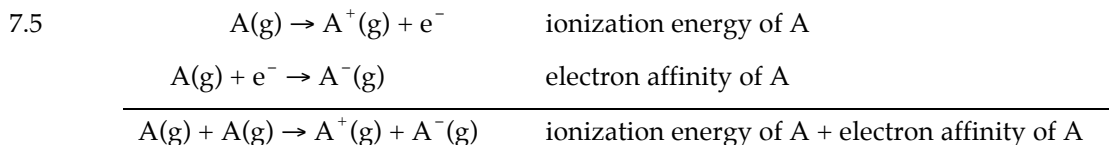


7 Periodic Properties of the Elements

Visualizing Concepts

- 7.2 A billiard ball is an imperfect model for an atom. The ball has a definite “hard” boundary, while an atom has no definite edge and can be reshaped by interactions with other atoms. That said, the billiard ball is a more appropriate analogy for the nonbonding radius of a fluorine atom. The ball’s radius is spherical, and not deformed by interaction (bonding) with a second ball.

If we use the billiard ball to represent the bonding atomic radius of a fluorine atom, we overestimate the bonding atomic radius. When atoms bond, attractive interactions cause their electron clouds to penetrate each other, bringing the nuclei closer together than during a nonbonding (billiard ball) collision.



The energy change for the reaction is the ionization energy of A plus the electron affinity of A.

This process is endothermic for both nonmetals and metals. Considering data for Cl and Na from Figures 7.12 and 7.14, the endothermic ionization energy term dominates the exothermic electron affinity term, even for Cl which has the most exothermic electron affinity listed.

Periodic Table; Effective Nuclear Charge

- 7.7 Mendeleev insisted that elements with similar chemical and physical properties be placed within a family or column of the table. Since many elements were as yet undiscovered, Mendeleev left blanks. He predicted properties for the “blanks” based on properties of other elements in the family and on either side.
- 7.9 According to Figure 7.2, many of the elements known since ancient times, Fe, Cu, Ag, Au, Hg, Sn, Pb, C and S, are present in nature in elemental form. These elements could be observed directly and their isolation did not require chemical processing. Even though Si is the second most abundant element in Earth’s crust, its abundant forms are compounds: silica, SiO_2 (sand, amethyst, quartz, etc.) or silicates (clay, granite, mica, etc.). In order to be ‘discovered’, elemental Si had to be chemically removed from one of its compounds. Discovery of elemental silicon awaited the more sophisticated

chemical techniques available in the nineteenth century.

- 7.11 (a) *Effective nuclear charge*, Z_{eff} is a representation of the average electrical field experienced by a single electron. It is the average environment created by the nucleus and the other electrons in the molecule, expressed as a net positive charge at the nucleus. It is approximately the nuclear charge, Z , minus the number of core electrons.
- (b) Going from left to right across a period, nuclear charge increases while the number of electrons in the core is constant. This results in an increase in Z_{eff} .
- 7.13 (a) *Analyze/Plan.* $Z_{\text{eff}} = Z - S$. Find the atomic number, Z , of Na and K. Write their electron configurations and count the number of core electrons. Assume S = number of core electrons.
- Solve.* Na: $Z = 11$; $[\text{Ne}]3s^1$. In the Ne core there are 10 electrons. $Z_{\text{eff}} = 11 - 10 = 1$.
K: $Z = 19$; $[\text{Ar}]4s^1$. In the Ar core there are 18 electrons. $Z_{\text{eff}} = 19 - 18 = 1$.
- (b) *Analyze/Plan.* $Z_{\text{eff}} = Z - S$. Write the complete electron configuration for each element to show counting for Slater's rules. $S = 0.35$ (# of electrons with same n) + 0.85 (# of electrons with $(n-1) + 1$ (# of electrons with $(n-2)$).
- Solve.* Na: $1s^2 2s^2 2p^6 3s^1$. $S = 0.35(0) + 0.85(8) + 1(2) = 8.8$. $Z_{\text{eff}} = 11 - 8.8 = 2.2$
K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. $S = 0.35(0) + 0.85(8) + 1(10) = 16.8$. $Z_{\text{eff}} = 19 - 16.8 = 2.2$
- (c) For both Na and K, the two values of Z_{eff} are 1.0 and 2.2. The Slater value of 2.2 is closer to the values of 2.51 (Na) and 3.49 (K) obtained from detailed calculations.
- (d) Both approximations, 'core electrons 100% effective' and Slater, yield the same value of Z_{eff} for Na and K. Neither approximation accounts for the gradual increase in Z_{eff} moving down a group.
- 7.15 Krypton has a larger nuclear charge ($Z = 36$) than argon ($Z = 18$). The shielding of electrons in the $n = 3$ shell by the 1s, 2s and 2p core electrons in the two atoms is approximately equal, so the $n = 3$ electrons in Kr experience a greater effective nuclear charge and are thus situated closer to the nucleus.

Atomic and Ionic Radii

- 7.17 (a) Atomic radii are determined by measuring distances between atoms (interatomic distances) in various situations.
- (b) Bonding radii are calculated from the internuclear separation of two atoms joined by a chemical bond. Nonbonding radii are calculated from the internuclear separation between two gaseous atoms that collide and move apart, but do not bond.
- (c) For a given element, the nonbonding radius is always larger than the bonding radius. When a chemical bond forms, electron clouds of the two atoms interpenetrate, bringing the two nuclei closer together and resulting in a smaller bonding atomic radius (Figure 7.6).

7 Periodic Properties of the Elements Solutions to Exercises

- 7.19 The atomic (*metallic*) radius of W is the interatomic W-W distance divided by 2, $2.74 \text{ \AA} / 2 = 1.37 \text{ \AA}$.
- 7.21 From atomic radii, $\text{As-I} = 1.19 \text{ \AA} + 1.33 \text{ \AA} = 2.52 \text{ \AA}$. This is very close to the experimental value of 2.55 \AA .
- 7.23 (a) Atomic radii decrease moving from left to right across a row and (b) increase from top to bottom within a group.
- (c) $\text{F} < \text{S} < \text{P} < \text{As}$. The order is unambiguous according to the trends of increasing atomic radius moving down a column and to the left in a row of the table.
- 7.25 *Plan.* Locate each element on the periodic charge and use trends in radii to predict their order. *Solve.*
- (a) $\text{Be} < \text{Mg} < \text{Ca}$ (b) $\text{Br} < \text{Ge} < \text{Ga}$ (c) $\text{Si} < \text{Al} < \text{Tl}$
- 7.27 (a) Electrostatic repulsions are reduced by removing an electron from a neutral atom, Z_{eff} increases, and the cation is smaller.
- (b) The additional electrostatic repulsion produced by adding an electron to a neutral atom causes the electron cloud to expand, so that the radius of the anion is larger than the radius of the neutral atom.
- (c) Going down a column, the n value of the valence electrons increases and they are farther from the nucleus. Valence electrons also experience greater shielding by core electrons. The greater radial extent of the valence electrons outweighs the increase in Z , and the size of particles with like charge increases.
- 7.29 The size of the red sphere decreases on reaction, so it loses one or more electrons and becomes a cation. Metals lose electrons when reacting with nonmetals, so the red sphere represents a metal. The size of the blue sphere increases on reaction, so it gains one or more electrons and becomes an anion. Nonmetals gain electrons when reacting with metals, so the blue sphere represents a nonmetal.
- 7.30 The order of radii is $\text{Ca} > \text{Ca}^{2+} > \text{Mg}^{2+}$, so the largest sphere is Ca, the intermediate one is Ca^{2+} , and the smallest is Mg^{2+} .
- 7.31 (a) An isoelectronic series is a group of atoms or ions that have the same number of electrons, and thus the same electron configuration.
- (b) (i) $\text{Al}^{3+}:\text{Ne}$ (ii) $\text{Ti}^{4+}:\text{Ar}$ (iii) $\text{Br}^{-}:\text{Kr}$ (iv) $\text{Sn}^{2+}:\text{Cd}$
- 7.33 (a) *Analyze/Plan.* Follow the logic in Sample Exercise 7.4.
- Solve.* Na^{+} is smaller. Since F^{-} and Na^{+} are isoelectronic, the ion with the larger nuclear charge, Na^{+} , has the smaller radius.
- (b) *Analyze/Plan.* The electron configuration of the ions is $[\text{Ne}]$ or $[\text{He}]2s^22p^6$. The ions have either 10 core electrons or 2 core electrons. Apply Equation 7.1 to both cases and check the result.
- Solve.* F^{-} : $Z = 9$. For 10 core electrons, $Z_{\text{eff}} = 9 - 10 = -1$. While we might be able to interpret a negative value for Z_{eff} , positive values will be easier to compare; we will assume a He core of 2 electrons.

7 Periodic Properties of the Elements Solutions to Exercises

$$\text{F}^-, Z = 9. Z_{\text{eff}} = 9 - 2 = 7. \quad \text{Na}^+: Z_{\text{eff}} = 11 - 2 = 9$$

- (c) *Analyze/Plan.* The electron of interest has $n = 2$. There are 7 other $n = 2$ electrons, and two $n = 1$ electrons.

$$\text{Solve. } S = 0.35(7) + 0.85(2) + 1(0) = 4.15$$

$$\text{F}^-, Z_{\text{eff}} = 9 - 4.15 = 4.85. \quad \text{Na}^+: Z_{\text{eff}} = 11 - 4.15 = 6.85$$

- (d) For isoelectronic ions, the electron configurations and therefore shielding values (S) are the same. Only the nuclear charge changes. So, as nuclear charge (Z) increases, effective nuclear charge (Z_{eff}) increases and ionic radius decreases.

7.35 *Analyze/Plan.* Use relative location on periodic chart and trends in atomic and ionic radii to establish the order.

(a) $\text{Cl} < \text{S} < \text{K}$

(b) $\text{K}^+ < \text{Cl}^- < \text{S}^{2-}$

- (c) Even though K has the largest Z value, the n -value of the outer electron is larger than the n -value of valence electrons in S and Cl so K atoms are largest. When the 4s electron is removed, K^+ is isoelectronic with Cl^- and S^{2-} . The larger Z value causes the 3p electrons in K^+ to experience the largest effective nuclear charge and K^+ is the smallest ion.

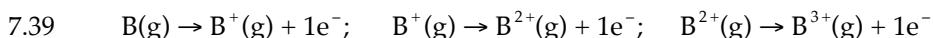
7.37 (a) O^{2-} is larger than O because the increase in electron repulsions that accompany addition of an electron causes the electron cloud to expand.

- (b) S^{2-} is larger than O^{2-} , because for particles with like charges, size increases going down a family.

- (c) S^{2-} is larger than K^+ because the two ions are isoelectronic and K^+ has the larger Z and Z_{eff} .

- (d) K^+ is larger than Ca^{2+} because for isoelectronic ions, the ion with the smaller Z has the larger radius.

Ionization Energies; Electron Affinities



7.41 (a) According to Coulomb's law, the energy of an electron in an atom is negative, because of the electrostatic attraction of the electron for the nucleus. In order to overcome this attraction, remove the electron and increase its energy; energy must be added to the atom. Ionization energy, ΔE for this process, is positive, regardless of the magnitude of Z or the quantum numbers of the electron.

- (b) F has a greater first ionization energy than O, because F has a greater Z_{eff} and the outer electrons in both elements are approximately the same distance from the nucleus.

- (c) The second ionization energy of an element is greater than the first because Z_{eff} is larger for the +1 cation than the neutral atom; more energy is required to overcome the larger Z_{eff} .

7.43 (a) In general, the smaller the atom, the larger its first ionization energy.

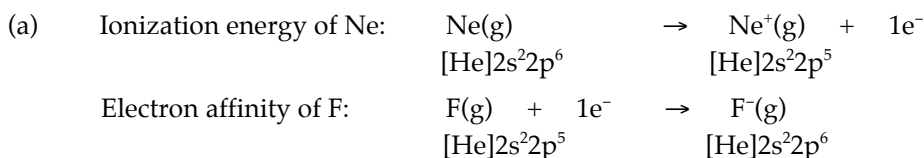
7 Periodic Properties of the Elements Solutions to Exercises

- (b) According to Figure 7.12, He has the largest and Cs the smallest first ionization energy of the nonradioactive elements.
- 7.45 *Plan.* Use periodic trends in first ionization energy. *Solve.*
 (a) Ar (b) Be (c) Co (d) S (e) Te
- 7.47 *Plan.* Follow the logic of Sample Exercise 7.7. *Solve.*
 (a) In^{3+} : $[\text{Kr}]4d^{10}$ (b) Sb^{3+} : $[\text{Kr}]5s^2 4d^{10}$
 (c) Te^{2-} : $[\text{Kr}]5s^2 4d^{10} 5p^6$ or $[\text{Xe}]$ (d) Te^{6+} : $[\text{Kr}]4d^{10}$
 (e) Hg^{2+} : $[\text{Xe}]4f^{14} 5d^{10}$ (f) Rh^{3+} : $[\text{Kr}]4d^6$
 [Note that In^{3+} and Te^{6+} (but not Sb^{3+}) above are isoelectronic.]
- 7.49 *Plan.* Follow the logic in Sample Exercise 7.7. Construct a mental box diagram for the outer electrons to determine how many are unpaired. *Solve.*
 (a) Ni^{2+} : $[\text{Ar}]3d^8$, 2 unpaired electrons. There are 5 degenerate d orbitals; 3 are filled, 2 contain single electrons.
 (b) Sn^{2+} : $[\text{Kr}]5s^2 4d^{10}$, 0 unpaired electrons. The 5s and five 4d orbitals are all filled.
- 7.51 *Analyze/Plan.* Consider the definitions of ionization energy, electron affinity and the electron configuration of Ar.
Solve. Argon is a noble gas, with a very stable core electron configuration. This causes the element to resist chemical change. Positive, endothermic, values for ionization energy and electron affinity mean that energy is required to either remove or add electrons. Valence electrons in Ar experience the largest Z_{eff} of any element in the third row, because the nuclear buildup is not accompanied by an increase in screening. This results in a large, positive ionization energy. When an electron is added to Ar, the $n = 3$ electrons become core electrons which screen the extra electrons so effectively that Ar^- has a higher energy than an Ar atom and a free electron. This results in a large positive electron affinity.
- 7.53 *Analyze/Plan.* Consider the definitions of ionization energy and electron affinity, along with pertinent electron configurations. *Solve.*
- Electron affinity $\text{Br}(\text{g}) + 1e^- \rightarrow \text{Br}^-(\text{g})$
 $[\text{Ar}]4s^2 3d^{10} 4p^5$ $[\text{Ar}]4s^2 3d^{10} 4p^6$
- When a Br atom gains an electron, the Br^- ion adopts the stable electron configuration of Kr. Since the electron is added to the same 4p subshell as other outer electrons, it experiences essentially the same attraction for the nucleus. Thus, the energy of the Br^- ion is lower than the total energy of a Br atom and an isolated electron, and electron affinity is negative.
- Electron affinity $\text{Kr}(\text{g}) + 1e^- \rightarrow \text{Kr}^-(\text{g})$
 $[\text{Ar}]4s^2 3d^{10} 4p^6$ $[\text{Ar}]4s^2 3d^{10} 4p^6 5s^1$
- Energy is required to add an electron to a Kr atom; Kr^- has a higher energy than the isolated Kr atom and free electron. In Kr^- the added electron would have to occupy the higher energy 5s orbital; a 5s electron is farther from the nucleus and effectively

7 Periodic Properties of the Elements Solutions to Exercises

shielded by the spherical Kr core and is not stabilized by the nucleus.

7.55 *Analyze/Plan.* Consider the definitions of ionization energy and electron affinity, along with the appropriate electron configurations. *Solve.*



(b) The I_1 of Ne is positive, while E_1 of F is negative. All ionization energies are positive.

(c) One process is apparently the reverse of the other, with one important difference. The Z (and Z_{eff}) for Ne is greater than Z (and Z_{eff}) for F^- . So we expect $I_1(\text{Ne})$ to be somewhat greater in magnitude and opposite in sign to $E_1(\text{F})$. [Repulsion effects approximately cancel; repulsion decrease upon I_1 causes smaller positive value; repulsion increase upon E_1 causes smaller negative value.]

Properties of Metals and Nonmetals

7.57 The smaller the first ionization energy of an element, the greater the metallic character of that element.

7.59 *Analyze/Plan.* Use first ionization energies for metals and metalloids from Figure 7.12 to inform our discussion.

Solve. I_1 for Al is 578 kJ/mol. This is similar to values for Ca and Sr group 2A, the alkaline earth metals. I_1 values for the four metalloids in group 4A and 5A range from 762 kJ/mol for Ge to 947 kJ/mol for As. The low value of I_1 for Al classifies it as a metal, rather than a metalloid.

7.61 *Analyze/Plan.* Ionic compounds are formed by combining a metal and a nonmetal; molecular compounds are formed by two or more nonmetals. *Solve.*

Ionic: MgO , Li_2O , Y_2O_3 ; molecular: SO_2 , P_2O_5 , N_2O , XeO_3

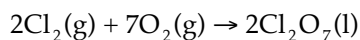
7.63 (a) When dissolved in water, an “acidic oxide” produces an acidic ($\text{pH} < 7$) solution. A “basic oxide” dissolved in water produces a basic ($\text{pH} > 7$) solution.

(b) Oxides of nonmetals are acidic. Example: $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$. Oxides of metals are basic. Example: CaO (quick lime). $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{aq})$.

7.65 *Analyze/Plan.* Cl_2O_7 is a molecular compound formed by two nonmetallic elements. More specifically, it is a nonmetallic oxide and acidic. *Solve.*

(a) Dichlorinesesptoxide

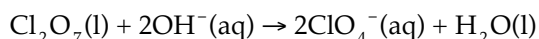
(b) Elemental chlorine and oxygen are diatomic gases.



(c) Most nonmetallic oxides we have seen, such as CO_2 and SO_3 , are gases. However, oxides with more atoms, such as $\text{P}_2\text{O}_3(\text{l})$ and $\text{P}_2\text{O}_5(\text{s})$, exist in other states. A boiling point of 81°C is not totally unexpected for a large molecule like



- (d) Cl_2O_7 is an acidic oxide, so it will be more reactive to base, OH^- .



- 7.67 (a) $\text{BaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ba}(\text{OH})_2(\text{aq})$
 (b) $\text{FeO}(\text{s}) + 2\text{HClO}_4(\text{aq}) \rightarrow \text{Fe}(\text{ClO}_4)_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 (c) $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$
 (d) $\text{CO}_2(\text{g}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$

Group Trends in Metals and Nonmetals

- | | | |
|------|-------------------|---|
| 7.69 | <u>Na</u> | <u>Mg</u> |
| (a) | $[\text{Ne}]3s^1$ | $[\text{Ne}]3s^2$ |
| (b) | +1 | +2 |
| (c) | +496 kJ/mol | +738 kJ/mol |
| (d) | very reactive | reacts with steam, but not $\text{H}_2\text{O}(\text{l})$ |
| (e) | 1.54 Å | 1.30 Å |
- (b) When forming ions, both adopt the stable configuration of Ne, but Na loses one electron and Mg two electrons to achieve this configuration.
- (c),(e) The nuclear charge of Mg ($Z = 12$) is greater than that of Na, so it requires more energy to remove a valence electron with the same n value from Mg than Na. It also means that the 2s electrons of Mg are held closer to the nucleus, so the atomic radius (e) is smaller than that of Na.
- (d) Mg is less reactive because it has a filled subshell and it has a higher ionization energy.
- 7.71 (a) Ca and Mg are both metals; they tend to lose electrons and form cations when they react. Ca is more reactive because it has a lower ionization energy than Mg. The Ca valence electrons in the 4s orbital are less tightly held because they are farther from the nucleus than the 3s valence electrons of Mg.
- (b) K and Ca are both metals; they tend to lose electrons and form cations when they react. K is more reactive because it has a lower ionization energy. The 4s valence electron in K is less tightly held because it experiences a smaller nuclear charge ($Z = 19$ for K versus $Z = 20$ for Ca) with similar shielding effects than the 4s valence electrons of Ca.
- 7.73 (a) $2\text{K}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{KCl}(\text{s})$
 (b) $\text{SrO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Sr}(\text{OH})_2(\text{aq})$
 (c) $4\text{Li}(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{Li}_2\text{O}(\text{s})$
 (d) $2\text{Na}(\text{s}) + \text{S}(\text{l}) \rightarrow \text{Na}_2\text{S}(\text{s})$

7 Periodic Properties of the Elements Solutions to Exercises

- 7.75 *Analyze/Plan.* Use first ionization energies from Figure 7.12 to inform our discussion.
- H ($I_1 = 1312 \text{ kJ/mol}$) fits between C ($I_1 = 1086 \text{ kJ/mol}$) and N ($I_1 = 1402 \text{ kJ/mol}$) in the second period. (Ignore the value for O, which is anomalously low due to exaggerated repulsion effects in the small 2p orbitals.)
 - Li ($I_1 = 520 \text{ kJ/mol}$) fits between Na ($I_1 = 496 \text{ kJ/mol}$) and Mg ($I_1 = 738 \text{ kJ/mol}$).
 - H definitely fits among the nonmetals of the second row, and Li fits among the metals of the third row, so positions in these series are consistent with their assignment as nonmetal (H) and metal (Li).
- 7.77
- | <u>F</u> | <u>Cl</u> |
|--------------------------------------|---------------------------|
| (a) $[\text{He}]2s^2 2p^5$ | $[\text{Ne}]3s^2 3p^5$ |
| (b) -1 | -1 |
| (c) 1681 kJ/mol | 1251 kJ/mol |
| (d) reacts exothermically to form HF | reacts slowly to form HCl |
| (e) -328 kJ/mol | -349 kJ/mol |
| (f) 0.71 Å | 0.99 Å |
- F and Cl are in the same group, have the same valence electron configuration and common ionic charge.
 - (c),(f) The $n = 2$ valence electrons in F are closer to the nucleus and more tightly held than the $n = 3$ valence electrons in Cl. Therefore, the ionization energy of F is greater, and the atomic radius is smaller.
 - In its reaction with H_2O , F is reduced; it gains an electron. Although the electron affinity, a gas phase single atom property, of F is less negative than that of Cl, the tendency of F to hold its own electrons (high ionization energy) coupled with a relatively large exothermic electron affinity makes it extremely susceptible to reduction and chemical bond formation. Cl is unreactive to water because it is less susceptible to reduction.
 - While F has approximately the same Z_{eff} as Cl, its small atomic radius gives rise to large repulsions when an extra electron is added, so the overall electron affinity of F is smaller (less exothermic) than that of Cl.
 - The $n = 2$ valence electrons in F are closer to the nucleus so the atomic radius is smaller than that of Cl.
- 7.79
- The term “inert” was dropped because it no longer described all the group 8A elements.
 - In the 1960s, scientists discovered that Xe would react with substances such as F_2 and PtF_6 that have a strong tendency to remove electrons. Thus, Xe could not be categorized as an “inert” gas.
 - The group is now called the noble gases.

- 7.81 (a) $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$
 (b) $\text{Xe}(\text{g}) + \text{F}_2(\text{g}) \rightarrow \text{XeF}_2(\text{g})$
 $\text{Xe}(\text{g}) + 2\text{F}_2(\text{g}) \rightarrow \text{XeF}_4(\text{s})$
 $\text{Xe}(\text{g}) + 3\text{F}_2(\text{g}) \rightarrow \text{XeF}_6(\text{s})$
 (c) $\text{S}(\text{s}) + \text{H}_2(\text{g}) \rightarrow \text{H}_2\text{S}(\text{g})$
 (d) $2\text{F}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{HF}(\text{aq}) + \text{O}_2(\text{g})$

Additional Exercises

- 7.83 Up to $Z = 82$, there are three instances where atomic weights are reversed relative to atomic numbers: Ar and K; Co and Ni; Te and I.

In each case, the most abundant isotope of the element with the larger atomic number (Z) has one more proton, but fewer neutrons than the element with the smaller atomic number. The smaller number of neutrons causes the element with the larger Z to have a smaller than expected atomic weight.

- 7.85 (a) P: $[\text{Ne}]3s^23p^3$. $Z_{\text{eff}} = Z - S = 15 - 10 = 5$.
 (b) Four other $n = 3$ electrons, eight $n = 2$ electrons, two $n = 1$ electron. $S = 0.35(4) + 0.85(8) + 1(2) = 10.2$. $Z_{\text{eff}} = Z - S = 15 - 10.2 = 4.8$. The approximation in (a) and Slater's rules give very similar values for Z_{eff} .
 (c) The 3s electrons penetrate the [Ne] core electrons (by analogy to Figure 7.4) and experience less shielding than the 3p electrons. That is, S is greater for 3p electrons, owing to the penetration of the 3s electrons, so $Z - S$ (3p) is less than $Z - S$ (3s).
 (d) The 3p electrons are the outermost electrons; they experience a smaller Z_{eff} than 3s electrons and thus a smaller attraction for the nucleus, given equal n -values. The first electron lost is a 3p electron. Each 3p orbital holds one electron, so there is no preference as to which 3p electron will be lost.

- 7.88 Atomic size (bonding atomic radius) is strongly correlated to Z_{eff} , which is determined by Z and S . Moving across the representative elements, electrons added to ns or np valence orbitals do not effectively screen each other. The increase in Z is not accompanied by a similar increase in S ; Z_{eff} increases and atomic size decreases. Moving across the transition elements, electrons are added to $(n-1)d$ orbitals and become part of the core electrons, which do significantly screen the ns valence electrons. The increase in Z is accompanied by a larger increase in S for the ns valence electrons; Z_{eff} increases more slowly and atomic size decreases more slowly.

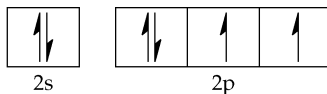
- 7.91 Y: $[\text{Kr}]5s^24d^1$, $Z = 39$ Zr: $[\text{Kr}] 5s^24d^2$, $Z = 40$
 La: $[\text{Xe}]6s^25d^1$, $Z = 57$ Hf: $[\text{Xe}] 6s^24f^{14}5d^2$, $Z = 72$

The completed 4f subshell in Hf leads to a much larger change in Z going from Zr to Hf ($72 - 40 = 32$) than in going from Y to La ($57 - 39 = 18$). The 4f electrons in Hf do not completely shield the valence electrons, so there is also a larger increase in Z_{eff} . This larger increase in Z_{eff} going from Zr to Hf leads to a smaller increase in atomic radius

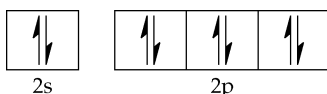
than in going from Y to La.

- 7.94 C: $1s^2 2s^2 2p^2$. I_1 through I_4 represent loss of the 2p and 2s electrons in the outer shell of the atom. The values of I_1 – I_4 increase as expected. The nuclear charge is constant, but removing each electron reduces repulsive interactions between the remaining electrons, so effective nuclear charge increases and ionization energy increases. I_5 and I_6 represent loss of the 1s core electrons. These 1s electrons are much closer to the nucleus and experience the full nuclear charge (they are not shielded), so the values of I_5 and I_6 are significantly greater than I_1 – I_4 . I_6 is larger than I_5 because all repulsive interactions have been eliminated.

- 7.96 O: $[\text{He}]2s^2 2p^4$



- O^{2-} : $[\text{He}]2s^2 2p^6 = [\text{Ne}]$



- O^{3-} : $[\text{Ne}]3s^1$ The third electron would be added to the 3s orbital, which is farther from the nucleus and more strongly shielded by the [Ne] core. The overall attraction of this 3s electron for the O nucleus is not large enough for O^{3-} to be a stable particle.

- 7.98 (a) The group 2B metals have complete $(n-1)d$ subshells. An additional electron would occupy an np subshell and be substantially shielded by both ns and $(n-1)d$ electrons. Overall this is not a lower energy state than the neutral atom and a free electron.
- (b) Valence electrons in Group 1B elements experience a relatively large effective nuclear charge due to the buildup in Z with the filling of the $(n-1)d$ subshell. Thus, the electron affinities are large and negative. Group 1B elements are exceptions to the usual electron filling order and have the generic electron configuration $ns^1(n-1)d^{10}$. The additional electron would complete the ns subshell and experience repulsion with the other ns electron. Going down the group, size of the ns subshell increases and repulsion effects decrease. That is, effective nuclear charge is greater going down the group because it is less diminished by repulsion, and electron affinities become more negative.
- 7.101 $\text{O}_2 < \text{Br}_2 < \text{K} < \text{Mg}$. O_2 and Br_2 are (nonpolar) nonmetals. We expect O_2 , with the much lower molar mass, to have the lower melting point. This is confirmed by data in Tables 7.6 and 7.7. K and Mg are metallic solids (all metals are solids), with higher melting points than the two nonmetals. Since alkaline earth metals (Mg) are typically harder, more dense and higher melting than alkali metals (K), we expect Mg to have the highest melting point of the group. This is confirmed by data in Tables 7.4 and 7.5.

Integrative Exercises

- 7.106 (a) Li: $[\text{He}]2s^1$. Assume that the $[\text{He}]$ core is 100% effective at shielding the 2s valence electron $Z_{\text{eff}} = Z - S \approx 3 - 2 = 1+$.

- (b) The first ionization energy represents loss of the 2s electron.

ΔE = energy of free electron ($n = \infty$) – energy of electron in ground state ($n = 2$)

$$\Delta E = I_1 = [-2.18 \times 10^{-18} \text{ J } (Z^2 / \infty^2)] - [-2.18 \times 10^{-18} \text{ J } (Z^2 / 2^2)]$$

$$\Delta E = I_1 = 0 + 2.18 \times 10^{-18} \text{ J } (Z^2 / 2^2)$$

For Li, which is not a one-electron particle, let $Z = Z_{\text{eff}}$.

$$\Delta E \approx 2.18 \times 10^{-18} \text{ J } (+1^2 / 4) \approx 5.45 \times 10^{-19} \text{ J/atom}$$

- (c) Change the result from part (b) to kJ/mol so it can be compared to the value in

$$\text{Table 7.4. } 5.45 \times 10^{-19} \frac{\text{J}}{\text{atom}} \times \frac{6.022 \times 10^{23} \text{ atom}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 328 \text{ kJ/mol}$$

The value in Table 7.4 is 520 kJ/mol. This means that our estimate for Z_{eff} was a lower limit, that the $[\text{He}]$ core electrons do not perfectly shield the 2s electron from the nuclear charge.

- (d) From Table 7.4, $I_1 = 520 \text{ kJ/mol}$.

$$\frac{520 \text{ kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 8.6350 \times 10^{-19} \text{ J/atom}$$

Use the relationship for I_1 and Z_{eff} developed in part (b).

$$Z_{\text{eff}}^2 = \frac{4(8.6350 \times 10^{-19} \text{ J})}{2.18 \times 10^{-18} \text{ J}} = 1.5844 \quad 1.58 Z_{\text{eff}} = 1.26$$

This value, $Z_{\text{eff}} = 1.26$, based on the experimental ionization energy, is greater than our estimate from part (a), which is consistent with the explanation in part (c).

- 7.109 (a) Mg_3N_2

- (b) $\text{Mg}_3\text{N}_2(\text{s}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 3\text{MgO}(\text{s}) + 2\text{NH}_3(\text{g})$

The driving force is the production of $\text{NH}_3(\text{g})$.

- (c) After the second heating, all the Mg is converted to MgO.

Calculate the initial mass Mg.

$$0.486 \text{ g MgO} \times \frac{24.305 \text{ g Mg}}{40.305 \text{ g MgO}} = 0.293 \text{ g Mg}$$

$x = \text{g Mg converted to MgO}$; $y = \text{g Mg converted to Mg}_3\text{N}_2$; $x = 0.293 - y$

$$\text{g MgO} = x \left(\frac{40.305 \text{ g MgO}}{24.305 \text{ g Mg}} \right); \text{g Mg}_3\text{N}_2 = y \left(\frac{100.929 \text{ g Mg}_3\text{N}_2}{72.915 \text{ g Mg}} \right)$$

$$\text{g MgO} + \text{g Mg}_3\text{N}_2 = 0.470$$

$$(0.293 - y) \left(\frac{40.305}{24.305} \right) + y \left(\frac{100.929}{72.915} \right) = 0.470$$

$$(0.293 - y)(1.6583) + y(1.3842) = 0.470$$

$$-1.6583 y + 1.3842 y = 0.470 - 0.48588$$

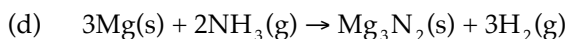
$$-0.2741 y = -0.016$$

$$y = 0.05794 = 0.058 \text{ g Mg in Mg}_3\text{N}_2$$

$$\text{g Mg}_3\text{N}_2 = 0.05794 \text{ g Mg} \times \frac{100.929 \text{ g Mg}_3\text{N}_2}{72.915 \text{ g Mg}} = 0.0802 \text{ g Mg}_3\text{N}_2$$

$$\text{mass\% Mg}_3\text{N}_2 = \frac{0.0802 \text{ g Mg}_3\text{N}_2}{0.470 \text{ g (MgO + Mg}_3\text{N}_2)} \times 100 = 17\%$$

(The final mass % has two sig figs because the mass of Mg obtained from solving simultaneous equations has two sig figs.)



$$6.3 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.305 \text{ g Mg}} = 0.2592 \text{ mol Mg}$$

$$2.57 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.031 \text{ g NH}_3} = 0.1509 \text{ mol NH}_3$$

$$0.2592 \text{ mol Mg} \times \frac{2 \text{ mol NH}_3}{3 \text{ mol Mg}} = 0.1728 \text{ mol NH}_3$$

0.26 mol Mg requires more than the available NH₃ so NH₃ is the limiting reactant.

$$0.1509 \text{ mol NH}_3 \times \frac{3 \text{ mol H}_2}{2 \text{ mol NH}_3} \times \frac{2.016 \text{ g H}_2}{\text{mol H}_2} = 0.4563 \text{ g H}_2$$



$$= -461.08 \text{ kJ} + 0 - 3(0) - 2(-46.19) = -368.70 \text{ kJ}$$