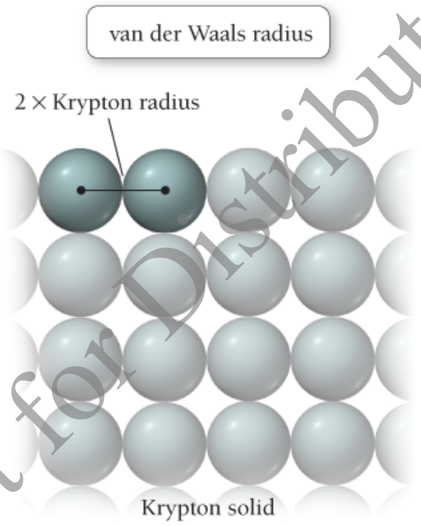
3.6: Periodic Trends in Atomic Size and Effective Nuclear Charge

Key Concept Video **Periodic Trends and Effective Nuclear Charge**

In previous chapters, we saw that the volume of an atom is taken up primarily by its electrons (Chapter 1) occupying quantum-mechanical orbitals (Chapter 2). We also saw that these orbitals do not have a definite boundary but represent only a statistical probability distribution for where the electron is found. So how do we define the size of an atom? One way to define atomic radii is to consider the distance between *nonbonding* atoms that are in direct contact. For example, krypton can be frozen into a solid in which the krypton atoms are touching each other but are not bonded together. The distance between the centers of adjacent krypton atoms—which can be determined from the solid's density—is then twice the radius of a krypton atom. An atomic radius determined in this way is the **nonbonding atomic radius** or the **van der Waals radius**. The van der Waals radius represents the radius of an atom when it is not bonded to another atom.

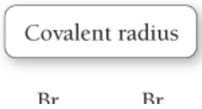


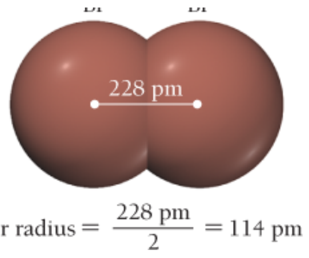
The van der Waals radius of an atom is one-half the distance between adjacent nuclei in the atomic solid.

Another way to define the size of an atom, the **bonding atomic radius** or **covalent radius**, is defined differently for nonmetals and metals, as follows:

> Nonmetals: one-half the distance between two of the atoms bonded together
>
> Metals: one-half the distance between two of the atoms next to each other in a crystal of the metal

For example, the distance between Br atoms in Br_2 is 228 pm; therefore, the Br covalent radius is assigned to be one-half of 228 pm, or 114 pm.





$$\text{Br radius} = \frac{228\ \text{pm}}{2} = 114\ \text{pm}$$

The covalent radius of bromine is one-half the distance between two bonded bromine atoms.

Using this method, we can assign radii to all elements in the periodic table that form chemical bonds or form metallic crystals. A more general term, the **atomic radius**, refers to a set of average bonding radii determined from measurements on a large number of elements and compounds. The atomic radius represents the radius of an atom when it is bonded to another atom and is always smaller than the van der Waals radius. The approximate bond length of any two covalently bonded atoms is the sum of their atomic radii. For example, the approximate bond length for ICl is iodine's atomic radius (133 pm) plus chlorine's atomic radius (99 pm), for a bond length of 232 pm. (The actual experimentally measured bond length in ICl is 232.07 pm.)

Figure 3.13 shows the atomic radius plotted as a function of atomic number for the first 57 elements in the periodic table. Notice the periodic trend in the radii. Atomic radii peak with each alkali metal. Figure 3.14 is a relief map of atomic radii for most of the elements in the periodic table. The general trends in the atomic radii of main-group elements, which are the same as trends observed in van der Waals radii, are as follows:

1. As we move down a column (or family) in the periodic table, the atomic radius increases.
2. As we move to the right across a period (or row) in the periodic table, the atomic radius decreases.

Figure 3.13 **Atomic Radius versus Atomic Number**

Notice the periodic trend in the atomic radius, starting at a peak with each alkali metal and falling to a minimum with each noble gas.

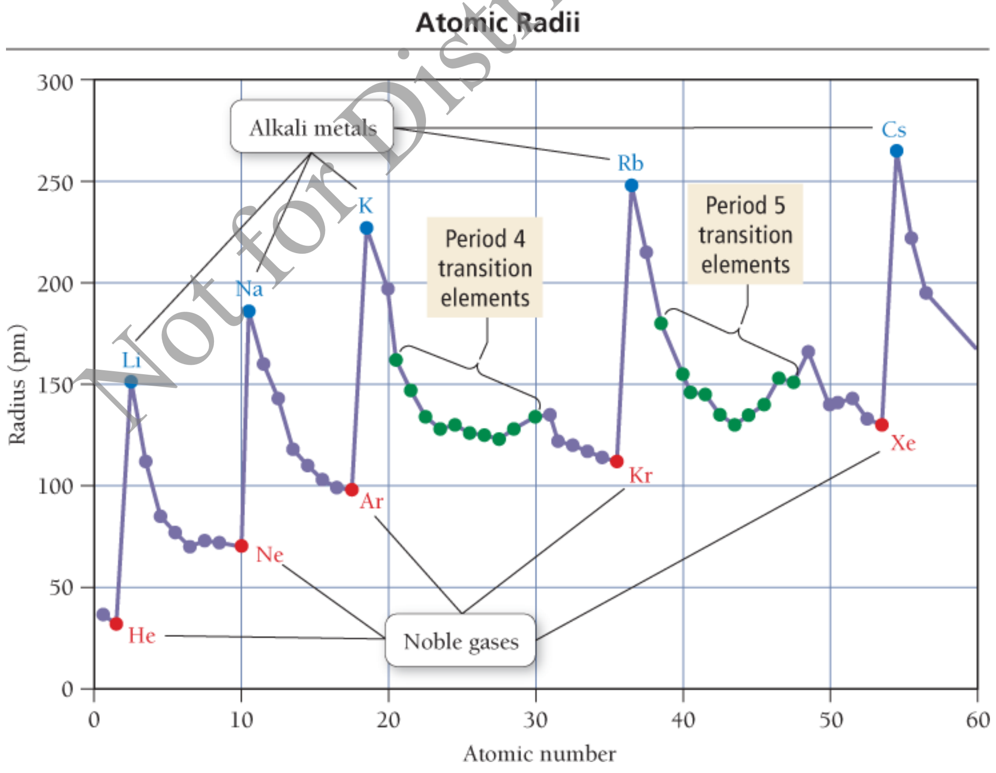
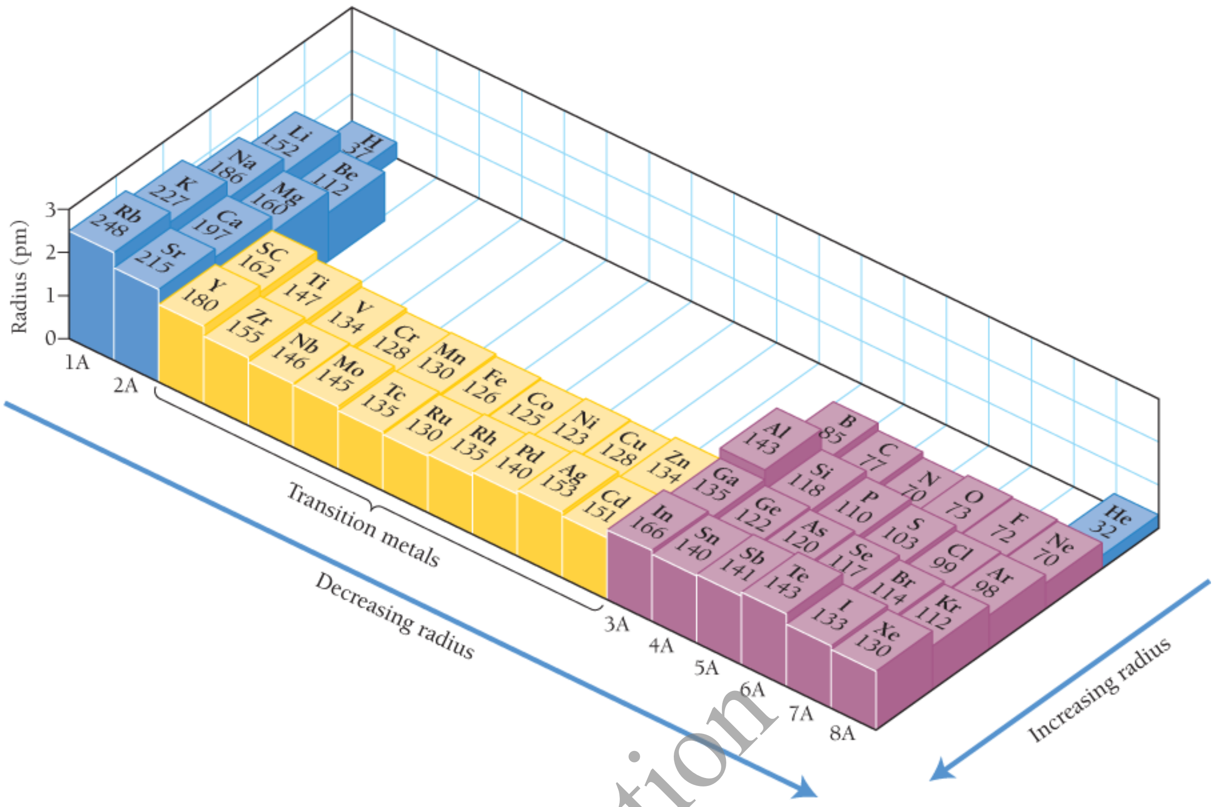


Figure 3.14 **Trends in Atomic Radius**

In general, atomic radii increase as we move down a column and decrease as we move to the right across a period in the periodic table.

Trends in Atomic Radius



We can understand the observed trend in radius as we move down a column based on the trends in the sizes of atomic orbitals. The atomic radius is largely determined by the valence electrons, the electrons farthest from the nucleus. As we move down a column in the periodic table, the highest principal quantum number (n) of the valence electrons increases. Consequently, the valence electrons occupy larger orbitals, resulting in larger atoms.

The observed trend in atomic radius as we move to the right across a row, however, is a bit more complex. To understand this trend, we now revisit some concepts from Section 3.3, including effective nuclear charge and shielding.

Effective Nuclear Charge

The trend in atomic radius as we move to the right across a row in the periodic table is determined by the inward pull of the nucleus on the electrons in the outermost principal energy level (highest n value). According to Coulomb's law, the attraction between a nucleus and an electron increases with increasing magnitude of nuclear charge. For example, compare the H atom to the He$^+$ ion:

$$\begin{array}{ll} \mathrm{H} & 1s^1 \\ \mathrm{He}^+ & 1s^1 \end{array}$$

It takes 1312 kJ/mol of energy to remove the $1s$ electron from H, but 5251 kJ/mol of energy to remove it from He$^+$. Why? Although each electron is in a $1s$ orbital, the electron in the helium ion is attracted to the nucleus by a 2+ charge, while the electron in the hydrogen atom is attracted to the nucleus by only a 1+ charge. Therefore, the electron in the helium ion is held more tightly (it has lower potential energy according to Coulomb's law), making it more difficult to remove and making the helium ion smaller than the hydrogen atom.

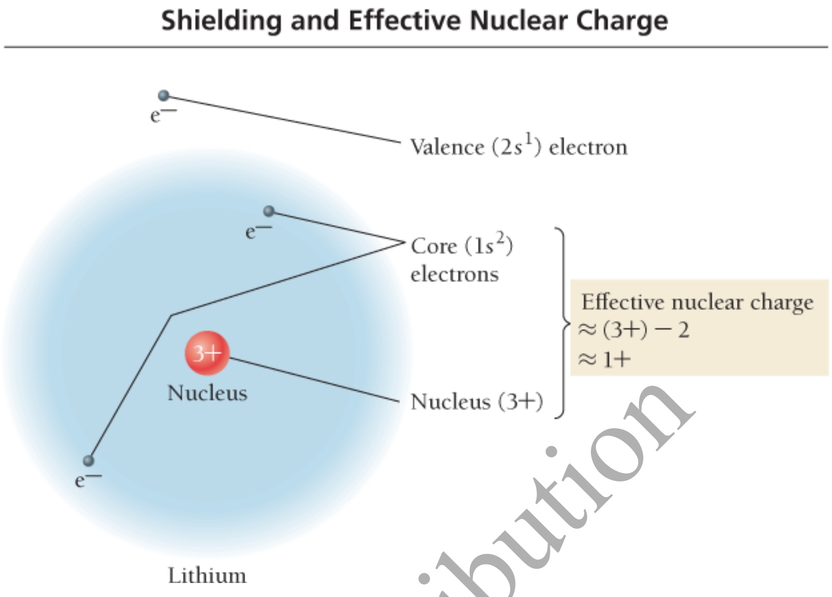
As we saw in Section 3.3, any one electron in a multi-electron atom experiences both the positive charge of the nucleus (which is attractive) and the negative charges of the other electrons (which are repulsive). Consider again the outermost electron in the lithium atom:

$$\text{Li} \quad 1s^2\ 2s^1$$

As shown in Figure 3.15, even though the $2s$ orbital penetrates into the $1s$ orbital to some degree, the majority of the $2s$ orbital is outside of the $1s$ orbital. Therefore, the electron in the $2s$ orbital is partially *screened* or *shielded* from the 3+ charge of the nucleus by the 2− charge of the $1s$ (or core) electrons, reducing the net charge experienced by the $2s$ electron.

Figure 3.15 Shielding and Effective Nuclear Charge

The valence electron in lithium experiences the 3+ charge of the nucleus through the shield of the 2− charge of the core electrons. The effective nuclear charge acting on the valence electron is approximately 1+.


Shielding and Effective Nuclear Charge
e−
Valence (2s¹) electron
e−
Core (1s²) electrons
Effective nuclear charge ≈ (3+) − 2 ≈ 1+
3+
Nucleus
Nucleus (3+)
e−
Lithium

Recall from Section 3.3 that we define the average or net charge experienced by an electron as the *effective nuclear charge*. The effective nuclear charge experienced by a particular electron in an atom is the *actual nuclear charge* (*Z*) minus *the charge shielded by other electrons* (*S*):

$$\underset{\text{Effective nuclear charge}}{Z_{\text{eff}}} = \underset{\text{Actual nuclear charge}}{Z} = \underset{\text{Charge shielded by other electrons}}{S}$$

For lithium, we estimate that the two core electrons shield the valence electron from the nuclear charge with high efficiency (S is nearly 2). The effective nuclear charge experienced by lithium's valence electron is therefore slightly greater than 1+.

Now consider the valence electrons in beryllium (Be), with atomic number 4. Its electron configuration is:

$$\text{Be} \quad 1s^2\ 2s^2$$

To estimate the effective nuclear charge experienced by the $2s$ electrons in beryllium, we must distinguish between two different types of shielding: (1) the shielding of the outermost electrons by the core electrons and (2) the shielding of the outermost electrons by *each other*. The key to understanding the trend in atomic radius is the difference between these two types of shielding:

> Core electrons efficiently shield electrons in the outermost principal energy level from nuclear charge, but outermost electrons do not efficiently shield one another from nuclear charge.

For example, the two outermost electrons in beryllium experience the 4+ charge of the nucleus through the shield of the two $1s$ core electrons without shielding each other from that charge very much. We estimate that the shielding (S) experienced by any one of the outermost electrons due to the core electrons is nearly 2, but that the shielding due to the other outermost electron is nearly 0. The effective nuclear charge experienced by beryllium's outermost electrons is therefore slightly greater than 2+.

The effective nuclear charge experienced by *beryllium's* outermost electrons is greater than that experienced by *lithium's* outermost electron. Consequently, beryllium's outermost electrons are held more tightly than lithium's, resulting in a smaller atomic radius for beryllium. The effective nuclear charge experienced by an atom's outermost electrons continues to become more positive as we move to the right across the rest of the second row in the periodic table, resulting in successively smaller atomic radii. The same trend is generally observed in all main-group elements.

Summarizing Atomic Radii for Main-Group Elements

- As we move down a column in the periodic table, the principal quantum number (n) of the electrons in the outermost principal energy level increases, resulting in larger orbitals and therefore larger atomic radii.
- As we move to the right across a row in the periodic table, the effective nuclear charge (Z_{eff}) experienced by the electrons in the outermost principal energy level increases, resulting in a stronger attraction between the outermost electrons and the nucleus, and smaller atomic radii.

Conceptual Connection 3.5 **Effective Nuclear Charge**

Interactive

Atomic Radii and the Transition Elements

Notice in Figure 3.14 that as *we move down the first two rows of a column* within the transition metals, the elements follow the same general trend in atomic radii as the main-group elements (the radii get larger). In contrast, with the exception of the first couple of elements in each transition series, the atomic radii of the transition elements *do not* follow the same trend as the main-group elements as *we move to the right across a row*. Instead of decreasing in size, *the radii of transition elements stay roughly constant across each row*. Why? The difference is that, across a row of transition elements, the number of electrons in the outermost principal energy level (highest n value) is nearly constant (recall from Section 3.3, for example, that the $4s$ orbital fills before the $3d$). As another proton is added to the nucleus of each successive element, another electron is added as well, but the electron goes into an $n_{\text{highest}} - 1$ orbital. The number of outermost electrons stays constant, and the electrons experience a roughly constant effective nuclear charge, keeping the radius approximately constant.

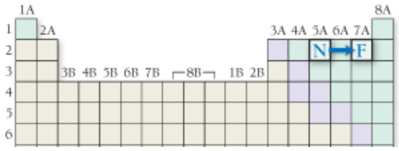
Example 3.6 Atomic Size

On the basis of periodic trends, choose the larger atom in each pair (if possible). Explain your choices.

a. N or F
b. C or Ge
c. N or Al
d. Al or Ge

SOLUTION

a. N atoms are larger than F atoms because, as you trace the path between N and F on the periodic table, you move to the right within the same period. As you move to the right across a period, the effective nuclear charge experienced by the outermost electrons increases, resulting in a smaller radius.



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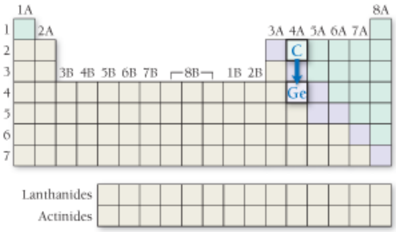
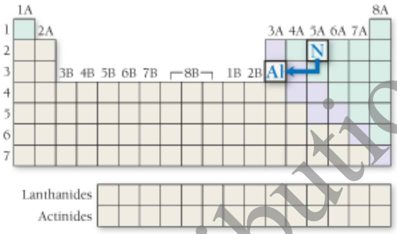
Lanthanides
Actinides

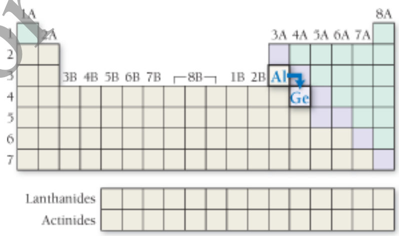
b. Ge atoms are larger than C atoms because, as you trace the path between C and Ge on the periodic table, you move down a column. Atomic size increases as you move down a column because the outermost electrons occupy orbitals with a higher principal quantum number that are therefore larger, resulting in a larger atom.


1A
8A
2A
3A 4A 5A 6A 7A
3B 4B 5B 6B 7B 8B 1B 2B
C
Ge
1
2
3
4
5
6
7
Lanthanides
Actinides

c. Al atoms are larger than N atoms because, as you trace the path between N and Al on the periodic table, you move down a column (atomic size increases) and then to the left across a period (atomic size increases). These effects add together for an overall increase.


1A
8A
2A
3A 4A 5A 6A 7A
3B 4B 5B 6B 7B 8B 1B 2B
N
Al
1
2
3
4
5
6
7
Lanthanides
Actinides

d. Based on periodic trends alone, you cannot tell which atom is larger, because as you trace the path between Al and Ge you go to the right across a period (atomic size decreases) and then down a column (atomic size increases). These effects tend to counter each other, and it is not easy to tell which will predominate.


1A
8A
2A
3A 4A 5A 6A 7A
3B 4B 5B 6B 7B 8B 1B 2B
Al
Ge
1
2
3
4
5
6
7
Lanthanides
Actinides

FOR PRACTICE 3.6 On the basis of periodic trends, choose the larger atom in each pair (if possible):

a. Sn or I

b. Ge or Po

c. Cr or W

d. F or Se

FOR MORE PRACTICE 3.6 Arrange the elements in order of decreasing radius: S, Ca, F, Rb, Si.

Interactive Worked Example 3.6 **Atomic Size**