
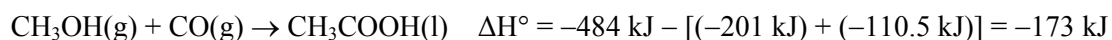
Using bond energies, $\Delta H = -20.$ kJ. For this reaction, bond energies give a much poorer estimate for ΔH as compared with gas phase reactions. The major reason for the large discrepancy is that not all species are gases in this exercise. Bond energies do not account for the energy changes that occur when liquids and solids form instead of gases. These energy changes are due to intermolecular forces and will be discussed in Chapter 16.

47.   a. $HF(g) \rightarrow H(g) + F(g)$ $\Delta H = 565 \ kJ$
               $H(g) \rightarrow H^+(g) + e^-$ $\Delta H = 1312 \ kJ$
               $F(g) + e^- \rightarrow F^-(g)$ $\Delta H = -327.8 \ kJ$
              ―――――――――――――――――――――――――――――――――――
               $HF(g) \rightarrow H^+(g) + F^-(g)$ $\Delta H = 1549 \ kJ$

    b. $HCl(g) \rightarrow H(g) + Cl(g)$ $\Delta H = 427 \ kJ$
               $H(g) \rightarrow H^+(g) + e^-$ $\Delta H = 1312 \ kJ$
               $Cl(g) + e^- \rightarrow Cl^-(g)$ $\Delta H = -348.7 \ kJ$
              ―――――――――――――――――――――――――――――――――――
               $HCl(g) \rightarrow H^+(g) + Cl^-(g)$ $\Delta H = 1390. \ kJ$

    c. $HI(g) \rightarrow H(g) + I(g)$ $\Delta H = 295 \ kJ$
               $H(g) \rightarrow H^+(g) + e^-$ $\Delta H = 1312 \ kJ$
               $I(g) + e^- \rightarrow I^-(g)$ $\Delta H = -295.2 \ kJ$
              ―――――――――――――――――――――――――――――――――――
               $HI(g) \rightarrow H^+(g) + I^-(g)$ $\Delta H = 1312 \ kJ$

    d. $H_2O(g) \rightarrow OH(g) + H(g)$ $\Delta H = 467 \ kJ$
               $H(g) \rightarrow H^+(g) + e^-$ $\Delta H = 1312 \ kJ$
               $OH(g) + e^- \rightarrow OH^-(g)$ $\Delta H = -180. \ kJ$
              ―――――――――――――――――――――――――――――――――――
               $H_2O(g) \rightarrow H^+(g) + OH^-(g)$ $\Delta H = 1599 \ kJ$

48.   a. Using SF_4 data: $SF_4(g) \rightarrow S(g) + 4 \ F(g)$
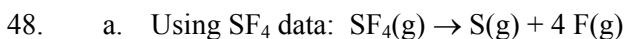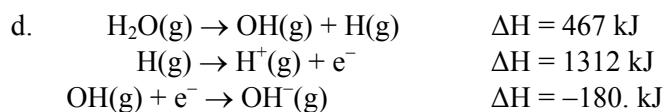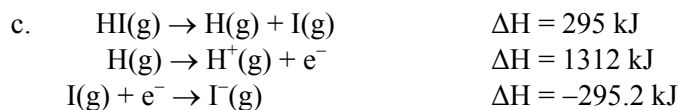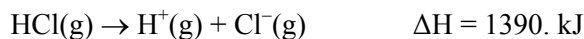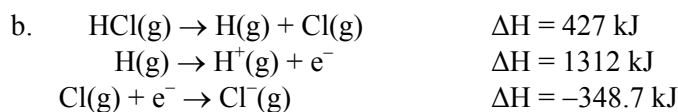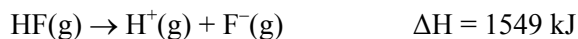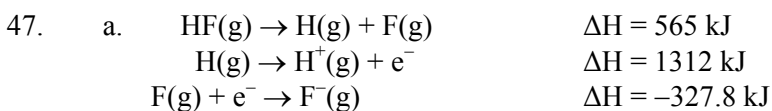
        $\Delta H° = 4D_{SF} = 278.8 \ kJ + 4(79.0 \ kJ) - (-775 \ kJ) = 1370. \ kJ$

$$D_{SF} = \frac{1370. \ kJ}{4 \ mol \ SF \ bonds} = 342.5 \ kJ/mol$$

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

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

$$D_{SF} = \frac{1962\ kJ}{6} = 327.0\ kJ/mol$$

b.   The S‒F bond energy in Table 13.6 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 form of the element at 25°C and 1 atm. The most stable forms are $S_8(s)$ and $F_2(g)$; $\Delta H_f° = 0$ for these two species.

49. $NH_3(g) \rightarrow N(g) + 3\ H(g)$

$\Delta H° = 3D_{NH} = 472.7\ kJ + 3(216.0\ kJ) - (-46.1\ kJ) = 1166.8\ kJ$

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

$D_{calc} = 389\ kJ/mol$ compared with 391 kJ/mol in the table. There is good agreement.

50. $\Delta H_f°$ for H(g) is $\Delta H°$ for the reaction: $1/2\ H_2(g) \rightarrow H(g)$; $\Delta H_f°$ for H(g) equals one-half the H‒H bond energy.

Lewis Structures and Resonance

51.   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.   HCN has $1 + 4 + 5 = 10$ valence electrons.

b. PH_3 has $5 + 3(1) = 8$ valence electrons.

H—C—N   H—C≡N:

Skeletal   Lewis
structure   structure

H—P—H   H—P̈—H
     | |
     H   H
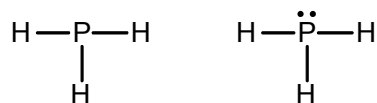
Skeletal   Lewis
structure   structure

Skeletal structure uses 4 e¯; 6 e¯ remain

Skeletal structures uses 6 e¯; 2 e¯ remain

c. $CHCl_3$ has $4 + 1 + 3(7) = 26$ valence electrons.
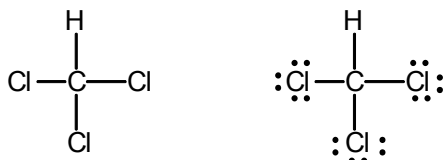
d. NH_4^+ has $5 + 4(1) - 1 = 8$ valence electrons.

Skeletal
structure

Lewis
structure

Lewis
structure

Note: Subtract valence electrons for positive charged ions.
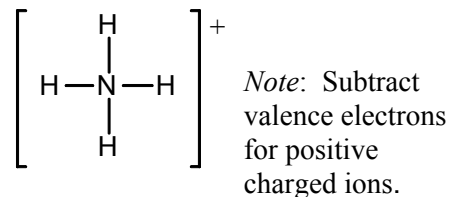
e. H_2CO has $2(1) + 4 + 6 = 12$ valence electrons.
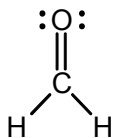
f. SeF_2 has $6 + 2(7) = 20$ valence electrons.
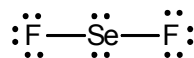
g. CO_2 has $4 + 2(6) = 16$ valence electrons.
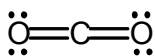
h. O_2 has $2(6) = 12$ valence electrons.

i.   HBr has $1 + 7 = 8$ valence electrons.
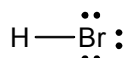
52.   a. $POCl_3$ has $5 + 6 + 3(7) = 32$ valence electrons.
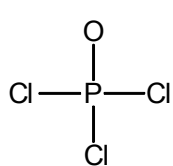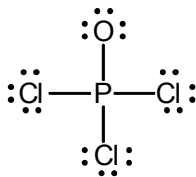
Skeletal   Lewis
structure   structure

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.
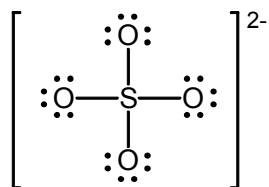
Note: A negatively charged ion will have additional electrons to those that come from the valence shell of the atoms.
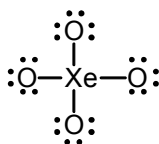
XeO_4, $8 + 4(6) = 32$ e⁻ PO_4^{3-}, $5 + 4(6) + 3 = 32$ e⁻
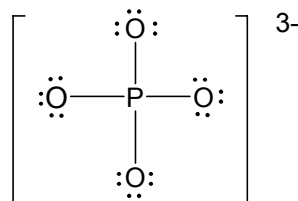
ClO_4^- has $7 + 4(6) + 1 = 32$ valence electrons.
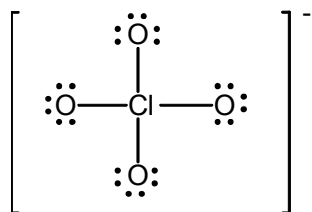
Note: All these species have the same number of atoms and the same number of valence electrons. They also have the same Lewis structure.

b. NF_3 has $5 + 3(7) = 26$ valence electrons. SO_3^{2-}, $6 + 3(6) + 2 = 26$ e⁻
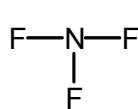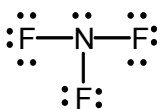
Skeletal   Lewis
structure   structure
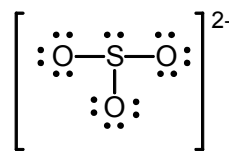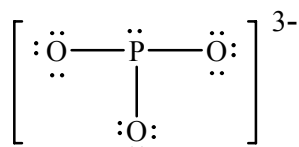
PO_3^{3-}, $5 + 3(6) + 3 = 26$ e⁻ ClO_3^-, $7 + 3(6) + 1 = 26$ e⁻
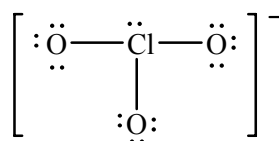
Note: Species with the same number of atoms and valence electrons have similar Lewis
structures.

c. ClO_2^- has $7 + 2(6) + 1 = 20$ valence electrons.
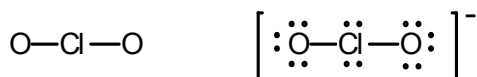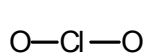
Skeletal structure   Lewis structure
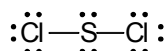
SCl_2, $6 + 2(7) = 20$ e⁻ PCl_2^-, $5 + 2(7) + 1 = 20$ e⁻
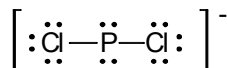
Note: Species with the same number of atoms and valence electrons have similar Lewis
structures.

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

54.   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.
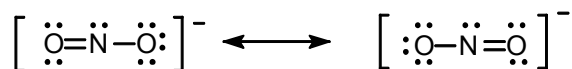
Because there is no reason to have the double bond to a particular oxygen atom, we can draw two resonance structures. Each Lewis structure uses the correct number of electrons and satisfies the octet rules, so each is a valid Lewis structure. Resonance structures occur when you have multiple bonds that 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 between the three oxygen atoms.
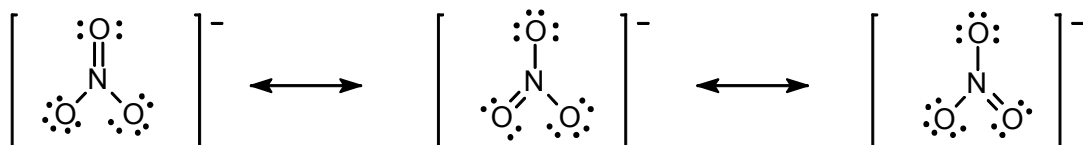
N_2O_4 has $2(5) + 4(6) = 34$ valence electrons. We can draw four resonance structures for N_2O_4.
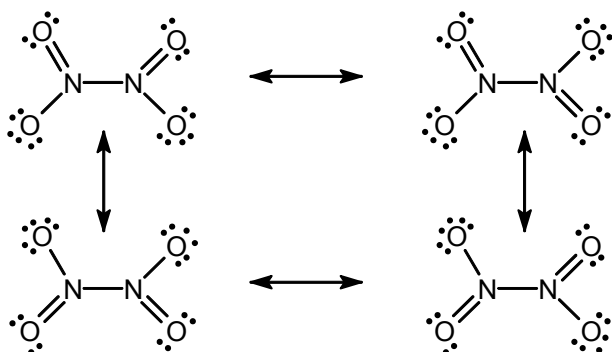
b. OCN^- has $6 + 4 + 5 + 1 = 16$ valence electrons. We can draw three resonance structures for OCN^-.
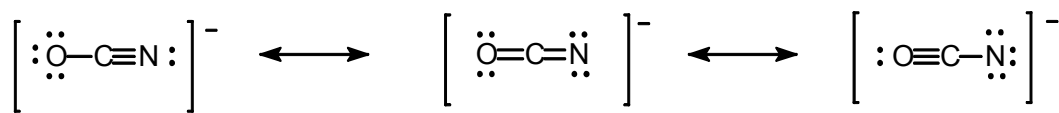
SCN^- has $6 + 4 + 5 + 1 = 16$ valence electrons. Three resonance structures can be drawn.
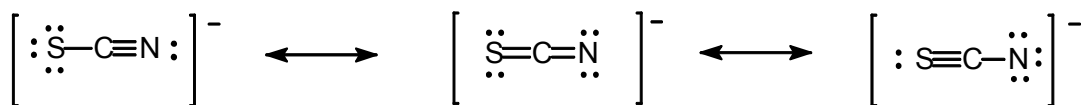
N_3^- has $3(5) + 1 = 16$ valence electrons. As with OCN^- and SCN^-, three different resonance structures can be drawn.
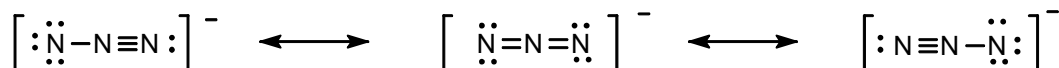
55.   Ozone: O_3 has $3(6) = 18$ valence electrons. Two resonance structures can be drawn.
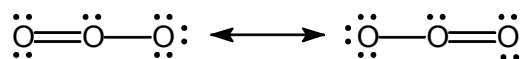
Sulfur dioxide: SO_2 has $6 + 2(6) = 18$ valence electrons. Two resonance structures are possible.
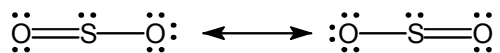
Sulfur trioxide: SO_3 has $6 + 3(6) = 24$ valence electrons. Three resonance structures are possible.
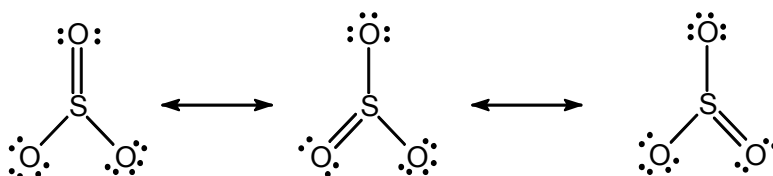
56.   PAN ($H_3C_2NO_5$) has $3(1) + 2(4) + 5 + 5(6) = 46$ valence electrons.
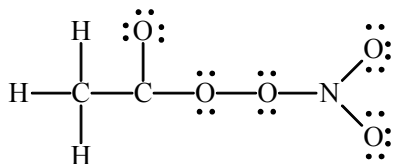
This is the skeletal structure with complete octets about oxygen atoms (46 electrons used).

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 form two double bonds.

(last form not important)
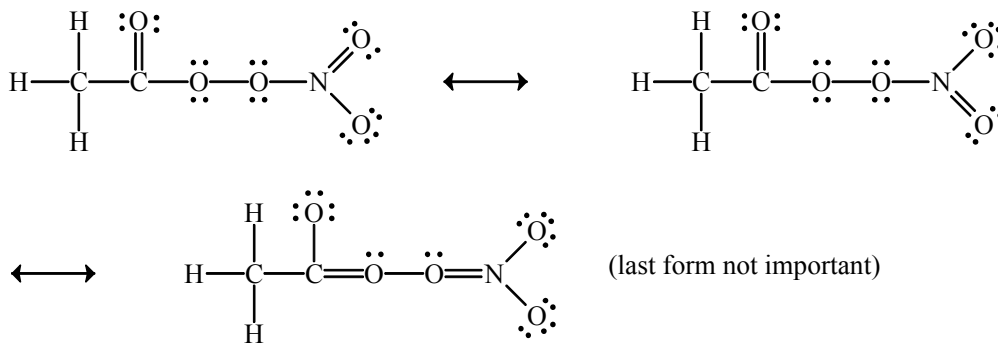
57. CH_3NCO has $4 + 3(1) + 5 + 4 + 6 = 22$ valence electrons. The order of the elements in the formula give the skeletal structure.
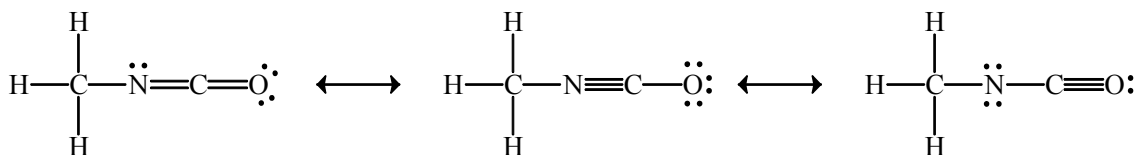
58.   Resonance occurs when more than one valid Lewis structure can be drawn for a particular
       molecule. A common characteristic of resonance structures is a multiple bond(s) that moves
       from one position to another. We say the electrons in the multiple bond(s) are delocalized in
       the molecule. This helps us rationalize why the bonds in a molecule that exhibit resonance are
       all equivalent in length and strength. Any one of the resonance structures indicates different
       types of bonds within that molecule. This is not correct, hence none of the individual
       resonance structures are correct. We think of the actual structure as an average of all the
       resonance structures; again, this helps explain the equivalent bonds within the molecule that
       experiment tells us we have.

59.   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.
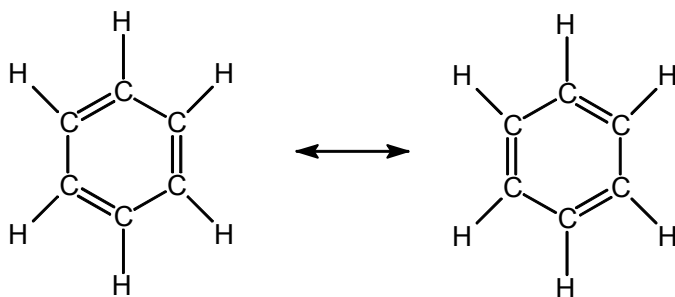
60.   We will use a hexagon to represent the six-membered carbon ring, and we will omit the four
       hydrogen atoms and the three lone pairs of electrons on each chlorine. If no resonance exists,
       we could draw four different molecules:
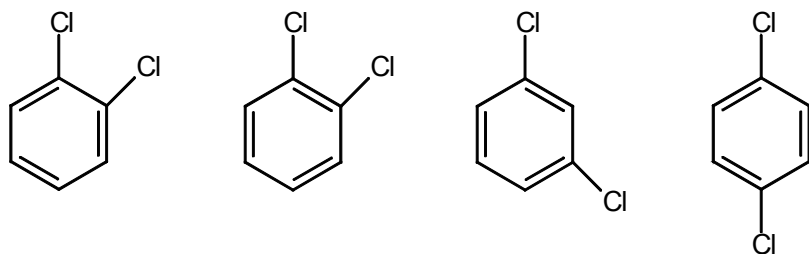
       If the double bonds in the benzene ring exhibit resonance, then we can draw only three
       different dichlorobenzenes. The circle in the hexagon in the following illustrations represent
       the delocalization of the three double bonds in the benzene ring (see Exercise 13.59).
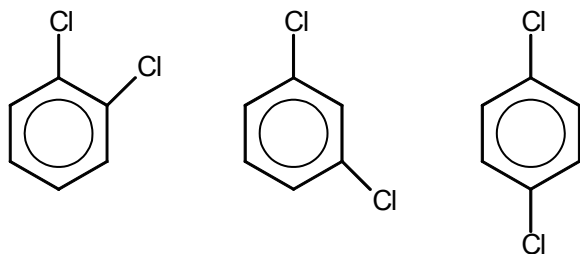
With resonance, all carbon-carbon bonds are equivalent. We can't distinguish between a single and double bond between adjacent carbons that have a chlorine attached. That only three isomers are observed supports the concept of resonance.

61.   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 13.59.
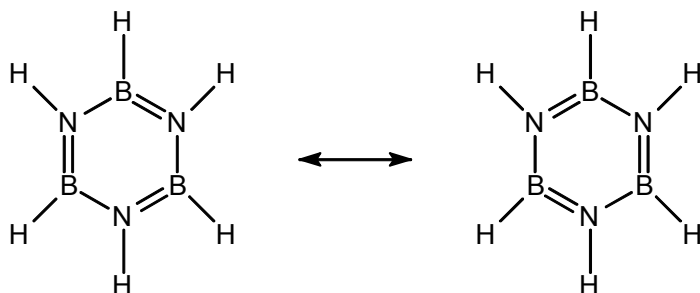
62.
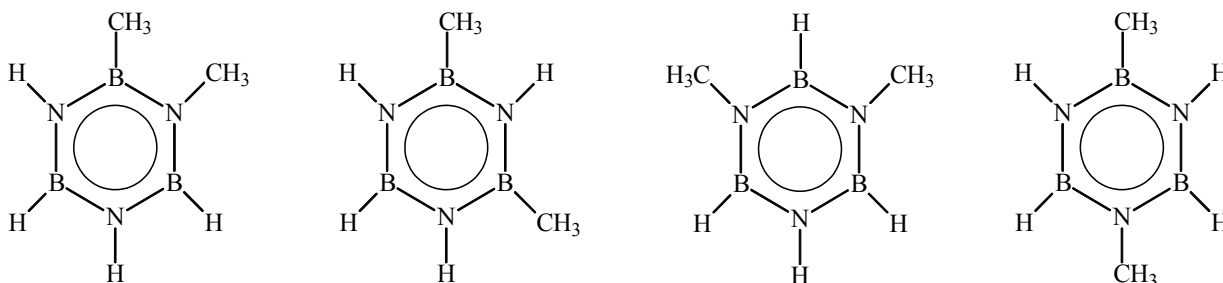
There are four different dimethylborazines. The circles in these structures represent the ability of borazine to form resonance structures (see Exercise 13.61), and CH_3 is shorthand for three hydrogen atoms singly bonded to a carbon atom.

There would be five structures if there were no resonance; all the structures drawn above plus an additional one related to the first Lewis structure above (see following illustration).
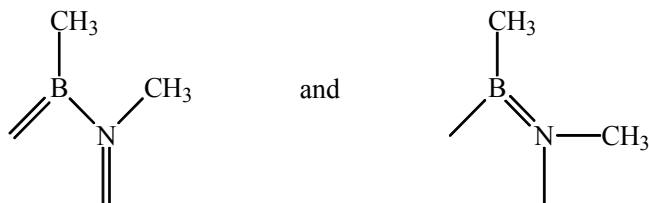
63.   Statements a and c are true. For statement a, XeF_2 has 22 valence electrons and it is impossible to satisfy the octet rule for all atoms with this number of electrons. The best Lewis structure is:
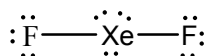
For statement c, NO^+ has 10 valence electrons, whereas NO^- has 12 valence electrons. The Lewis structures are:

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:
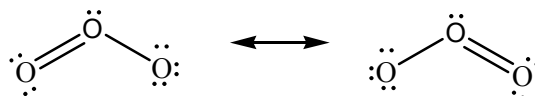
When resonance structures can be drawn, the actual bond lengths and strengths are all equal to each other. Even though each Lewis structure implies the two O−O bonds are different, this is not the case in real life. In real life, both of the O−O bonds are equivalent. When resonance structures can be drawn, you can think of the bonding as an average of all of the resonance structures.
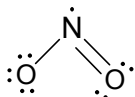
64.   a. NO_2, $5 + 2(6) = 17$ e$^-$ N_2O_4, $2(5) + 4(6) = 34$ e$^-$
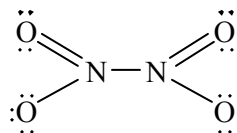
       Plus others   Plus other resonance structures

       b. BH_3, $3 + 3(1) = 6$ e$^-$ NH_3, $5 + 3(1) = 8$ e$^-$
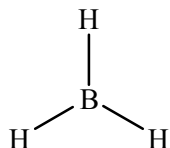
BH_3NH_3, $6 + 8 = 14$ e$^-$
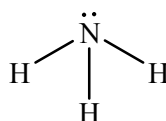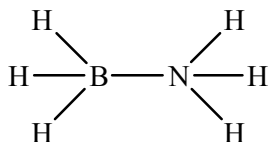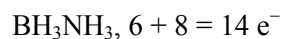
In reaction a, NO_2 has an odd number of electrons, so it is impossible to satisfy the octet rule. By dimerizing to form N_2O_4, the odd electron on two NO_2 molecules can pair up, giving a species whose Lewis structure can satisfy the octet rule. In general, odd-electron species are very reactive. In 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.

65. 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$^-$
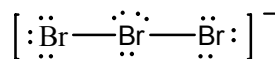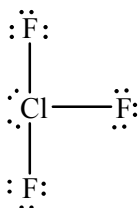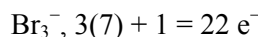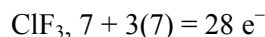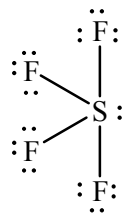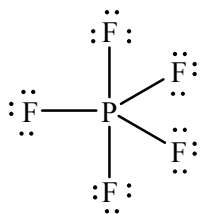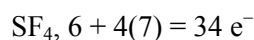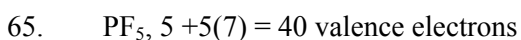
Row 3 and heavier nonmetals can have more than 8 electrons around them when they have to. Row 3 and heavier elements have empty d orbitals that are close in energy to valence s and p orbitals. These empty d orbitals can accept extra electrons.

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.

66. SF_6, $6 + 6(7) = 48$ e$^-$ ClF_5, $7 + 5(7) = 42$ e$^-$
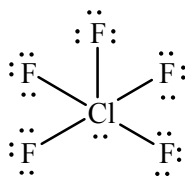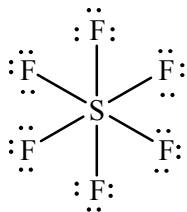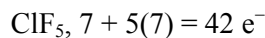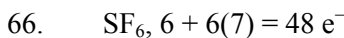
XeF_4, $8 + 4(7) = 36$ e^-
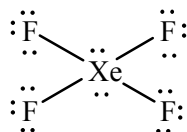
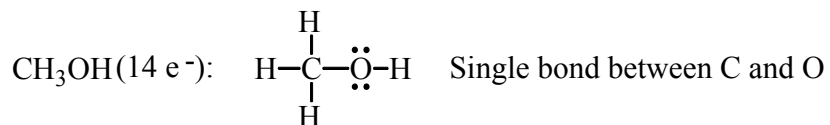67. CO_3^{2-} has $4 + 3(6) + 2 = 24$ valence electrons.
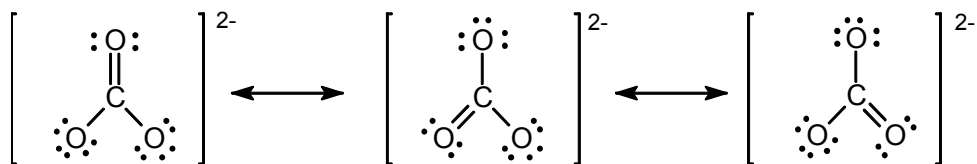
Three resonance structures can be drawn for CO_3^{2-}. The actual structure for CO_3^{2-} is an average of these three resonance structures. That is, the three C–O bond lengths are all equivalent, with a length somewhere between a single and a double bond. The actual bond length of 136 pm is consistent with this resonance view of CO_3^{2-}.
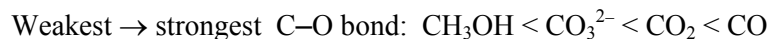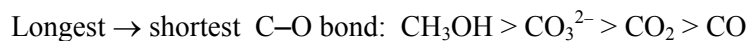
68.   The Lewis structures for the various species are below:

CO (10 e^-):   :C≡O: Triple bond between C and O.

CO_2 (16 e^-):   Ö=C=Ö   Double bond between C and O.

CO_3^{2-} (24 e⁻):
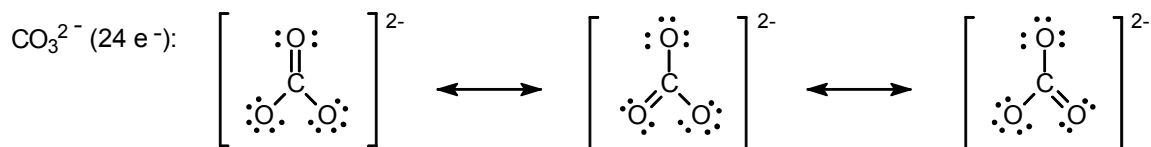
Average of 1 1/3 bond between C and O

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: $CH_3OH < CO_3^{2-} < CO_2 < CO$

69.

N_2 (10 e⁻):   :N≡N: Triple bond between N and N.

N_2F_4 (38 e⁻):   :F̈—N̈—N̈—F̈:   Single bond between N and N.
                           | |
                         :F̈: :F̈:

N_2F_2 (24 e⁻):   :F̈—N≡N—F̈:   Double bond between N and N.
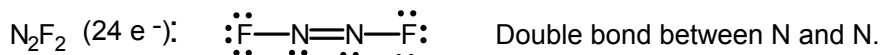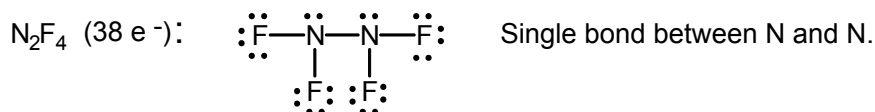
As the number of bonds increase between two atoms, bond strength increases and bond length decreases. From the Lewis structure, the shortest to longest N-N bonds is $N_2 < N_2F_2 < N_2F_4$.

Formal Charge

70.   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:

N̈=N=Ö   ⟷   :N≡N—Ö:
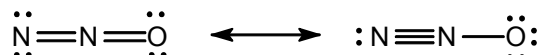
Assigning formal charges for all three resonance forms:

N̈=N=Ö   ⟷   :N≡N—Ö: ⟷   :N̈—N≡O:
-1   +1   0   0   +1   -1   -2   +1   +1
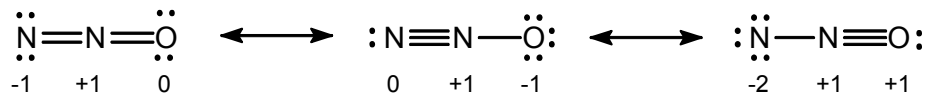
For:

(N̈=), FC = 5 - 4 - 1/2(4) = -1

(=N=), FC = 5 - 1/2(8) = +1 , Same for (≡N—) and (—N≡)

(:N̈—), FC = 5 - 6 - 1/2(2) = -2 ; (:N≡), FC = 5 - 2 - 1/2(6) = 0

(=Ö), FC = 6 - 4 - 1/2(4) = 0 ; (—Ö:), FC = 6 - 6 - 1/2(2) = -1

(≡O:), FC = 6 - 2 - 1/2(6) = +1

We should eliminate N−N≡O since 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.

71.   See Exercise 13.52a for the Lewis structures of $POCl_3$, SO_4^{2-}, ClO_4^- and PO_4^{3-}. All of these compounds/ions have similar Lewis structures to those of SO_2Cl_2 and XeO_4 shown below.

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$^-$ f. XeO_4, 8 + 4(6) = 32 e$^-$
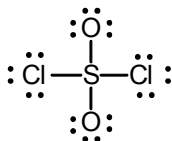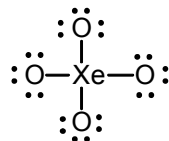
S, FC = 6 − 1/2(8) = +2   Xe, FC = 8 − 1/2(8) = +4

g. ClO_3^-, 7 + 3(6) + 1 = 26 e$^-$ h. NO_4^{3-}, 5 + 4(6) + 3 = 32 e$^-$
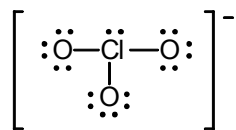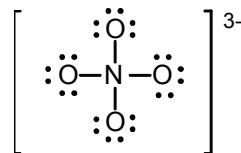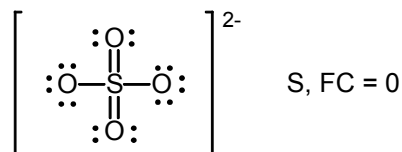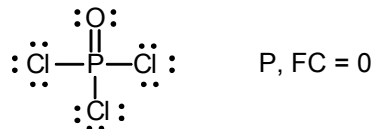

Cl, FC = 7 − 2 − 1/2(6) = +2   N, FC = 5 − 1/2(8) = +1

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

a. Must have five bonds to P to minimize   b. Must form six bonds to S to minimize
    formal charge of P. The best choice is   formal charge of S.
    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
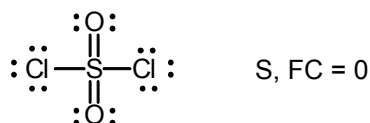   reason.

c.   Must form seven bonds to Cl
to minimize formal charge.
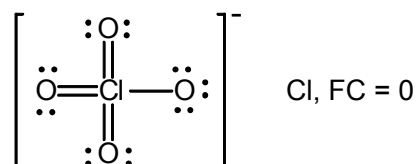
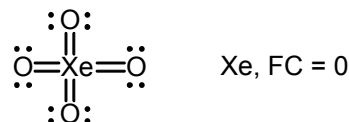d.   Must form five bonds to P to
to minimize formal charge.

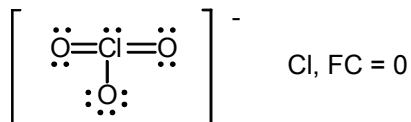Cl, FC = 0
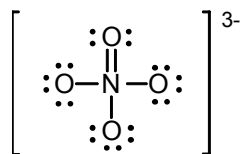
P, FC = 0
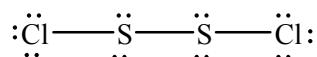
e.

f.

S, FC = 0

Xe, FC = 0

g.

Cl, FC = 0
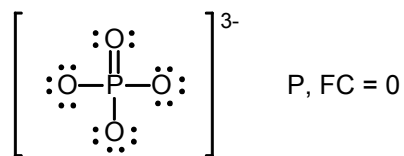
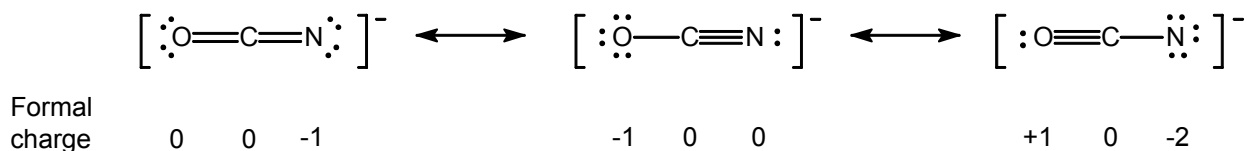h.   We can't . The following structure has a zero formal charge for N:

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

73.   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:
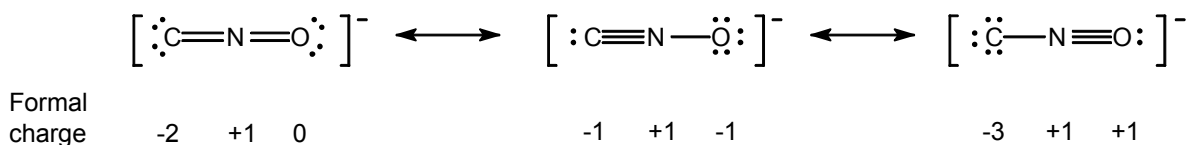
:Cl——S——S——Cl:

74.   OCN⁻ has 6 + 4 + 5 + 1 = 16 valence electrons.

$$\left[:\ddot{O}=C=\ddot{N}: \right]^- \longleftrightarrow \left[:\ddot{O}—C\equiv N: \right]^- \longleftrightarrow \left[:O\equiv C—\ddot{N}: \right]^-$$

Formal
charge   0   0   -1   -1   0   0   +1   0   -2

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^-:

Formal
charge   -2   +1   0   -1   +1   -1   -3   +1   +1

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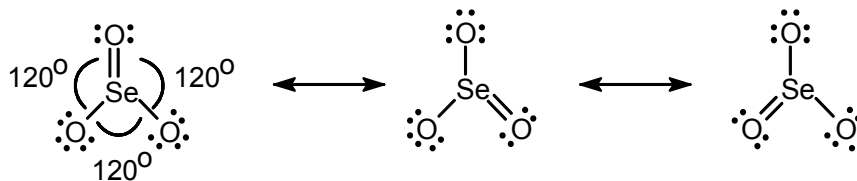

Molecular Structure and Polarity

75.   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 13.51, 13.52 and 13.54. The structures and bond angles for each follow.

13.51   a.   HCN: linear, 180°   b. PH_3: trigonal pyramid, <109.5°

        c. $CHCl_3$: tetrahedral, 109.5°   d. NH_4^+: tetrahedral, 109.5°

        e. H_2CO: trigonal planar, 120°   f. SeF_2: V-shaped or bent, <109.5°

        g. CO_2: linear, 180°   h and i. O_2 and HBr are both linear, but
                                                              there is no bond angle in either.

Note: PH_3 and SeF_2 both have lone pairs of electrons on the central atom, which result in bond angles that are something less than predicted from a tetrahedral arrangement (109.5°). However, we cannot predict the exact number. For these cases we will just insert a less than sign to indicate this phenomenon.

13.52   a.   All are tetrahedral; 109.5°

        b.   All are trigonal pyramid; <109.5°

        c.   All are V-shaped; <109.5°

13.54   a. NO_2^-: V-shaped, $\approx$ 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.

76.   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^-
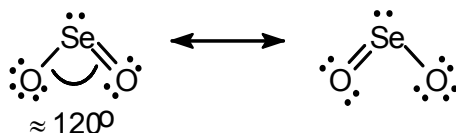
SeO$_2$ has a V-shaped molecular structure.   We would expect the bond angle to be approximately 120° as expected for trigonal planar geometry.

Note: Both SeO$_3$ and SeO$_2$ structures have three effective pairs of electrons about the central atom. All 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.
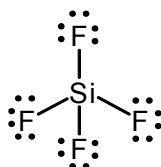
c.   PCl$_3$ has $5 + 3(7) =$
     26 valence electrons.

d.   SCl$_2$ has $6 + 2(7) =$
     20 valence electrons
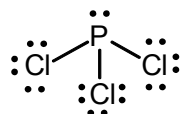
Trigonal pyramid; all angles are <109.5°.
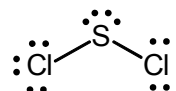
V-shaped; angle is <109.5°.

e.   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. All 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.

77.   From the Lewis structures (see Exercise 13.65), 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):
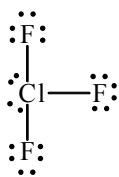
The central Cl atom is surrounded by five electron pairs, which requires a trigonal bipyramid geometry. Since there are three bonded atoms and two lone pairs of electrons about Cl, we describe the molecular structure of ClF_3 as T-shaped with predicted bond angles of about 90°. The actual bond angles will be slightly less than 90° due to the stronger repulsive effect of the lone pair electrons as compared to the bonding electrons.

78.   From the Lewis structures (see Exercise 13.66), XeF_4 would have a square planar molecular structure and ClF_5 would have a square pyramid molecular structure.

79.   a. $XeCl_2$ has $8 + 2(7) = 22$ valence electrons.
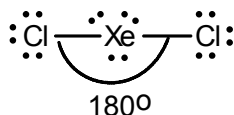
There are five pairs of electrons about the central Xe atom. The structure will be based on a trigonal bipyramid geometry. The most stable arrangement of the atoms in $XeCl_2$ is a linear molecular structure with a 180° bond angle.

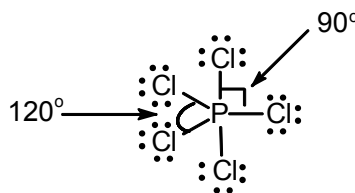   b. ICl_3 has $7 + 3(7) = 28$ valence electrons.
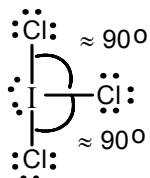
T-shaped; The ClICl angles are ≈ 90°. Since the lone pairs will take up more space, the ClICl bond angles will probably be slightly less than 90°.

        c. TeF_4 has $6 + 4(7) = 34$ d. PCl_5 has $5 + 5(7) = 40$
             valence electrons.   valence electrons.
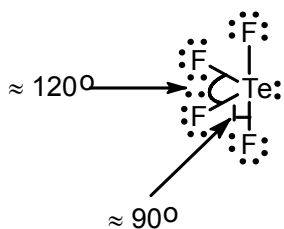
             See-saw or teeter-totter   Trigonal bipyramid
             or distorted tetrahedron
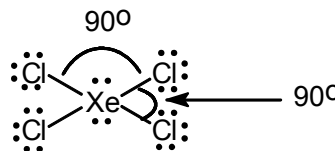
All the species in this exercise have five pairs of electrons around the central atom. All the structures are based on a trigonal bipyramid geometry, but only in PCl_5 are all the pairs bonding pairs. Thus PCl_5 is the only one we describe the molecular structure as trigonal bipyramid. Still, we had to begin with the trigonal bipyramid geometry to get to the structures (and bond angles) of the others.
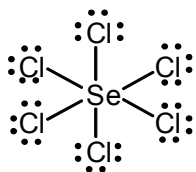
80.   a. ICl_5, $7 + 5(7) = 42$ e⁻   b. $XeCl_4$, $8 + 4(7) = 36$ e⁻
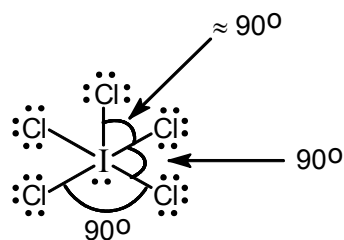
Square pyramid, $\approx 90°$ bond angles   Square planar, 90° bond angles

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.

81.   Let us consider the molecules with three pairs of electrons around the central atom first; these molecules are SeO_3 and SeO_2, and both have a trigonal planar arrangement of electron pairs. Both these molecules have polar bonds, but only SeO_2 has an overall net dipole moment. The net effect of the three bond dipoles from the three polar Se–O bonds in SeO_3 will be to cancel each other out 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.
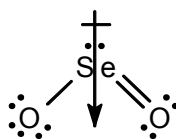
The other molecules in Exercise 13.76 (PCl_3, SCl_2, and SiF_4) have a tetrahedral arrangement of electron pairs. All have polar bonds; in SiF_4 the individual bond dipoles cancel when summed together, and in PCl_3 and SCl_2 the individual bond dipoles do not cancel. Therefore, SiF_4 has no net dipole 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.

82.   The molecules in Exercise 13.79 ($XeCl_2$, ICl_3, TeF_4, and PCl_5) all have a trigonal bipyramid arrangement of electron pairs. All of these molecules 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 dipole moment. The bond dipoles in $XeCl_2$ also cancel:
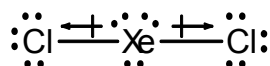

Since the bond dipoles from the two Xe–Cl bonds are equal in magnitude but point in opposite directions, they cancel each other, and $XeCl_2$ has no dipole moment (is nonpolar). For TeF_4 and ICl_3, the arrangement of these molecules is such that the individual bond dipoles do *not* all cancel, so each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

The molecules in Exercise 13.80 (ICl_5, $XeCl_4$, and $SeCl_6$) all have an octahedral arrangement of electron pairs. All of these molecules have polar bonds, but only ICl_5 has an overall dipole moment. The six bond dipoles in $SeCl_6$ all cancel each other, so $SeCl_6$ has no dipole moment. The same is true for $XeCl_4$:
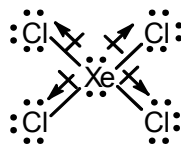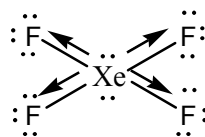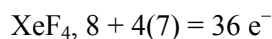

When the four bond dipoles are added together, they all cancel each other and $XeCl_4$ has no overall dipole moment. ICl_5 has a structure in which the individual bond dipoles do *not* all cancel, hence ICl_5 has a dipole moment.
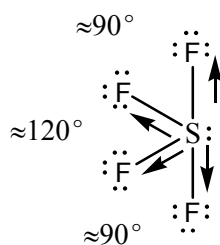
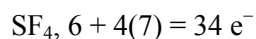83.   The two general requirements for a polar molecule are:

1. Polar bonds

2. A structure such that the bond dipoles of the polar bonds do not cancel

CF_4, $4 + 4(7) = 32$ valence electrons XeF_4, $8 + 4(7) = 36$ e$^-$
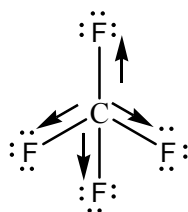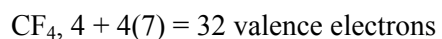
Tetrahedral, 109.5°   Square planar, 90°

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

See-saw, ≈90°, ≈120°

The arrows indicate the individual bond dipoles in the three molecules (the arrows point to the more electronegative atom in the bond, which will be the partial negative end of the bond dipole). All three of these molecules have polar bonds. To determine the polarity of the overall molecule, we sum the effect of all of the individual bond dipoles. In CF_4, the fluorines are symmetrically arranged about the central carbon atom. The net result is for all the individual C–F bond dipoles to cancel each other out, giving a nonpolar molecule. In XeF_4, the 4 Xe–F bond dipoles are also symmetrically arranged, and XeF_4 is also nonpolar. The individual bond dipoles cancel out when summed together. In SF_4, we also have four polar bonds. But in SF_4 the bond dipoles are not symmetrically arranged, and they do not cancel each other out. SF_4 is polar. It is the positioning of the lone pair that disrupts the symmetry in SF_4.

CO_2, $4 + 2(6) = 16$ e$^-$ COS, $4 + 6 + 6 = 16$ e$^-$
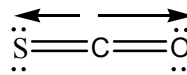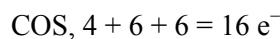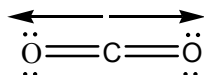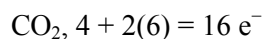
CO_2 and COS both have linear molecular structures with a 180° bond angle. CO_2 is nonpolar because the individual bond dipoles cancel each other out, but COS is polar. By replacing an O with a less electronegative S atom, the molecule is not symmetric any more. The individual bond dipoles do not cancel because the C–S bond dipole is smaller than the C–O bond dipole resulting in a polar molecule.

84.   a. $XeCl_4$, $8 + 4(7) = 36$ e⁻ $XeCl_2$, $8 + 2(7) = 22$ e⁻
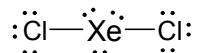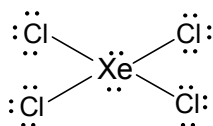
        Square planar, 90°, nonpolar   Linear, 180°, nonpolar

        Both compounds have a central Xe atom 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 angle between the Cl atoms on the diagonal in $XeCl_4$ are 180°
        apart from each other.

        b.   We didn't draw the Lewis structures, but all 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.

85.   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 com-
        pounds do not have the same bond angle. For statement d, central atoms adopt a geometry to
        minimize electron repulsions, not maximize them.

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

            $26 = x + 3(6) + 1$, $x = 7$ 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°.

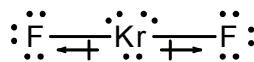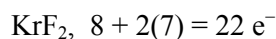87.   The formula is EF_2O^{2-}, and the Lewis structure has 28 valence electrons.

            $28 = x + 2(7) + 6 + 2$, $x = 6$ 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 (see Exercise 13.77) with bond angles of ≈90°.

88. H_2O and NH_3 have lone pair electrons on the central atoms. These lone pair electrons require more room than the bonding electrons, which tends to compress the angles between the bonding pairs. The bond angle for H_2O is the smallest because oxygen has two lone pairs on the central atom, and the bond angle is compressed more than in NH_3 where N has only one lone pair.

89.   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.
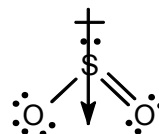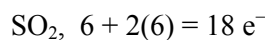
a. OCl_2, $6 + 2(7) = 20$ e⁻ KrF_2, $8 + 2(7) = 22$ e⁻
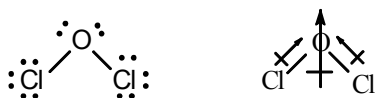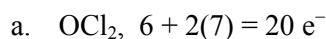
V-shaped, polar; OCl_2 is polar because   Linear, nonpolar; The molecule is
the two O–Cl bond dipoles don't cancel   nonpolar because the two Kr–F
each other. The resulting dipole moment   bond dipoles cancel each other.
is shown in the drawing.

BeH_2, $2 + 2(1) = 4$ e⁻ SO_2, $6 + 2(6) = 18$ e⁻
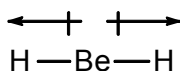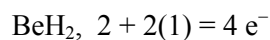
Linear, nonpolar; Be–H bond dipoles   V-shaped, polar; The S–O bond
are equal and point in opposite directions.   dipoles do not cancel, so SO_2 is polar
They cancel each other. BeH_2 is nonpolar.   (has a net dipole moment). Only one
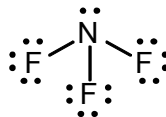   resonance structure is shown.

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.
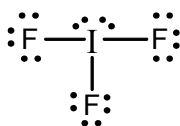
b. SO_3, $6 + 3(6) = 24$ e$^-$ NF_3, $5 + 3(7) = 26$ e$^-$
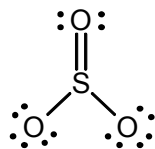
Trigonal planar, nonpolar;
bond dipoles cancel. Only one
resonance structure is shown.

Trigonal pyramid, polar;
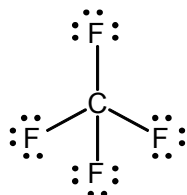bond dipoles do not cancel.

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

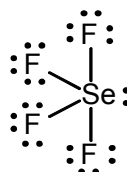T-shaped, polar; bond dipoles do not cancel.

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

Tetrahedral, nonpolar;
bond dipoles cancel.

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.
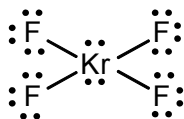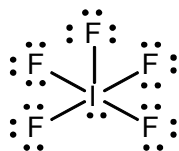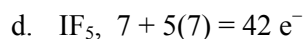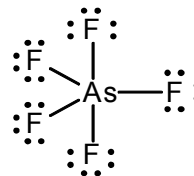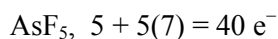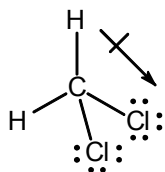
d.   IF$_5$, $7 + 5(7) = 42$ e$^-$ AsF$_5$, $5 + 5(7) = 40$ e$^-$

Square pyramid, polar;   Trigonal bipyramid, nonpolar;
bond dipoles do not cancel.   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.

90.   a.

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

δ+ δ−
C–Cl is the charge distribution for each C–Cl bond.
In CH$_2$Cl$_2$, 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.
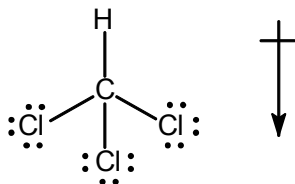
CCl$_4$ is nonpolar. CCl$_4$ is a tetrahedral molecule where all four C–Cl bond dipoles cancel
when added together. Let's consider just the C and two of the Cl atoms. There will be a
net dipole pointing in the direction of the middle of the two Cl atoms.
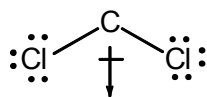
There will be an equal and opposite dipole arising from the other two Cl atoms. Combining:
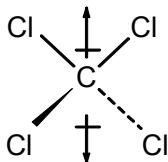
The two dipoles cancel, and CCl_4 is nonpolar.

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, 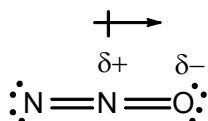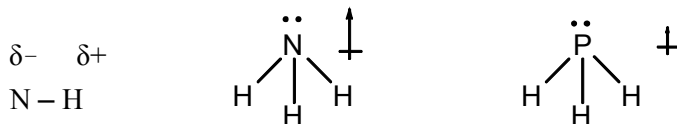the presence of the lone pair makes the PH_3 molecule slightly polar. The net dipole is in the direction of the lone pair and has a magnitude about one third that of the NH_3 dipole.

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

Additional Exercises

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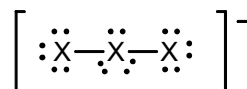
Bromine and iodine are large enough and have low-energy, empty d orbitals to accommodate the expanded octet. Fluorine is small, and its valence shell contains only 2s and 2p orbitals (four orbitals) and cannot expand its octet. The lowest-energy d orbitals in F are 3d; they are too high in energy compared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

93. CO_3^{2-} has $4 + 3(6) + 2 = 24$ valence electrons.
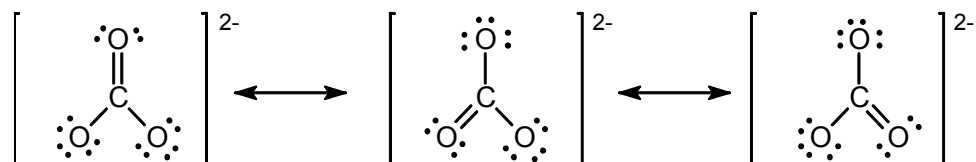
HCO$_3^-$ has $1 + 4 + 3(6) + 1 = 24$ valence electrons.
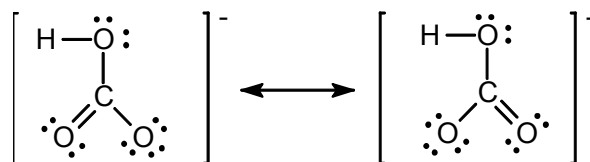
H_2CO_3 has $2(1) + 4 + 3(6) = 24$ valence electrons.
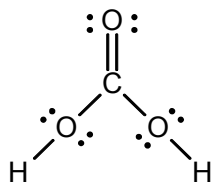
The Lewis structures for the reactants and products are:
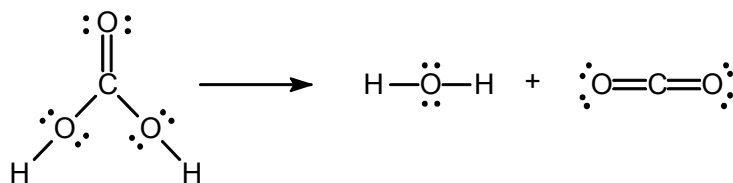
Bonds broken: Bonds formed:

  2 C–O (358 kJ/mol)   1 C=O (799 kJ/mol)
  1 O–H (467 kJ/mol)   1 O–H (467 kJ/mol)

$\Delta H = 2(358) + 467 - (799 + 467) = -83$ 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.

94.   TeF$_5^-$ has $6 + 5(7) + 1 = 42$ valence electrons.
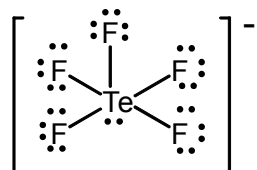
The lone pair of electrons around Te exerts a stronger repulsion than the bonding pairs, pushing the four square-planar F's away from the lone pair and thus reducing the bond angles between the axial F atom and the square-planar F atoms.

95.   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.

96. 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 out each other, a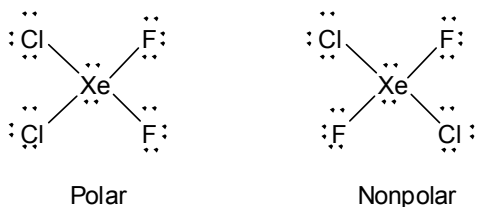nd this molecule is nonpolar. Therefore, measurement of the dipole moment would differentiate between the two compounds. These are different compounds and not resonance structures.

97.   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+} 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 with 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).

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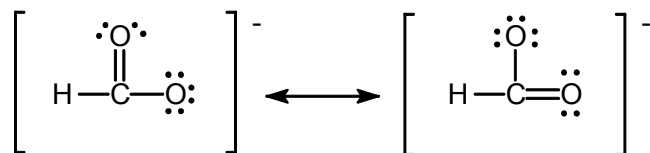
b.
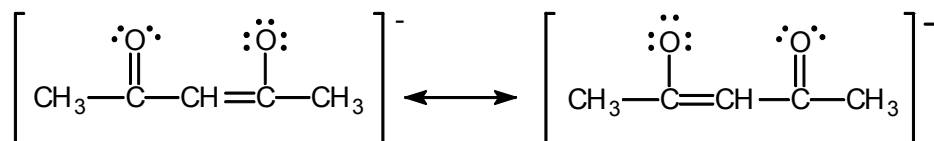
c.
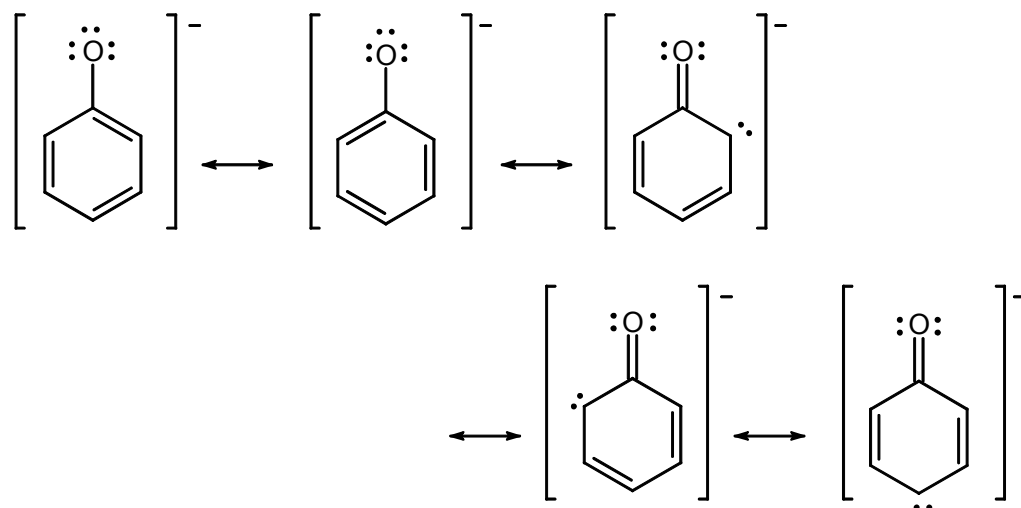
In all three cases, extra resonance forms can be drawn for the anion that are not possible when the H^+ is present, which leads to enhanced stability.

99.   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.

100.
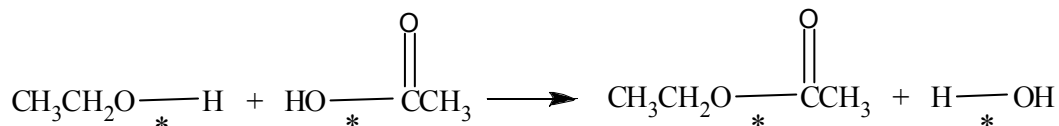
Bonds broken (*):   Bonds formed (*)
   O–H   O–H
   C–O   C–O

We make the same bonds that we have to break in order to convert reactants into products. Therefore, we would predict ΔH = 0 for this reaction using bond energies. This is probably not a great estimate for this reaction because this is not a gas-phase reaction, where bond energies work best.

101.   Nonmetals, which form covalent bonds to each other, have valence electrons in the s and p orbitals. Since there are four total s and p orbitals, there is room for only eight valence electrons (the octet rule). The valence shell for hydrogen is just the 1s orbital. This orbital can hold two electrons, so hydrogen follows the duet rule.

102.   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).
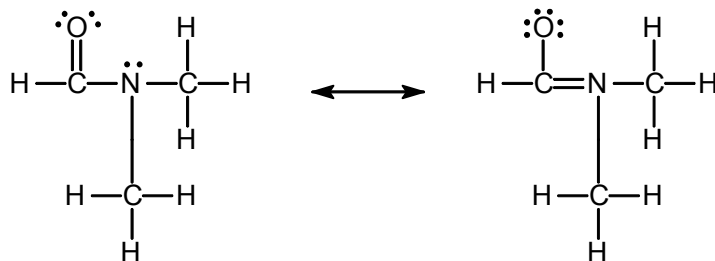
103.   Assuming 100.00 g of compound: $42.81 \text{ g F } \times \dfrac{1 \text{ mol F}}{19.00 \text{ g F}} = 2.253 \text{ mol F}$

The number of moles of X in XF_5 is: $2.253 \text{ mol F} \times \dfrac{1 \text{ mol X}}{5 \text{ mol F}} = 0.4506 \text{ mol X}$

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:

$$\frac{57.19 \text{ g X}}{0.4506 \text{ mol X}} = 126.9 \text{ g/mol; This is element I.}$$
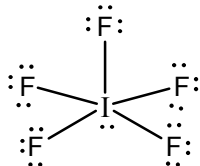
IF_5, $7 + 5(7) = 42$ e$^-$

The molecular structure is square pyramid.

104.   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:
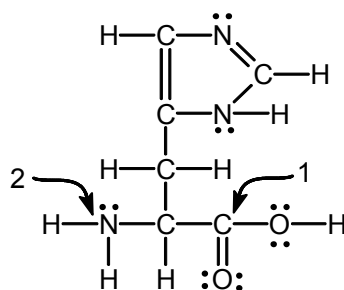
We would expect 120° bond angles about the carbon atom labeled 1 and ~109.5° bond angles about the nitrogen atom labeled 2. The nitrogen bond angles should be slightly smaller than 109.5° due to the lone pair of electrons on nitrogen.

105.   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.)

106.   a. $BrFI_2$, $7 + 7 + 2(7) = 28$ e$^-$; two possible structures exist; each has a T-shaped molecular structure.
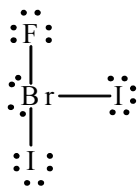
90° bond angles between I atoms   180° bond angle between I atoms
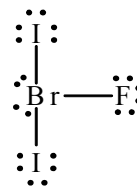
b. XeO_2F_2, $8 + 2(6) + 2(7) = 34$ e⁻; three possible structures exist; each has a see-saw
      molecular structure.
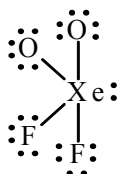
90° bond angle   180° bond angle   120° bond angle
between O atoms   between O atoms   between O atoms

c. $TeF_2Cl_3^-$, $6 + 2(7) + 3(7) + 1 = 42$ e⁻; three possible structures exist; each has a square
      pyramid molecular structure.
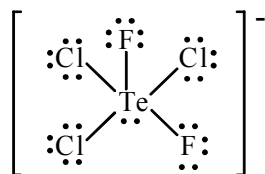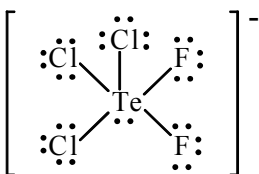
One F is 180° from   Both F atoms are 90° from   Both F atoms are 90° from
the lone pair.   the lone pair and 90° from   the lone pair and 180° from
                                     each other.   each other.

Challenge Problems

107. KrF_2, $8 + 2(7) = 22$ e⁻; from the Lewis structure, we have a trigonal bipyramid arrangement
         of electron pairs with a linear molecular structure.
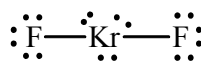
Hyperconjugation assumes that the overall bonding in KrF_2 is a combination of covalent and
ionic contributions (see Section 13.12 of the text for discussion of hyperconjugation). Using
hyperconjugation, two resonance structures are possible that keep the linear structure.
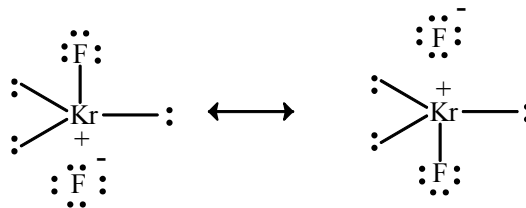
108.   The skeletal structure of caffeine is:
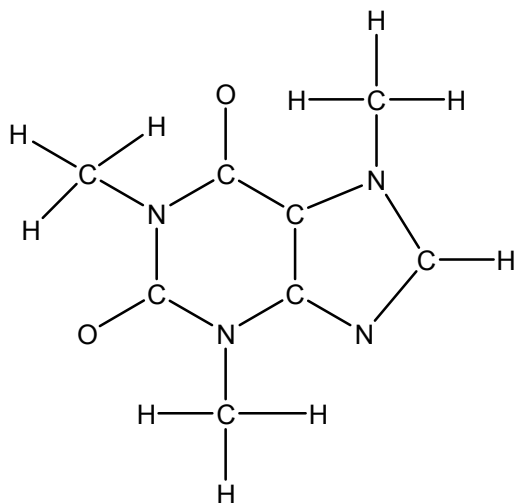
For a formal charge of zero on all atoms, the bonding requirements are:

    a.   Four bonds and no lone pairs for each carbon atom
    b.   Three bonds and one lone pair for each nitrogen atom
    c.   Two bonds and two lone pairs for each oxygen atom
    d.   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:

109. $2\ Li^+(g) + 2\ Cl^-(g) \rightarrow\ 2\ LiCl(s)$ $\Delta H = 2(-829\ kJ)$
              $2\ Li(g) \rightarrow 2\ Li^+(g) + 2\ e^-$ $\Delta H = 2(520.\ kJ)$
              $2\ Li(s) \rightarrow 2\ Li(g)$ $\Delta H = 2(166\ kJ)$
              $2\ HCl(g) \rightarrow\ 2\ H(g) + 2\ Cl(g)$ $\Delta H = 2(427\ kJ)$
              $2\ Cl(g) + 2\ e^- \rightarrow\ 2\ Cl^-(g)$ $\Delta H = 2(-349\ kJ)$
              $2\ H(g) \rightarrow\ H_2(g)$ $\Delta H = -(432\ kJ)$
_____

        $2\ Li(s) + 2\ HCl(g) \rightarrow\ 2\ LiCl(s) + H_2(g)$ $\Delta H = -562\ kJ$
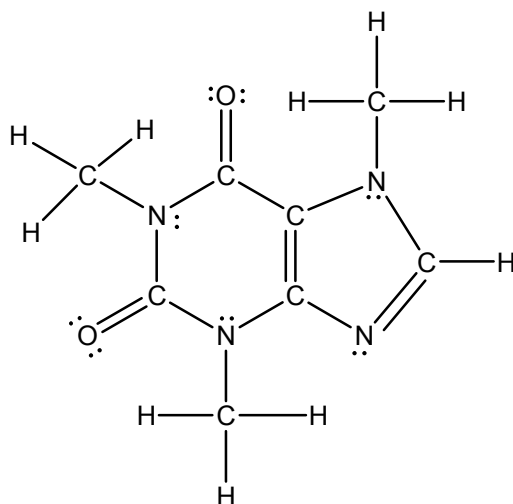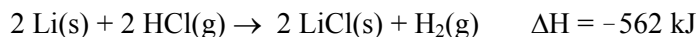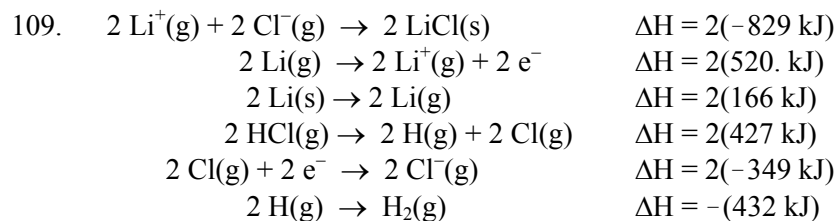
110.   See Figure 13.11 to see the data supporting MgO as an ionic compound. Note that the lattice
        energy is large enough to overcome all of the other processes (removing two electrons from
        Mg, etc.). The bond energy for O_2 (247 kJ/mol) and electron affinity (737 kJ/mol) are the
        same when making CO. However, ionizing carbon to form a C^{2+} ion must be too large. See
        Figure 12.35 to see that the first ionization energy for carbon is about 400 kJ/mol greater
        than the first IE for magnesium. If all other numbers were equal, the overall energy change
        would be down to ~200 kJ/mol (see Figure 13.11). It is not unreasonable that the second
        ionization energy for carbon is more than 200 kJ/mol greater than the second ionization
        energy of magnesium.

111.   a. $N(NO_2)_2^-$ contains $5 + 2(5) + 4(6) + 1 = 40$ valence electrons.

             The most likely structures are:
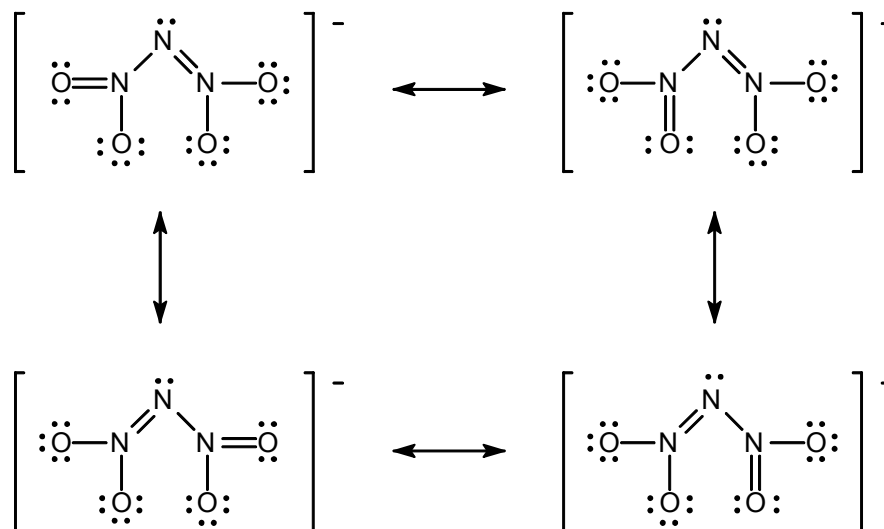
             There are other possible resonance structures, but these are most likely.

        b.   The NNN and all ONN and ONO bond angles should be about 120°.

c. $NH_4N(NO_2)_2 \rightarrow 2\ N_2 + 2\ H_2O + O_2$; break and form all bonds.

Bonds broken: Bonds formed:

    4 N–H (391 kJ/mol)   2 N≡N (941 kJ/mol)

    1 N–N (160. kJ/mol)   4 H–O (467 kJ/mol)

    1 N=N (418 kJ/mol)   1 O=O (495 kJ/mol)

    3 N–O (201 kJ/mol)   _____

    1 N=O (607 kJ/mol) ΣD_{formed} = 4245 kJ

_____

    ΣD_{broken} = 3352 kJ

    $\Delta H = \Sigma D_{broken} - \Sigma D_{formed}$ = 3352 kJ – 4245 kJ = –893 kJ

d.   To estimate ΔH, we completely ignored the ionic interactions between NH_4^+ and $N(NO_2)_2^-$. In addition, we assumed the bond energies in Table 13.6 applied to the $N(NO_2)^-$ bonds in any one of the resonance structures above. This is a bad assumption since molecules that exhibit resonance generally have stronger overall bonds than predicted. All these assumptions give an estimated ΔH value which is too negative.

112.   a.   (1) Removing an electron from the metal: IE, positive ($\Delta H > 0$)
        (2) Adding an electron to the nonmetal: EA, often negative ($\Delta H < 0$)
        (3) Allowing the metal cation and nonmetal anion to come together: LE, 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 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.

113.   a.   i. $C_6H_6N_{12}O_{12} \rightarrow 6\ CO + 6\ N_2 + 3\ H_2O + 3/2\ O_2$
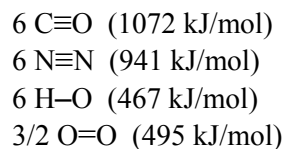
The NO_2 groups have one N–O single bond and one N=O double bond, and each carbon atom has one C–H single bond. We must break and form all bonds.
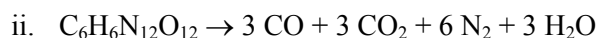
Bonds broken: Bonds formed:

 3 C–C (347 kJ/mol)   6 C≡O (1072 kJ/mol)
 6 C–H (413 kJ/mol)   6 N≡N (941 kJ/mol)
 12 C–N (305 kJ/mol)   6 H–O (467 kJ/mol)
 6 N–N (160. kJ/mol)   3/2 O=O (495 kJ/mol)
 6 N–O (201 kJ/mol)   —————————————
 6 N=O (607 kJ/mol) ΣD_{formed} = 15,623 kJ
 —————————————
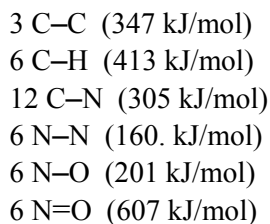
 ΣD_{broken} = 12,987 kJ

$\Delta H = \Sigma D_{broken} - \Sigma D_{formed}$ = 12,987 kJ − 15,623 kJ = −2636 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)
 —————————————
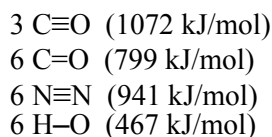
 ΣD_{formed} = 16,458 kJ

ΔH = 12,987 kJ − 16,458 kJ = −3471 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)
 —————————————
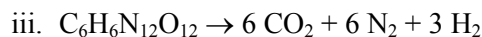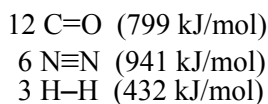
 ΣD_{formed} = 16,530. kJ

ΔH = 12,987 kJ − 16,530. kJ = −3543 kJ

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

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

114.   For acids containing the H–O–X grouping, as the electronnegativity of X increases, it becomes more effective at withdrawing electron density from the O–H bond, thereby weakening and polarizing the bond. This increases the tendency for the molecule to produce a proton, and so its acid strength increases. Consider HOBr with $K_a = 2 \times 10^{-11}$. When Br is replaced by the more electronegative Cl, the K_a value increases to 4×10^{-8} for HOCl.

What determines whether X–O–H type molecules are acids or bases in water lies mainly in the nature of the O–X bond. If X has a relatively high electronegativity, the O–X bond will be covalent and strong. When the compound containing the H–O–X grouping is dissolved in water, the O–X bond will remain intact. It will be the polar and relatively weak H–O bond that will tend to break, releasing a proton. On the other hand, if X has a very low electronegativity, the O–X bond will be ionic and subject to being broken in polar water. Examples of these ionic substances are the strong bases NaOH and KOH.
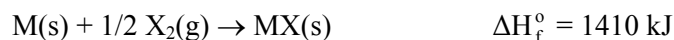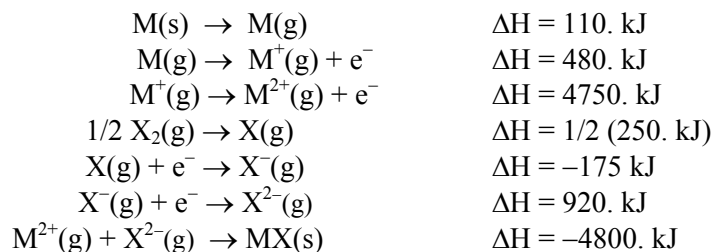
115.   The reaction is:

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

Using Hess's law:

$1/2 \ I_2(s) \rightarrow 1/2 \ I_2(g)$	$\Delta H = 1/2 \ (62 \ kJ)$	(Appendix 4)
$1/2 \ I_2(g) \rightarrow I(g)$	$\Delta H = 1/2 \ (149 \ kJ)$	(Table 13.6)
$1/2 \ Cl_2(g) \rightarrow Cl(g)$	$\Delta H = 1/2 \ (239 \ kJ)$	(Table 13.6)
$I(g) + Cl(g) \rightarrow ICl(g)$	$\Delta H = -208 \ kJ$	(Table 13.6)

$$1/2 \ I_2(s) + 1/2 \ Cl_2(g) \rightarrow ICl(g) \qquad \Delta H = 17 \ kJ \ so \ \Delta H_f^o = 17 \ kJ/mol$$
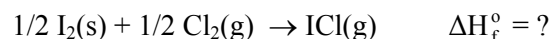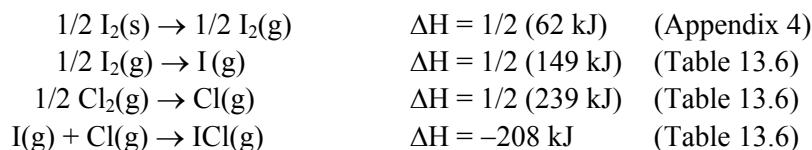
116.   There are four possible ionic compounds we need to consider. They are MX, composed of either M^+ and X^- ions or M^{2+} and X^{2-} ions, M_2X composed of M^+ and X^{2-} ions; or MX_2 composed of M^{2+} and X^- ions. For each possible ionic compound, let's calculate ΔH_f^o, the enthalpy of formation. The compound with the most negative enthalpy of formation will be the ionic compound most likely to form.

For MX composed of M^{2+} and X^{2-}:

$M(s) \rightarrow M(g)$	$\Delta H = 110. \ kJ$
$M(g) \rightarrow M^+(g) + e^-$	$\Delta H = 480. \ kJ$
$M^+(g) \rightarrow M^{2+}(g) + e^-$	$\Delta H = 4750. \ kJ$
$1/2 \ X_2(g) \rightarrow X(g)$	$\Delta H = 1/2 \ (250. \ kJ)$
$X(g) + e^- \rightarrow X^-(g)$	$\Delta H = -175 \ kJ$
$X^-(g) + e^- \rightarrow X^{2-}(g)$	$\Delta H = 920. \ kJ$
$M^{2+}(g) + X^{2-}(g) \rightarrow MX(s)$	$\Delta H = -4800. \ kJ$

$$M(s) + 1/2 \ X_2(g) \rightarrow MX(s) \qquad \Delta H_f^o = 1410 \ kJ$$

For MX composed of M^+ and X^-, $M(s) + 1/2 \ X_2(g) \rightarrow MX(s)$:

$$\Delta H_f^o = 110. + 480. + 1/2 \ (250.) - 175 - 1200. = -660. \ kJ$$

For M_2X composed of M^+ and X^{2-}, $2 \ M(s) + 1/2 \ X_2(g) \rightarrow M_2X(s)$:

$$\Delta H_f^o = 2(110.) + 2(480.) + 1/2 \ (250.) - 175 + 920. - 3600. = -1550. \ kJ$$

For MX_2 composed of M^{2+} and X^-, $M(s) + X_2(g) \rightarrow MX_2(s)$:

$$\Delta H_f^o = 110. + 480. + 4750. + 250 + 2(-175) - 3500. = 1740. \text{ kJ}$$

Only M^+X^- and $(M^+)_2X^{2-}$ have exothermic enthalpies of formation, so these are both theo-retically possible. Because M_2X has the more negative (more favorable) ΔH_f^o value, we would predict the M_2X compound most likely to form. The charges of the ions in M_2X are M^+ and X^{2-}.

Marathon Problem

117.   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:
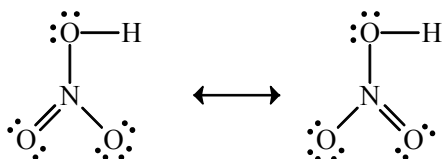
Compound B: This compound is basic (part g) and has one nitrogen (part b). The formal charge of zero (part b) tells us that there are three bonds to the nitrogen and the nitrogen has one lone pair. Assuming compound B is monobasic, then the data in part g tells us that the molar mass of B is 33.0 g/mol (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:
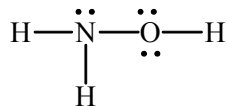
Compound C: From parts a and f and assuming compound A is HNO_3 , then compound C contains the nitrate ion, NO_3^-. Because part b tells us that there are two nitrogens, the other ion needs to have one N and some H's. In addition, compound C must be a weak acid (part g), which must be due to the other 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:
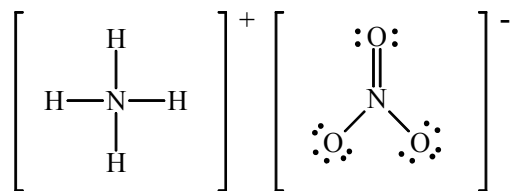
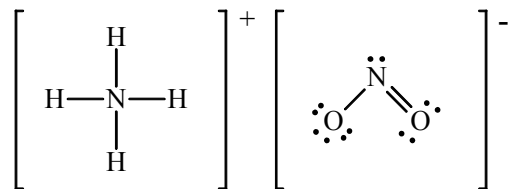*Note*: Two more resonance structures can be drawn for NO_3^-.

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 of N:O:H. The empirical formula is NOH_2, which has an empirical formula mass of 32.0 g/mol.

$$\text{Molar mass} = \frac{dRT}{P} = \frac{2.86 \text{ g/L}(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(273 \text{ K})}{1.00 \text{ atm}} = 64.1 \text{ g/mol}$$

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.

Compound E: 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: