

CHAPTER 8

PERIODIC RELATIONSHIPS AMONG THE ELEMENTS

8.19 Hydrogen forms the H^+ ion (resembles the alkali metals) and the H^- ion (resembles the halogens).

8.20 Strategy: (a) We refer to the building-up principle discussed in Section 7.9 of the text. We start writing the electron configuration with principal quantum number $n = 1$ and continue upward in energy until all electrons are accounted for. (b) What are the electron configuration characteristics of representative elements, transition elements, and noble gases? (c) Examine the pairing scheme of the electrons in the outermost shell. What determines whether an element is diamagnetic or paramagnetic?

Solution:

- (a) We know that for $n = 1$, we have a $1s$ orbital (2 electrons). For $n = 2$, we have a $2s$ orbital (2 electrons) and three $2p$ orbitals (6 electrons). For $n = 3$, we have a $3s$ orbital (2 electrons). The number of electrons left to place is $17 - 12 = 5$. These five electrons are placed in the $3p$ orbitals. The electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^5$ or $[\text{Ne}]3s^2 3p^5$.
- (b) Because the $3p$ subshell is not completely filled, this is a *representative element*. Without consulting a periodic table, you might know that the halogen family has seven valence electrons. You could then further classify this element as a *halogen*. In addition, all halogens are *nonmetals*.
- (c) If you were to write an orbital diagram for this electron configuration, you would see that there is *one* unpaired electron in the p subshell. Remember, the three $3p$ orbitals can hold a total of six electrons. Therefore, the atoms of this element are paramagnetic.

Check: For (b), note that a transition metal possesses an incompletely filled d subshell, and a noble gas has a completely filled outer-shell. For (c), recall that if the atoms of an element contain an odd number of electrons, the element must be paramagnetic.

8.21 (a) and (d); (b) and (f); (c) and (e).

8.22 Elements that have the same number of valence electrons will have similarities in chemical behavior. Looking at the periodic table, elements with the same number of valence electrons are in the same group. Therefore, the pairs that would represent similar chemical properties of their atoms are:

(a) and (d) (b) and (e) (c) and (f).

8.23 (a) $1s^2 2s^2 2p^5$ (halogen) (c) $[\text{Ar}]4s^2 3d^6$ (transition metal)
(b) $[\text{Ar}]4s^2$ (alkaline earth metal) (d) $[\text{Ar}]4s^2 3d^{10} 4p^3$ (Group 5A)

8.24 (a) Group 1A (b) Group 5A (c) Group 8A (d) Group 8B

Identify the elements.

- 8.25** There are no electrons in the $4s$ subshell because transition metals lose electrons from the ns valence subshell before they are lost from the $(n-1)d$ subshell. For the neutral atom there are only six valence electrons. The element can be identified as Cr (chromium) simply by counting six across starting with potassium (K, atomic number 19).

What is the electron configuration of neutral chromium?

- 8.26** You should realize that the metal ion in question is a transition metal ion because it has five electrons in the $3d$ subshell. Remember that in a transition metal ion, the $(n-1)d$ orbitals are more stable than the ns orbital. Hence, when a cation is formed from an atom of a transition metal, electrons are *always* removed first from the ns orbital and then from the $(n-1)d$ orbitals if necessary. Since the metal ion has a +3 charge, three electrons have been removed. Since the $4s$ subshell is less stable than the $3d$, two electrons would have been lost from the $4s$ and one electron from the $3d$. Therefore, the electron configuration of the neutral atom is $[\text{Ar}]4s^23d^6$. This is the electron configuration of iron. Thus, the metal is **iron**.

- 8.27** Determine the number of electrons, and then “fill in” the electrons as you learned (Figure 7.23 and Table 7.3 of the text).

(a) $1s^2$	(g) $[\text{Ar}]4s^23d^{10}4p^6$	(m) $[\text{Xe}]$
(b) $1s^2$	(h) $[\text{Ar}]4s^23d^{10}4p^6$	(n) $[\text{Xe}]6s^24f^{14}5d^{10}$
(c) $1s^22s^22p^6$	(i) $[\text{Kr}]$	(o) $[\text{Kr}]5d^{10}$
(d) $1s^22s^22p^6$	(j) $[\text{Kr}]$	(p) $[\text{Xe}]6s^24f^{14}5d^{10}$
(e) $[\text{Ne}]3s^23p^6$	(k) $[\text{Kr}]5s^24d^{10}$	(q) $[\text{Xe}]4f^{14}5d^{10}$
(f) $[\text{Ne}]$	(l) $[\text{Kr}]5s^24d^{10}5p^6$	

- 8.28 Strategy:** In the formation of a **cation** from the neutral atom of a representative element, one or more electrons are *removed* from the highest occupied n shell. In the formation of an **anion** from the neutral atom of a representative element, one or more electrons are *added* to the highest partially filled n shell. Representative elements typically gain or lose electrons to achieve a stable noble gas electron configuration. When a cation is formed from an atom of a transition metal, electrons are *always* removed first from the ns orbital and then from the $(n-1)d$ orbitals if necessary.

Solution:

(a) $[\text{Ne}]$	(e) Same as (c)
(b) same as (a). Do you see why?	(f) $[\text{Ar}]3d^6$. Why isn't it $[\text{Ar}]4s^23d^4$?
(c) $[\text{Ar}]$	(g) $[\text{Ar}]3d^9$. Why not $[\text{Ar}]4s^23d^7$?
(d) Same as (c). Do you see why?	(h) $[\text{Ar}]3d^{10}$. Why not $[\text{Ar}]4s^23d^8$?

- 8.29** This exercise simply depends on determining the total number of electrons and using Figure 7.23 and Table 7.3 of the text.

(a) $[\text{Ar}]$	(f) $[\text{Ar}]3d^6$	(k) $[\text{Ar}]3d^9$
(b) $[\text{Ar}]$	(g) $[\text{Ar}]3d^5$	(l) $[\text{Kr}]4d^{10}$
(c) $[\text{Ar}]$	(h) $[\text{Ar}]3d^7$	(m) $[\text{Xe}]4f^{14}5d^{10}$
(d) $[\text{Ar}]3d^3$	(i) $[\text{Ar}]3d^8$	(n) $[\text{Xe}]4f^{14}5d^8$
(e) $[\text{Ar}]3d^5$	(j) $[\text{Ar}]3d^{10}$	(o) $[\text{Xe}]4f^{14}5d^8$

- 8.30 (a) Cr^{3+} (b) Sc^{3+} (c) Rh^{3+} (d) Ir^{3+}

8.31 Two species are isoelectronic if they have the same number of electrons. Can two neutral atoms of different elements be isoelectronic?

- (a) C and B^- are isoelectronic. (b) Mn^{2+} and Fe^{3+} are isoelectronic.
 (c) Ar and Cl^- are isoelectronic. (d) Zn and Ge^{2+} are isoelectronic.

With which neutral atom are the positive ions in (b) isoelectronic?

8.32 Isoelectronic means that the species have the same number of electrons and the same electron configuration.

- Be^{2+} and He (2e^-) F^- and N^{3-} (10e^-) Fe^{2+} and Co^{3+} (24e^-) S^{2-} and Ar (18e^-)

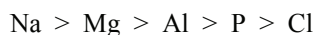
- 8.37 (a) Cs is larger. It is below Na in Group 1A. (d) Br is larger. It is below F in Group 7A.
 (b) Ba is larger. It is below Be in Group 2A. (e) Xe is larger. It is below Ne in Group 8A.
 (c) Sb is larger. It is below N in Group 5A.

8.38 **Strategy:** What are the trends in atomic radii in a periodic group and in a particular period. Which of the above elements are in the same group and which are in the same period?

Solution: Recall that the general periodic trends in atomic size are:

- (1) Moving from left to right across a row (period) of the periodic table, the atomic radius *decreases* due to an increase in effective nuclear charge.
- (2) Moving down a column (group) of the periodic table, the atomic radius *increases* since the orbital size increases with increasing principal quantum number.

The atoms that we are considering are all in the same period of the periodic table. Hence, the atom furthest to the left in the row will have the largest atomic radius, and the atom furthest to the right in the row will have the smallest atomic radius. Arranged in order of decreasing atomic radius, we have:



Check: See Figure 8.5 of the text to confirm that the above is the correct order of decreasing atomic radius.

8.39 Pb, as can be seen in Figure 8.5 of the text.

8.40 **Fluorine** is the smallest atom in Group 7A. Atomic radius increases moving down a group since the orbital size increases with increasing principal quantum number, n .

8.41 The electron configuration of lithium is $1s^2 2s^1$. The two $1s$ electrons shield the $2s$ electron effectively from the nucleus. Consequently, the lithium atom is considerably larger than the hydrogen atom.

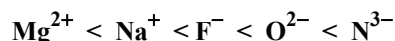
8.42 The atomic radius is largely determined by how strongly the outer-shell electrons are held by the nucleus. The larger the effective nuclear charge, the more strongly the electrons are held and the smaller the atomic radius. For the second period, the atomic radius of Li is largest because the $2s$ electron is well shielded by the filled $1s$ shell. The effective nuclear charge that the outermost electrons feel increases across the period as a result of incomplete shielding by electrons in the same shell. Consequently, the orbital containing the electrons is compressed and the atomic radius decreases.

- 8.43** (a) Cl is smaller than Cl^- . An atom gets bigger when more electrons are added.
 (b) Na^+ is smaller than Na. An atom gets smaller when electrons are removed.
 (c) O^{2-} is smaller than S^{2-} . Both elements belong to the same group, and ionic radius increases going down a group.
 (d) Al^{3+} is smaller than Mg^{2+} . The two ions are isoelectronic (What does that mean? See Section 8.2 of the text) and in such cases the radius gets smaller as the charge becomes more positive.
 (e) Au^{3+} is smaller than Au^+ for the same reason as part (b).

In each of the above cases from which atom would it be harder to remove an electron?

- 8.44 Strategy:** In comparing ionic radii, it is useful to classify the ions into three categories: (1) isoelectronic ions, (2) ions that carry the same charges and are generated from atoms of the same periodic group, and (3) ions that carry different charges but are generated from the same atom. In case (1), ions carrying a greater negative charge are always larger; in case (2), ions from atoms having a greater atomic number are always larger; in case (3), ions have a smaller positive charge are always larger.

Solution: The ions listed are all isoelectronic. They each have ten electrons. The ion with the fewest protons will have the largest ionic radius, and the ion with the most protons will have the smallest ionic radius. The effective nuclear charge increases with increasing number of protons. The electrons are attracted more strongly by the nucleus, decreasing the ionic radius. N^{3-} has only 7 protons resulting in the smallest attraction exerted by the nucleus on the 10 electrons. N^{3-} is the largest ion of the group. Mg^{2+} has 12 protons resulting in the largest attraction exerted by the nucleus on the 10 electrons. Mg^{2+} is the smallest ion of the group. The order of increasing atomic radius is:



- 8.45** The Cu^+ ion is larger than Cu^{2+} because it has one more electron.
8.46 Both selenium and tellurium are Group 6A elements. Since atomic radius increases going down a column in the periodic table, it follows that Te^{2-} must be larger than Se^{2-} .
8.47 Bromine is liquid; all the others are solids.
8.48 We assume the approximate boiling point of argon is the mean of the boiling points of neon and krypton, based on its position in the periodic table being between Ne and Kr in Group 8A.

$$\text{b.p.} = \frac{-245.9^\circ\text{C} + (-152.9^\circ\text{C})}{2} = -199.4^\circ\text{C}$$

The actual boiling point of argon is -185.7°C .

- 8.51** Ionization energy increases across a row of the periodic table and decreases down a column or group. The correct order of increasing ionization energy is:



- 8.52** The general periodic trend for first ionization energy is that it increases across a period (row) of the periodic table and it decreases down a group (column). Of the choices, K will have the smallest ionization energy. Ca, just to the right of K, will have a higher first ionization energy. Moving to the right across the periodic

table, the ionization energies will continue to increase as we move to P. Continuing across to Cl and moving up the halogen group, F will have a higher ionization energy than P. Finally, Ne is to the right of F in period two, thus it will have a higher ionization energy. The correct order of increasing first ionization energy is:



You can check the above answer by looking up the first ionization energies for these elements in Table 8.2 of the text.

- 8.53** Apart from the small irregularities, the ionization energies of elements in a period increase with increasing atomic number. We can explain this trend by referring to the increase in effective nuclear charge from left to right. A larger effective nuclear charge means a more tightly held outer electron, and hence a higher first ionization energy. Thus, in the third period, sodium has the lowest and neon has the highest first ionization energy.
- 8.54** The Group 3A elements (such as Al) all have a single electron in the outermost p subshell, which is well shielded from the nuclear charge by the inner electrons and the ns^2 electrons. Therefore, less energy is needed to remove a single p electron than to remove a paired s electron from the same principal energy level (such as for Mg).
- 8.55** To form the +2 ion of calcium, it is only necessary to remove two valence electrons. For potassium, however, the second electron must come from the atom's noble gas core which accounts for the much higher second ionization energy. Would you expect a similar effect if you tried to form the +3 ion of calcium?
- 8.56** **Strategy:** Removal of the outermost electron requires less energy if it is shielded by a filled inner shell.

Solution: The lone electron in the $3s$ orbital will be much easier to remove. This lone electron is shielded from the nuclear charge by the filled inner shell. Therefore, the ionization energy of 496 kJ/mol is paired with the electron configuration $1s^2 2s^2 2p^6 3s^1$.

A noble gas electron configuration, such as $1s^2 2s^2 2p^6$, is a very stable configuration, making it extremely difficult to remove an electron. The $2p$ electron is not as effectively shielded by electrons in the same energy level. The high ionization energy of 2080 kJ/mol would be associated with the element having this noble gas electron configuration.

Check: Compare this answer to the data in Table 8.2. The electron configuration of $1s^2 2s^2 2p^6 3s^1$ corresponds to a Na atom, and the electron configuration of $1s^2 2s^2 2p^6$ corresponds to a Ne atom.

- 8.57** The ionization energy is the difference between the $n = \infty$ state (final) and the $n = 1$ state (initial).

$$\Delta E = E_{\infty} - E_1 = (-2.18 \times 10^{-18} \text{ J})(2)^2 \left(\frac{1}{\infty}\right)^2 - (-2.18 \times 10^{-18} \text{ J})(2)^2 \left(\frac{1}{1}\right)^2$$

$$\Delta E = 0 + (2.18 \times 10^{-18} \text{ J})(2)^2 \left(\frac{1}{1}\right)^2 = 8.72 \times 10^{-18} \text{ J}$$

$$\text{In units of kJ/mol: } (8.72 \times 10^{-18} \text{ J}) \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{6.022 \times 10^{23}}{1 \text{ mol}} = 5.25 \times 10^3 \text{ kJ/mol}$$

Should this be larger than the first ionization energy of helium (see Table 8.2 of the text)?

- 8.58** The atomic number of mercury is 80. We carry an extra significant figure throughout this calculation to avoid rounding errors.

$$\Delta E = (2.18 \times 10^{-18} \text{ J})(80^2) \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) = 1.395 \times 10^{-14} \text{ J/ion}$$

$$\Delta E = \frac{1.395 \times 10^{-14} \text{ J}}{1 \text{ ion}} \times \frac{6.022 \times 10^{23} \text{ ions}}{1 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \mathbf{8.40 \times 10^6 \text{ kJ/mol}}$$

- 8.61** (a) $\text{K} < \text{Na} < \text{Li}$ (b) $\text{I} < \text{Br} < \text{F} < \text{Cl}$

- 8.62 Strategy:** What are the trends in electron affinity in a periodic group and in a particular period. Which of the above elements are in the same group and which are in the same period?

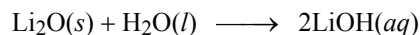
Solution: One of the general periodic trends for electron affinity is that the tendency to accept electrons increases (that is, electron affinity values become more positive) as we move from left to right across a period. However, this trend does not include the noble gases. We know that noble gases are extremely stable, and they do not want to gain or lose electrons.

Based on the above periodic trend, **Cl** would be expected to have the highest electron affinity. Addition of an electron to Cl forms Cl^- , which has a stable noble gas electron configuration.

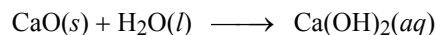
- 8.63** Based on electron affinity values, we would not expect the alkali metals to form anions. A few years ago most chemists would have answered this question with a loud "No"! In the early seventies a chemist named J.L. Dye at Michigan State University discovered that under very special circumstances alkali metals could be coaxed into accepting an electron to form negative ions! These ions are called alkalide ions.
- 8.64** Alkali metals have a valence electron configuration of ns^1 so they can accept another electron in the ns orbital. On the other hand, alkaline earth metals have a valence electron configuration of ns^2 . Alkaline earth metals have little tendency to accept another electron, as it would have to go into a higher energy p orbital.
- 8.67** Basically, we look for the process that will result in forming a cation of the metal that will be isoelectronic with the noble gas preceding the metal in the periodic table. Since all alkali metals have the ns^1 outer electron configuration, we predict that they will form unipositive ions: M^+ . Similarly, the alkaline earth metals, which have the ns^2 outer electron configuration, will form M^{2+} ions.
- 8.68** Since ionization energies decrease going down a column in the periodic table, francium should have the lowest first ionization energy of all the alkali metals. As a result, Fr should be the most reactive of all the Group 1A elements toward water and oxygen. The reaction with oxygen would probably be similar to that of K, Rb, or Cs.
- What would you expect the formula of the oxide to be? The chloride?
- 8.69** The electron configuration of helium is $1s^2$ and that of the other noble gases is ns^2np^6 . The completely filled subshell represents great stability. Consequently, these elements are chemically unreactive.
- 8.70** The Group 1B elements are much less reactive than the Group 1A elements. The 1B elements are more stable because they have much higher ionization energies resulting from incomplete shielding of the nuclear charge by the inner d electrons. The ns^1 electron of a Group 1A element is shielded from the nucleus more effectively by the completely filled noble gas core. Consequently, the outer s electrons of 1B elements are more strongly attracted by the nucleus.

- 8.71** Across a period, oxides change from basic to amphoteric to acidic. Going down a group, the oxides become more basic.

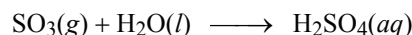
- 8.72 (a)** Lithium oxide is a basic oxide. It reacts with water to form the metal hydroxide:



- (b)** Calcium oxide is a basic oxide. It reacts with water to form the metal hydroxide:



- (c)** Sulfur trioxide is an acidic oxide. It reacts with water to form sulfuric acid:



- 8.73** LiH (lithium hydride): ionic compound; BeH₂ (beryllium hydride): covalent compound; B₂H₆ (diborane, you aren't expected to know that name): molecular compound; CH₄ (methane, do you know that one?): molecular compound; NH₃ (ammonia, you should know that one): molecular compound; H₂O (water, if you didn't know that one, you should be ashamed): molecular compound; HF (hydrogen fluoride): molecular compound. LiH and BeH₂ are solids, B₂H₆, CH₄, NH₃, and HF are gases, and H₂O is a liquid.

- 8.74** As we move down a column, the metallic character of the elements increases. Since magnesium and barium are both Group 2A elements, we expect barium to be more metallic than magnesium and **BaO** to be more basic than MgO.

- 8.75 (a)** Metallic character decreases moving left to right across a period and increases moving down a column (Group).
(b) Atomic size decreases moving left to right across a period and increases moving down a column (Group).
(c) Ionization energy increases (with some exceptions) moving left to right across a period and decreases moving down a column.
(d) Acidity of oxides increases moving left to right across a period and decreases moving down a column.

- 8.76 (a)** bromine **(b)** nitrogen **(c)** rubidium **(d)** magnesium

- 8.77 (a)** $\text{S}^- + \text{e}^- \rightarrow \text{S}^{2-}$
(b) $\text{Ti}^{2+} \rightarrow \text{Ti}^{3+} + \text{e}^-$
(c) $\text{Mg}^{2+} + \text{e}^- \rightarrow \text{Mg}^+$
(d) $\text{O}^{2-} \rightarrow \text{O}^- + \text{e}^-$

- 8.78** This is an isoelectronic series with ten electrons in each species. The nuclear charge interacting with these ten electrons ranges from +8 for oxygen to +12 for magnesium. Therefore the +12 charge in Mg²⁺ will draw in the ten electrons more tightly than the +11 charge in Na⁺, than the +9 charge in F⁻, than the +8 charge in O²⁻. Recall that the largest species will be the *easiest* to ionize.

- (a)** increasing ionic radius: $\text{Mg}^{2+} < \text{Na}^+ < \text{F}^- < \text{O}^{2-}$
(b) increasing ionization energy: $\text{O}^{2-} < \text{F}^- < \text{Na}^+ < \text{Mg}^{2+}$

8.79 Ionic compounds are usually combinations of a metal and a nonmetal. Molecular compounds are usually nonmetal–nonmetal combinations.

(a) Na_2O (ionic); MgO (ionic); Al_2O_3 (ionic); SiO_2 (molecular);
 P_4O_6 and P_4O_{10} (both molecular); SO_2 or SO_3 (molecular);
 Cl_2O and several others (all molecular).

(b) NaCl (ionic); MgCl_2 (ionic); AlCl_3 (ionic); SiCl_4 (molecular);
 PCl_3 and PCl_5 (both molecular); SCl_2 (molecular).

8.80 According to the *Handbook of Chemistry and Physics* (1966-67 edition), potassium metal has a melting point of 63.6°C , bromine is a reddish brown liquid with a melting point of -7.2°C , and potassium bromide (KBr) is a colorless solid with a melting point of 730°C . **M** is **potassium** (K) and **X** is **bromine** (Br).

8.81 (a) matches bromine (Br_2), (b) matches hydrogen (H_2), (c) matches calcium (Ca),
 (d) matches gold (Au), (e) matches argon (Ar)

8.82 O^+ and N Ar and S^{2-} Ne and N^{3-} Zn and As^{3+} Cs^+ and Xe

8.83 Only (b) is listed in order of decreasing radius. Answer (a) is listed in increasing size because the radius increases down a group. Answer (c) is listed in increasing size because the number of electrons is increasing.

8.84 (a) and (d)

8.85 The equation is: $\text{CO}_2(g) + \text{Ca}(\text{OH})_2(aq) \rightarrow \text{CaCO}_3(s) + \text{H}_2\text{O}(l)$

The milky white color is due to calcium carbonate. Calcium hydroxide is a base and carbon dioxide is an acidic oxide. The products are a salt and water.

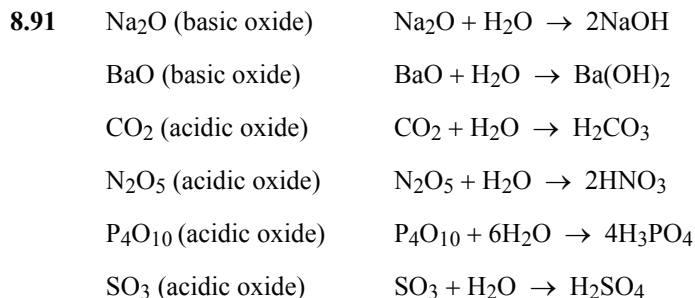
8.86 Fluorine is a yellow-green gas that attacks glass; chlorine is a pale yellow gas; bromine is a fuming red liquid; and iodine is a dark, metallic-looking solid.

8.87 (a) (i) Both react with water to produce hydrogen;
 (ii) Their oxides are basic;
 (iii) Their halides are ionic.
 (b) (i) Both are strong oxidizing agents;
 (ii) Both react with hydrogen to form HX (where X is Cl or Br);
 (iii) Both form halide ions (Cl^- or Br^-) when combined with electropositive metals (Na, K, Ca, Ba).

8.88 Fluorine

8.89 Sulfur has a ground state electron configuration of $[\text{Ne}]3s^23p^4$. Therefore, it has a tendency to accept one electron to become S^- . Although adding another electron makes S^{2-} , which is isoelectronic with Ar, the increase in electron repulsion makes the process unfavorable.

8.90 H^- and He are isoelectronic species with two electrons. Since H^- has only one proton compared to two protons for He, the nucleus of H^- will attract the two electrons less strongly compared to He. Therefore, H^- is larger.



8.92

<u>Oxide</u>	<u>Name</u>	<u>Property</u>
Li ₂ O	lithium oxide	basic
BeO	beryllium oxide	amphoteric
B ₂ O ₃	boron oxide	acidic
CO ₂	carbon dioxide	acidic
N ₂ O ₅	dinitrogen pentoxide	acidic

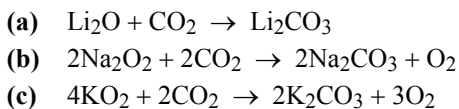
Note that only the highest oxidation states are considered.

8.93

<u>Element</u>	<u>State</u>	<u>Form</u>
Mg	solid	three dimensional
Cl	gas	diatomic molecules
Si	solid	three dimensional
Kr	gas	monatomic
O	gas	diatomic molecules
I	solid	diatomic molecules
Hg	liquid	liquid (metallic)
Br	liquid	diatomic molecules

8.94 In its chemistry, hydrogen can behave like an alkali metal (H^+) and like a halogen (H^-). H^+ is a single proton.

8.95 The reactions are:



8.96 Replacing Z in the equation given in Problem 8.57 with $(Z - \sigma)$ gives:

$$E_n = (2.18 \times 10^{-18} \text{ J})(Z - \sigma)^2 \left(\frac{1}{n^2} \right)$$

For helium, the atomic number (Z) is 2, and in the ground state, its two electrons are in the first energy level, so $n = 1$. Substitute Z , n , and the first ionization energy into the above equation to solve for σ .

$$E_1 = 3.94 \times 10^{-18} \text{ J} = (2.18 \times 10^{-18} \text{ J})(2 - \sigma)^2 \left(\frac{1}{1^2} \right)$$

$$(2 - \sigma)^2 = \frac{3.94 \times 10^{-18} \text{ J}}{2.18 \times 10^{-18} \text{ J}}$$

$$2 - \sigma = \sqrt{1.81}$$

$$\sigma = 2 - 1.35 = \mathbf{0.65}$$

8.97 Noble gases have filled shells or subshells. Therefore, they have little tendency to accept electrons (endothermic).

8.98 The percentage of volume occupied by K^+ compared to K is:

$$\frac{\text{volume of } \text{K}^+ \text{ ion}}{\text{volume of K atom}} \times 100\% = \frac{\frac{4}{3}\pi(133 \text{ pm})^3}{\frac{4}{3}\pi(216 \text{ pm})^3} \times 100\% = 23.3\%$$

Therefore, there is a decrease in volume of $(100 - 23.3)\% = \mathbf{76.7\%}$ when K^+ is formed from K.

8.99 The volume of a sphere is $4/3\pi r^3$.

The percent change in volume from F to F^- is:

$$\frac{\text{volume of } \text{F}^- \text{ ion}}{\text{volume of F atom}} \times 100\% = \frac{\frac{4}{3}\pi(136 \text{ pm})^3}{\frac{4}{3}\pi(72 \text{ pm})^3} \times 100\% = 674\%$$

Therefore, there is an increase in volume of $(674 - 100)\%$ or $\mathbf{574\%}$ as a result of the formation of the F^- ion.

8.100 Rearrange the given equation to solve for ionization energy.

$$IE = h\nu - \frac{1}{2}mu^2$$

or,

$$IE = \frac{hc}{\lambda} - KE$$

The kinetic energy of the ejected electron is given in the problem. Substitute h , c , and λ into the above equation to solve for the ionization energy.

$$IE = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{162 \times 10^{-9} \text{ m}} - (5.34 \times 10^{-19} \text{ J})$$

$$IE = \mathbf{6.94 \times 10^{-19} \text{ J}}$$

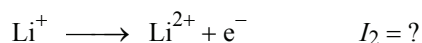
We might also want to express the ionization energy in kJ/mol.

$$\frac{6.94 \times 10^{-19} \text{ J}}{1 \text{ photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \mathbf{418 \text{ kJ/mol}}$$

To ensure that the ejected electron is the valence electron, UV light of the *longest* wavelength (lowest energy) should be used that can still eject electrons.

- 8.101**
- (a) Because of argon's lack of reactivity.
 - (b) Once Ar was discovered, scientists began to look for other unreactive elements.
 - (c) Atmosphere's content of helium is too low to be detected.

8.102 We want to determine the second ionization energy of lithium.



The equation given in Problem 8.57 allows us to determine the third ionization energy for Li. Knowing the total energy needed to remove all three electrons from Li, we can calculate the second ionization energy by difference.

$$\text{Energy needed to remove three electrons} = I_1 + I_2 + I_3$$

First, let's calculate I_3 . For Li, $Z = 3$, and $n = 1$ because the third electron will come from the $1s$ orbital.

$$I_3 = \Delta E = E_\infty - E_3$$

$$I_3 = -(2.18 \times 10^{-18} \text{ J})(3)^2 \left(\frac{1}{\infty^2} \right) + (2.18 \times 10^{-18} \text{ J})(3)^2 \left(\frac{1}{1^2} \right)$$

$$I_3 = +1.96 \times 10^{-17} \text{ J}$$

Converting to units of kJ/mol:

$$I_3 = (1.96 \times 10^{-17} \text{ J}) \times \frac{6.022 \times 10^{23} \text{ ions}}{1 \text{ mol}} = 1.18 \times 10^7 \text{ J/mol} = 1.18 \times 10^4 \text{ kJ/mol}$$

$$\text{Energy needed to remove three electrons} = I_1 + I_2 + I_3$$

$$1.96 \times 10^4 \text{ kJ/mol} = 520 \text{ kJ/mol} + I_2 + (1.18 \times 10^4 \text{ kJ/mol})$$

$$I_2 = 7.28 \times 10^3 \text{ kJ/mol}$$

8.103 The first equation is: $\text{X} + \text{H}_2 \rightarrow \text{Y}$. We are given sufficient information from the decomposition reaction (the reverse reaction) to calculate the relative number of moles of X and H. At STP, 1 mole of a gas occupies a volume of 22.4 L.

$$0.559 \text{ L} \times \frac{1 \text{ mol}}{22.4 \text{ L}} = 0.0250 \text{ mol H}_2$$

$$0.0250 \text{ mol H}_2 \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2} = 0.0500 \text{ mol H}$$

Let $\mathcal{M}$ be the molar mass of X. If we assume that the formula for Y is either XH, XH_2 , or XH_3 , then if $\text{Y} = \text{XH}$, then

$$\frac{\text{mol H}}{\text{mol X}} = 1 = \frac{0.0500 \text{ mol}}{1.00 \text{ g} \times \frac{1}{\mathcal{M}(\text{g/mol})}}$$

$$\mathcal{M} = 20.0 \text{ g/mol} = \text{the element Ne (closest mass)}$$

if $\text{Y} = \text{XH}_2$, then

$$\frac{\text{mol H}}{\text{mol X}} = 2 = \frac{0.0500 \text{ mol}}{1.00 \text{ g} \times \frac{1}{\mathcal{M}(\text{g/mol})}}$$

$$\mathcal{M} = 40.0 \text{ g/mol} = \text{the element Ca (closest mass)}$$

if $Y = \text{XH}_3$, then

$$\frac{\text{mol H}}{\text{mol X}} = 3 = \frac{0.0500 \text{ mol}}{1.00 \text{ g} \times \frac{1}{\mathcal{M}(\text{g/mol})}}$$

$$\mathcal{M} = 60.0 \text{ g/mol} = ? \text{ (no element of close mass)}$$

If we deduce that the element $X = \text{Ca}$, then the formula for the chloride Z is CaCl_2 (why?). (Why couldn't X be Ne ?) Calculating the mass percent of chlorine in CaCl_2 to compare with the known results.

$$\% \text{Cl} = \frac{(2)(35.45)}{[40.08 + (2)(35.45)]} \times 100\% = 63.89\%$$

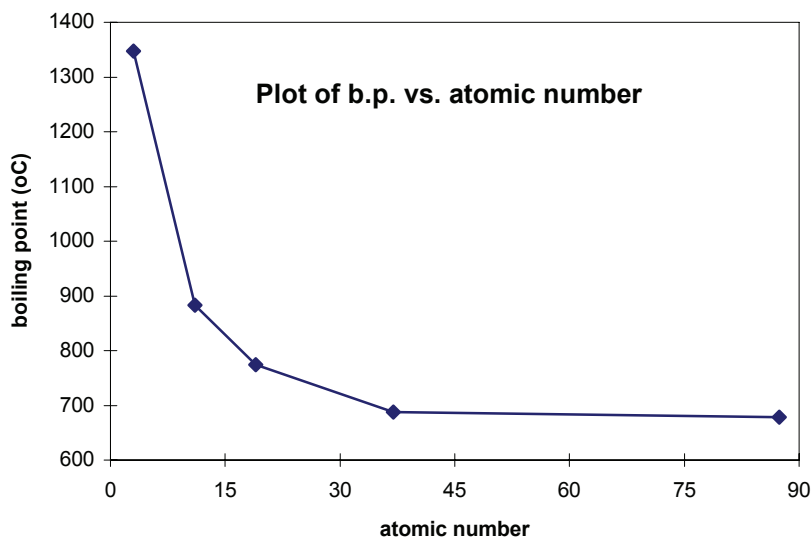
Therefore X is **calcium**.

8.104 X must belong to Group 4A; it is probably **Sn** or **Pb** because it is not a very reactive metal (it is certainly not reactive like an alkali metal).

Y is a nonmetal since it does *not* conduct electricity. Since it is a light yellow solid, it is probably **phosphorus** (Group 5A).

Z is an **alkali metal** since it reacts with air to form a basic oxide or peroxide.

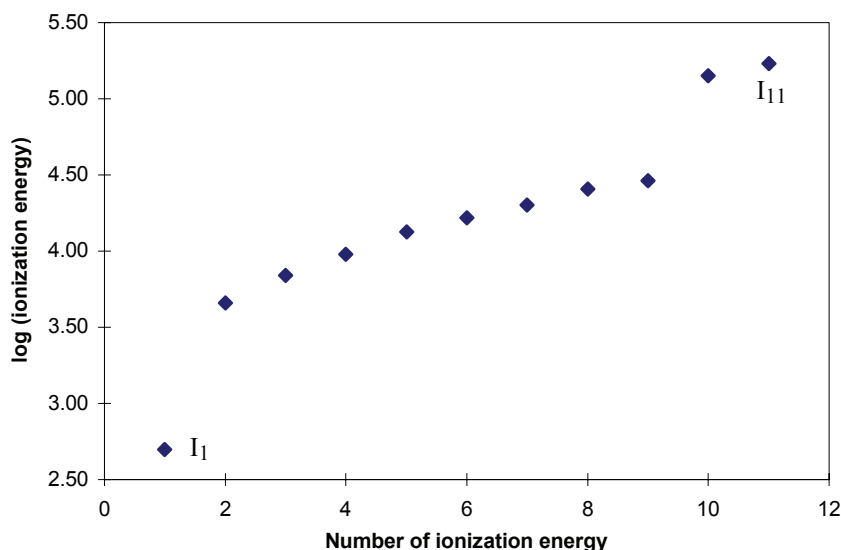
8.105 Plotting the boiling point versus the atomic number and extrapolating the curve to francium, the estimated boiling point is 670°C .



8.106 $\text{Na} \longrightarrow \text{Na}^+ + \text{e}^- \quad I_1 = 495.9 \text{ kJ/mol}$

This equation is the reverse of the electron affinity for Na^+ . Therefore, the electron affinity of Na^+ is **+495.9 kJ/mol**. Note that the electron affinity is positive, indicating that energy is liberated when an electron is added to an atom or ion. You should expect this since we are adding an electron to a positive ion.

8.107 The plot is:

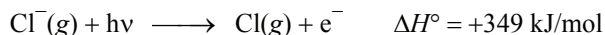


- (a) I_1 corresponds to the electron in $3s^1$ I_7 corresponds to the electron in $2p^1$
 I_2 corresponds to the first electron in $2p^6$ I_8 corresponds to the first electron in $2s^2$
 I_3 corresponds to the first electron in $2p^5$ I_9 corresponds to the electron in $2s^1$
 I_4 corresponds to the first electron in $2p^4$ I_{10} corresponds to the first electron in $1s^2$
 I_5 corresponds to the first electron in $2p^3$ I_{11} corresponds to the electron in $1s^1$
 I_6 corresponds to the first electron in $2p^2$
- (b) It requires more energy to remove an electron from a closed shell. The breaks indicate electrons in different shells and subshells.

8.108 The reaction representing the electron affinity of chlorine is:



It follows that the energy needed for the reverse process is also +349 kJ/mol.



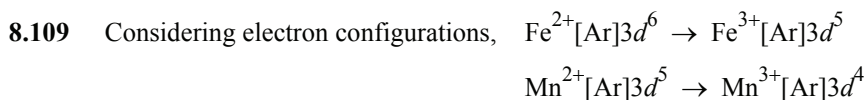
The energy above is the energy of one mole of photons. We need to convert to the energy of one photon in order to calculate the wavelength of the photon.

$$\frac{349 \text{ kJ}}{1 \text{ mol photons}} \times \frac{1 \text{ mol photons}}{6.022 \times 10^{23} \text{ photons}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 5.80 \times 10^{-19} \text{ J/photon}$$

Now, we can calculate the wavelength of a photon with this energy.

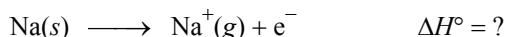
$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{5.80 \times 10^{-19} \text{ J}} = 3.43 \times 10^{-7} \text{ m} = \mathbf{343 \text{ nm}}$$

The radiation is in the **ultraviolet** region of the electromagnetic spectrum.

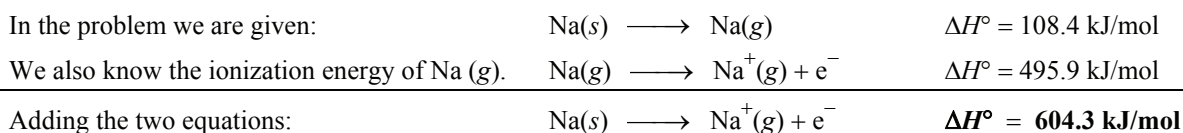


A half-filled shell has extra stability. In oxidizing Fe^{2+} the product is a d^5 -half-filled shell. In oxidizing Mn^{2+} , a d^5 -half-filled shell electron is being lost, which requires more energy.

8.110 The equation that we want to calculate the energy change for is:



Can we take information given in the problem and other knowledge to end up with the above equation? This is a Hess's law problem (see Chapter 6).



8.111 The hydrides are: LiH (lithium hydride), CH_4 (methane), NH_3 (ammonia), H_2O (water), and HF (hydrogen fluoride).

The reactions with water: $\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2$

$\text{CH}_4 + \text{H}_2\text{O} \rightarrow$ no reaction at room temperature.

$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-$

$\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^-$

$\text{HF} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{F}^-$

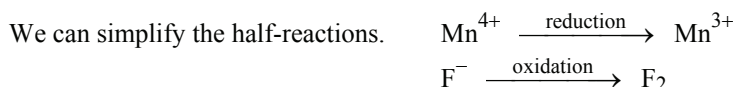
The last three reactions involve *equilibria* that will be discussed in later chapters.

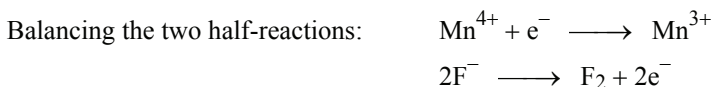
8.112 The electron configuration of titanium is: $[\text{Ar}]4s^23d^2$. Titanium has four valence electrons, so the maximum oxidation number it is likely to have in a compound is +4. The compounds followed by the oxidation state of titanium are: K_3TiF_6 , +3; $\text{K}_2\text{Ti}_2\text{O}_5$, +4; TiCl_3 , +3; K_2TiO_4 , +6; and K_2TiF_6 , +4. **K_2TiO_4** is unlikely to exist because of the oxidation state of Ti of +6. Titanium in an oxidation state greater than +4 is unlikely because of the very high ionization energies needed to remove the fifth and sixth electrons.

- | | | |
|---|----------------------------|---|
| 8.113 (a) Mg in $\text{Mg}(\text{OH})_2$ | (d) Na in NaHCO_3 | (g) Ca in CaO |
| (b) Na, liquid | (e) K in KNO_3 | (h) Ca |
| (c) Mg in $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ | (f) Mg | (i) Na in NaCl ; Ca in CaCl_2 |

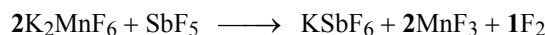


In this redox reaction, Mn^{4+} is reduced to Mn^{3+} , and F^- from both MnF_6^{2-} and SbF_5 is oxidized to F_2 .

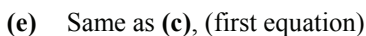
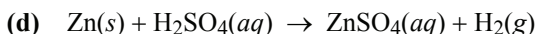
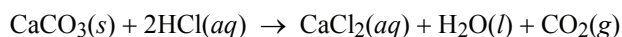
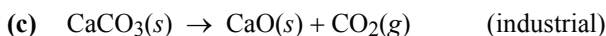
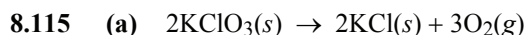
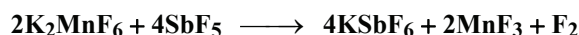




We can now reconstruct the complete balanced equation. In the balanced equation, we have 2 moles of Mn ions and 1 mole of F_2 on the products side.



We can now balance the remainder of the equation by inspection. Notice that there are 4 moles of K^{+} on the left, but only 1 mole of K^{+} on the right. The balanced equation is:



8.116 To work this problem, assume that the oxidation number of oxygen is -2 .

<u>Oxidation number</u>	<u>Chemical formula</u>
+1	N_2O
+2	NO
+3	N_2O_3
+4	$\text{NO}_2, \text{N}_2\text{O}_4$
+5	N_2O_5

8.117 Examine a solution of Na_2SO_4 which is colorless. This shows that the SO_4^{2-} ion is colorless. Thus the blue color is due to $\text{Cu}^{2+}(aq)$.

8.118 The larger the effective nuclear charge, the more tightly held are the electrons. Thus, the atomic radius will be small, and the ionization energy will be large. The quantities show an opposite periodic trend.

8.119 Z_{eff} increases from left to right across the table, so electrons are held more tightly. (This explains the electron affinity values of C and O.) Nitrogen has a zero value of electron affinity because of the stability of the half-filled $2p$ subshell (that is, N has little tendency to accept another electron).

- 8.120** We assume that the m.p. and b.p. of bromine will be between those of chlorine and iodine.

Taking the average of the melting points and boiling points:

$$\text{m.p.} = \frac{-101.0^{\circ}\text{C} + 113.5^{\circ}\text{C}}{2} = \mathbf{6.3^{\circ}\text{C}} \quad (\text{Handbook: } -7.2^{\circ}\text{C})$$

$$\text{b.p.} = \frac{-34.6^{\circ}\text{C} + 184.4^{\circ}\text{C}}{2} = \mathbf{74.9^{\circ}\text{C}} \quad (\text{Handbook: } 58.8^{\circ}\text{C})$$

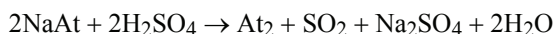
The estimated values do not agree very closely with the actual values because $\text{Cl}_2(g)$, $\text{Br}_2(l)$, and $\text{I}_2(s)$ are in different physical states. If you were to perform the same calculations for the noble gases, your calculations would be much closer to the actual values.

- 8.121** Once an atom gains an electron forming a negative ion, adding additional electrons is typically an unfavorable process due to electron-electron repulsions. 2nd and 3rd electron affinities do not occur spontaneously and are therefore difficult to measure.

- 8.122** The heat generated from the radioactive decay can break bonds; therefore, few radon compounds exist.

- 8.123** Physical characteristics: Solid; metallic appearance like iodine; melting point greater than 114°C .

Reaction with sulfuric acid:



- 8.124 (a)** It was determined that the periodic table was based on atomic number, not atomic mass.

(b) Argon:

$$(0.00337 \times 35.9675 \text{ amu}) + (0.00063 \times 37.9627 \text{ amu}) + (0.9960 \times 39.9624 \text{ amu}) = \mathbf{39.95 \text{ amu}}$$

Potassium:

$$(0.93258 \times 38.9637 \text{ amu}) + (0.000117 \times 39.9640 \text{ amu}) + (0.0673 \times 40.9618 \text{ amu}) = \mathbf{39.10 \text{ amu}}$$

- 8.125** $\text{Na}(g) \rightarrow \text{Na}^+(g) + e^- \quad I_1 = 495.9 \text{ kJ/mol}$

Energy needed to ionize one Na atom:

$$\frac{495.9 \times 10^3 \text{ J}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 8.235 \times 10^{-19} \text{ J/atom}$$

The corresponding wavelength is:

$$\lambda = \frac{hc}{I_1} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{8.235 \times 10^{-19} \text{ J}} = 2.42 \times 10^{-7} \text{ m} = \mathbf{242 \text{ nm}}$$

- 8.126** $Z = 119$

Electron configuration: $[\text{Rn}]7s^2 5f^{14} 6d^{10} 7p^6 8s^1$

- 8.127** Both ionization energy and electron affinity are affected by atomic size – the smaller the atom, the greater the attraction between the electrons and the nucleus. If it is difficult to remove an electron from an atom (that is, high ionization energy), then it follows that it would also be favorable to add an electron to the atom (large electron affinity).

Noble gases would be an exception to this generalization.

- 8.128** There is a large jump from the second to the third ionization energy, indicating a change in the principal quantum number n . In other words, the third electron removed is an inner, noble gas core electron, which is difficult to remove. Therefore, the element is in **Group 2A**.

- 8.129** Helium should be named helon to match the other noble gases: neon, argon, xenon, krypton, and radon. In addition, the ending, -ium, suggests that helium has properties similar to some metals (i.e., sodium, magnesium, barium, etc.). Since helium is an unreactive gas, this ending is not appropriate.

- 8.130** (a) SiH_4 , GeH_4 , SnH_4 , PbH_4
(b) Metallic character increases going down a family of the periodic table. Therefore, RbH would be more ionic than NaH .
(c) Since Ra is in Group 2A, we would expect the reaction to be the same as other alkaline earth metals with water.

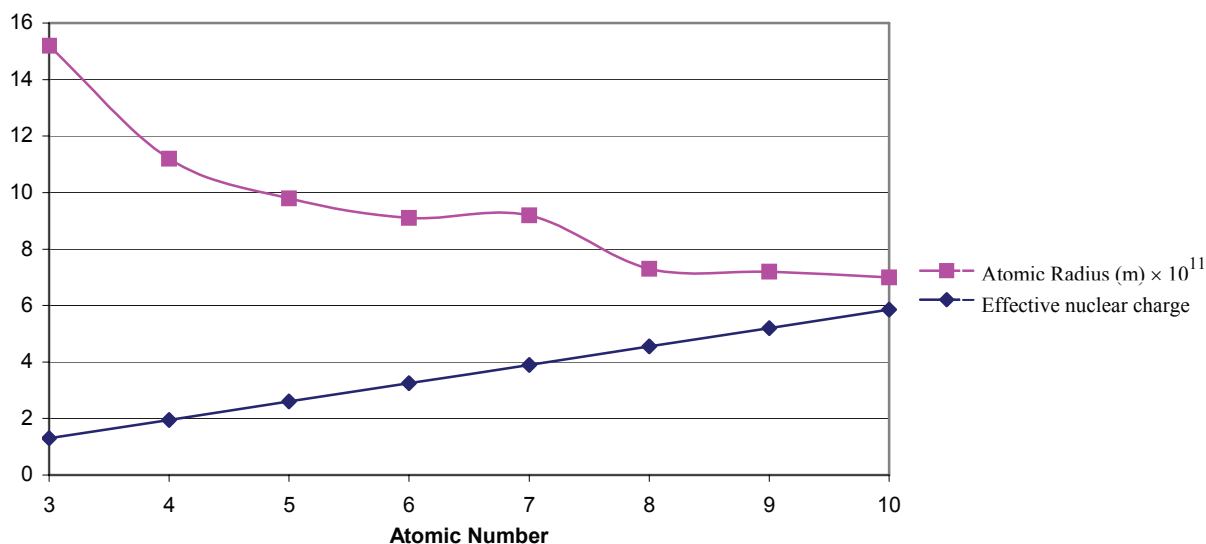


- (d) Beryllium (diagonal relationship)

- 8.131** (a) F_2 (b) Na (c) B (d) N_2 (e) Al

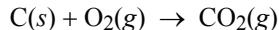
- 8.132** The importance and usefulness of the periodic table lie in the fact that we can use our understanding of the general properties and trends within a group or a period to predict with considerable accuracy the properties of any element, even though the element may be unfamiliar to us. For example, elements in the same group or family have the same valence electron configurations. Due to the same number of valence electrons occupying similar orbitals, elements in the same family have similar chemical properties. In addition, trends in properties such as ionization energy, atomic radius, electron affinity, and metallic character can be predicted based on an element's position in the periodic table. Ionization energy typically increases across a period of the periodic table and decreases down a group. Atomic radius typically decreases across a period and increases down a group. Electron affinity typically increases across a period and decreases down a group. Metallic character typically decreases across a period and increases down a group. The periodic table is an extremely useful tool for a scientist. Without having to look in a reference book for a particular element's properties, one can look at its position in the periodic table and make educated predictions as to its many properties such as those mentioned above.

8.133

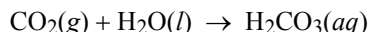


Note that the atomic radius values (in meters) have been multiplied by 1×10^{11} , so that the effective nuclear charge and radius data would fit better on the same graph. In general, as the effective nuclear charge increases, the outer-shell electrons are held more strongly, and hence the atomic radius decreases.

- 8.134** The first statement that an allotropic form of the element is a colorless crystalline solid, might lead you to think about diamond, a form of carbon. When carbon is reacted with excess oxygen, the colorless gas, carbon dioxide is produced.

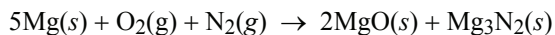


When $\text{CO}_2(g)$ is dissolved in water, carbonic acid is produced.

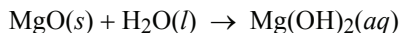


Element X is most likely carbon, choice (c).

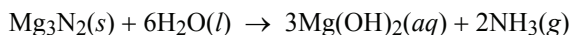
- 8.135** Referring to the Chemistry in Action in Section 8.6 of the text, Mg will react with air (O_2 and N_2) to produce $\text{MgO}(s)$ and $\text{Mg}_3\text{N}_2(s)$. The reaction is:



$\text{MgO}(s)$ will react with water to produce the basic solution, $\text{Mg}(\text{OH})_2(aq)$. The reaction is:



The problem states that B forms a similar solution to A, plus a gas with a pungent odor. This gas is ammonia, NH_3 . The reaction is:



A is **MgO**, and **B** is **Mg₃N₂**.

- 8.136** The ionization energy of 412 kJ/mol represents the energy difference between the ground state and the dissociation limit, whereas the ionization energy of 126 kJ/mol represents the energy difference between the first excited state and the dissociation limit. Therefore, the energy difference between the ground state and the excited state is:

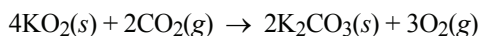
$$\Delta E = (412 - 126) \text{ kJ/mol} = 286 \text{ kJ/mol}$$

The energy of light emitted in a transition from the first excited state to the ground state is therefore 286 kJ/mol. We first convert this energy to units of J/photon, and then we can calculate the wavelength of light emitted in this electronic transition.

$$E = \frac{286 \times 10^3 \text{ J}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ photons}} = 4.75 \times 10^{-19} \text{ J/photon}$$

$$\lambda = \frac{hc}{E} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{4.75 \times 10^{-19} \text{ J}} = 4.19 \times 10^{-7} \text{ m} = 419 \text{ nm}$$

- 8.137 (a)** The reactions are:



- (b)** First, we calculate the density of O₂ in KO₂ using the mass percentage of O₂ in the compound.

$$\frac{32.00 \text{ g O}_2}{71.10 \text{ g KO}_2} \times \frac{2.15 \text{ g}}{1 \text{ cm}^3} = 0.968 \text{ g/cm}^3$$

Now, we can use Equation (5.11) of the text to calculate the pressure of oxygen gas that would have the same density as that provided by KO₂.

$$\frac{0.968 \text{ g}}{1 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1 \text{ L}} = 968 \text{ g/L}$$

$$d = \frac{P\mathcal{M}}{RT}$$

or

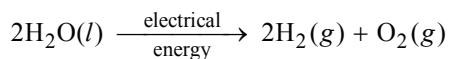
$$P = \frac{dRT}{\mathcal{M}} = \frac{\left(\frac{968 \text{ g}}{1 \text{ L}}\right)\left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(293 \text{ K})}{\left(\frac{32.00 \text{ g}}{1 \text{ mol}}\right)} = 727 \text{ atm}$$

Obviously, using O₂ instead of KO₂ is not practical.

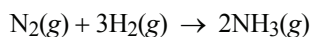
- 8.138** In He, r is greater than that in H. Also, the shielding in He makes Z_{eff} less than 2. Therefore, $I_1(\text{He}) < 2I(\text{H})$. In He⁺, there is only one electron so there is no shielding. The greater attraction between the nucleus and the lone electron reduces r to less than the r of hydrogen. Therefore, $I_2(\text{He}) > 2I(\text{H})$.

- 8.139** Air contains O_2 and N_2 . Our aims are first to prepare NH_3 and HNO_3 . The reaction of NH_3 and HNO_3 produces NH_4NO_3 .

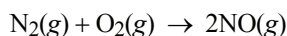
To prepare NH_3 , we isolate N_2 from air. H_2 can be obtained by the electrolysis of water.



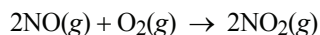
Under suitable conditions,



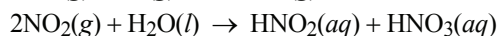
To prepare HNO_3 , we first react N_2 with O_2 (from air or water).



Next,



Then,



Finally,



We will study the conditions for carrying out the reactions in later chapters.

- 8.140** We rearrange the equation given in the problem to solve for Z_{eff} .

$$Z_{\text{eff}} = n \sqrt{\frac{I_1}{1312 \text{ kJ/mol}}}$$

$$\text{Li: } Z_{\text{eff}} = (2) \sqrt{\frac{520 \text{ kJ/mol}}{1312 \text{ kJ/mol}}} = 1.26$$

$$\text{Na: } Z_{\text{eff}} = (3) \sqrt{\frac{495.9 \text{ kJ/mol}}{1312 \text{ kJ/mol}}} = 1.84$$

$$\text{K: } Z_{\text{eff}} = (4) \sqrt{\frac{418.7 \text{ kJ/mol}}{1312 \text{ kJ/mol}}} = 2.26$$

As we move down a group, Z_{eff} increases. This is what we would expect because shells with larger n values are less effective at shielding the outer electrons from the nuclear charge.

$$\text{Li: } \frac{Z_{\text{eff}}}{n} = \frac{1.26}{2} = 0.630$$

$$\text{Na: } \frac{Z_{\text{eff}}}{n} = \frac{1.84}{3} = 0.613$$

$$\text{K: } \frac{Z_{\text{eff}}}{n} = \frac{2.26}{4} = 0.565$$

The Z_{eff}/n values are fairly constant, meaning that the screening per shell is about the same.