



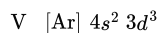
3.7: Ions: Electron Configurations, Magnetic Properties, Radii, and Ionization Energy

Recall that ions are atoms (or groups of atoms) that have lost or gained electrons. In this section, we examine periodic trends in ionic electron configurations, magnetic properties, radii, and ionization energies.

Electron Configurations and Magnetic Properties of Ions

As we saw in [Section 3.5](#), we can deduce the electron configuration of a main-group monoatomic ion from the electron configuration of the neutral atom and the charge of the ion. For anions, we *add* the number of electrons indicated by the magnitude of the charge of the anion. For example, the electron configuration of fluorine (F) is $1s^2 2s^2 2p^5$, and that of the fluoride ion (F^-) is $1s^2 2s^2 2p^6$.

We determine the electron configuration of cations by *subtracting* the number of electrons indicated by the magnitude of the charge. For example, the electron configuration of lithium (Li) is $1s^2 2s^1$, and that of the lithium ion (Li^+) is $1s^2 2s^0$ (or simply $1s^2$). For main-group cations, we remove the required number of electrons in the reverse order of filling. However, for transition metal cations, the trend is different. When writing the electron configuration of a transition metal cation, we *remove the electrons in the highest n -value orbitals first, even if this does not correspond to the reverse order of filling*. For example, the electron configuration of vanadium is:



The V^{2+} ion, however, has the following electron configuration:



In other words, for transition metal cations, the order in which electrons are removed upon ionization is *not* the reverse of the filling order. During filling, the $4s$ orbital normally fills before the $3d$ orbital. When a fourth-period transition metal ionizes, however, it normally loses its $4s$ electrons before its $3d$ electrons. Why this unexpected behavior?

The full answer to this question is beyond our scope, but the following two factors contribute to this phenomenon:

- As discussed previously, the ns and $(n-1)d$ orbitals are extremely close in energy and, depending on the exact configuration, can vary in relative energy ordering.
- As the $(n-1)d$ orbitals begin to fill in the first transition series, the increasing nuclear charge

stabilizes the $(n-1)d$ orbitals relative to the ns orbitals. This happens because the $(n-1)d$ orbitals are not the outermost (or highest n) orbitals and are therefore not effectively shielded from the increasing nuclear charge by the ns orbitals.

The bottom-line experimental observation is that an $ns^0(n-1)d^x$ configuration is lower in energy than an $ns^2(n-1)d^{x-2}$ configuration for transition metal ions. Therefore, we remove the ns electrons before the $(n-1)d$ electrons when writing electron configurations for transition metal ions.

The magnetic properties of transition metal ions support these assignments. Recall from Section 3.3 that an unpaired electron has spin. This spin generates a tiny magnetic field. Consequently, an atom or ion that contains unpaired electrons is attracted to an external magnetic field, and we say that the atom or ion is **paramagnetic**. For example, consider the electron configuration of silver:

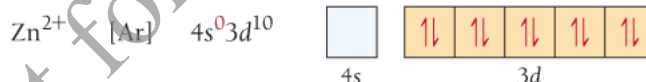


Silver's unpaired 5s electron causes silver to be paramagnetic. In fact, an early demonstration of electron spin—called the Stern–Gerlach experiment—involved the interaction of a beam of silver atoms with a magnetic field.

An atom or ion in which all electrons are paired is not attracted to an external magnetic field—it is instead slightly repelled—and we say that the atom or ion is **diamagnetic**. The zinc atom is diamagnetic.



The magnetic properties of the zinc ion provide confirmation that the 4s electrons are indeed lost before 3d electrons in the ionization of zinc. If zinc lost two 3d electrons upon ionization, then the Zn^{2+} would become paramagnetic (because the two electrons would come out of two different filled d orbitals, leaving each of them with one unpaired electron). But the zinc ion, like the zinc atom, is diamagnetic because the 4s electrons are lost instead.



Observations in other transition metals confirm that the ns electrons are lost before the $(n-1)d$ electrons upon ionization.

Example 3.7 Electron Configurations and Magnetic Properties for Ions

Write the electron configuration and orbital diagram for each ion and determine whether each is diamagnetic or paramagnetic.

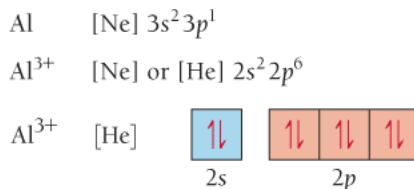
- Al^{3+}
- S^{2-}
- Fe^{3+}

SOLUTION

- Al^{3+}

Begin by writing the electron configuration of the neutral atom.

Since this ion has a 3+ charge, remove three electrons to write the electron configuration of the ion. Write the orbital diagram by drawing half-arrows to represent each electron in boxes representing the orbitals. Because there are no unpaired electrons, Al^{3+} is diamagnetic.

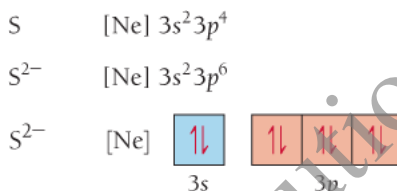


Diamagnetic

b. S^{2-}

Begin by writing the electron configuration of the neutral atom.

Since this ion has a 2- charge, add two electrons to write the electron configuration of the ion. Write the orbital diagram by drawing half-arrows to represent each electron in boxes representing the orbitals. Because there are no unpaired electrons, S^{2-} is diamagnetic.

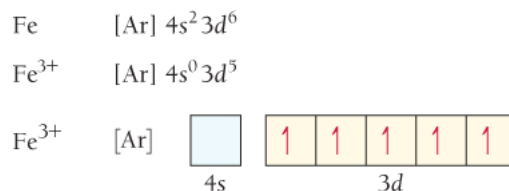


Diamagnetic

c. Fe^{3+}

Begin by writing the electron configuration of the neutral atom.

Since this ion has a 3+ charge, remove three electrons to write the electron configuration of the ion. Since it is a transition metal, remove the electrons from the 4s orbital before removing electrons from the 3d orbitals. Write the orbital diagram by drawing half-arrows to represent each electron in boxes representing the orbitals. There are unpaired electrons, so Fe^{3+} is paramagnetic.



Paramagnetic

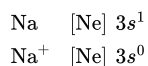
FOR PRACTICE 3.7 Write the electron configuration and orbital diagram for each ion and predict whether each will be paramagnetic or diamagnetic.

- Co^{2+}
- N^{3-}
- Ca^{2+}

Interactive Worked Example 3.7 Electron Configurations and Magnetic Properties for Ions

Ionic Radii

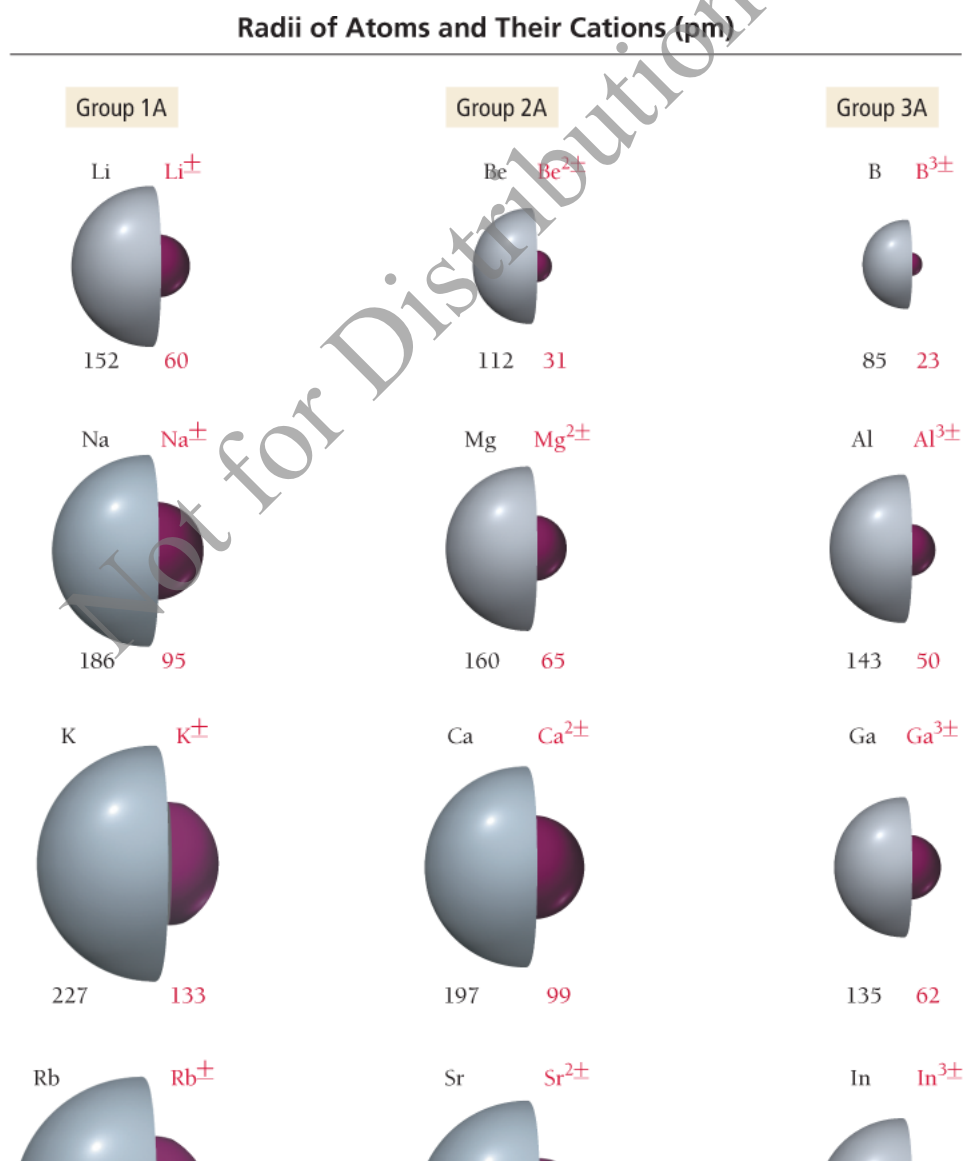
What happens to the radius of an atom when it becomes a cation? An anion? Consider, for example, the difference between the Na atom and the Na^+ ion. Their electron configurations are:

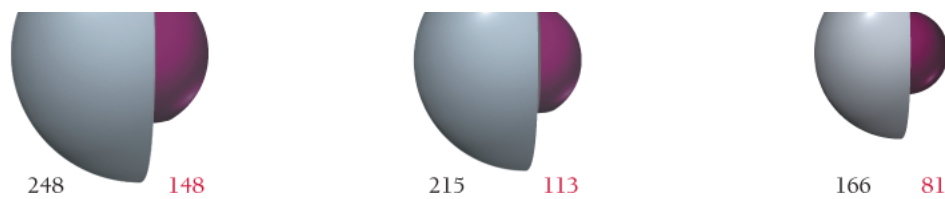


The sodium atom has an outer 3s electron and a neon core. Because the 3s electron is the outermost electron and that electron is shielded from the nuclear charge by the core electrons, it contributes greatly to the size of the sodium atom. The sodium cation, having lost the outermost 3s electron, has only the neon core and carries a charge of 1+. Without the 3s electron, the sodium cation (ionic radius = 95 pm) is much smaller than the sodium atom (covalent radius = 186 pm). The trend is the same with all cations and their atoms, as illustrated in Figure 3.16.

Figure 3.16 Sizes of Atoms and Their Cations

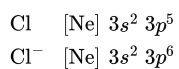
Atomic and ionic radii (pm) for the first three columns of main-group elements





Cations are much smaller than their corresponding neutral atoms.

What about anions? Consider, for example, the difference between Cl and Cl^- . Their electron configurations are:

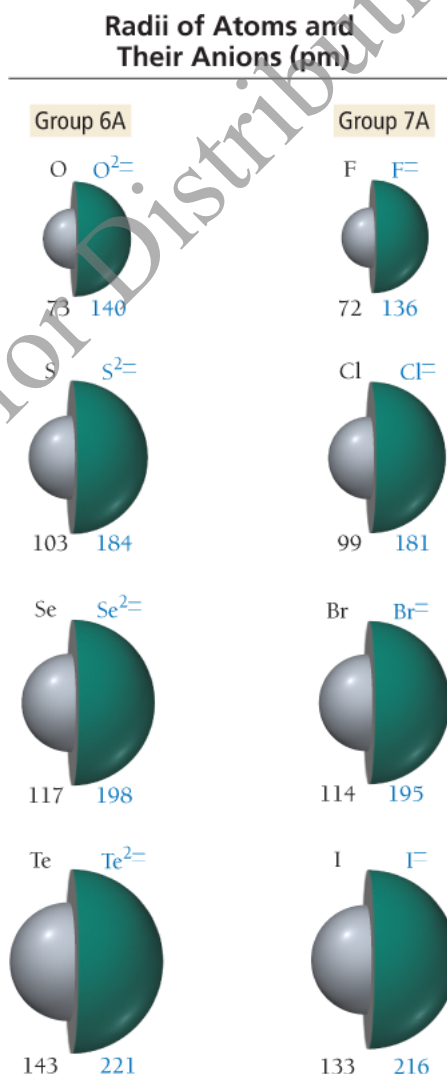


The chlorine anion has one additional outermost electron but no additional proton to increase the nuclear charge. The extra electron increases the repulsions among the outermost electrons, resulting in a chloride anion that is larger than the chlorine atom. The trend is the same with all anions and their atoms, as shown in Figure 3.17.

Anions are much larger than their corresponding neutral atoms.

Figure 3.17 Sizes of Atoms and Their Anions

Atomic and ionic radii for groups 6A and 7A in the periodic table.



We can observe an interesting trend in ionic size by examining the radii of an *isoelectronic* series of ions—ions with the same number of electrons. Consider the following ions and their radii:

S^{2-} (184 pm)	Cl^- (181 pm)	K^+ (133 pm)	Ca^{2+} (99 pm)
18 electrons	18 electrons	18 electrons	18 electrons
16 protons	17 protons	19 protons	20 protons

All of these ions have 18 electrons in exactly the same orbitals, but the radius of each ion gets successively smaller. Why? The reason is the progressively greater number of protons. The S^{2-} ion has 16 protons, and therefore a charge of 16+ pulling on 18 electrons. The Ca^{2+} ion, however, has 20 protons, and therefore a charge of 20+ pulling on the same 18 electrons. The result is a much smaller radius. In general, the greater the nuclear charge in atoms or ions with the same number of electrons, the smaller the atom or ion.

Example 3.8 Ion Size

Choose the larger atom or ion from each pair.

- S or S^{2-}
- Ca or Ca^{2+}
- Br^- or Kr

SOLUTION

- The S^{2-} ion is larger than an S atom because the S^{2-} ion has the same number of protons as S but two more electrons. The additional electron–electron repulsions cause the anion to be larger than the neutral atom.
- A Ca atom is larger than a Ca^{2+} ion because the Ca atom has an argon core and two 4s electrons. Because the 4s electrons are the outermost electrons and they are shielded from the nuclear charge by the core electrons, they contribute greatly to the size of the Ca atom. The Ca^{2+} cation, having lost the outermost 4s electrons, has only the argon core and carries a charge of 2+, which makes it smaller than the Ca atom.
- A Br^- ion is larger than a Kr atom because, although they are isoelectronic, Br^- has one fewer proton than Kr, resulting in a smaller pull on the electrons and therefore a larger radius.

FOR PRACTICE 3.8 Choose the larger atom or ion from each pair.

- K or K^+
- F or F^-
- Ca^{2+} or Cl^-

Conceptual Connection 3.6 Ions, Isotopes, and Atomic Size

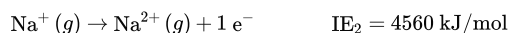
Ionization Energy

The **ionization energy (IE)** of an atom or ion is the energy required to remove an electron from the

atom or ion in the gaseous state. Ionization energy is always positive because removing an electron always takes energy. (The process is endothermic, which, as we discussed in Chapter E, absorbs heat and therefore carries a positive sign.) The energy required to remove the first electron is the *first ionization energy* (IE_1). For example, we represent the first ionization of sodium with the equation:



The energy required to remove the second electron is the *second ionization energy* (IE_2), the energy required to remove the third electron is the *third ionization energy* (IE_3), and so on. We represent the second ionization energy of sodium as:



Notice that the second ionization energy is not the energy required to remove *two* electrons from sodium (that quantity is the sum of IE_1 and IE_2), but rather the energy required to remove one electron from Na^+ . We look at trends in IE_1 and IE_2 separately.

Trends in First Ionization Energy

The first ionization energies of the elements through Xe are shown in Figure 3.18. Notice the periodic trend in ionization energy, peaking at each noble gas and bottoming at each alkali metal. Based on what we have learned about electron configurations and effective nuclear charge, how can we account for the observed trend? As we have seen, the principal quantum number, n , increases as we move down a column. For a given sublevel, orbitals with higher principal quantum numbers are larger than orbitals with smaller principal quantum numbers. (For example, a 4s orbital is larger than a 3s orbital.) Consequently, electrons in the outermost principal level are farther away from the positively charged nucleus—and are therefore held less tightly—as we move down a column. This results in lower ionization energies as we move down a column, as shown in Figure 3.19.

Figure 3.18 First Ionization Energy versus Atomic Number for the Elements through Xenon

First ionization energy starts at a minimum with each alkali metal and rises to a peak with each noble gas.

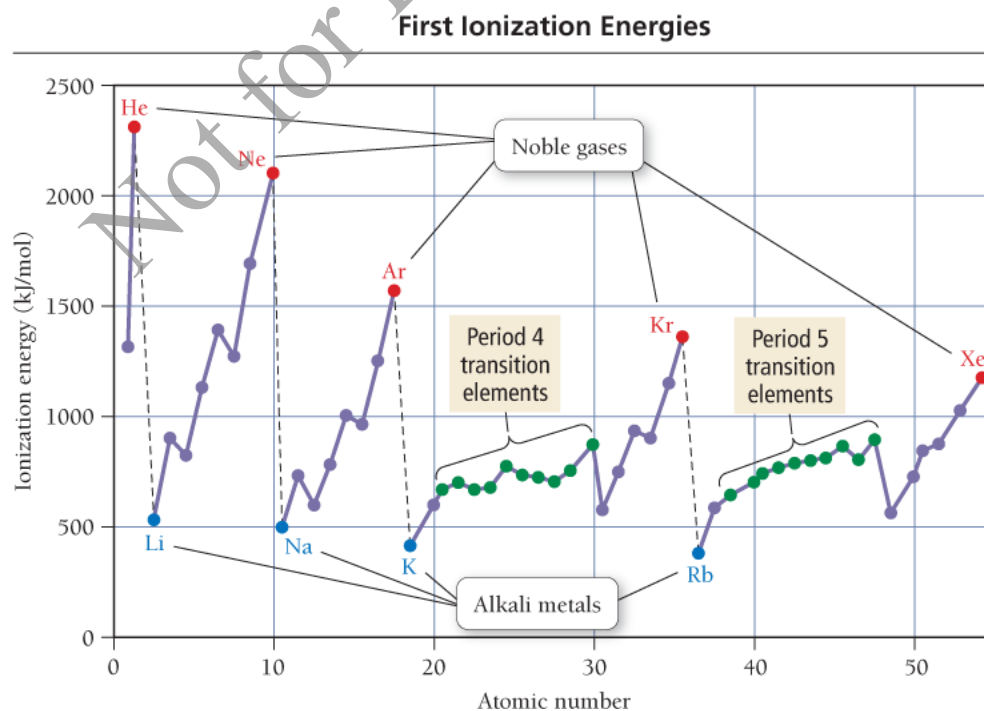
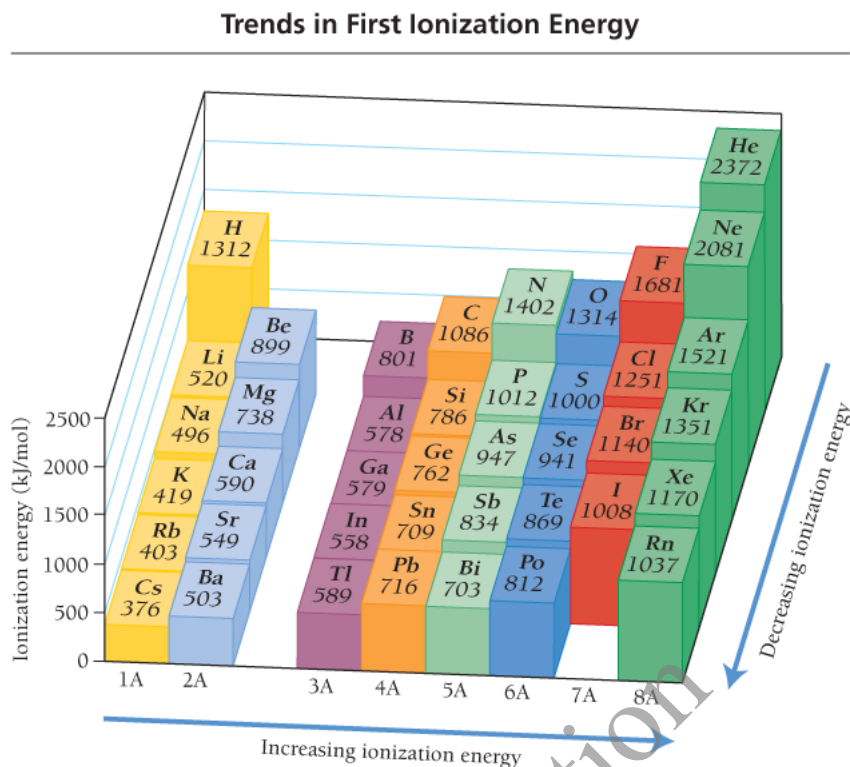


Figure 3.19 Trends in Ionization Energy

Ionization energy increases as we move to the right across a period and decreases as we move down a column in the periodic table.



What about the trend as we move to the right across a row? For example, does it take more energy to remove an electron from Na or from Cl, two elements on either end of the third row in the periodic table? We know that Na has an outer electron configuration of $3s^1$ and Cl has an outer electron configuration of $3s^2 3p^5$. As discussed previously, the outermost electrons in chlorine experience a higher effective nuclear charge than the outermost electrons in sodium (which is why chlorine has a smaller atomic radius than sodium). Consequently, we would expect chlorine to have a higher first ionization energy than sodium, which is indeed the case. We can make a similar argument for the other main-group elements: First ionization energy generally increases as we move to the right across a row in the periodic table, as shown in Figure 3.19.

Summarizing First Ionization Energy for Main-Group Elements

- First ionization energy generally *decreases* as we move down a column (or family) in the periodic table because electrons in the outermost principal level are increasingly farther away from the positively charged nucleus and are therefore held less tightly.
- First ionization energy generally *increases* as we move to the right across a row (or period) in the periodic table because electrons in the outermost principal energy level generally experience a greater effective nuclear charge (Z_{eff}).

Example 3.9 First Ionization Energy

On the basis of periodic trends, determine which element in each pair has the higher first ionization energy (if possible).

- Al or S
- As or Sb
- N or Si
- O or Cl

SOLUTION

a. Al or S

S has a higher first ionization energy than Al because, as you trace the path between Al and S on the periodic table, you move to the right within the same row. First ionization energy increases as you go to the right due to increasing effective nuclear charge.

b. As or Sb

As has a higher first ionization energy than Sb because, as you trace the path between As and Sb on the periodic table, you move down a column. First ionization energy decreases as you go down a column as a result of the increasing size of orbitals with increasing n .

c. N or Si

N has a higher first ionization energy than Si because, as you trace the path between N and Si on the periodic table, you move down a column (first ionization energy decreases due to increasing size of outermost orbitals) and then to the left across a row (first ionization energy decreases due to decreasing effective nuclear charge). These effects sum together for an overall decrease.

d. O or Cl

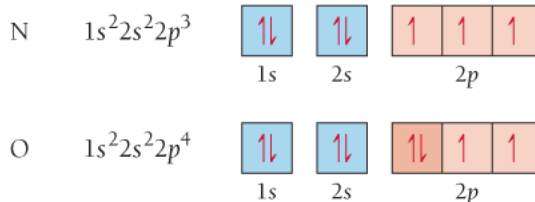
Based on periodic trends alone, it is impossible to tell which has a higher first ionization energy because, as you trace the path between O and Cl, you go to the right across a row (first ionization energy increases) and then down a column (first ionization energy decreases). These effects tend to counter each other, and it is not obvious which will dominate.

- Sn or I
- Ca or Sr
- C or P
- F or S

Interactive Worked Example 3.9 First Ionization Energy

If we carefully examine [Figure 3.19](#), we can see some exceptions to the trends in first ionization energies. For example, boron has a smaller ionization energy than beryllium, even though it lies to the right of beryllium in the same row. This exception is caused by the change in going from the s block to the p block. Recall from [Section 3.3](#) that the $2p$ orbital penetrates into the nuclear region *less than* the $2s$ orbital. Consequently, the $1s$ electrons shield the electron in the $2p$ orbital from nuclear charge more than they shield the electrons in the $2s$ orbital. The result is that the $2p$ orbitals are higher in energy, and therefore the electron is easier to remove (it has a lower first ionization energy). Similar exceptions occur for aluminum and gallium, both directly below boron in group 3A.

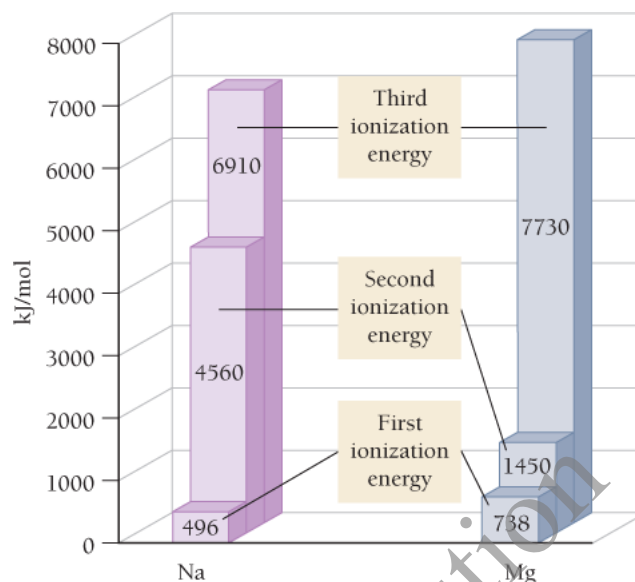
Another exception occurs between nitrogen and oxygen. Although oxygen is to the right of nitrogen in the same row, it has a lower first ionization energy. This exception is caused by the repulsion between electrons when they occupy the same orbital. Examine the electron configurations and orbital diagrams of nitrogen and oxygen shown here:



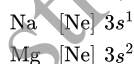
Trends in Second and Successive Ionization

Energies

Notice the trends in the first, second, and third ionization energies of sodium (group 1A) and magnesium (group 2A), as shown in the margin. For sodium, there is a huge jump between the first and second ionization energies. For magnesium, the ionization energy roughly doubles from the first to the second, but then a huge jump occurs between the second and third ionization energies. What is the reason for these jumps?



We can understand these trends by examining the electron configurations of sodium and magnesium:



The first ionization of sodium involves removing the valence electron in the 3s orbital. Recall that these valence electrons are held more loosely than the core electrons and that the resulting ion has a noble gas configuration, which is particularly stable. Consequently, the first ionization energy is fairly low. The second ionization of sodium, however, involves removing a core electron from an ion with a noble gas configuration. This requires a tremendous amount of energy, making the value of IE_2 very high.

As with sodium, the first ionization of magnesium involves removing a valence electron in the 3s orbital. This requires a bit more energy than the corresponding ionization of sodium because of the trends in Z_{eff} that we discussed earlier (Z_{eff} increases as we move to the right across a row). The second ionization of magnesium also involves removing an outer electron in the 3s orbital, but this time from an ion with a 1+ charge (instead of from a neutral atom). This requires roughly twice the energy as removing the electron from the neutral atom. The third ionization of magnesium is analogous to the second ionization of sodium—it requires removing a core electron from an ion with a noble gas configuration. This requires a tremendous amount of energy, making IE_3 very high.

As shown in [Table 3.1](#), similar trends exist for the successive ionization energies of many elements. Ionization energies increase fairly uniformly with each successive removal of an outermost electron but take a large jump with the removal of the first core electron.

Table 3.1 Successive Values of Ionization Energies for the Elements Sodium through Argon (kJ/mol)

Element	IE ₁	IE ₂	IE ₃	IE ₄	IE ₅	IE ₆	IE ₇
Na	496	4560					
Mg	738	1450	7730				
Al	578	1820	2750	11,600			
Si	786	1580	3230	4360	16,100		
P	1012	1900	2910	4960	6270	22,200	
S	1000	2250	3360	4560	7010	8500	27,100
Cl	1251	2300	3820	5160	6540	9460	11,000
Ar	1521	2670	3930	5770	7240	8780	12,000

Conceptual Connection 3.7 Ionization Energies and Chemical Bonding

Interactive

Not for Distribution

Not for Distribution

Not for Distribution

Not for Distribution