Learning Objectives

- To understand periodic trends in atomic radii.
- To predict relative ionic sizes within an isoelectronic series.

Although some people fall into the trap of visualizing atoms and ions as small, hard spheres similar to miniature table-tennis balls or marbles, the quantum mechanical model tells us that their shapes and boundaries are much less definite than those images suggest. As a result, atoms and ions cannot be said to have exact sizes; however, some atoms are larger or smaller than others, and this influences their chemistry. In this section, we discuss how atomic and ion “sizes” are defined and obtained.

Atomic Radii

Recall that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure 1 (Figure 1) which shows a plot of total electron density for all occupied orbitals for three noble gases as a function of their distance from the nucleus. Electron density diminishes gradually with increasing distance, which makes it impossible to draw a sharp line marking the boundary of an atom.

Figure 1: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1s electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1s electrons have a maximum at ≈8 pm, and the 2s and 2p electrons combine to form another maximum at ≈35 pm (the n = 2 shell). In Ar, the 1s electrons have a maximum at ≈2 pm, the 2s and 2p electrons combine to form a maximum at ≈18 pm, and the 3s and 3p electrons combine to form a maximum at ≈70 pm.

Figure 1 also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell. Because helium has only one filled shell (n = 1), it shows only a single peak. In contrast, neon, with filled n = 1 and 2 principal shells, has two peaks. Argon, with filled n = 1, 2, and 3 principal shells, has three peaks. The peak for the filled n = 1 shell occurs at successively shorter distances for neon (Z = 10) and argon (Z = 18) because, with a greater number of protons, their nuclei are more positively charged than that of helium.
Because the 1s\(^2\) shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of \(n\). Consequently, the two electrons in the \(n = 1\) shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus. The energy of the \(n = 1\) shell also decreases tremendously (the filled 1s orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled \(n = 2\) shell in argon is located closer to the nucleus and has a lower energy than the \(n = 2\) shell in neon.

Figure \(\PageIndex{1}\) illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic \(\text{Cl}_2\) molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a **covalent atomic radius** (\(r_{\text{cov}}\)), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (Figure \(\PageIndex{2a}\)). Atomic radii are often measured in angstroms (Å), a non-SI unit: 1 Å = 1 \times 10^{-10} \text{ m} = 100 \text{ pm}.

Figure \(\PageIndex{2}\): Definitions of the Atomic Radius. (a) The covalent atomic radius, \(r_{\text{cov}}\), is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as \(\text{Cl}_2\). (b) The metallic atomic radius, \(r_{\text{met}}\), is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, \(r_{\text{vdW}}\), is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of \(\text{Cl}_2\) is half the distance between the two chlorine atoms in a single molecule of \(\text{Cl}_2\). The van der Waals radius is half the distance between chlorine nuclei in two different but touching \(\text{Cl}_2\) molecules. Which do you think is larger? Why?

In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds. A similar approach for measuring the size of ions is discussed later in this section.

Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the **metallic atomic radius** (\(r_{\text{met}}\)) is defined as half the distance between the nuclei of two adjacent metal atoms in the solid (Figure \(\PageIndex{2b}\)). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the **van der Waals atomic radius** (\(r_{\text{vdW}}\)), which is half the internuclear distance between two nonbonded atoms in the solid (Figure \(\PageIndex{2c}\)). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a \(\text{Cl}_2\)) molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, \(\text{Cl}_2(s)\)) at low temperatures). These radii are generally not the same (Figure \(\PageIndex{2d}\)).
Periodic Trends in Atomic Radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure 1).

Figure 1: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table

In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure 2).

Figure 2: Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: [http://www.webelements.com](http://www.webelements.com). Web Elements is an excellent online source for looking up atomic properties.

Trends in atomic size result from differences in the effective nuclear charges ($Z_{\text{eff}}$) experienced by electrons in the outermost orbitals of the elements. For all elements except H, the effective nuclear charge is always less than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.

Atomic radii decrease from left to right across a row and increase from top to bottom down a column.

The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10.
Although electrons are being added to the 2s and 2p orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2s electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled 1s$^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of $Z_{\text{eff}} = +1.26$ for Li.) In contrast, the two 2s electrons in beryllium do not shield each other very well, although the filled 1s$^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2s electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium.

Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2s and 2p orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size (Figure \(\PageIndex{5}\)).

![Increasing](image)

**Calculated atomic radius (pm), s-, p-, and d-block elements**

![Figure](image)

The increase in atomic size going down a column is also due to electron shielding, but the situation is more complex because the principal quantum number $n$ is not constant. As we saw in Chapter 2, the size of the orbitals increases as $n$ increases, *provided the nuclear charge remains the same*. In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to $ns$ orbitals with increasing values of $n$. However, it is important to remember that the radius of an orbital depends dramatically on the nuclear charge. As we go down the column of the group 1 elements, the principal quantum number $n$ increases from 2 to 6, but the nuclear charge increases from +3 to +55!

As a consequence the radii of the *lower electron orbitals* in Cesium are much smaller than those in lithium and the electrons in those orbitals experience a much larger force of attraction to the nucleus. That force depends on the effective nuclear charge experienced by the inner electrons. If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a 6s$^1$ valence electron configuration, is much larger than lithium, with a 2s$^1$ valence electron configuration. The effective nuclear charge changes relatively little for electrons in the outermost, or valence shell, from lithium to cesium because
Electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled 1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$4s$^2$3d$^{10}$4p$^6$5s$^2$4d$^{10}$5p$^6$ shells, abbreviated as [Xe]5s$^2$4d$^{10}$5p$^6$, which effectively neutralize most of the 55 positive charges in the nucleus. The same dynamic is responsible for the steady increase in size observed as we go down the other columns of the periodic table. Irregularities can usually be explained by variations in effective nuclear charge.

Not all Electrons shield equally

Electrons in the same principal shell are not very effective at shielding one another from the nuclear charge, whereas electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge.

Example \(\PageIndex{1}\)

On the basis of their positions in the periodic table, arrange these elements in order of increasing atomic radius: aluminum, carbon, and silicon.

**Given:** three elements

**Asked for:** arrange in order of increasing atomic radius

**Strategy:**

A. Identify the location of the elements in the periodic table. Determine the relative sizes of elements located in the same column from their principal quantum number \(n\). Then determine the order of elements in the same row from their effective nuclear charges. If the elements are not in the same column or row, use pairwise comparisons.

B. List the elements in order of increasing atomic radius.

**Solution:**

A These elements are not all in the same column or row, so we must use pairwise comparisons. Carbon and silicon are both in group 14 with carbon lying above, so carbon is smaller than silicon (C < Si). Aluminum and silicon are both in the third row with aluminum lying to the left, so silicon is smaller than aluminum (Si < Al) because its effective nuclear charge is greater.

B Combining the two inequalities gives the overall order: C < Si < Al.

**Exercise \(\PageIndex{1}\)**

On the basis of their positions in the periodic table, arrange these elements in order of increasing size: oxygen, phosphorus, potassium, and sulfur.

**Answer**

\(O < S < P < K\)
Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom to form a positive ion (cation) or when additional electrons attach themselves to neutral atoms to form a negative one (anion). The designations cation or anion come from the early experiments with electricity which found that positively charged particles were attracted to the negative pole of a battery, the cathode, while negatively charged ones were attracted to the positive pole, the anode.

![Figure 6: Definition of Ionic Radius](image)

(a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na\(^+\) and Cl\(^-\) in sodium chloride. (b) This depiction of electron density contours for a single plane of atoms in the NaCl structure shows how the lines connect points of equal electron density. Note the relative sizes of the electron density contour lines around Cl\(^-\) and Na\(^+\).

Ionic compounds consist of regular repeating arrays of alternating positively charged cations and negatively charged anions. Although it is not possible to measure an ionic radius directly for the same reason it is not possible to directly measure an atom's radius, it is possible to measure the distance between the nuclei of a cation and an adjacent anion in an ionic compound to determine the ionic radius (the radius of a cation or anion) of one or both. As illustrated in Figure 6, the internuclear distance corresponds to the sum of the radii of the cation and anion. A variety of methods have been developed to divide the experimentally measured distance proportionally between the smaller cation and larger anion. These methods produce sets of ionic radii that are internally consistent from one ionic compound to another, although each method gives slightly different values. For example, the radius of the Na\(^+\) ion is essentially the same in NaCl and Na\(_2\)S, as long as the same method is used to measure it. Thus despite minor differences due to methodology, certain trends can be observed.

A comparison of ionic radii with atomic radii (Figure 7) shows that a cation, having lost an electron, is always smaller than its parent neutral atom, and an anion, having gained an electron, is always larger than the parent neutral atom. When one or more electrons is removed from a neutral atom, two things happen: (1) repulsions between electrons in the same principal shell decrease because fewer electrons are present, and (2) the effective nuclear charge felt by the remaining electrons increases because there are fewer electrons to shield one another from the nucleus. Consequently, the size of the region of space occupied by electrons decreases and the ion shrinks (compare Li at 167 pm with Li\(^+\) at 76 pm). If different numbers of electrons can be removed to produce ions with different charges, the ion with the greatest positive charge is the smallest (compare Fe\(^{2+}\) at 78 pm with Fe\(^{3+}\) at 64.5 pm). Conversely, adding one or more electrons to a neutral atom causes electron–electron repulsions to increase and the effective nuclear charge to decrease, so the size of the probability region increases and the ion expands (compare F at 42 pm with F\(^-\) at 133 pm).
Cations are always smaller than the neutral atom and anions are always larger.

Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na\(^-\) ion, allowing comparison of its size with that of the far more familiar Na\(^+\) ion, which is found in many compounds. The radius of sodium in each of its three known oxidation states is given in Table \(\PageIndex{1}\). All three species have a nuclear charge of +11, but they contain 10 (Na\(^+\)), 11 (Na\(^0\)), and 12 (Na\(^-\)) electrons. The Na\(^+\) ion is significantly smaller than the neutral Na atom because the 3s\(^1\) electron has been removed to give a closed shell with \(n = 2\). The Na\(^-\) ion is larger than the parent Na atom because the additional electron produces a 3s\(^2\) valence electron configuration, while the nuclear charge remains the same.

**Table \(\PageIndex{1}\): Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States**

<table>
<thead>
<tr>
<th>Electron Configuration</th>
<th>Na(^+)</th>
<th>Na(^0)</th>
<th>Na(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (pm)</td>
<td>102</td>
<td>154*</td>
<td>202†</td>
</tr>
</tbody>
</table>


Ionic radii follow the same vertical trend as atomic radii; that is, for ions with the same charge, the ionic radius increases going down a column. The reason is the same as for atomic radii: shielding by filled inner shells produces little change in the effective nuclear charge felt by the outermost electrons. Again, principal shells with larger values of \(n\) lie at successively greater distances from the nucleus.

Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table. Instead, elements that are next to each other tend to form ions with the...
same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an **isoelectronic series**. For example, the isoelectronic series of species with the neon closed-shell configuration \((1s^22s^22p^6)\) is shown in Table \(\PageIndex{3}\).

The sizes of the ions in this series decrease smoothly from \(\text{N}^{3−}\) to \(\text{Al}^{3+}\). All six of the ions contain 10 electrons in the 1s, 2s, and 2p orbitals, but the nuclear charge varies from +7 (N) to +13 (Al). As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge \((\text{Al}^{3+})\) is the smallest, and the ion with the smallest nuclear charge \((\text{N}^{3−})\) is the largest. The neon atom in this isoelectronic series is not listed in Table \(\PageIndex{3}\), because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.


<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius (pm)</th>
<th>Atomic Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{N}^{3−})</td>
<td>146</td>
<td>7</td>
</tr>
<tr>
<td>(\text{O}^{2−})</td>
<td>140</td>
<td>8</td>
</tr>
<tr>
<td>(\text{F}^{−})</td>
<td>133</td>
<td>9</td>
</tr>
<tr>
<td>(\text{Na}^{+})</td>
<td>98</td>
<td>11</td>
</tr>
<tr>
<td>(\text{Mg}^{2+})</td>
<td>79</td>
<td>12</td>
</tr>
<tr>
<td>(\text{Al}^{3+})</td>
<td>57</td>
<td>13</td>
</tr>
</tbody>
</table>

Example \(\PageIndex{2}\)

Based on their positions in the periodic table, arrange these ions in order of increasing radius: \(\text{Cl}^{−}\), \(\text{K}^{+}\), \(\text{S}^{2−}\), and \(\text{Se}^{2−}\).

**Given:** four ions

**Asked for:** order by increasing radius
Strategy:

A. Determine which ions form an isoelectronic series. Of those ions, predict their relative sizes based on their nuclear charges. For ions that do not form an isoelectronic series, locate their positions in the periodic table.

B. Determine the relative sizes of the ions based on their principal quantum numbers \( n \) and their locations within a row.

Solution:

A We see that S and Cl are at the right of the third row, while K and Se are at the far left and right ends of the fourth row, respectively. \( \text{K}^+ \), \( \text{Cl}^- \), and \( \text{S}^{2-} \) form an isoelectronic series with the [Ar] closed-shell electron configuration; that is, all three ions contain 18 electrons but have different nuclear charges. Because \( \text{K}^+ \) has the greatest nuclear charge (\( Z = 19 \)), its radius is smallest, and \( \text{S}^{2-} \) with \( Z = 16 \) has the largest radius. Because selenium is directly below sulfur, we expect the \( \text{Se}^{2-} \) ion to be even larger than \( \text{S}^{2-} \).

B The order must therefore be \( \text{K}^+ < \text{Cl}^- < \text{S}^{2-} < \text{Se}^{2-} \).

Exercise \( \PageIndex{2} \)

Based on their positions in the periodic table, arrange these ions in order of increasing size: \( \text{Br}^- \), \( \text{Ca}^{2+} \), \( \text{Rb}^+ \), and \( \text{Sr}^{2+} \).

Answer

\( \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Rb}^+ < \text{Br}^- \)

Summary

Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges. A variety of methods have been established to measure the size of a single atom or ion. The covalent atomic radius (\( r_{\text{cov}} \)) is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the metallic atomic radius (\( r_{\text{met}} \)) is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The van der Waals radius (\( r_{\text{vdW}} \)) of an element is half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The ionic radii of cations and anions are always smaller or larger, respectively, than the parent atom due to changes in electron–electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an isoelectronic series, shows a clear correlation between increasing nuclear charge and decreasing size.

Contributors

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