Periodic Trends in Atomic Size

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Concept 1 Periodic Trends in Atomic Size

Lesson Objectives

The student will:

- define atomic radius.
- define the shielding effect.
- describe the factors that determine the trend in atomic size.
- describe the general trend in atomic size for groups and periods.
- use the general trends to predict the relative sizes of atoms.
- describe variations that occur in the general trend of atomic size in the transition metals.

Vocabulary

atomic radius one-half the distance between the centers of a homonuclear diatomic molecule

diatomic molecule a molecule containing exactly two atoms

nuclear charge the number of protons in the nucleus

shielding effect the effect where the inner electrons help "shield" the outer electrons and the nucleus from each other

Introduction

In the periodic table, there are a number of physical properties that are trend-like. This means that as you move down a group or across a period, you will see the properties changing in a general direction. The actual trends that are observed with atomic size have to do with three factors. These factors are:

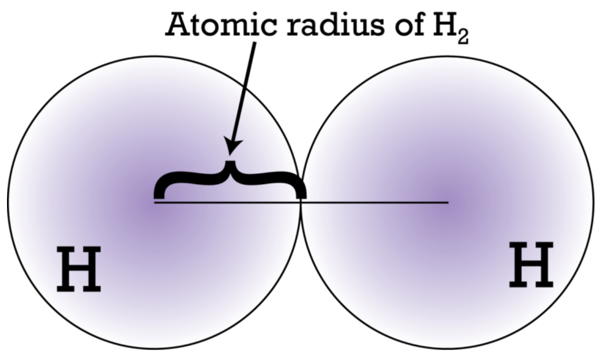
a. the number of protons in the nucleus (called the **nuclear charge**).
b. the number of energy levels holding electrons and the number of electrons in the outer energy level.
c. the number of electrons held between the nucleus and its outermost electrons (called the **shielding effect**).

Atomic Radius Defined

The gold foil experiment performed by Rutherford in 1911 (see the chapter "The Atomic Theory" for more details), was the first experiment that gave scientists an approximate measurement for the size of the atom. The atomic size is the distance from the nucleus to the valence shell, where the valence electrons are located. Using the technology available in the early part of the 1900s, Rutherford was able to determine quantitatively that the nucleus had a radius size smaller than 3×10^{-12} cm. The size of the atom is significantly larger, being approximately 2×10^{-8} cm in diameter.

The region in space occupied by the electron cloud of an atom is often thought of as a probability distribution of the electron positions. Consequently, there is no well-defined outer edge of the electron cloud. Because it is so difficult to measure atomic size from the nucleus to the outermost edge of the electron cloud, chemists use other approaches to get consistent measurements of atomic sizes.

Atomic size is defined in several different ways, which often produce some variations in the measurement of atomic sizes. One way that chemists define atomic size is by using the atomic radius. The **atomic radius** is one-half the distance between the centers of a homonuclear diatomic molecule, as illustrated below. A **diatomic molecule** is a molecule made of exactly two atoms, while homonuclear means both atoms are the same element.



Group Trends in Atomic Radii

Let's now look at how the atomic radii changes from the top of a family to the bottom. Take, for example, the Group 1A metals (see **Table** 1.1). Every atom in this family has the same number of electrons in the outer energy level (true for all main group families). Each period in the periodic table represents another added energy level. When we first learned about principal energy levels, we learned that each new energy level was larger than the one before. Therefore, as we move down the periodic table, each successive period represents the addition of a larger energy level, thus increasing the atomic radius.

TABLE 1.1: Group 1A Data

Element	Number of Protons	Electron Configuration
Lithium (Li)	3	$[He]2s^1$
Sodium (Na)	11	$[Ne]3s^1$
Potassium (K)	19	$[Ar]4s^1$
Rubidium (Rb)	37	$[Kr]5s^1$
Cesium (Cs)	55	$[Xe]6s^1$

One other contributing factor to atomic size is the shielding effect. The protons in the nucleus attract the valence electrons in the outer energy level, but the strength of this attraction depends on the size of the charges, the distance between the charges, and the number of electrons between the nucleus and the valence electrons. The presence of the core electrons weakens the attraction between the nucleus and the valence electrons. This weakening is called the shielding effect. Note that although valence electrons do participate in shielding, electrons in the same energy level do not shield each other as effectively as the core electrons do. As a result, the amount of shielding primarily depends on the number of electrons between the nucleus and the valence electrons. When the nucleus pulls strongly on the valence electrons, the valence shell can be pulled in tighter and closer to the nucleus. When the attraction is weakened by shielding, the valence shell cannot be pulled in as close. The more shielding that occurs, the further the valence shell can spread out.

For example, if you are looking at the element sodium, it has the electron configuration:

Na $1s^2 2s^2 2p^6 3s^1$

The outer energy level is $n = 3$. There is one valence electron, but the attraction between this lone valence electron and the nucleus, which has 11 protons, is shielded by the other 10 inner (or core) electrons.

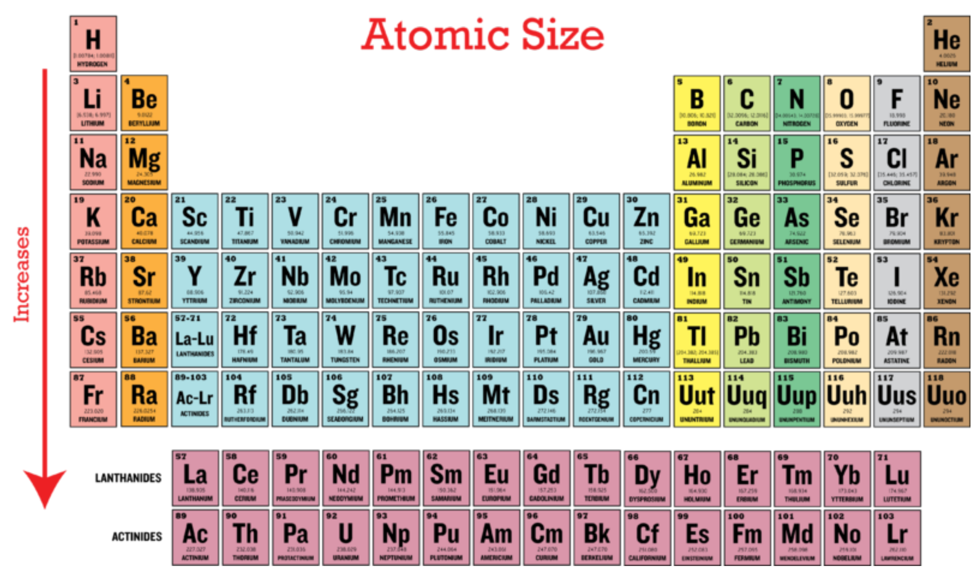
When we compare an atom of sodium to one of cesium, we notice that the number of protons increases, as well as the number of energy levels occupied by electrons. The increase in the number of protons, however, is also accompanied by the same increase in the number of shielding electrons.

Cs $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^1$

The result is that the valence electron in both atoms feels a similar pull from the nucleus, but the valence electron in the cesium atom is further from the nucleus because it is in a higher energy level. Compared to the shielding effect, the increase in the number of energy levels has a greater impact on the atom's size. Consequently, the size of a cesium atom is larger than that of a sodium atom.

This is true for not only Group 1A metals, but for all of the groups across the periodic table. For any given group, as you move downward in the periodic table, the size of the atoms increases. For instance, the largest atoms in the halogen family are bromine and iodine (astatine is radioactive and only exists for short periods of time, so we won't include it in the discussion). You can imagine that with the increase in the number of energy levels, the size of the atom must increase. The increase in the number of energy levels in the electron cloud takes up more space.

The periodic table below shows the trend of atomic size for groups, with the arrow indicating the direction of the increase.



Example:

Which of the following is larger? Explain.

a. As or Sb
b. Ca or Be
c. polonium or sulfur

Solution:

a. Sb, because it is below As in Group 15.
b. Ca, because it is below Be in Group 2.
c. Polonium, because it is below sulfur in Group 16.

Period Trends in Atomic Radii

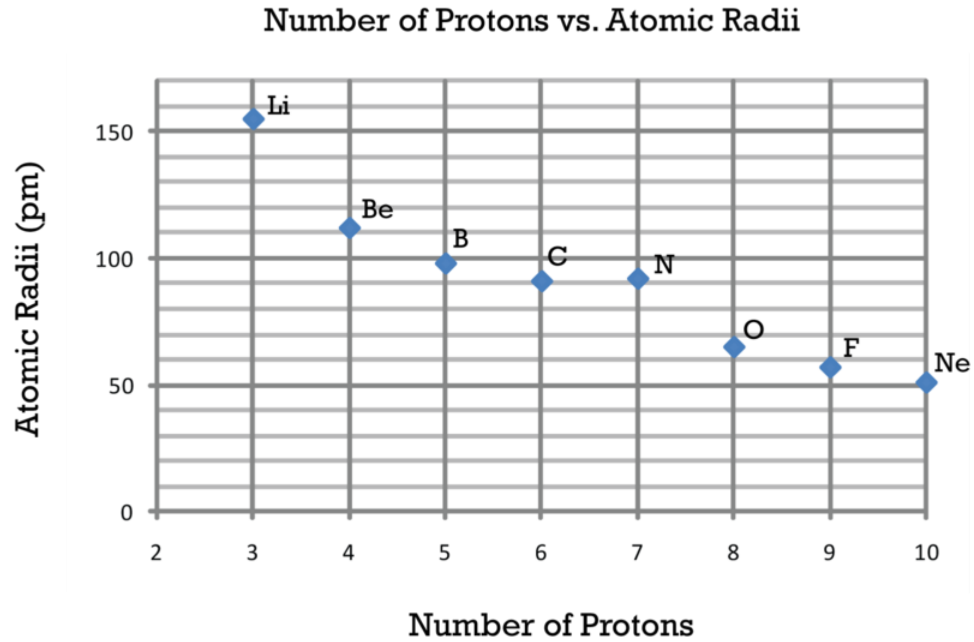
In order to determine the trend for the periods, we need to look at the number of protons (nuclear charge), the number of energy levels, and the shielding effect. For a row in the periodic table, the atomic number still increases (as it did for the groups), and thus the number of protons would increase. For a given period, however, we find that the outermost energy level does not change as the number of electrons increases. In period 2, for example, each additional electron goes into the second energy level, so the total number of energy levels does not go up. **Table** 1.2 shows the electron configuration for the elements in period 2.

TABLE 1.2: Electron Configurations for Elements in Period 2

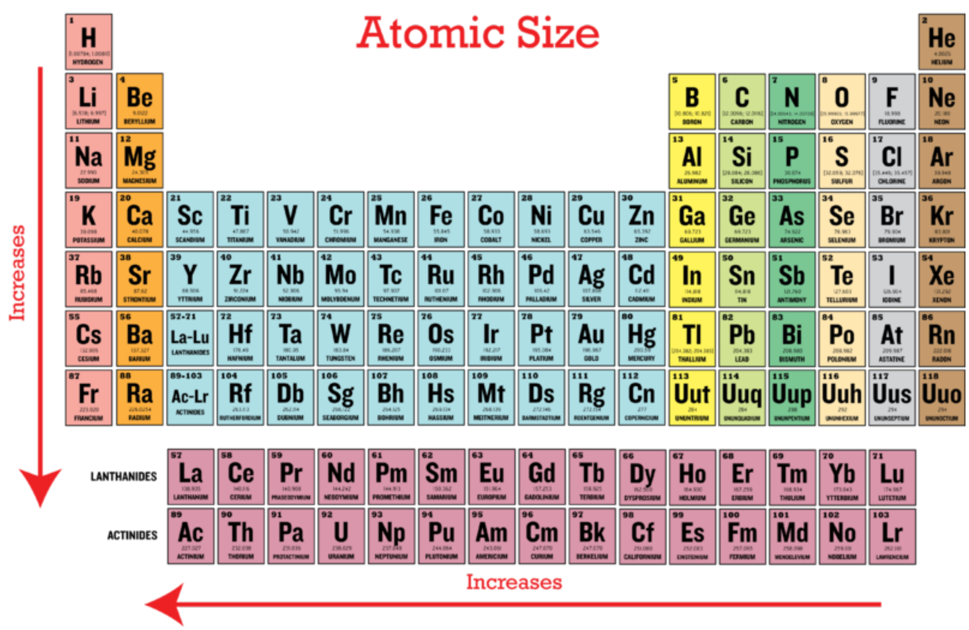
Element	Number of Protons	Electron Configuration
Lithium (Li)	3	$1s^2 2s^1$
Beryllium (Be)	4	$1s^2 2s^2$
Boron (B)	5	$1s^2 2s^2 2p^1$
Carbon (C)	6	$1s^2 2s^2 2p^2$
Nitrogen (N)	7	$1s^2 2s^2 2p^3$
Oxygen (O)	8	$1s^2 2s^2 2p^4$
Fluorine (F)	9	$1s^2 2s^2 2p^5$

Looking at the elements in period 2, the number of protons increases from three (for lithium) to nine (for fluorine). Therefore, the nuclear charge increases across a period. Meanwhile, the number of energy levels occupied by the electrons remains the same. How will this affect the radius? We know that every one of the elements in this period has two core electrons in the inner energy level ($n = 1$). The core electrons shield the outer electrons from the charge of the nucleus. Since the number of protons attracting the outer electrons increases while the shielding remains the same, the valence electrons are pulled closer to the nucleus, making the atom smaller.

Consider the elements lithium, beryllium, and fluorine from period 2. With lithium, the two core electrons will shield the one valence electron from three protons. Beryllium has four protons being shielded by the $1s^2$ electrons. For fluorine, there are nine protons and nine electrons. All three of these elements have the same core electrons: the $1s^2$ electrons. As the number of protons increases, the nuclear charge increases. With an increase in nuclear charge, there is an increase in the pull between the protons and the outer level, pulling the outer electrons toward the nucleus. The amount of shielding from the nucleus does not increase because the number of core electrons remains the same. The net result is that the atomic size decreases going across the row. In the graph below, the values are shown for the atomic radii for period 2.

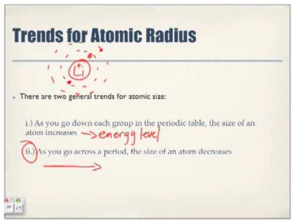


Let's add this new trend to the periodic table. In the diagram below, you will notice that the trend arrow for the period shows the atomic radii increase going from right to left, which is the equivalent to saying that the atomic radii decrease from left to right.



Considering these two trends, you will recognize that the largest atom, francium (atomic number 87), is at the bottom left-hand corner of the periodic table, while the smallest atom, helium (atomic number 2) is at the top right-hand corner of the table.

For an introduction to the electronic organization of the periodic table **(1c)**, see http://www.youtube.com/watch?v=35cWAxtHUGw (4:20).



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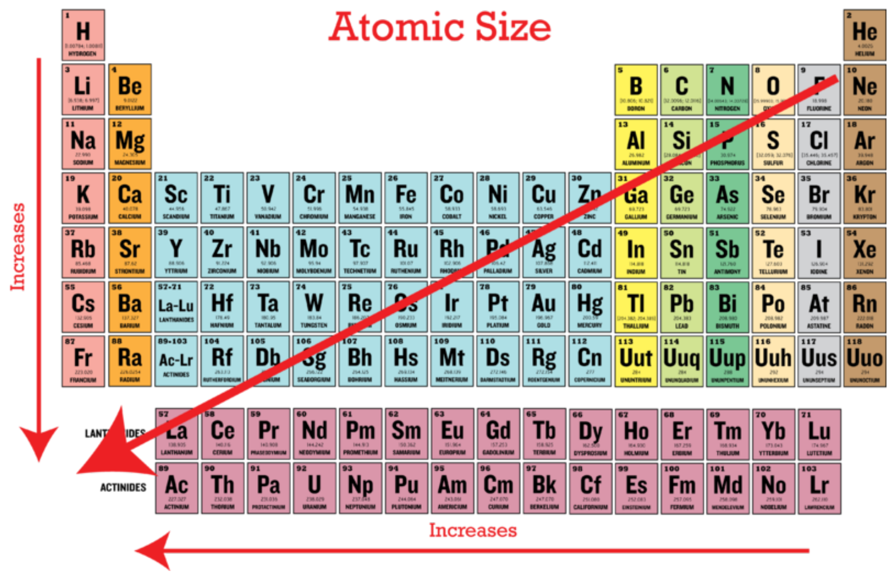
Atomic Radii of Transition Elements

The general trend for atomic radii in the periodic table would look similar to that illustrated in the diagram below. The elements with the smallest atomic radii are found in the upper right; those with the largest atomic radii are found in the lower left.



Until now, we have worked solely with the main group elements. Let's consider how three factors affecting atomic size affect transition metals. The first row of the transition metals all contain electrons in the 3*d* sublevel and are referred to as the 3*d* metals. **Table** 1.3 shows the electron configuration for the ten elements in this row. The number of protons is increasing, so the nuclear charge is increasing.

TABLE 1.3: **Electron Configuration for 3**

Element	Number of Protons	Electron Configuration
Scandium (Sc)	21	$[Ar]3d^14s^2$
Titanium (Ti)	22	$[Ar]3d^24s^2$
Vanadium (V)	23	$[Ar]3d^34s^2$
Chromium (Cr)	24	$[Ar]3d^54s^1$
Manganese (Mn)	25	$[Ar]3d^54s^2$
Iron (Fe)	26	$[Ar]3d^64s^2$
Cobalt (Co)	27	$[Ar]3d^74s^2$
Nickel (Ni)	28	$[Ar]3d^84s^2$
Copper (Cu)	29	$[Ar]3d^{10}4s^1$
Zinc (Zn)	30	$[Ar]3d^{10}4s^2$

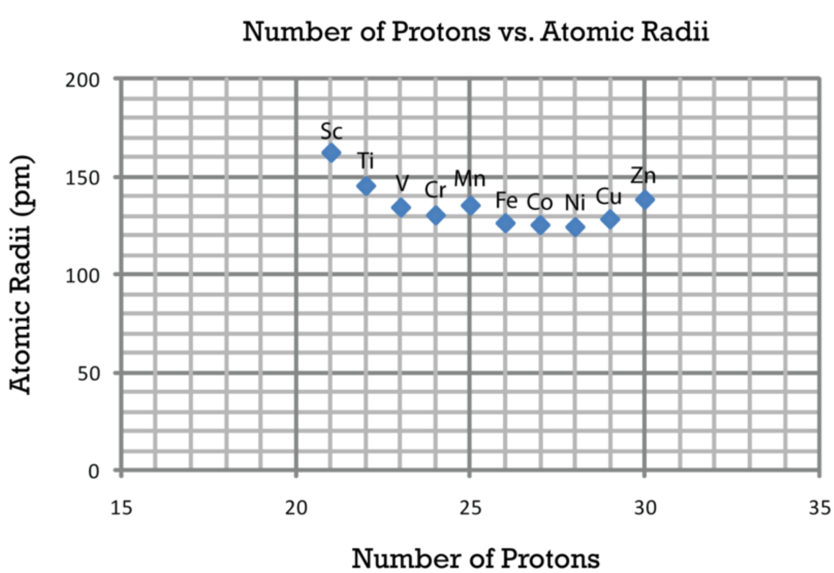
You may notice that some of these configurations are not what you would expect based on the information presented so far. Both chromium and copper have one of the 4*s* electrons moved to a 3*d* orbital. A simplified explanation for these unusual electron configurations is that the *d* sub-level is particularly stable when it is half-full (5 electrons) or completely full (10 electrons). Since the 4*s* and 3*d* orbitals are close in energy, this added stabilization is enough to change the location of one valence electron.

TABLE 1.4: Atomic Radii for 3d Metals

Element	Atomic Radii (pm)
Scandium (Sc)	164
Titanium (Ti)	147
Vanadium (V)	135
Chromium (Cr)	129
Manganese (Mn)	137
Iron (Fe)	126
Cobalt (Co)	125
Nickel (Ni)	125
Copper (Cu)	128
Zinc (Zn)	137

Table 1.4 lists the atomic radii for the first row of the transition metals. It can be seen from this table that the period trend in atomic radii is not followed as closely by the transition metals. Since we are adding electrons to the 3*d* orbitals, we are actually adding to the core electrons and *not* to the valence orbitals. Although the nuclear charge is going up, the shielding is also increasing with each added electron. Because of this, there is less atomic contraction throughout the transition metals.

The graph of the number of protons versus the atomic radii for the 3*d* metals is shown below. Compared to the same graph for the elements in period 2, the graph for transition metals shows the trend for atomic radii is not as straightforward.



Lesson Summary

- Atomic size is the distance from the nucleus to the valence shell.

- Atomic size is difficult to measure because it has no definite boundary.
- Atomic radius is a more definite and measurable way of defining atomic size. It is half the distance from the center of one atom to the center of another atom in a homonuclear diatomic molecule.
- There are three factors that help in the prediction of the trends in the periodic table: number of protons in the nucleus, number of energy levels, and the shielding effect.
- The atomic radii increase from top to the bottom in any group.
- The atomic radii decrease from left to right across a period.
- This trend is not as systematic for the transition metals because other factors come into play.

Review Questions

1. Why is the atomic size considered to have "no definite boundary"?
2. How is atomic size measured?
    a. using a spectrophotometer
    b. using a tiny ruler (called a nano ruler)
    c. indirectly
    d. directly
3. Which of the following would be smaller: indium or gallium?
4. Which of the following would be smaller: potassium or cesium?
5. Which of the following would be smaller: titanium or polonium?
6. Explain why iodine is larger than bromine.
7. What are three factors that affect atomic size?
8. Which of the following would have the largest atomic radius?
    a. Si
    b. C
    c. Sn
    d. Pb
9. Which of the following would have the smallest atomic radius?
    a. $1s^2 2s^2$
    b. $1s^2 2s^2 2p^6 3s^1$
    c. $1s^2$
    d. $1s^1$
10. Arrange the following in order of increasing atomic radius: Tl, B, Ga, Al, In.
11. Arrange the following in order of increasing atomic radius: Ga, Sn, C.
12. Which of the following would be larger: Rb or Sn?
13. Which of the following would be larger: Ca or As?
14. Describe the trend for the atomic size of elements in a row in the periodic table.
15. Which of the following would have the largest atomic radius?
    a. Sr
    b. Sn
    c. Rb
    d. In
16. Which of the following would have the smallest atomic radius?
    a. K
    b. Kr
    c. Ga

d. Ge

17. Arrange the following in order of decreasing atomic radius: Ba, Tl, Se, Bi, Cs.