CHAPTER 14 PERIODIC PATTERNS IN THE MAIN-GROUP ELEMENTS

14.1   a) Electron configuration: the distribution of electrons in the energy levels and sublevels of an atom; atomic size: the atomic radius or one-half the distance between nuclei of identical bonded atoms; ionization energy: the energy required to remove the highest energy electron from one mole of gaseous atoms; electronegativity: the relative ability of an atom in a covalent bond to attract shared electrons.
b) The principal quantum number n is related to the size and energy of the orbital. The azimuthal quantum number l gives the shape of the orbital. The superscript tells the number of electrons in the subshell.
c) The value of n determines the size.
d) In a group, n varies. Across a period, the number of electrons varies.
e) The number of valence shell electrons is given by the "old" group number, or by the "new" group number minus ten for the representative elements.

14.2   a) Z_{eff}, the effective nuclear charge, increases across a period and decreases down a group.
b) As you move to the right across a period, the atomic size decreases, the IE_1 increases, and the electronegativity increases, all because of the increased Z_{eff}.

14.3   a) Polarity is the molecular property that is responsible for the difference in boiling points between iodine monochloride and bromine. The stronger the intermolecular forces holding molecules together, the higher the boiling point. More polar molecules have stronger intermolecular forces and higher boiling points. Molecular polarity is a result of the difference in electronegativity, an atomic property, of the atoms in the molecule.
b) ICl is a polar molecule while Br_2 is nonpolar. The dipole-dipole forces between polar molecules are stronger than the dispersion forces between nonpolar molecules. The boiling point of the polar ICl is higher than the boiling point of Br_2.

14.4   As an atom becomes smaller, its electrons are closer to the nucleus and are therefore more tightly held, therefore increasing the ionization energy. The two trends are opposite to one another.

14.5   In general, stronger bonds (higher bond energy) are also shorter and less reactive. (This assumes the same number and type of bonds.)

14.6   Covalent and metallic bonding are similar in that they involve sharing of electrons between atoms. They are different in that covalent bonding includes sharing between a small number of atoms (usually two), while metallic bonding involves essentially all the atoms in a given sample.

14.7   The leftmost element in a period is an alkali metal [except for hydrogen, Group 1A(1)]. As the other bonding atom moved to the right, the bonding would change from metallic to polar covalent to ionic. The atomic properties (IE, EA, and electronegativity) of the leftmost element and the "other" element become increasingly different, causing changes in the character of the bond between the two elements.

14.8   A pair of atoms bonded only by a single bond use a σ bond, which is cylindrically symmetric, i.e., its energy will not change significantly with rotation. The "second" bond of the double bond is a π bond, which needs to be in a specific geometric orientation to form. Rotation of the molecule about this bond would break this π bond, a process that requires more energy than is available under ordinary circumstances.

14.9   The most stable ion of elements in groups 1A, 2A, and 3A is a cation with an electron configuration of the noble gas from the previous period. The most stable ion of the elements in groups 5A, 6A, and 7A is an anion with electron configuration of the noble gas of the same period. For ions in the nth period, the outer level electrons for the cations are in the $n – 1$ level, whereas the outer level electrons for the anions are in the n level. Ions with an $n – 1$ outer level are smaller than ions with n as the outer level since the size of the electron cloud increases as the principle quantum number, n, increases. Thus, the cations will be significantly smaller than the anions in a period.

As an example, look at period 3. The cations Na^+, Mg^{2+}, and Al^{3+} have electron configurations $1s^22s^22p^6$, isoelectronic with neon. The anions P^{3-}, S^{2-}, and Cl^- have electron configurations $1s^22s^22p^63s^23p^6$, isoelectronic with argon. Figure 8.29 shows the cations decrease in size from 102 pm for Na^+ to 54 pm for Al^{3+}, then a jump to 212 pm for the first anion, P^{3-}. Moving across the anions, the ionic radius decreases from the 212 pm for P^{3-} to 181 pm for Cl^-. The irregularity in the trend occurs in the change from positively charged ions to negatively charged ions.

14.10   **S^{2-} would be larger** than Cl^-, since Cl has one additional proton in its nucleus. **Mg^{2+} would be smaller** than Na^+ for the same reason.

14.11   a) Element oxides are either ionic or covalent molecules. Elements with low electronegativity (metals) form ionic oxides, whereas elements with relatively high electronegativity (nonmetals) form covalent oxides. The greater the electronegativity of the element, the more covalent the bonding is in its oxide.
        b) Oxide acidity increases to the right across a period and decreases down a group, so increasing acidity directly correlates with increasing electronegativity.

14.12   a) The metallic character of an element and the acidity of its oxide are inversely related.
        b) In general, oxide basicity decreases as you move to the right in a period and increases as you move down a group.

14.13   As you move down a group, atomic size increases, IE_1 and electronegativity decrease. This makes the Group 1A(1) and 2A(2) elements easier to oxidize as you move toward the bottom, and makes the Group 6A(16) and 7A(17) elements easier to reduce as you move toward the top.

14.14   Network covalent solids differ from molecular solids in that they are harder and have higher melting points than molecular solids. A network solid is held together by covalent bonds while intermolecular forces hold molecules in molecular solids together. Covalent bonds are much stronger than intermolecular forces and require more energy to break. To melt a network solid, more energy (higher temperature) is required to break the covalent bonds than is required to break the intermolecular forces in the molecular solid, so the network solid has a higher melting point. The covalent bonds also hold the atoms in a much more rigid structure than the intermolecular forces hold the molecules. Thus, a network solid is much harder than a molecular solid.

14.15   a) **Mg < Sr < Ba**   Atomic size increases down a group.
        b) **Na < Al < P** IE_1 increases across a period.
        c) **Se < Br < Cl**   Electronegativity increases across a period and up a group.
        d) **Ga < Sn < Bi**   Ga has three valence electrons, whereas Sn has four valence electrons and Bi has five valence p electrons.

14.16   a) **Si > P > N**   b) **Ar > Kr > K**   c) **I > In > Rb**   d) **S > Sb > Cs**

14.17   a) Chlorine and bromine will not form ionic compounds since they are both nonmetals that form anions.
        b) Sodium and bromine will form an ionic compound because sodium is a metal that forms a cation and bromine is a nonmetal that forms an anion.
        c) Phosphorus and selenium will not form ionic compounds since they are both nonmetals that form anions.
        d) Hydrogen and barium will form barium hydride, an ionic compound. Hydrogen reacts with reactive metals, such as Ba, to form ionic hydrides and reacts with nonmetals to form covalent hydrides.
        Compounds formed in cases **b and d** are ionic.

14.18   Compounds formed in cases **a and d** are covalent.

14.19   Recall in the Lewis structure model, bond order is the number of electron pairs shared between 2 bonded atoms (bond order is defined differently in molecular orbital theory). A bond order of 2 refers to two shared pairs of electrons in a double bond. There are several possibilities, with carbon dioxide being one example.

$$\ddot{O}\!\!=\!\!C\!\!=\!\!\ddot{O}$$
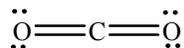
14.20   There are several possibilities, with the nitrite ion being one example.

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

14.21   Bond length increases as the size of the atoms in the bond increases. Silicon, carbon, and germanium are all in group 4A and chlorine, fluorine, and bromine are all in group 7A. Size increases down a group, so carbon is the smallest and germanium the largest in group 4A and fluorine is the smallest and bromine the largest in group 7A. The order of increasing bond length follows increasing size of atoms: **$CF_4 < SiCl_4 < GeBr_4$**.
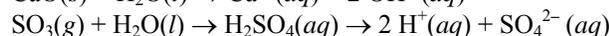
14.22   **$NF_3 > NCl_3 > NI_3$**

14.23   a) **$Na^+ < F^- < O^{2-}$** In an isoelectronic series, ionic size decreases due to an increase in Z_{eff}.
b) **$Cl^- < 2^{2-} < P^{3-}$** This series is also isoelectronic. Recall that anions are larger than their respective atoms due to electron repulsion; the more electrons added, the greater the repulsion and the larger space they will occupy.

14.24   a) **$K^+ > Ca^{2+} > Ga^{3+}$**   b) **$Br^- > Rb^+ > Sr^{2+}$**

14.25   The difference in the three species is in the number of electrons in the outer level. As the number of electrons increase, electron repulsion increases which increases the size of the electron cloud. Thus, O^{2-} will be the largest of the three since it contains the most electrons. In order of increasing size, the rank is **$O < O^- < O^{2-}$**.

14.26   **$Tl > Tl^+ > Tl^{3+}$**

14.27   a) Metals form basic oxides, whereas nonmetals form acidic oxides. **Calcium oxide** (CaO) will form the more basic oxide.
$$CaO(s) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2\ OH^-\ (aq)$$
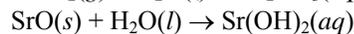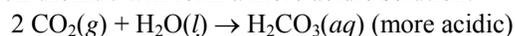$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq) \rightarrow 2\ H^+(aq) + SO_4^{2-}\ (aq)$$
b) Oxide basicity increases down a group as the element becomes less electronegative. **Barium oxide** (BaO) produces the more basic solution.
c) Oxide basicity decreases to the right across a period because the element becomes less electronegative. **Carbon dioxide** (CO_2) produces the more basic solution.
d) **Potassium oxide** (K_2O) produces the more basic solution because K is more metallic (lower electronegativity) than P.

14.28   a) **Carbon dioxide** will form a more acidic solution.
$$2\ CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq) \text{ (more acidic)}$$
$$SrO(s) + H_2O(l) \rightarrow Sr(OH)_2(aq)$$
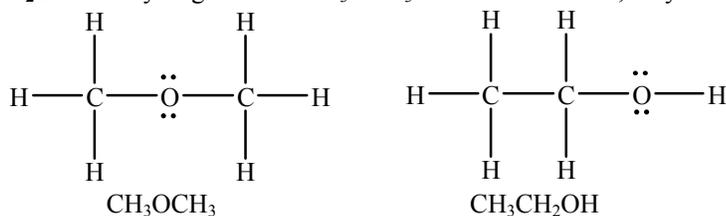b) **Tin(IV) oxide** (SnO_2)
c) **Dichlorine oxide** (Cl_2O)
d) **Sulfur dioxide** (SO_2)

14.29   Covalent character increases as the electronegativity difference between the atoms decreases.
a) **Lithium chloride** will have more covalent character than potassium chloride because Li is more electronegative than K (electronegativity increases up a group) so the electronegativity difference with chlorine will be smaller for LiCl than for KCl.
b) **Phosphorus trichloride** will have more covalent character than aluminum chloride because P is more electronegative than Al (electronegativity increases across a period) so the electronegativity difference with chlorine will be smaller for PCl_3 than for $AlCl_3$.

c) **Nitrogen trichloride** will have more covalent character than arsenic trichloride since the electronegativity of N is closer to the electronegativity of Cl. To answer this question, the trends in electronegativity are not sufficient since the electronegativity needs to be compared with that of chlorine. From Figure 9.20, the electronegativity values are 3.0 for Cl, 3.0 for N, and 2.0 for As. Δelectronegativity for NCl_3 is 0 and Δelectronegativity for $AsCl_3$ is 1.0.

14.30　a) **Calcium fluoride** (CaF_2)　　b) **Lead(II) fluoride** (PbF_2)　　c) **Germanium tetrafluoride** (GeF_4)

14.31　a) **Ar < Na < Si**. Ar forms an atomic solid held together only by dispersion forces. Na is a metallic solid and Si is a network covalent solid, requiring the most energy to separate.
b) **Cs < Rb < Li**. The heat of fusion, ΔH_{fus}, is the amount of energy needed to melt the solid. As melting point increases, so does ΔH_{fus}. All three are metallic solids, so the intermolecular forces are metallic bonds. Li has the highest melting point because smaller atoms attract delocalized electrons more strongly and produce stronger metallic bonds.

14.32　a) **As > Br$_2$ > O$_2$**　　　b) **I$_2$ > Cl$_2$ > Ar**

14.33　Ionization energy is defined as the energy required to remove the outermost electron from an atom. The further the outermost electron is from the nucleus, the less energy is required to remove it from the attractive force of the nucleus. In hydrogen, the outermost electron is in the $n = 1$ level and in lithium the outermost electron is in the $n = 2$ level. Therefore, the outermost electron in lithium requires less energy to remove, resulting in a lower ionization energy.

14.34

14.35　a) **NH$_3$** will hydrogen bond because H is attached to one of three atoms (N, O, and F) necessary for hydrogen bonding.

b) **CH₃CH₂OH** will hydrogen bond. CH₃OCH₃ has no O–H bonds, only C-H bonds.

CH₃OCH₃   CH₃CH₂OH

14.36   a) **NH₃** will form hydrogen bonds.
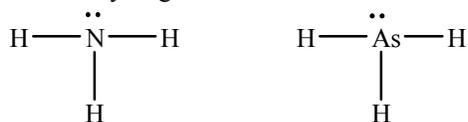
b) **H₂O** will form hydrogen bonds.
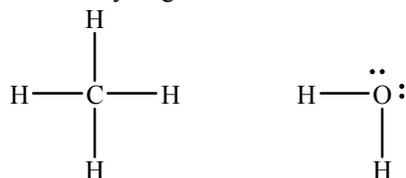
14.37   a) $2 \text{Al}(s) + 6 \text{HCl}(aq) \rightarrow 2\text{AlCl}_3(aq) + 3 \text{H}_2(g)$
         Active metals displace hydrogen from HCl by reducing the H^+ to H_2.
   b) $\text{LiH}(s) + \text{H}_2\text{O}(l) \rightarrow \text{LiOH}(aq) + \text{H}_2(g)$
         In water, H^- (here in LiH) reacts as a strong base to form H_2 and OH^-.

14.38   a) $\text{CaH}_2(s) + 2 \text{H}_2\text{O}(l) \rightarrow \text{Ca(OH)}_2(aq) + 2 \text{H}_2(g)$
         b) $\text{PdCl}_2(aq) + \text{H}_2(g) \rightarrow \text{Pd}(s) + 2 \text{HCl}(aq)$

14.39   a)   Na = +1   B = +3   H = −1 in NaBH₄
               Al = +3   B = +3   H = −1 in Al(BH₄)₃
               Li = +1   Al = +3   H = −1 in LiAlH₄
         b) The polyatomic ion in NaBH₄ is $[\text{BH}_4]^-$. There are $[1 \times \text{B}(3e^-)] + [4 \times \text{H}(1e^-)] + [1e^-$ from charge$] = 8$
         valence electrons. All eight electrons are required to form the four bonds from the 4 hydrogen atoms to
         the boron atom. Boron is the central atom and has four surrounding electron groups; therefore, its shape is
         tetrahedral.
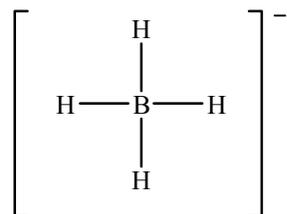
14.40   Since the nucleus of H contains only one proton, the electrons are not very tightly held and the H^- ion will be very
         polarizible (i.e., its electron cloud can be very easily distorted by a neighboring ion). Stated differently, there will
         be different amounts of covalent character in the different compounds.

14.41   In general, the maximum oxidation number increases as you move to the right. (Max. O.N. = (old) group number.)
         In the second period, the maximum oxidation number drops off below the group number in Groups 6A(16) and
         7A(17).

14.42   For period 2 elements in the first four groups, the number of covalent bonds equals the number of electrons in the outer level, so it increases from 1 covalent bond for lithium in group 1A(1) to 4 covalent bonds for carbon in group 4A(14). For the rest of period 2 elements, the number of covalent bonds equals the difference between 8 and the number of electrons in the outer level. So for nitrogen, $8 - 5 = 3$ covalent bonds; for oxygen, $8 - 6 = 2$ covalent bonds; for fluorine, $8 - 7 = 1$ covalent bond; and for neon, $8 - 8 = 0$, no bonds.
         For elements in higher periods, the same pattern exists but with exceptions for groups 3A(13) to 7A(17) when an expanded octet allows for more covalent bonds.

14.43   a) Lithium fluoride, LiF   beryllium fluoride, BeF_2 boron trifluoride, BF_3 carbon tetrafluoride, CF_4
         nitrogen trifluoride, NF_3 oxygen difluoride, OF_2 fluorine, F_2
         b) Δelectronegativity decreases
         c) % ionic character decreases
         d)
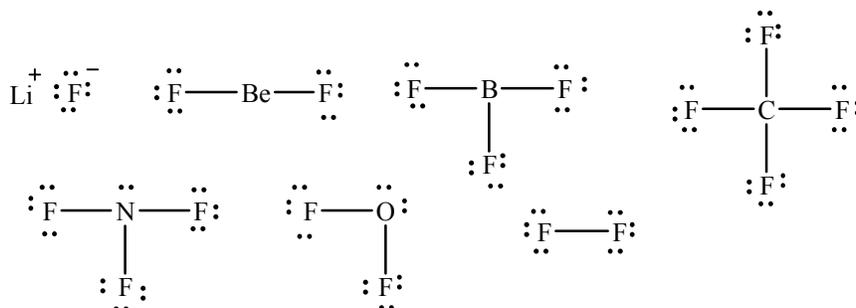
14.44   a) **32 elements**, **30 metals**
         b) **Between Po and At**

14.45   a) E must have an oxidation of +3 to form an oxide E_2O_3 or fluoride EF_3. E is in group **3A(13) or 3B(3)**.
         b) If E were in Group 3B(3), the oxide and fluoride would have more ionic character because 3B elements have lower electronegativity than 3A element. The Group 3B(3) oxides would be more basic.

14.46   Oxygen and fluorine have almost-filled outer shells ($2s^22p^4$ and $2s^22p^5$, respectively), so they both have a great ability to attract and hold bonded electrons (i.e., a large electronegativity). Neon, on the other hand, has a filled outer shell ($2s^22p^6$), so has little desire to hold additional electrons, and has essentially a zero electronegativity.

14.47   The small size of Li^+ leads to a large lattice energy for LiF, which lowers its solubility.

14.48   a) Alkali metals generally lose electrons (act as **reducing agents**) in their reactions.
         b) Alkali metals have relatively low ionization energies, meaning they easily lose the outermost electron. The electron configurations of alkali metals have one more electron than a noble gas configuration, so losing an electron gives a stable electron configuration.
         c) $2\ Na(s) + 2\ H_2O(l) \rightarrow 2\ Na^+(aq) + 2\ OH^-(aq) + H_2(g)$
           $2\ Na(s) + Cl_2(g) \rightarrow 2\ NaCl(s)$

14.49   The large atomic radii of the Group 1A(1) elements mean that their atomic volumes are large. Since density = mass/volume, the densities will be small.

14.50   a) Density increases down a group. The increasing atomic size (volume) is not offset by the increasing size of the nucleus (mass), so m/V increases.
         b) Ionic size increases down a group. Electron shells are added down a group, so both atomic and ionic size increase.
         c) E–E bond energy decreases down a group. Shielding of the outer electron increases as the atom gets larger, so the attraction responsible for the E–E bond decreases.
         d) IE_1 decreases down a group. Increased shielding of the outer electron is the cause of the decreasing IE_1.

e) ΔH_{hydr} decreases down a group. ΔH_{hydr} is the heat released when the metal salt dissolves in, or is hydrated by, water. Hydration energy decreases as ionic size increases.
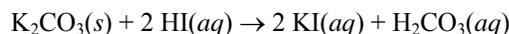**Increasing down: a and b;   Decreasing down: c, d, and e**

14.51   **Increasing up the group a, c, and e**
Decreasing up the group b and d

14.52   Peroxides are oxides in which oxygen has a –1 oxidation state. Sodium peroxide has the formula Na_2O_2 and is formed from the elements Na and O_2.
$$2 \, Na(s) + O_2(g) \rightarrow Na_2O_2(s)$$
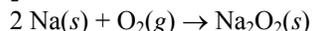
14.53 $RbOH(aq) + HBr(aq) \rightarrow RbBr(aq) + H_2O(l)$

14.54   The problem specifies that an alkali halide is the desired product. The alkali metal is K (comes from potassium carbonate, $K_2CO_3(s)$) and the halide is I (comes from hydroiodic acid, $HI(aq)$). Treat the reaction as a double displacement reaction.
$$K_2CO_3(s) + 2 \, HI(aq) \rightarrow 2 \, KI(aq) + H_2CO_3(aq)$$
However, $H_2CO_3(aq)$ is unstable and decomposes to $H_2O(l)$ and $CO_2(g)$, so the final reaction is:
$$K_2CO_3(s) + 2 \, HI(aq) \rightarrow 2 \, KI(aq) + H_2O(l) + CO_2(g)$$

14.55   a)% Li $= \dfrac{6.941 \text{ g Li/mol}}{290.40 \text{ g/mol}}$ x 100% = 2.39015 = **2.390% Li**

a)% Li $= \dfrac{6.941 \text{ g Li/mol}}{64.05 \text{ g/mol}}$ x 100% = 10.8368 = **10.84% Li**

14.56   The Group 1A(1) elements react more vigorously with water than those in Group 2A(2).

14.57   a) Li/Mg and Be/Al
b) Li and Mg both form ionic nitrides and thermally unstable carbonates. Be and Al both form amphoteric oxides; their oxide coatings make both metals unreactive to water.
c) The charge density (i.e., charge/radius ratio) is similar.

14.58   Metal atoms are held together by metallic bonding, a sharing of valence electrons. Alkaline earth metal atoms have one more valence electron than alkali metal atoms, so the number of electrons shared is greater. Thus, metallic bonds in alkaline earth metals are stronger than in alkali metals. Melting requires overcoming the metallic bonds. To overcome the stronger alkaline earth metal bonds requires more energy (higher temperature) than to overcome the alkali earth metal bonds.
First ionization energy, density, and boiling points will be larger for alkaline earth metals than for alkali metals.

14.59   a) A base forms when a basic oxide, such as CaO, is added to water.
$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$
b) Alkaline earth metals reduce O_2 to form the oxide.
$$2 \, Ca(s) + O_2(g) \rightarrow 2 \, CaO(s)$$
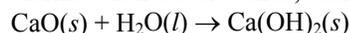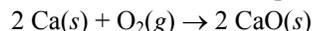
14.60   a) $BaCO_3(s) \xrightarrow{\Delta} BaO(s) + CO_2(g)$
b) $Mg(OH)_2(s) + 2 \, HCl(aq) \rightarrow MgCl_2(aq) + 2 \, H_2O(l)$

14.61   a) $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$ ($CaCO_3$ from limestone)
b) $Ca(OH)_2(s) + SO_2(g) \rightarrow CaSO_3(s) + H_2O(l)$
c) $3 \, CaO(s) + 2 \, H_3AsO_4(aq) \rightarrow Ca_3(AsO_4)_2(s) + 3 \, H_2O(l)$
d) $Na_2CO_3(aq) + CaO(s) + H_2O(l) \rightarrow CaCO_3(s) + 2 \, NaOH(aq)$

14.62 Beryllium is generally the exception to properties exhibited by other alkaline earth elements.
a) Here, Be does not behave like other alkaline earth metals: $BeO(s) + H_2O(l) \rightarrow NR$.
The oxides of alkaline earth metals are strongly basic, but BeO is amphoteric. BeO will react with both acids and bases to form salts, but an amphoteric substance does not react with water.
b) Here, Be does behave like other alkaline earth metals:
$$BeCl_2(l) + 2\ Cl^-(\text{solvated}) \rightarrow BeCl_4^{2-}(\text{solvated})$$
Each chloride ion donates a lone pair of electrons to form a covalent bond with the Be in $BeCl_2$. Metal ions form similar covalent bonds with ions or molecules containing a lone pair of electrons. The difference in beryllium is that the orbital involved in the bonding is a p-orbital, whereas in metal ions it is usually the d-orbitals that are involved.

14.63 The pattern of ionization energies in Group 3A(13) is irregular; there is not a smooth decrease in ionization energy as you proceed down the group. This is due to the appearance of the transition metals (and the 10 additional protons in the nucleus) preceding Ga, In and Tl. The presence of the transition elements causes a contraction of the atoms and a resulting increase in ionization energy for these three elements. There is a smoother decrease in ionization energy for the elements in Group 3B(3).

14.64 Tl_2O is more basic (i.e., less acidic) than Tl_2O_3. Acidity increases with increasing oxidation number.

14.65 The electron removed in Group 2A(2) atoms is from the outer level s orbital, whereas in Group 3A(13) atoms the electron is from the outer level p orbital. For example, the electron configuration for Be is $1s^22s^2$ and for B is $1s^22s^22p^1$. It is easier to remove the p electron of B than the s electron of Be, because the energy of a p-orbital is slightly higher than that of the s orbital from the same level. Even though the atomic size decreases from increasing Z_{eff}, the IE decreases from 2A(2) to 3A(13).

14.66 a) Compounds of Group 3A(13) elements, like boron, have only six electrons in their valence shell when combined with halogens to form three bonds. Having six electrons, rather than an octet, results in an "electron deficiency."
b) As an electron deficient central atom, B is trigonal planar. Upon accepting an electron pair to form a bond, the shape changes to tetrahedral.
$BF_3(g) + NH_3(g) \rightarrow F_3B{-}NH_3(g)$
$B(OH)_3(aq) + OH^-(aq) \rightarrow B(OH)_4^-(aq)$

14.67 a) Boron is a metalloid, while the other elements in the group show predominately metallic behavior. It forms covalent bonds exclusively; the others at best occasionally form ions. It is also much less chemically reactive in general.
b) The small size of B is responsible for these differences.

14.68 Acidity of oxides increases up a group: **$In_2O_3 < Ga_2O_3 < Al_2O_3$**.

14.69 **$B(OH)_3 < Al(OH)_3 < In(OH)_3$**

14.70 Halogens typically have a –1 oxidation state in metal-halide combinations, so the apparent oxidation state of Tl = +3. However, the anion I_3^- combines with Tl in the +1 oxidation state. The anion I_3^- has [3 x (I)7e$^-$] + [1e$^-$ from the charge] = 22 valence electrons; 4 of these electrons are used to form the two single bonds between iodine atoms and 16 electrons are used to give every atom an octet. The remaining two electrons belong to the central I atom; therefore the central iodine has five electron groups (2 single bonds and 3 lone pairs) and has a general formula of AX_2E_3. The electrons are arranged in a trigonal bipyramid with the three lone pairs in the trigonal plane. It is a linear molecule with bond angles = 180°. $(Tl^{3+})\ (I^-)_3$ does not exist because of the low strength of the Tl–I bond.
**O.N. = +3 (apparent); = +1 (actual)**
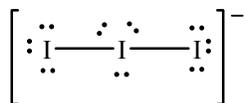
14.71   **O.N. = +2 (apparent); = +1(Ga^+) and +3 ($GaCl_4^-$) (actual)**
         class = AX_4; bond angles = 109.5°; tetrahedral
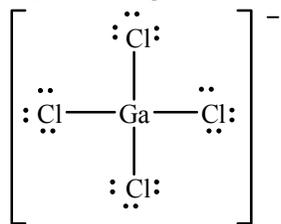
14.72   a) **boron, B**   b) **gallium, Ga**   c) **gallium, Ga**   d) **boron, B**
         e) **aluminum, Al**   f) **boric acid, $B(OH)_3$**   g) **thallium, Tl**

14.73   a) In: $[Kr]4d^{10}5s^25p^1$ In^+ : $[Kr]4d^{10}5s^2$ In^{2+} : $[Kr]4d^{10}5s^1$ In^{3+}: $[Kr]4d^{10}$
         a) In^+ and In^{3+} are diamagnetic while In and In^{2+} are paramagnetic.
         c) In^{2+}
         d) There can be no In^{2+} present. Half the indium is In^+ and half is In^{3+}.

14.74
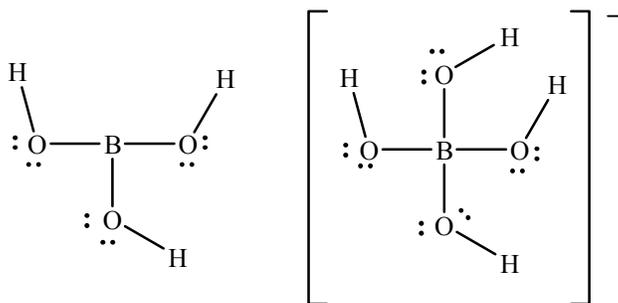
         $B(OH)_3$ has 120° angles $B(OH)_4^-$ has 109.5° angles around B
         around B

14.75   a) $B_2O_3(s) + 2\ NH_3(g) \rightarrow 2\ BN(s) + 3\ H_2O(g)$
         b) $\Delta H_{rxn} = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$
             $= [2\ \text{mol}\ \Delta H_f\ BN(s) + 3\ \text{mol}\ \Delta H_f\ H_2O(g)] - [1\ \text{mol}\ \Delta H_f\ B_2O_3(s) + 2\ \text{mol}\ \Delta H_f\ NH_3(g)]$
             $= [2\ \text{mol}\ (-254\ \text{kJ/mol}) + 3\ (-241.826\ \text{mol kJ/mol})] - [1\ \text{mol}\ (-1272\ \text{kJ/mol}) + 2\ \text{mol}\ (-45.9\ \text{kJ/mol})]$
             $= 130.322 = \mathbf{1.30 \times 10^2\ kJ}$
         c) Mass borax

$$= (1.0\ \text{kg BN})\left(\frac{10^3\ \text{g}}{1\ \text{kg}}\right)\left(\frac{1\ \text{mol BN}}{24.82\ \text{g BN}}\right)\left(\frac{1\ \text{mol B}}{1\ \text{mol BN}}\right)\left(\frac{1\ \text{mol Na}_2\text{B}_4\text{O}_7 \bullet 10\ \text{H}_2\text{O}}{4\ \text{mol B}}\right)\left(\frac{381.38\ \text{g}}{1\ \text{mol}}\right)\left(\frac{100\%}{72\%}\right)$$
$$= 5.335359 \times 10^3 = \mathbf{5.3 \times 10^3\ g\ borax}$$

14.76   Oxide basicity is greater for the oxide of a metal atom. Tin(IV) oxide is more basic than carbon dioxide since tin
         has more metallic character than carbon.

14.77   a) The increased stability of the lower oxidation state as one goes down a group.
         b) As the atoms become larger, the strength of the bonds to other elements becomes weaker, and insufficient
         energy is gained in forming the bonds to offset the additional ionization or promotion energy.
         c) Tl^+ is more stable than Tl^{3+}, but Al^{3+} is the only stable oxidation state for Al.

14.78   a) IE_1 values generally decrease down a group.
         b) The increase in Z_{eff} from Si to Ge is larger than the increase from C to Si because more protons have been added. Between C and Si an additional 8 protons have been added, whereas between Si and Ge an additional 18 (includes the protons for the *d*-block) protons have been added. The same type of change takes place when going from Sn to Pb, when the 14 *f*-block protons are added.
         c) Group 3A(13) would show greater deviations because the single *p* electron receives no shielding effect offered by other *p* electrons.

14.79   The drop between C and Si is due to a weakening of the bonds due to increased atomic size. The drop between Ge and Sn is due to a change in bonding from covalent to metallic.

14.80   Allotropes are two forms of a chemical element which have different bonding and physical properties. C forms graphite, diamond and buckminsterfullerene; Sn has gray (α) and white (β) forms.

14.81   Atomic size increases moving down a group. As atomic size increases, ionization energy decreases so that it is easier to form a positive ion. An atom that is easier to ionize exhibits greater metallic character.

14.82   Having four valence electrons allows all of the Group 4A(14) elements to form a large number of bonds, hence, many compounds. However, the small size of the C atom makes its bonds stronger and gives stability to a wider variety of compounds than for the heavier members of the group.
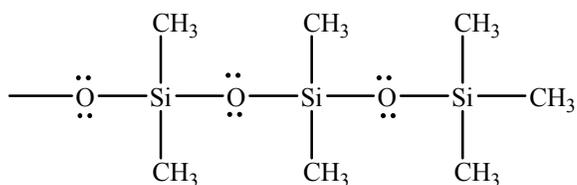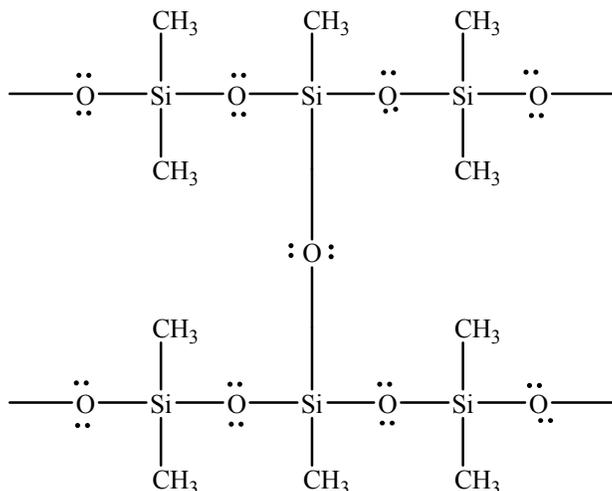
14.83
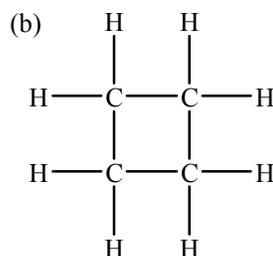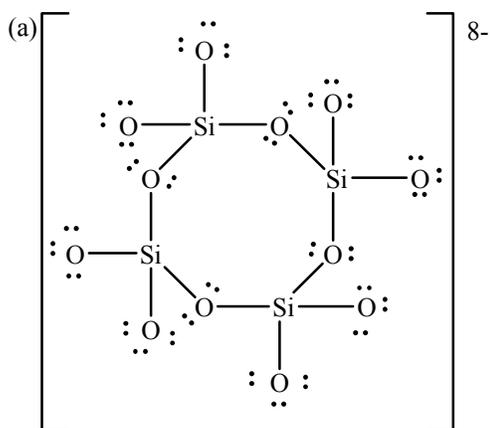
There is another answer possible for C_4H_8.

14.84   There are numerous alternate answers for C_6H_{12}.

14-10
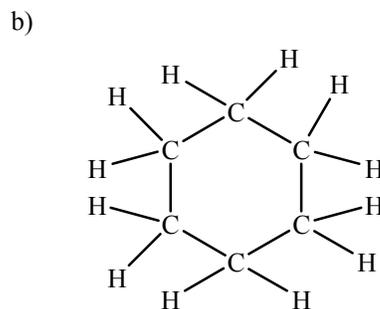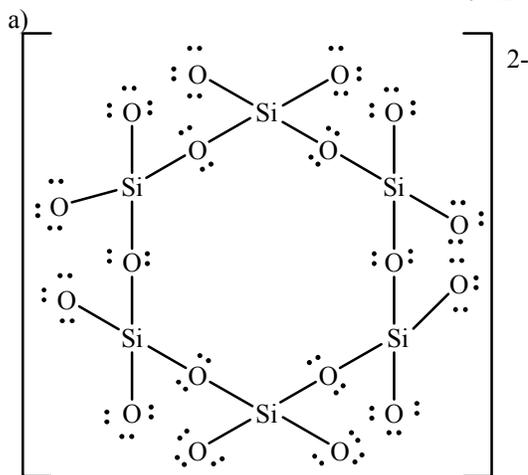
14.85

14.86

14.87 Each alkaline earth metal ion will displace two sodium ions because of the charge difference.
Determine the moles of alkaline earth metal ions:
Moles Ca^{2+} = (4.5 x 10^{-3} mol/L) (25,000 L) = 112.5 mol Ca^{2+} (unrounded)
Moles Mg^{2+} = (9.2 x 10^{-4} mol/L) (25,000 L) = 23 mol Mg^{2+}
Total moles of M^{2+} = (112.5 + 23) mol = 135.5 mol M^{2+} (unrounded)
Determine the moles of Na^+ needed:
Moles Na^+ = (135.5 mol M^{2+}) (2 mol Na^+ / 1 mol M^{2+}) = 271 mol Na^+ (unrounded)
Determine the molar mass of the zeolite:
12 Na (22.99) + 12 Al (26.98) + 12 Si (28.09) + 54 H (1.008) + 75 O (16.00) = 2191.15 g/mol
Determine mass of zeolite:
Mass = (271 mol Na^+)(1 mol zeolite/12 mol Na^+)(2191.15 g zeolite/mol zeolite)(1 kg/10^3 g) (100% / 85%)
= 58.215848 = **58 kg zeolite**

14.88 a) **Diamond**, **C**, a network covalent solid of carbon
b) **Calcium carbonate**, **CaCO₃** (Brands that use this compound as an antacid also advertise them as an important source of calcium).
c) **Carbon dioxide**, **CO₂**, is the most widely known greenhouse gas; CH₄ is also implicated.
d) **Silicone [(CH₃)₂SiO]ₙ**
e) **Carborundum**, **SiC**
f) **Carbon monoxide**, **CO**, is formed in combustion when the amount of O_2 (air) is limited.
g) **Lead**, **Pb** (in old plumbing as lead solder, and in paint as a pigment)

14.89 $B_2H_6(g) + 3\,O_2(g) \rightarrow B_2O_3(s) + 3\,H_2O(g)$
$2\,Si_4H_{10}(g) + 13\,O_2(g) \rightarrow 8\,SiO_2(s) + 10\,H_2O(g)$
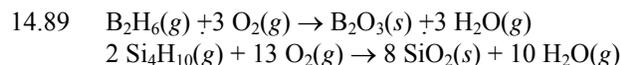
14.90 All of the elements in Group 5A(15) form trihalides, but only P, As, and Sb form pentahalides. N cannot expand its octet, so it cannot form a pentahalide. The large Bi atom forms weak bonds, so it is unfavorable energetically for it to form 5 bonds, except with fluorine. It would also require too much energy to remove 5 electrons.

14.91 The bonding changes from covalent small molecules, to larger molecules, to metallic bonding in Bi. The first two elements (N, P) are nonmetals, followed by two metalloid elements (As, Sb) and then by a metallic element (Bi).

14.92 a) In Group 5A(15), all elements except bismuth have a range of oxidation states from –3 to +5.
b) For nonmetals, the range of oxidation states is from the lowest at group number (A) – 8, which is 5 – 8 = –3 for Group 5A, to the highest equal to the group number (A), which is +5 for Group 5A.

14.93 In general, high oxidation states are less stable towards the bottom of the periodic table.

14.94 **$Bi_2O_3 < Sb_2O_3 < Sb_2O_5 < P_4O_{10}$**

14.95 Arsenic is less electronegative than phosphorus, which is less electronegative than nitrogen. Therefore, arsenic acid is the weakest acid and nitric acid is the strongest. Order of increasing strength: **$H_3AsO_4 < H_3PO_4 < HNO_3$**

14.96 **$HNO_3 > HNO_2 > H_2N_2O_2$**

14.97 a) With excess oxygen arsenic will form the oxide with arsenic in its highest possible oxidation state, +5.
$$4\ As(s) + 5\ O_2(g) \rightarrow 2\ As_2O_5(s)$$
b) Trihalides are formed by direct combination of the elements (except N).
$$2\ Bi(s) + 3\ F_2(g) \rightarrow 2\ BiF_3(s)$$
c) Metal phosphides, arsenides, and antimonides react with water to form Group 5A hydrides.
$$Ca_3As_2(s) + 6\ H_2O(l) \rightarrow 3\ Ca(OH)_2(s) + 2\ AsH_3(g)$$

14.98 a) $2\ Sb(s) + 3\ Br_2(l) \rightarrow 2\ SbBr_3(s)$
b) $2\ HNO_3(aq) + MgCO_3(s) \rightarrow Mg(NO_3)_2(aq) + CO_2(g) + H_2O(l)$
c) $2\ K_2HPO_4(s) \xrightarrow{\Delta} K_4P_2O_7(s) + H_2O(g)$

14.99 a) Aluminum is not as active a metal as Li or Mg, so heat is needed to drive this reaction.
$$N_2(g) + 2\ Al(s) \xrightarrow{\Delta} 2\ AlN(s)$$
b) The 5A halides react with water to form the oxoacid with the same oxidation state as the original halide.
$$PF_5(g) + 4\ H_2O(l) \rightarrow H_3PO_4(aq) + 5\ HF(g)$$

14.100 a) $AsCl_3(l) + 3\ H_2O(l) \rightarrow H_3AsO_3(aq) + 3\ HCl(g)$
b) $Sb_2O_3(s) + 6\ NaOH(aq) \rightarrow 2\ Na_3SbO_3(aq) + 3\ H_2O(l)$

14.101 From the Lewis structure, the phosphorus has 5 electron groups for a trigonal bipyramidal molecular shape. In this shape, the three groups in the equatorial plane have greater bond angles (120°) than the two groups above and below this plane (90°). The chlorine atoms would occupy the planar sites where there is more space for the larger atoms.
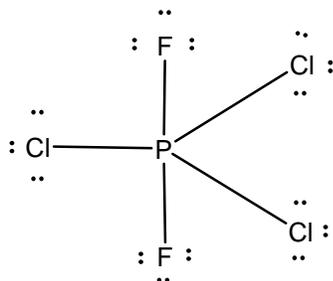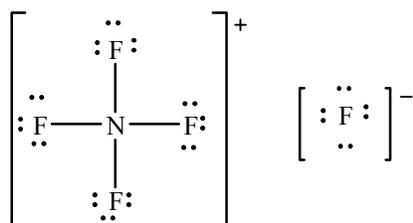
14.102
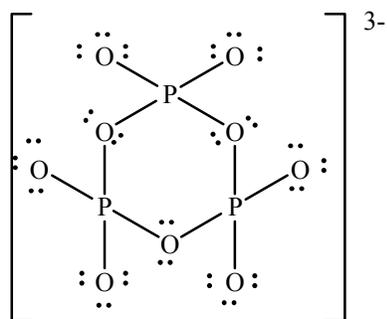
The structure would be tetrahedral at the P atoms and bent at the O atoms.

14.103

14.104   a) **Ammonia, NH$_3$**   b) **Nitrogen, N**; **Phosphorus, P**
c) **Ammonia, NH$_3$**   d) **Nitrogen monoxide, NO**; **nitrogen dioxide, NO$_2$**
e) **Antimony hydroxide, Sb(OH)$_3$** f) **Sodium tripolyphosphate, Na$_5$P$_3$O$_{10}$**
g) **Bismuth, Bi**

14.105   Set the atoms into the positions described, and then complete the Lewis structures.
a) and b) N$_2$O$_2$ has [2 x 5e$^-$ (N) + 2 x 6e$^-$ (O)] = 22 valence electrons. Six of these electrons are used to make the single bonds between the atoms, leaving 22 – 6 = 16 electrons. Since 20 electrons are needed to complete the octets of all of the atoms, two double bonds are needed.
c) N$_2$O$_3$ has [2 x 5e$^-$ (N) + 3 x 6e$^-$ (O)] = 28 valence electrons. Eight of these electrons are used to make the single bonds between the atoms, leaving 28 – 8 = 20 electrons. Since 24 electrons are needed to complete the octets of all of the atoms, two double bonds are needed.
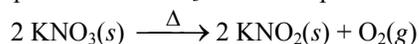d) NO$^+$ has [1x 5e$^-$ (N) + 1 x 6e$^-$ (O) – 1 e$^-$ (due to the + charge)] = 10 valence electrons. Two of these electrons are used to make the single bond between the atoms, leaving 10 – 2 = 8 electrons. Since 12 electrons are needed to complete the octets of both atoms, a triple bond is needed.
NO$_3^-$ has [1x 5e$^-$ (N) + 3 x 6e$^-$ (O) + 1 e$^-$ (due to the – charge)] = 24 valence electrons. Six of these electrons are used to make the single bond between the atoms, leaving 24 – 6 = 18 electrons. Since 20 electrons are needed to complete the octets of all of the atoms, a double bond is needed.

(a)

(b)

(c)

(d)

14.106   NH$_4$NO$_3$(s) $\xrightarrow{\Delta}$ N$_2$O(g) +2 H$_2$O(l)
O.N.:   –3 +5   +1
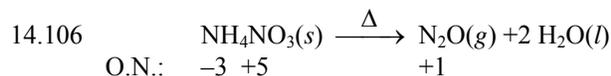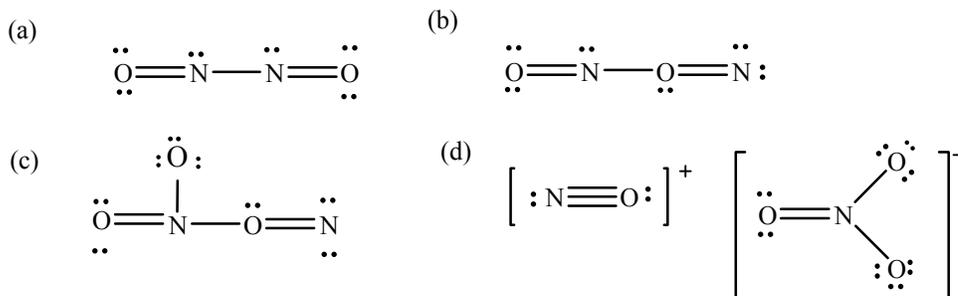
14.107 a) Thermal decomposition of KNO_3 at low temperatures:
$$2\ KNO_3(s) \xrightarrow{\Delta} 2\ KNO_2(s) + O_2(g)$$
b) Thermal decomposition of KNO_3 at high temperatures:
$$4\ KNO_3(s) \xrightarrow{\Delta} 2\ K_2O(s) + 2\ N_2(g) + 5\ O_2(g)$$

14.108 **S < Se < Po**; nonmetal < metalloid < metal

14.109 a) Both groups have elements that range from gas to metalloid to metal. Thus, their boiling points and conductivity vary in similar ways down a group.
b) The degree of metallic character and methods of bonding vary in similar ways down a group.
c) Both P and S have allotropes and both bond covalently with almost every other nonmetal.
d) Both N and O are diatomic gases at normal temperatures and pressures. Both N and O have very low melting and boiling points.
e) Oxygen, O_2, is a reactive gas whereas nitrogen, N_2, is not. Nitrogen can exist in multiple oxidation states, whereas oxygen has 2 oxidation states.
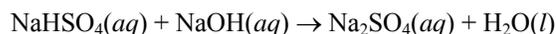
14.110 a) The change occurs between periods two and three.
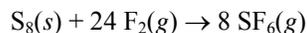b) The H−E−H bond angle changes.
c) The hybridization changes from sp^3 in H_2O to p (unhybridized) in the others.
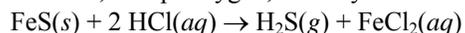d) Group 5A(15) is similar.

14.111 a) To decide what type of reaction will occur, examine the reactants. Notice that sodium hydroxide is a strong base. Is the other reactant an acid? If we separate the salt, sodium hydrogen sulfate, into the two ions, Na^+ and HSO_4^-, then it is easier to see the hydrogen sulfate ion as the acid. The sodium ions could be left out for the net ionic reaction.
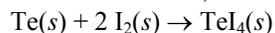$$NaHSO_4(aq) + NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$$
b) As mentioned in the book, hexafluorides are known to exist for sulfur. These will form when excess fluorine is present.
$$S_8(s) + 24\ F_2(g) \rightarrow 8\ SF_6(g)$$
c) Group 6A(16) elements, except oxygen, form hydrides in the following reaction.
$$FeS(s) + 2\ HCl(aq) \rightarrow H_2S(g) + FeCl_2(aq)$$
d) Tetraiodides, but not hexaiodides, of tellurium are known.
$$Te(s) + 2\ I_2(s) \rightarrow TeI_4(s)$$

14.112 a) $2\ H_2S(g) + 3\ O_2(g) \rightarrow 2\ SO_2(g) + 2\ H_2O(g)$
     or: $8\ H_2S(g) + 4\ O_2(g) \rightarrow S_8(s) + 8\ H_2O(g)$
b) $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$
c) $SF_4(g) + 2\ H_2O(l) \rightarrow SO_2(g) + 4\ HF(g)$
d) $Al_2Se_3(s) + 6\ H_2O(l) \rightarrow 2\ Al(OH)_3(s) + 3\ H_2Se(g)$
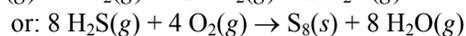
14.113 a) Se is a nonmetal; its oxide is **acidic**.
b) N is a nonmetal; its oxide is **acidic**.
c) K is a metal; its oxide is **basic**.
d) Be is an alkaline earth metal, but all of its bonds are covalent; its oxide is **amphoteric**.
e) Ba is a metal; its oxide is **basic**.

14.114 a) **basic**   b) **acidic**   c) **basic**   d) **acidic**   e) **amphoteric**

14.115 Acid strength of binary acids increases down a group: $\mathbf{H_2O < H_2S < H_2Te}$.

14.116 $\mathbf{H_2SO_4 > H_2SO_3 > HSO_3^-}$

14.117 When solid sulfur is heated, it melts at about 115°C to a mobile liquid consisting of S_8 molecules. Above 150°C, the rings begin to open and become tangled, increasing the viscosity of the liquid, and causing a darkening of the 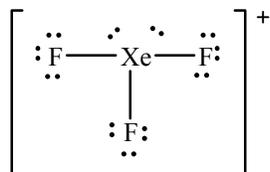liquid. At about 180°C, the dark brown mass has its highest viscosity. At higher temperatures, the chains break and untangle, decreasing the viscosity until the liquid boils at 444°C (above the end point specified). If the heated liquid (above 300°C) is poured into water, a rubbery mass ("plastic" sulfur) forms, which consists of short, tangled chains; left at room temperature for a few days, it reverts to the original crystalline solid containing S_8 molecules.

14.118   a) **SF_6, sulfur hexafluoride**
b) **O_3, ozone**
c) **SO_3, sulfur trioxide** (+6 oxidation state)
d) **SO_2, sulfur dioxide**
e) **H_2SO_4, sulfuric acid**
f) **$Na_2S_2O_3 \cdot 5H_2O$, sodium thiosulfate pentahydrate**
g) **H_2S, hydrogen sulfide**

14.119   a) **0**   b) **+4**   c) **+6**   d) **–2**   e) **–1**   f) **+6**   g) **+2**

14.120 $S_2F_{10}(g) \rightarrow SF_4(g) + SF_6(g)$
O.N. of S in S_2F_{10}: – (10 x –1 for F) / 2 = +5
O.N. of S in SF_4: – (4 x –1 for F) = +4
O.N. of S in SF_6: – (6 x –1 for F) = +6

14.121   a) F_2 is a pale yellow gas; Cl_2 is a green gas; Br_2 is a red-orange liquid; I_2 is a purple-black solid.
b) As the mass of the molecules increases, the strength of the dispersion forces will increase as well, and the melting and boiling points will parallel this trend by increasing with increasing molar mass.

14.122   a) Bonding with very electronegative elements: **+1, +3, +5, +7**. Bonding with other elements: **–1**
b) The electron configuration for Cl is $[Ne]3s^23p^5$. By adding one electron to form Cl^-, Cl achieves an octet similar to the noble gas Ar. By forming covalent bonds, Cl completes or expands its octet by maintaining its electrons paired in bonds or lone pairs.
c) Fluorine only forms the –1 oxidation state because its small size and no access to *d*-orbitals prevent it from forming multiple covalent bonds. Fluorine's high electronegativity also prevents it from sharing its electrons.

14.123   The halogens need one electron to complete their octets. This can be accomplished by gaining one electron (to form Cl^-) or by sharing a pair of electrons to form one covalent bond (as in HCl or CCl_4).

14.124   a) The Cl–Cl bond is stronger than the Br–Br bond since the chlorine atoms are smaller than the bromine atoms, so the shared electrons are held more tightly by the two nuclei.
b) The Br–Br bond is stronger than the I–I bond since the bromine atoms are smaller than the iodine atoms.
c) The Cl–Cl bond is stronger than the F–F bond. The fluorine atoms are smaller than the chlorine but they are so small that electron-electron repulsion of the lone pairs decreases the strength of the bond.

14.125   You would expect them to contain an *odd* number of atoms, so that you would have an *even* number of electrons.

14.126   a) A substance that disproportionates serves as both an oxidizing and reducing agent. Assume that OH^- serves as the base. Write the reactants and products of the reaction, and balance like a redox reaction.
        $3\ Br_2(l) + 6\ OH^-\ (aq) \rightarrow 5\ Br^-\ (aq) + BrO_3^-\ (aq) + 3\ H_2O(l)$
b) In the presence of base, instead of water, only the oxy*anion* (not oxo*acid*) and fluoride (not *hydro*fluoride) form. No oxidation or reduction takes place, because Cl maintains its +5 oxidation state and F maintains its –1 oxidation state.
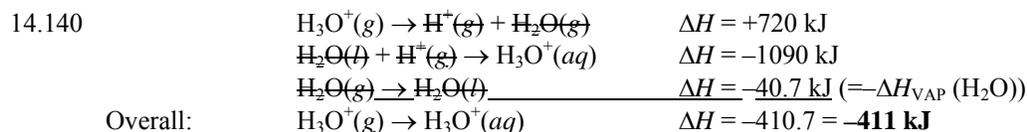 $ClF_5(l) + 6\ OH^-\ (aq) \rightarrow 5\ F^-\ (aq) + ClO_3^-\ (aq) + 3\ H_2O(l)$

14.127 a) $2 \, Rb(s) + Br_2(l) \rightarrow 2 \, RbBr(s)$
b) $I_2(s) + H_2O(l) \rightarrow HI(aq) + HIO(aq)$
c) $Br_2(l) + 2 \, I^-(aq) \rightarrow I_2(s) + 2 \, Br^-(aq)$
d) $CaF_2(s) + H_2SO_4(l) \rightarrow CaSO_4(s) + 2 \, HF(g)$

14.128 a) $H_3PO_4(l) + NaI(s) \rightarrow NaH_2PO_4(s) + HI(g)$
b) $Cl_2(g) + 2 \, I^-(aq) \rightarrow 2 \, Cl^-(aq) + I_2(s)$
c) $Br_2(l) + Cl^-(aq) \rightarrow NR$
d) $ClF(g) + F_2(g) \rightarrow ClF_3(g)$

14.129 Acid strength increases with increasing electronegativity of the central atom and increasing number of oxygen atoms. Therefore, **HIO < HBrO < HClO < HClO$_2$**

14.130 **HClO$_4$ > HBrO$_4$ > HBrO$_3$ > HIO$_3$**

14.131 a) **hydrogen fluoride, HF**   b) **calcium fluoride, CaF$_2$**
c) **chlorine dioxide, ClO$_2$**   d) **hydrogen fluoride, HF**
e) **potassium iodide, KI**   f) **chlorine, Cl$_2$**
g) **vinyl chloride, C$_2$H$_3$Cl**

14.132 a) In the reaction between NaI and H$_2$SO$_4$ the oxidation states of iodine and sulfur change, so the reaction is an **oxidation-reduction** reaction.
b) The reducing ability of X$^-$ increases down the group since the larger the ion the more easily it loses an electron. Therefore, **I$^-$ is more easily oxidized than Cl$^-$.**
c) Some acids, such as HCl, are not oxidizers, so substituting a non-oxidizing acid for H$_2$SO$_4$ would produce HI.

14.133 $I_2 < Br_2 < Cl_2$, since Cl_2 is able to oxidize Re to the +6 oxidation state, Br_2 only to +5, and I_2 only to +4.

14.134 **Helium** is the second most abundant element in the universe. **Argon** is the most abundant noble gas in Earth's atmosphere, the third most abundant constituent after N_2 and O_2.

14.135 **+2, +4, +6, +8**

14.136 Whether a boiling point is high or low is a result of the strength of the forces between particles. Dispersion forces, the weakest of all the intermolecular forces, hold atoms of noble gases together. Only a relatively low temperature is required for the atoms to have enough kinetic energy to break away from the attractive force of other atoms and go into the gas phase. The boiling points are so low that all the noble gases are gases at room temperature.

14.137 The electrons on the larger atoms are more easily removed, transferred or shared with another atom than those on the smaller atoms.

14.138 a) This allows the resulting ions to have an even number of electrons.
b) Xenon fluorides containing an odd number of fluorine atoms need an odd charge to maintain an even number of electrons around xenon.
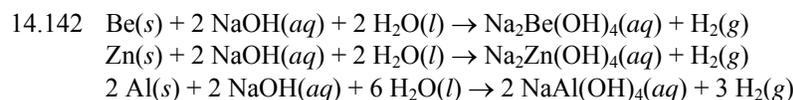c) XeF$_3$$^+$ would be T-shaped.

14.139 a)Xenon tetrafluoride, XeF_4, is an AX_4E_2 molecule with square planar geometry. Antimony pentafluoride, SbF_5, is an AX_5 molecule with trigonal bipyramidal molecule geometry. XeF_3^+ is an AX_3E_2 ion with a T-shaped geometry and SbF_6^- is an AX_6 ion with octahedral molecular geometry. **C** best shows the molecular geometries of these substances.
b) Xe in XeF_4 utilizes sp^3d^2 hybrid orbitals; in XeF_3^+, xenon utilizes sp^3d hybrid orbitals.

14.140
$$H_3O^+(g) \rightarrow \text{H}^+\text{(g)} + \text{H}_2\text{O(g)} \qquad \Delta H = +720 \text{ kJ}$$
$$\text{H}_2\text{O(l)} + \text{H}^+\text{(g)} \rightarrow H_3O^+(aq) \qquad \Delta H = -1090 \text{ kJ}$$
$$\underline{\text{H}_2\text{O(g)} \rightarrow \text{H}_2\text{O(l)} \qquad\qquad \Delta H = -40.7 \text{ kJ } (=-\Delta H_{VAP} (H_2O))}$$
Overall: $\qquad H_3O^+(g) \rightarrow H_3O^+(aq) \qquad \Delta H = -410.7 = \textbf{--411 kJ}$

14.141 Calculation of energy from wavelength: $\Delta E = hc / \lambda$.
$$\Delta E = \frac{\left(6.626 \text{ x } 10^{-34} \text{ J•s}\right)\left(2.9979 \text{ x } 10^8 \text{ m/s}\right)}{(589.2 \text{ nm})}\left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) = 3.3713654 \text{ x } 10^{-19} = \textbf{3.371 x } 10^{-19} \textbf{ J}$$

14.142 $Be(s) + 2 NaOH(aq) + 2 H_2O(l) \rightarrow Na_2Be(OH)_4(aq) + H_2(g)$
$Zn(s) + 2 NaOH(aq) + 2 H_2O(l) \rightarrow Na_2Zn(OH)_4(aq) + H_2(g)$
$2 Al(s) + 2 NaOH(aq) + 6 H_2O(l) \rightarrow 2 NaAl(OH)_4(aq) + 3 H_2(g)$
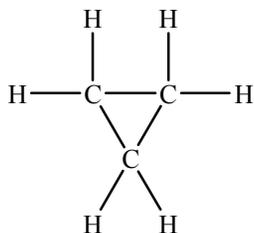
14.143 a) $5 \text{ IF} \rightarrow IF_5 + 2 I_2$
b) Iodine pentafluoride
c) This is a disproportionation redox reaction. IF acts both as the oxidizing and reducing agents.
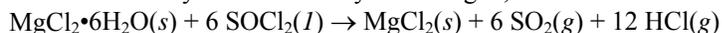d) Mass $IF_5 = \left(10 \text{ IF molecules}\right)\left(\frac{2.50 \text{ x } 10^{-3} \text{ mol IF}}{1 \text{ IF molecule}}\right)\left(\frac{1 \text{ mol } IF_5}{5 \text{ mol IF}}\right)\left(\frac{221.9 \text{ g } IF_5}{1 \text{ mol } IF_5}\right) = 1.1095 = 1.11 \text{ g } IF_5$

Mass of $I_2 = \left(10 \text{ IF molecules}\right)\left(\frac{2.50 \text{ x } 10^{-3} \text{ mol IF}}{1 \text{ IF molecule}}\right)\left(\frac{2 \text{ mol } I_2}{5 \text{ mol IF}}\right)\left(\frac{253.8 \text{ g } I_2}{1 \text{ mol } I_2}\right) = 2.538 = 2.54 \text{ g } I_2$

14.144 The compound would have 60° bond angles. The "normal" hybridization for a C atom with four bonds is sp^3, with 109°28' bond angles. The small size of the ring means that the orbital overlap will be small also; this weakens the bonds, making the compound reactive.

14.145 a) No oxidation state changes occur in this reaction; S maintains a +4 oxidation state. The prefix "hexa-" denotes 6, in this case 6 waters of hydration. Start by balancing H, then balance O.
$$MgCl_2•6H_2O(s) + 6 SOCl_2(l) \rightarrow MgCl_2(s) + 6 SO_2(g) + 12 HCl(g)$$
b) Sulfur is the central atom because it is the least electronegative element. The molecule has $[1 \text{ x } 6e^- \text{ (S)} + 1 \text{ x } 6e^-$ (O) $+ 2 \text{ x } 7e^-$ (Cl)$] = 26$ valence e^-. Six electrons are used for the three single bonds between the atoms, leaving $26 - 6 = 20e^-$. The remaining $20e^-$ electrons are distributed to the atoms to give each an octet. This results in structure **I**. An analysis of formal charges shows that structure **II** is more stable.
Formal charge = # of valence electrons – [# of unshared electrons + ½(#bonding electrons)]

I	II

I $FC_S = 6 - (2 + 1/2(6)) = +1$ II $FC_S = 6 - (2 + 1/2(8)) = 0$
    $FC_O = 6 - (6 + 1/2(2)) = -1$ $FC_O = 6 - (4 + 1/2(4)) = 0$
    $FC_{Cl} = 7 - (6 + 1/2(2)) = 0$ $FC_{Cl} = 7 - (6 + 1/2(2)) = 0$

14.146 a) Alkali metals have an outer electron configuration of ns^1. The first electron lost by the metal is the ns electron, giving the metal a noble gas configuration. Second ionization energies for alkali metals are high because the electron being removed is from the next lower energy level and electrons in a lower level are more tightly held by the nucleus. The metal would also lose its noble gas configuration.
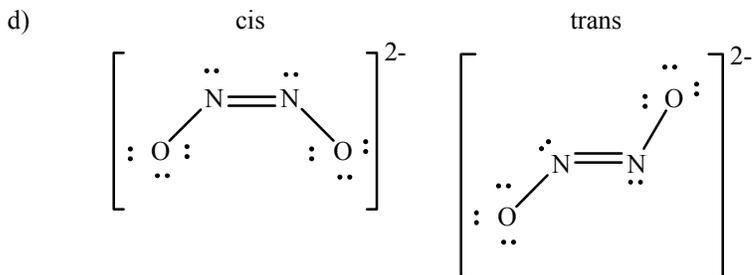b) The reaction is $2\ CsF_2(s) \rightarrow 2\ CsF(s) + F_2(g)$.
You know the ΔH_f for the formation of CsF:
    $Cs(s) + 1/2F_2(g) \rightarrow CsF(s)$ $\Delta H_f = -530$ kJ/mol
You also know the ΔH_f for the formation of CsF_2:
    $Cs(s) + F_2(g) \rightarrow CsF_2(s)$ $\Delta H_f = -125$ kJ/mol
To obtain the heat of reaction for the breakdown of CsF_2 to CsF, combine the formation reaction of CsF with the reverse of the formation reaction of CsF_2, both multiplied by 2:
    $2\ \overline{Cs(s)} + \overline{F_2(g)} \rightarrow 2\ CsF(s)$ $\Delta H = 2\ x\ (-530$ kJ$)$
    $2\ CsF_2(s) \rightarrow 2\overline{Cs(s)} + 2\overline{F_2(g)}$ $\Delta H = 2\ x\ (+125$ kJ$)$ (Note sign change)
    $2\ CsF_2(s) \rightarrow 2\ CsF(s) + F_2(g)$ $\Delta H = -810$ kJ
810 kJ of energy are released when 2 moles of CsF_2 convert to 2 moles of CsF, so heat of reaction for one mole of CsF is $-810/2$ or **−405 kJ/mol**.

14.147 $4\ Ga(l) + P_4(g) \rightarrow 4\ GaP(s)$
Finding the limiting reagent:

$$\text{Mass of GaP from Ga} = (32.5\ \text{g Ga})\left(\frac{1\ \text{mol Ga}}{69.72\ \text{g Ga}}\right)\left(\frac{4\ \text{mol GaP}}{4\ \text{mol Ga}}\right)\left(\frac{100.69\ \text{g GaP}}{1\ \text{mol GaP}}\right)$$
$$= 46.9367\ \text{g GaP}$$

$$\text{Moles } P_4 = n = \frac{PV}{RT} = \frac{(195\ \text{kPa})(20.4\ \text{L})}{\left(0.0821\dfrac{\text{L·atm}}{\text{mol·K}}\right)(515\ \text{K})}\left(\frac{1\ \text{atm}}{101.325\ \text{kPa}}\right) = 0.92853\ \text{mol } P_4\ \text{(unrounded)}$$

$$\text{Mass of GaP from } P_4: (0.92853\ \text{mol } P_4)\left(\frac{4\ \text{mol GaP}}{1\ \text{mol } P_4}\right)\left(\frac{100.69\ \text{g GaP}}{1\ \text{mol GaP}}\right) = 373.976\ \text{g GaP}$$

Since a smaller amount of product is obtained with Ga, Ga is the limiting reactant. Assuming 100% yield, 46.9367 g of GaP would be produced. Accounting for a loss of 7.2% by mass or a $100.0 - 7.2 = 92.8\%$ yield:
46.9367 g GaP (0.928) = 43.5573 = **43.6 g GaP**

14.148   a) Empirical formula HNO has a molar mass of 31.02, so hyponitrous acid with a molar mass of 62.04 g/mol which is twice 31.02 would have a molecular formula twice the empirical formula, $H_2N_2O_2$. In addition, the molecular formula of nitroxyl would be the same as the empirical formula, HNO, since the molar mass of nitroxyl is the same as the empirical formula.

b) $H_2N_2O_2$ has [2 x 1e⁻ (H) + 2 x 5e⁻ (N) + 2 x 6e⁻ (O)] = 24 valence e⁻. Ten electrons are used for single bonds between the atoms, leaving 24 – 10 = 14e⁻. 16 electrons are needed to give every atom an octet; since only 16 electrons are available, one double bond (between the N atoms) is needed.
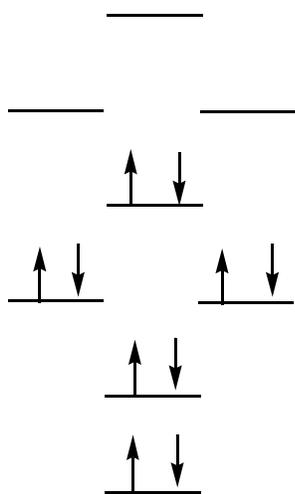HNO has [1 x 1e⁻ (H) + 1 x 5e⁻ (N) + 1 x 6e⁻ (O)] = 12 valence e⁻. Four electrons are used for single bonds between the atoms, leaving 12 – 4 = 8e⁻. 10 electrons are needed to give every atom an octet; since only 8 electrons are available, one double bond is needed between the N and O atoms.

c) In both hyponitrous acid and nitroxyl, the nitrogens are surrounded by 3 electron groups (one single bond, one double bond and one unshared pair), so the electron arrangement is trigonal planar and the molecular shape is **bent**.

d)
           cis   trans

14.149 a)

b) All have configuration $(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^2(\pi_{2p})^2(\sigma_{2p})^2$; bond order = 3.

14.150   The three steps of the Ostwald process are given in the chapter.
a) $4 NH_3(g) + 5 O_2(g) \rightarrow 4 NO(g) + 6 H_2O(g)$
           $2 NO(g) + O_2(g) \rightarrow 2 NO_2(g)$
           $3 NO_2(g) + H_2O(l) \rightarrow 2 HNO_3(l) + NO(g)$
b) If NO is not recycled, the reaction steps proceed as written above. The molar relationships for each reaction yield NH_3 consumed per mole HNO_3 produced:

$$\frac{\text{mol } NH_3 \text{ consumed}}{\text{mol } HNO_3 \text{ produced}} = \left(\frac{3 \text{ mol } NO_2}{2 \text{ mol } HNO_3}\right)\left(\frac{2 \text{ mol } NO}{2 \text{ mol } NO_2}\right)\left(\frac{4 \text{ mol } NH_3}{4 \text{ mol } NO}\right) = \textbf{1.5} \text{ mol } NH_3 \text{ / mol } HNO_3$$

c) The goal is to find the mass of HNO_3 produced, which can be converted to volume of aqueous solution using the density and mass percent. To find mass of HNO_3, determine the number of moles of NH_3 present in 1 m^3 of gas mixture (ideal gas law) and convert moles of NH_3 to moles HNO_3 using the mole ratio in b). Convert moles to grams using the molar mass of HNO_3 and convert to volume.

$$\text{Moles } NH_3 = \frac{PV}{RT} = \frac{(5.0 \text{ atm})(1 \text{ m}^3)}{\left(0.0821 \dfrac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)((273 + 850.) \text{K})} \left(\frac{1 \text{ L}}{10^{-3} \text{ m}^3}\right)\left(\frac{10.\% \text{ NH}_3}{100\% \text{ gas}}\right)$$

= 5.42309 mol NH_3 (unrounded)

Mass HNO_3 = (5.42309 mol NH_3) (1 mol HNO_3 / 1.5 mol NH_3) (63.02 g HNO_3 / 1 mol HNO_3) (96% / 100%)

= 218.728 g HNO_3 (unrounded)

Volume HNO_3 = (218.728 g HNO_3) (100% / 60.%) (1 mL / 1.37 g) = 266.092 = **2.7 x 10^2 mL** solution

14.151 Determine the volume of a unit cell:

$$\text{Volume} = \left(\frac{\text{cm}^3}{1.693 \text{ g}}\right)\left(\frac{12.01 \text{ g C}}{1 \text{ mol C}}\right)\left(\frac{1 \text{ mol C}}{6.022 \times 10^{23} \text{ C atoms}}\right)\left(\frac{240 \text{ C atoms}}{1 \text{ unit cell}}\right)$$

= 2.8272 x 10^{-21} = **2.827 x 10^{-21} cm^3**

Since the cell is cubic, the length of an edge is the cube root of the volume:

Cell edge = (2.8272 x 10^{-21} cm^3)$^{1/3}$ = 1.414009 x 10^{-7} = **1.414 x 10^{-7} cm**

The low density arises because even though the spheres are closest packed, the spheres are hollow.

14.152 2 $BrF_3(l) \rightarrow BrF_2^+(solvated) + BrF_4^-$ (solvated)

14.153 a) Percent N = (mass N / mass NH_3) x 100% = (14.01 g N / 17.03 g NH_3) x 100% = 82.266588 = **82.27% N**
b) Percent N = (mass N / mass NH_4NO_3) x 100% = (2 x 14.01 g N / 80.05 g NH_4NO_3) x 100%
= 35.00312 = **35.00% N**
c) Percent N = (mass N / mass $(NH_4)_2HPO_4$) x 100% = (2 x 14.01 g N / 132.06 g $(NH_4)_2HPO_4$) x 100%
= 21.2176 = **21.22% N**

14.154 Carbon monoxide and carbon dioxide would be formed from the reaction of coke (carbon) with the oxygen in the air. The nitrogen in the producer gas would come from the nitrogen already in the air. So, the calculation of mass of product is based on the mass of CO and CO_2 that can be produced from 1.75 metric tons of coke.
Using 100 grams of sample, the percentages simply become grams.
Since 5.0 grams of CO_2 is produced for each 25 grams of CO, we can calculate a mass ratio of carbon that produces each:

$$\frac{(25 \text{ g CO})\left(\dfrac{12.01 \text{ g C}}{28.01 \text{ g CO}}\right)}{(5.0 \text{ g CO}_2)\left(\dfrac{12.01 \text{ g C}}{44.01 \text{ g CO}_2}\right)} = 7.85612 / 1 \text{ (unrounded)}$$

Using the ratio of carbon that reacts as 7.85612:1, the total C reacting is 7.85612 + 1 = 8.85612. The mass fraction of the total carbon that produces CO is 7.85612/8.85612 and the mass fraction of the total carbon reacting that produces CO_2 is 1.00/8.85612. To find the mass of CO produced from 1.75 metric tons of carbon with an 87% yield:

Mass CO = (7.85612 / 8.85612) (1.75 ton) (28.01 ton CO / 12.01 ton C) (87% / 100%)
= 3.1498656 ton CO (unrounded)

Mass CO_2 = (1 / 8.85612) (1.75 ton) (44.01 ton CO_2 / 12.01 ton C) (87% / 100%)
= 0.6299733 ton CO_2 (unrounded)

The mass of CO and CO_2 represent a total of 30% (= 100% – 70.% N_2) of the mass of the producer gas, so the total mass would be (3.1498656 + 0.6299733) (100% / 30%) = 12.59946 = **13 metric tons**.
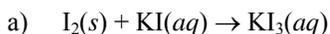
14.155   a) $2 F_2(g) + 2 H_2O(l) \rightarrow 4 HF(aq) + O_2(g)$
Oxidation states of oxygen: –2 in H_2O and 0 in O_2
Oxidizing agent: F_2; Reducing agent: H_2O
              $2 NaOH(aq) + 2 F_2(g) \rightarrow 2 NaF(aq) + H_2O(l) + OF_2(g)$
Oxidation states of oxygen: –2 in NaOH and H_2O, +2 in OF_2
Oxidizing agent: F_2; Reducing agent: NaOH
              $OF_2(g) + 2 OH^- (aq) \rightarrow O_2(g) + H_2O(l) + 2 F^- (aq)$
Oxidation states of oxygen: +2 in OF_2, 0 in O_2, –2 in OH^- and H_2O
Oxidizing agent: OF_2; Reducing agent: OH^-
b)

The oxygen is AX_2E_2, thus it is a **bent** molecule.

14.156   In a disproportionation reaction, a substance acts as both a reducing agent and oxidizing agent because an atom within the substance reacts to form atoms with higher and lower oxidation states.
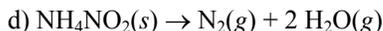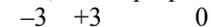   0   –1   –1/3
a) $I_2(s) + KI(aq) \rightarrow KI_3(aq)$
I in I_2 reduces to I in KI_3. I in KI oxidizes to I in KI_3. This is not a disproportionation reaction since different substances have atoms that reduce or oxidize. The *reverse* direction would be a disproportionation reaction because a single substance (I in KI) both oxidizes and reduces.
          +4   +5   +3
b) $2 ClO_2(g) + H_2O(l) \rightarrow HClO_3(aq) + HClO_2(aq)$
Yes, ClO_2 disproportionates, as the chlorine reduces from +4 to +3 and oxidizes from +4 to +5.
          0   –1   +1
c) $Cl_2(g) + 2 NaOH(aq) \rightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$
Yes, Cl_2 disproportionates, as the chlorine reduces from 0 to –1 and oxidizes from 0 to +1.
     –3   +3   0
d) $NH_4NO_2(s) \rightarrow N_2(g) + 2 H_2O(g)$
Yes, NH_4NO_2 disproportionates; the ammonium (NH_4^+) nitrogen oxidizes from –3 to 0, and the nitrite (NO_2^-) nitrogen reduces from +3 to 0.
          +6   +7   +4
e) $3 MnO_4^{2-}(aq) + 2 H_2O(l) \rightarrow 2 MnO_4^-(aq) + MnO_2(s) + 4 OH^-(aq)$
Yes, MnO_4^{2-} disproportionates, the manganese oxidizes from +6 to +7 and reduces from +6 to +4.
          +1   +3   0
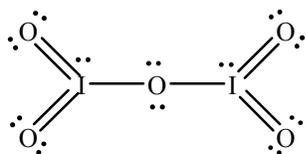f) $3 AuCl(s) \rightarrow AuCl_3(s) + 2 Au(s)$
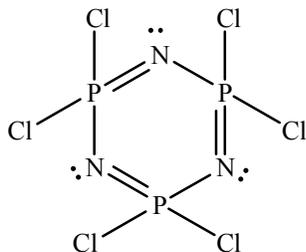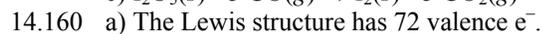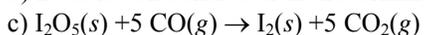Yes, AuCl disproportionates, the gold oxidizes from +1 to +3 and reduces from +1 to 0.

14.157   a) N lacks the *d* orbitals needed to expand its octet.
b) Si has empty low-energy *d* orbitals which can act as a "pathway" for electron donation from the O of H_2O (to form SiO_2 + HCl).
c) There is partial double-bond character in the S-O bond.
d) ClF_4 would be a free radical (odd number of electrons, one electron unpaired), which would be unstable.

14.158   a) Group **5A(15)** elements have 5 valence electrons and typically form three bonds with a lone pair to complete the octet. An example is NH_3.
b) Group **7A(17)** elements readily gain an electron causing the other reactant to be oxidized. They form monatomic ions of formula X^- and oxoanions. Examples would be Cl^- and ClO^-.
c) Group **6A(16)** elements have six valence electrons and gain a complete octet by forming two covalent bonds. An example is H_2O.
d) Group **1A(1)** elements are the strongest reducing agents because they most easily lose an electron. As the least electronegative and most metallic of the elements, they are not likely to form covalent bonds. Group **2A(2)** have similar characteristics. Thus, either Na or Ca could be an example.

e) Group **3A(13)** elements have only three valence electrons to share in covalent bonds, but with an empty orbital they can accept an electron pair from another atom. Boron would be an example of an element of this type.

f) Group **8A(18)**, the noble gases, are the least reactive of all the elements. Xenon is an example that forms compounds, while helium does not form compounds.
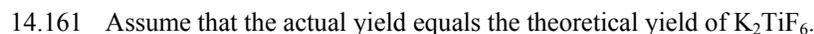
14.159 a) iodic acid; $2\ HIO_3(s) \xrightarrow{\Delta} I_2O_5(s) + H_2O(l)$

b) Double bond character in the terminal I–O bonds gives shorter bonds than the single bonds to the central O.

c) $I_2O_5(s) + 5\ CO(g) \rightarrow I_2(s) + 5\ CO_2(g)$

14.160 a) The Lewis structure has 72 valence e^-.

b) Three lone pairs appear on N ring atoms.

c) The bond order is 1.5. The molecule has a resonance structure, similar to the "alternating" bonds of benzene. The single-double bonds do not really alternate, but rather the valence electrons are delocalized on the ring, resulting in a bond order of 1.5.
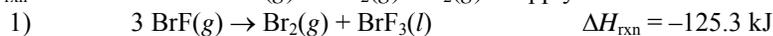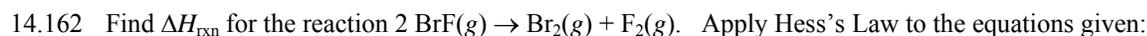
14.161 Assume that the actual yield equals the theoretical yield of K_2TiF_6.

$$\text{Mass of } K_2TiF_6 = \left(5.00\ \text{g TiO}_2\right)\left(\frac{1\ \text{mol TiO}_2}{79.88\ \text{g TiO}_2}\right)\left(\frac{1\ \text{mol } K_2TiF_6}{1\ \text{mol TiO}_2}\right)\left(\frac{240.08\ \text{g } K_2TiF_6}{1\ \text{mol } K_2TiF_6}\right)$$
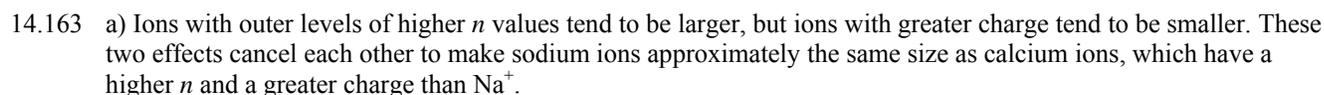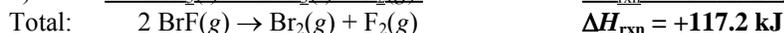
$$= 15.02754\ \text{g } K_2TiF_6\ \text{(unrounded)}$$

$$\text{Mass } K_2TiF_6 \text{ remaining in solution} = \left(250.\ \text{mL}\right)\left(\frac{0.60\ \text{g } K_2TiF_6}{100\ \text{mL}}\right) = 1.5\ \text{g } K_2TiF_6$$

Mass K_2TiF_6 obtained = (15.02754 – 1.5) g = 13.52754 = **13.5 g K_2TiF_6**

14.162 Find ΔH_{rxn} for the reaction $2\ BrF(g) \rightarrow Br_2(g) + F_2(g)$. Apply Hess's Law to the equations given:

1)	$3\ BrF(g) \rightarrow Br_2(g) + BrF_3(l)$	$\Delta H_{rxn} = -125.3\ \text{kJ}$
2)	$5\ BrF(g) \rightarrow 2\ Br_2(g) + BrF_5(l)$	$\Delta H_{rxn} = -166.1\ \text{kJ}$
3)	$BrF_3(l) + F_2(g) \rightarrow BrF_5(l)$	$\Delta H_{rxn} = -158.0\ \text{kJ}$

Reverse equations 1 and 3, and add to equation 2:

1)	$Br_2(g) + \cancel{BrF_3(l)} \rightarrow 3\ BrF(g)$	$\Delta H_{rxn} = +125.3\ \text{kJ (note sign change)}$
2)	$5\ BrF(g) \rightarrow 2\ Br_2(g) + \cancel{BrF_5(l)}$	$\Delta H_{rxn} = -166.1\ \text{kJ}$
3)	$\cancel{BrF_5(l)} \rightarrow \cancel{BrF_3(l)} + F_2(g)$	$\underline{\Delta H_{rxn} = +158.0\ \text{kJ (note sign change)}}$
Total:	$2\ BrF(g) \rightarrow Br_2(g) + F_2(g)$	$\Delta H_{rxn} = +117.2\ \text{kJ}$

14.163 a) Ions with outer levels of higher n values tend to be larger, but ions with greater charge tend to be smaller. These two effects cancel each other to make sodium ions approximately the same size as calcium ions, which have a higher n and a greater charge than Na^+.
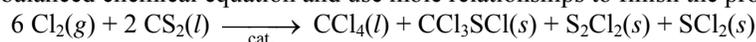
b) Dissolution is a process that involves the breaking of the force holding ions together (lattice energy) and the formation of ion-dipole forces between the ions and water molecules. If a salt (ionic compound) is soluble, the ion-dipole forces are greater than the lattice energy and if a salt is insoluble, the lattice energy is greater. Lattice energy is greater with greater ionic charge. The CaF_2 salt with Ca^{2+} ions will have greater lattice energy, and lower solubility, than the NaF salt with Na^+ ions.

c) Beryllium is unusual in Group 2A(2) in that all its compounds are covalent. Covalent compounds do not conduct electricity since they do not involve any ions. All other members of Group 2A(2) including calcium form ionic compounds that do conduct electricity when melted.

14.164   a) $Al^{3+}(aq) + 3\ H_2O(l) \rightarrow Al(OH)_3(s) + 3\ H^+(aq)$
b) $H^+(aq) + SO_4^{2-}(aq) \rightarrow HSO_4^-(aq)$

14.165   Write a balanced chemical equation and use mole relationships to finish the problem.
$$6\ Cl_2(g) + 2\ CS_2(l) \xrightarrow{\text{cat.}} CCl_4(l) + CCl_3SCl(s) + S_2Cl_2(s) + SCl_2(s)$$

In this reaction, the only source of carbon is CS_2. The number of grams of carbon in the products must equal the number of grams of carbon in the reactant.

Mass of carbon from $CCl_4 = \left(50.0\ \text{g } CCl_4\right)\left(\dfrac{1\ \text{mol } CCl_4}{153.81\ \text{g } CCl_4}\right)\left(\dfrac{1\ \text{mol C}}{1\ \text{mol } CCl_4}\right)\left(\dfrac{12.01\ \text{g C}}{1\ \text{mol C}}\right)$

   $= 3.904167$ g C (unrounded)

Mass of carbon from $CCl_3SCl = \left(0.500\ \text{g } CCl_3SCl\right)\left(\dfrac{1\ \text{mol } CCl_3SCl}{185.88\ \text{g } CCl_3SCl}\right)\left(\dfrac{1\ \text{mol C}}{1\ \text{mol } CCl_3SCl}\right)\left(\dfrac{12.01\ \text{g C}}{1\ \text{mol C}}\right)$

   $= 0.032305788$ g C (unrounded)
Total mass of carbon $= (3.904167 + 0.032305788)$ g C $= 3.93647$ g C (unrounded)

Mass of $CS_2 = \left(3.93647\ \text{g C}\right)\left(\dfrac{1\ \text{mol C}}{12.01\ \text{g C}}\right)\left(\dfrac{1\ \text{mol } CS_2}{1\ \text{mol C}}\right)\left(\dfrac{76.15\ \text{g } CS_2}{1\ \text{mol } CS_2}\right)$

   $= 24.95938 = \textbf{25.0 g } CS_2$
It is not possible to determine how much S_2Cl_2 and SCl_2 are formed. The total number of grams of sulfur in products can be calculated, but without knowing the ratio of S_2Cl_2 to SCl_2, no further determination can be made. Knowing the amount of $Cl_2(g)$ would also allow for the determination of the amount of SCl_2 and S_2Cl_2 made.

14.166   Hydrogen can act as a reducing agent by losing an electron and can act as an oxidizing agent by gaining an electron.
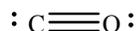 $2\ Na(s) + H_2(g) \rightarrow 2\ NaH(s)$ Na loses an electron, so H_2 is oxidizing agent.
   $H_2(g) + Cl_2(g) \rightarrow 2\ HCl(g)$ Cl gains an electron, so H_2 is reducing agent.

14.167 $2\ Ca_3(PO_4)_2(s) + 6\ SiO_2(s) + 10\ C(s) \rightarrow 6\ CaSiO_3(s) + 10\ CO(g) + P_4(g)$

Mass $= \left(315\ \text{mol } P_4\right)\left(\dfrac{2\ \text{mol } Ca_3(PO_4)_2}{1\ \text{mol } P_4}\right)\left(\dfrac{310.18\ \text{g } Ca_3(PO_4)_2}{1\ \text{mol } Ca_3(PO_4)_2}\right)\left(\dfrac{1\ \text{kg}}{10^3\ \text{g}}\right)\left(\dfrac{100\%}{90.\%}\right)$

   $= 2.17126 \times 10^2 = \textbf{2.2} \times \textbf{10}^2 \textbf{ kg } Ca_3(PO_4)_2$

14.168   a) E is a Group 16 element and has 6 valence electrons. EF_5^- would have $[1 \times 6e^-\ (E) + 5 \times 7e^-\ (F) + 1\ e^-$ from charge)] $= 42$ valence electrons. 10 electrons are used in the single bonds between the atoms. Thirty electrons are used to complete the octets of the fluorine atoms. The remaining 2 electrons reside on the E atom. EF_5^- is thus an AX_5E substance and has **square pyramidal** molecule geometry.
b) Since element E has six regions of electron density, six hybrid orbitals are required. The hybridization is $\textbf{sp}^3\textbf{d}^2$.
c) The oxidation number of E in EF_5^- is $\textbf{+4}$.
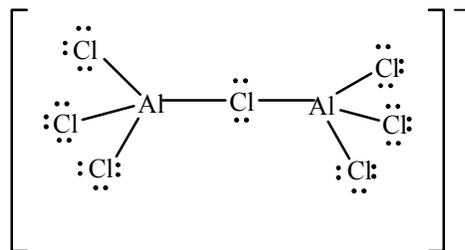
14.169   a)
   $$:C \equiv\!\equiv\!\equiv O:$$
b)   The formal charge on carbon is -1, and the formal charge on oxygen is $+1$.
   $FC_C = 4 - [2 + \frac{1}{2}(6)] = -1$ $FC_O = 6 - [2 + \frac{1}{2}(6)] = +1$

c) The electronegativity of oxygen partially compensates for the formal charge difference.

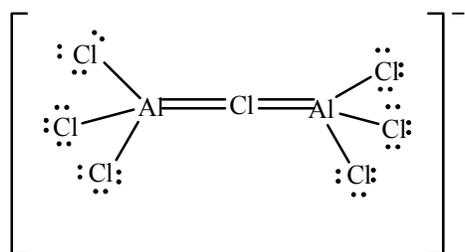14.170 To answer these questions, draw an initial structure for $Al_2Cl_7^-$:

a) Aluminum uses its $3s$ and $3p$ valence orbitals to form sp^3 hybrid orbitals for bonding.
b) With formula AX_4, the shape is **tetrahedral** around each aluminum atom.
c) Since the Al–Cl–Al bond is linear (180°Al–Cl–Al bond angle), the central atom must be sp hybridized.
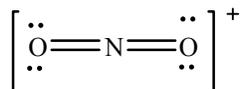d) The sp hybridization suggests that there are no lone pairs on the central chlorine. Instead, the extra four electrons participate in bonding with the empty d-orbitals on the aluminum to form double bonds between the chlorine and each aluminum.

14.171 a) Ionic size increases and charge density decreases down the column. When the charge density decreases, the ionic bond strength between the alkaline earth cation and carbonate anion will decrease. Therefore, the smaller cations release CO_2 more easily at lower temperatures.
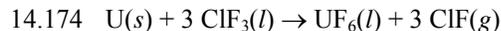b) To prepare a mixture of $CaCO_3$ and MgO from $CaCO_3$ and $MgCO_3$, heat the mixture to a temperature slightly higher than 542°C, but much lower than 882°C. This should drive off CO_2 from $MgCO_3$ without significantly affecting $CaCO_3$

14.172 The Lewis structures are

The nitronium ion (NO_2^+) has a linear shape because the central N atom has 2 surrounding electron groups, which achieve maximum repulsion at 180°. Both the nitrite ion (NO_2^-) and nitrogen dioxide (NO_2) have a central N surrounded by three electron groups. The electron group arrangement would be trigonal planar with an ideal bond angle of 120°. The bond angle in NO_2^- is more compressed than that in NO_2 since the lone pair of electrons in NO_2^- takes up more space than the lone electron in NO_2. Therefore the bond angle in NO_2^- is smaller (115°) than that of NO_2 (134°)

14.173 a)   1) $CaF_2(s) + H_2SO_4(l) \rightarrow 2\ HF(g) + CaSO_4(s)$
        2) $NaCl(s) + H_2SO_4(l) \rightarrow HCl(g) + NaHSO_4(s)$
        3) $FeS(s) + 2\ HCl(aq) \rightarrow FeCl_2(aq) + H_2S(g)$
     b) $Ca_3P_2(s) + 6\ H_2O(l) \rightarrow 2\ PH_3(g) + 3\ Ca(OH)_2(s)$
     c) $Al_4C_3(s) + 12\ H_2O(l) \rightarrow 4\ Al(OH)_3(s) + 3\ CH_4(g)$

14.174 $U(s) + 3\ ClF_3(l) \rightarrow UF_6(l) + 3\ ClF(g)$
    To find the limiting reactant, calculate the amount of UF_6 that would form from each reactant.
    (1 metric ton = 1 t = 1000 kg)
    From U:
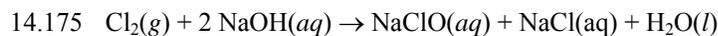
$$\text{Mole } UF_6 = (1.00\text{ t Ore})\left(\frac{10^3\text{ kg}}{1\text{ t}}\right)\left(\frac{10^3\text{ g}}{1\text{ kg}}\right)\left(\frac{1.55\%}{100\%}\right)\left(\frac{1\text{ mol U}}{238.0\text{ g U}}\right)\left(\frac{1\text{ mol }UF_6}{1\text{ mol U}}\right)$$

        $= 65.12605$ mol UF_6 (unrounded)
    From ClF_3:

$$\text{Mole } UF_6 = (12.75\text{ L})\left(\frac{1\text{ mL}}{10^{-3}\text{ L}}\right)\left(\frac{1.88\text{ g }ClF_3}{1\text{ mL}}\right)\left(\frac{1\text{ mol }ClF_3}{92.45\text{ g }ClF_3}\right)\left(\frac{1\text{ mol }UF_6}{3\text{ mol }ClF_3}\right)$$

        $= 86.42509$ mol UF_6 (unrounded)
    Since the amount of uranium will produce less uranium hexafluoride, it is the limiting reactant.
    Mass UF_6 = (65.12605 mol UF_6) (352.0 g UF_6 / 1 mol UF_6) = 2.2924×10^4 = **2.29×10^4 g UF_6**

14.175 $Cl_2(g) + 2\ NaOH(aq) \rightarrow NaClO(aq) + NaCl(aq) + H_2O(l)$
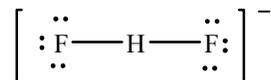
$$\text{Volume} = (1000.\text{ L})\left(\frac{5.25\%}{100\%}\right)\left(\frac{1\text{ mL}}{10^{-3}\text{ L}}\right)\left(\frac{1.07\text{ g}}{\text{mL}}\right)\left(\frac{1\text{ mol }NaClO}{74.44\text{ g }NaClO}\right)\left(\frac{1\text{ mol }Cl_2}{1\text{ mol }NaClO}\right)\left(\frac{22.4\text{ L}}{\text{mol}}\right)$$

        $= 1.69038 \times 10^4$ = **1.69×10^4 L Cl_2**

14.176 Apply Hess's Law to the two-step process below. The bond energy (BE) of H_2 is exothermic because heat is
    given off as the two H atoms at higher energy combine to form the H_2 molecule at lower energy.
        $H + H \rightarrow \cancel{H_2}$ BE = –432 kJ/mol
        $\cancel{H_2} + H^+ \rightarrow H_3^+$ ΔH = –337 kJ/mol
    Overall: $H + H + H^+ \rightarrow H_3^+$ ΔH_{rxn} = **–769 kJ/mol**

14.177 reverse and double: $1/2\ H_2(g) \rightarrow H(g)$ ΔH = 218.0 kJ
        1) $2\ H(g) \rightarrow \cancel{H_2(g)}$ ΔH = –436.0 kJ
        2) $\cancel{H_2(g)} + 1/2\ O_2(g) \rightarrow H_2O(g)$ ΔH = –241.826 kJ
        Overall: $2\ H(g) + 1/2\ O_2(g) \rightarrow H_2O(g)$ ΔH = –677.826 = **–677.8 kJ**

14.178 The H was covalently bonded to fluorine. The second fluorine was originally attracted to form a hydrogen bond.

$$\left[\ :\!\overset{..}{\underset{..}{F}}\!\!-\!\!H\!\!-\!\!\overset{..}{\underset{..}{F}}\!\!:\ \right]^{-}$$

14.179 Determine the electron configuration of each species. Partially filled orbitals lead to paramagnetism. If there are
    an odd number of electrons present, the species will be paramagnetic.
    O^+ $1s^2 2s^2 2p^3$ **paramagnetic**   odd number of electrons
    O^- $1s^2 2s^2 2p^5$ **paramagnetic**   odd number of electrons
    O^{2-} $1s^2 2s^2 2p^6$ diamagnetic   all orbitals filled (all electrons paired)
    O^{2+} $1s^2 2s^2 2p^2$ **paramagnetic**   Two of the $2p$ orbitals have one electron each. These electrons are
                        spin parallel (Hund's rule).

14.180   a) Determine the mass of As in a formula mass of the compound.

$$\% \text{ As in CuHAsO}_3 = \frac{74.92 \text{ g As}}{187.48 \text{ g CuHAsO}_3} \times 100\% = 39.96160 = \textbf{39.96\% As}$$

$$\% \text{ As in (CH}_3)_3\text{As} = \frac{74.92 \text{ g As}}{120.02 \text{ g (CH}_3)_3\text{As}} \times 100\% = 62.4229 = \textbf{62.42\% As}$$

b) Mass As $= \left(\dfrac{0.50 \text{ mg As}}{\text{m}^3} \right)\left(\dfrac{10^{-3} \text{ g}}{1 \text{ mg}} \right)\big((12.35 \text{ m})(7.52 \text{ m})(2.98 \text{ m})\big) = 0.13838 \text{ g As}$

Mass CuHAsO$_3$ $= (0.13838 \text{ g As})\left(\dfrac{100 \text{ g CuHAsO}_3}{39.96160 \text{ g As}} \right) = 0.346282 = \textbf{0.35 g CuHAsO}_3$

14.181   a) **oxidizing agent**, producing **H₂O**.
         b) **reducing agent**, producing **O₂**.