Excerpted from the Prentice Hall Book Chemistry by Antony C. Wilbraham, 5th Edition, (c) 2000

This explains material that we covered in class. Two pages are missing because they cover material that we do not need to know.

section 14.2

objectives

- Interpret group trends in atomic radii, ionic radii, ionization energies, and electronegativities
- Interpret period trends in atomic radii, ionic radii, ionization energies, and electronegativities

key terms

- atomic radius
- ionization energy
- electronegativity

PERIODIC TRENDS

Have you ever noticed physical similarities between relatives at a family reunion? The relatives may have similar-shaped noses or faces, or have lots of freckles. These characteristics generally indicate a relationship among the family members. As you know, the elements also belong to families—chemical families. **What trends in physical and chemical properties exist among the families and periods of the periodic table?**

Trends in Atomic Size

You know from the quantum mechanical model, which you read about in Chapter 13, that an atom does not have a sharply defined boundary that sets the limit of its size. Therefore, the radius of an atom cannot be measured directly. There are, however, several ways to estimate the relative sizes of atoms. If the atoms are in a solid crystalline structure, a technique called x-ray diffraction can provide an estimate of the distance between the nuclei. For elements that exist as diatomic molecules, the distance between the nuclei of the atoms bonded in the molecule can be estimated. The **atomic radius** is one-half of the distance between the nuclei of two like atoms in a diatomic molecule. Look at **Figure 14.7,** which shows the distance between the nuclei in the diatomic molecules of seven elements. The separation between the nuclei in a diatomic bromine molecule (Br_2) is 228 pm (1 pm = 1 picometer = 1×10^{-12} m). As you can see, because the atomic radius is one-half the distance between the nuclei, a value of 114 pm (228/2) is assigned as the radius of the bromine atom. **Figure 14.8** shows atomic radii for most of the representative elements. Remember, the atomic radius of an element indicates its relative size.

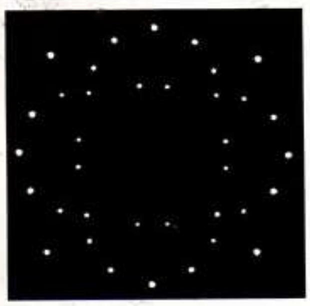


Figure 14.6
Analysis of this x-ray diffraction pattern of NaCl will reveal the distance between the two nuclei in the crystalline structure.

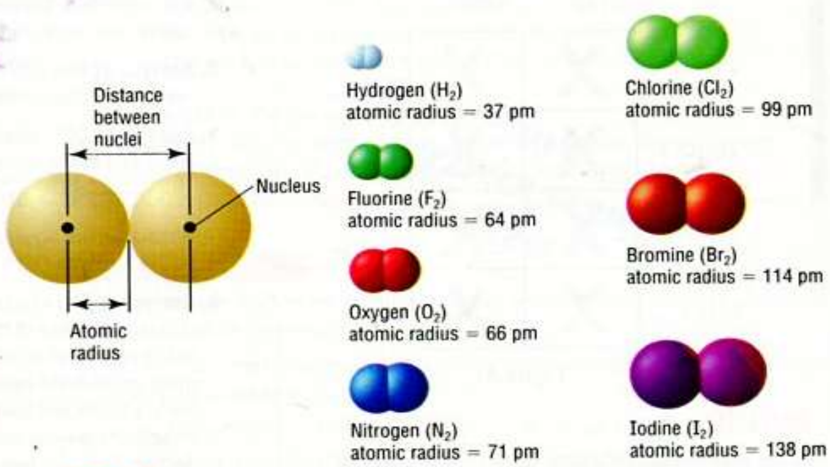


Figure 14.7
Seven elements exist as diatomic molecules. In the bromine molecule (Br_2), the distance between the nuclei is 228 pm and the atomic radius is 114 pm. What is the atomic radius, in meters, of a bromine atom? What is the diameter, in nanometers?

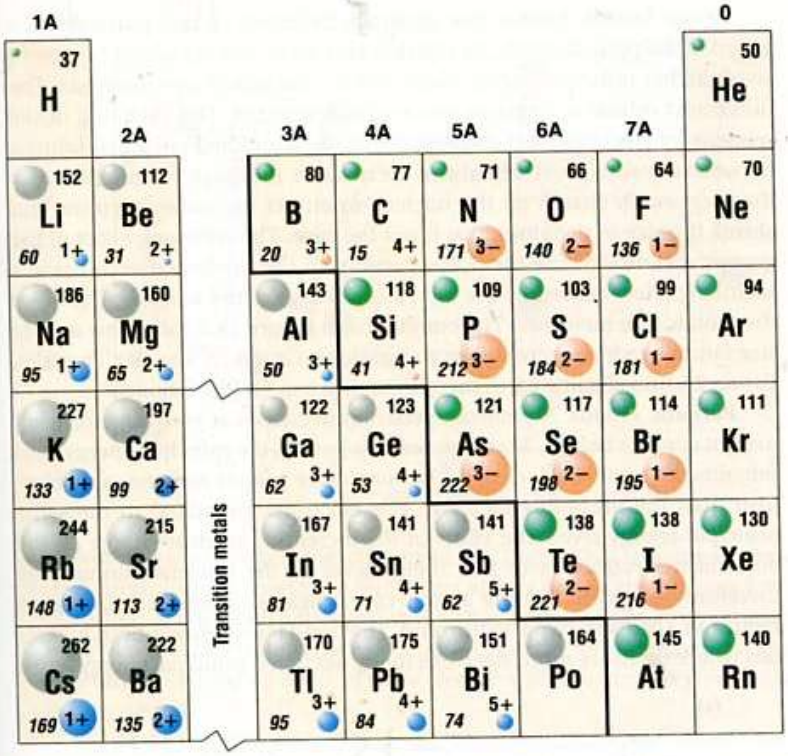
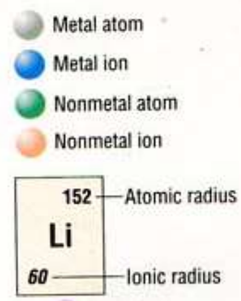


Figure 14.8

Atomic and ionic radii of the representative elements are given here in picometers. Transition metals are omitted from the figure because they show many exceptions to the general trend.



MINI LAB

Periodic Trends in Atomic Radii

PURPOSE

To graph ionic radius versus atomic number for the representative elements in periods 2–5 and to examine the graph for periodic and group trends.

MATERIALS

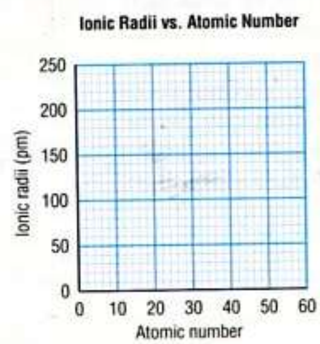
- graph paper
- pencil

PROCEDURE

Use the information presented in **Figure 14.8** to plot ionic radius versus atomic number.

ANALYSIS AND CONCLUSIONS

1. Comment on the sizes of cations compared with the sizes of anions. How do these sizes compare with those of the atoms?
2. Are the general trends shown for periods 2, 3, 4, and 5 similar or different?



3. Describe and explain the shape of each period's portion of the graph.
4. How do the radii for anions and cations change as you go down a group? Explain.

Group Trends Atomic size generally increases as you move down a group of the periodic table. As you descend, electrons are added to successively higher principal energy levels and the nuclear charge increases. The outermost orbital is larger as you move downward. The shielding of the nucleus by electrons also increases with the additional occupied orbitals between the outermost orbital and the nucleus. Although you might expect the increase in charge on the nucleus to attract the outer electrons and shrink the size of the atom, this is not the case. The enlarging effect of the greater distance of the outer electrons from the nucleus overcomes the shrinking effect caused by the increasing charge of the nucleus. Therefore the atomic size increases. The bar graphs in **Figure 14.9** show how atomic size (atomic radius) increases as you go down Group 1A (the alkali metals), Group 2A (the alkaline earth metals), and Group 7A (the halogens).

Periodic Trends Atomic size generally decreases as you move from left to right across a period. As you go across a period, the principal energy level remains the same. Each element has one more proton and one more electron than the preceding element. The electrons are added to the same principal energy level. The effect of the increasing nuclear charge on the outermost electrons is to pull them closer to the nucleus. Atomic size therefore decreases. Plotting atomic radius against atomic number, as in **Figure 14.10**, reveals a periodic trend. The trend is less pronounced in periods where there are more electrons in the occupied principal energy levels

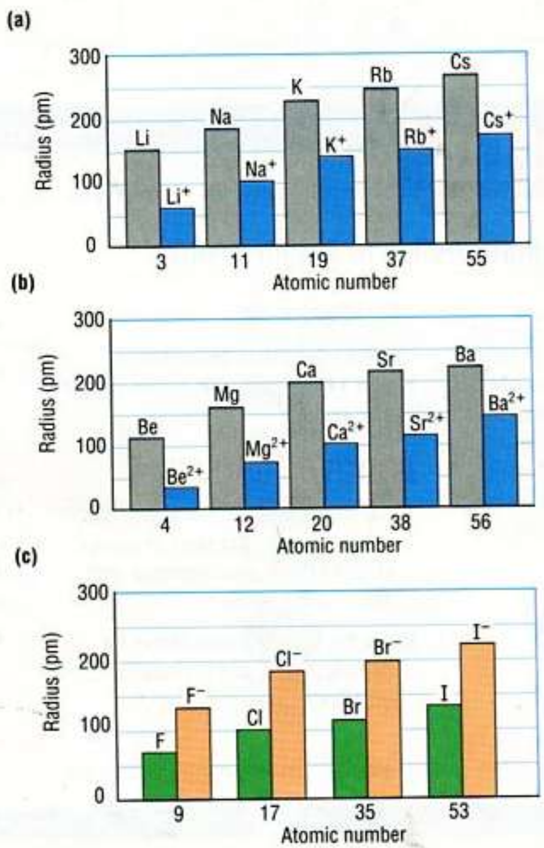


Figure 14.9

*The atomic radii of **(a)** Group 1A, **(b)** Group 2A, and **(c)** Group 7A elements increase as you go down the group, or as the atomic number increases. The ions (cations) in **(a)** and **(b)** are smaller than the neutral atoms. In contrast, the ions (anions) in **(c)** are larger than the neutral atoms. Why is a potassium atom larger than a potassium ion?*

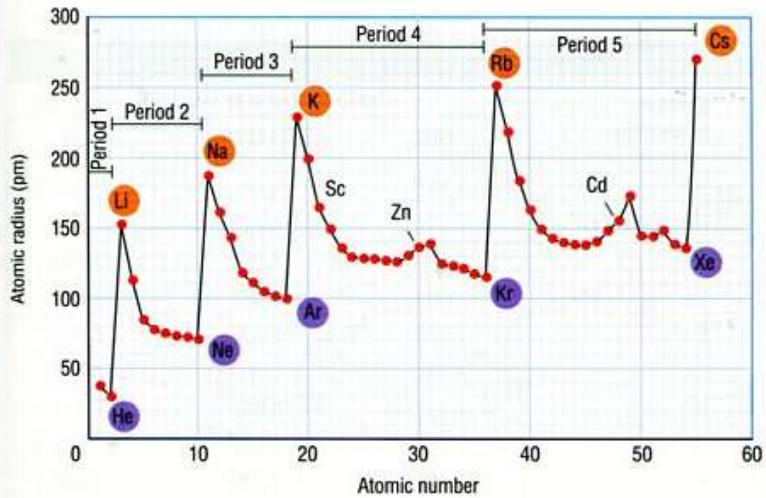


Figure 14.10
This graph of atomic radius versus atomic number shows a periodic trend.

between the nucleus and the outermost electrons. This is because these inner electrons help shield the outermost electrons and the nucleus from each other. In any given period, however, the number of electrons between the nucleus and the outermost electrons is the same for all elements. Consequently, the shielding effect of these electrons on the nucleus is constant within a period.

Figure 14.11 summarizes the group and period trends in atomic size. How would you describe the atomic radius of a period-2 alkaline earth metal compared with that of a period-4 alkaline earth metal?

Trends in Ionization Energy

When an atom gains or loses an electron, it becomes an ion. The energy required to overcome the attraction of the nuclear charge and remove an electron from a gaseous atom is called the **ionization energy.** Removing one electron results in the formation of a positive ion with a 1+ charge.

$$Na(g) \longrightarrow Na^{+}(g) + e^{-}$$

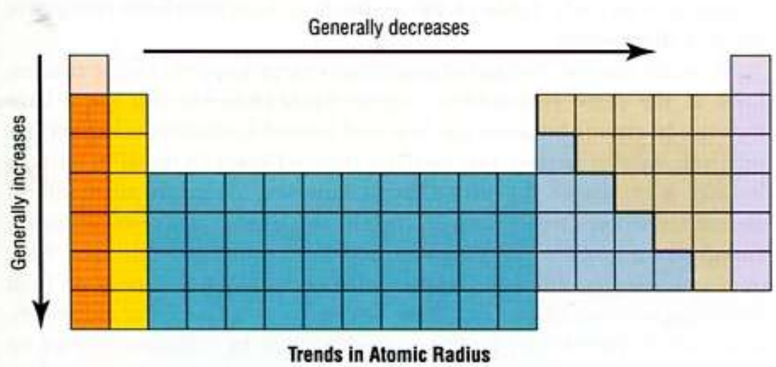


Figure 14.11
Atomic radii generally decrease across periods and increase down groups. Which has the larger atomic radius within the same period: a halogen or an alkali metal?

Link TO ASTRONOMY

The Big Bang

Astronomers have evidence that the material universe began with an event of indescribable energy. At the moment of this event, called the Big Bang, the

temperature was many billions of degrees. As a result of the Big Bang, the elements formed. Neutrons, protons, and electrons may have formed within 10^{-4} second after the Big Bang, and the lightest nuclei formed within 3 minutes. At this time, the temperature was still probably 70 times the temperature of Earth's sun. Matter was in the form of plasma, a sea of positive nuclei and negative electrons. It took an estimated 500 000 years for electrons and nuclei to cool enough to form atoms. According to the Big Bang theory, planet Earth, with its wealth of chemical elements, is the debris of supernova explosions. It is this literal star dust that contains all the elements essential for life.

Table 14.1

Ionization Energies of the First 20 Elements

Symbol of element	Ionization energy (kJ/mol) First	Second	Third
H	1 312		
He (noble gas)	2 371	5 247	
Li	520	7 297	11 810
Be	900	1 757	14 840
B	800	2 430	3 659
C	1 086	2 352	4 619
N	1 402	2 857	4 577
O	1 314	3 391	5 301
F	1 681	3 375	6 045
Ne (noble gas)	2 080	3 963	6 276
Na	495.8	4 565	6 912
Mg	737.6	1 450	7 732
Al	577.4	1 816	2 744
Si	786.2	1 577	3 229
P	1 012	1 896	2 910
S	999.6	2 260	3 380
Cl	1 255	2 297	3 850
Ar (noble gas)	1 520	2 665	3 947
K	418.8	3 069	4 600
Ca	589.5	1 146	4 941

The energy required to remove this first outermost electron is called the first ionization energy. To remove the outermost electron from the gaseous 1+ ion requires an amount of energy called the second ionization energy, and so forth. **Table 14.1** gives the first three ionization energies of the first 20 elements.

You can use the concept of ionization energy to predict ionic charges. Look at the three Group 1A metals in **Table 14.1.** Do you see a large increase in energy between the first and second ionization energies? It is relatively easy to remove one electron from a Group 1A metal to form an ion with a 1+ charge. It is very difficult, however, to remove an additional electron. For the three Group 2A metals, the large increase in ionization energy occurs between the second and third ionization energies. What does this tell you about the relative ease of removing one electron from these metals? Two electrons? Three electrons? You know that aluminum, in Group 3A, forms a 3+ ion. The large increase in ionization energy for aluminum occurs after the third electron is removed.

Group Trends As you can see from **Table 14.1,** the first ionization energy generally decreases as you move down a group of the periodic table. This is because the size of the atoms increases as you descend, so the

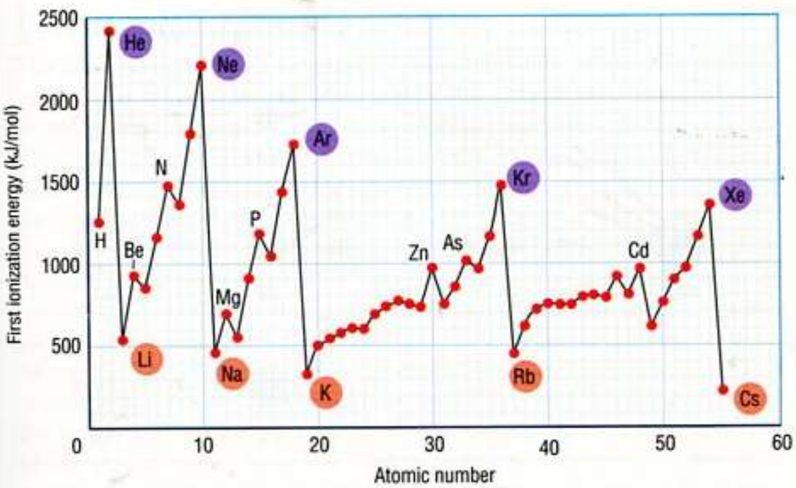


Figure 14.12

This graph of first ionization energy versus atomic number shows a periodic trend. Notice the ease with which Group 1A elements are ionized and the difficulty of ionizing noble gases. What is the group trend for the noble gases?

outermost electron is farther from the nucleus. The outermost electron should be more easily removed, and the element should have a lower ionization energy.

Periodic Trends For the representative elements, the first ionization energy generally increases as you move from left to right across a period. See **Figure 14.12**. The nuclear charge increases and the shielding effect is constant as you move across. A greater attraction of the nucleus for the electron leads to the increase in ionization energy.

Figure 14.13 summarizes the group and periodic trends in first ionization energies. Which element in Group 6A has the highest first ionization energy? In period 2?

Trends in Ionic Size

The atoms of metallic elements have low ionization energies. They form positive ions easily. By contrast, the atoms of nonmetallic elements readily form negative ions. Let's look at how the loss or gain of electrons affects the size of the ion formed.

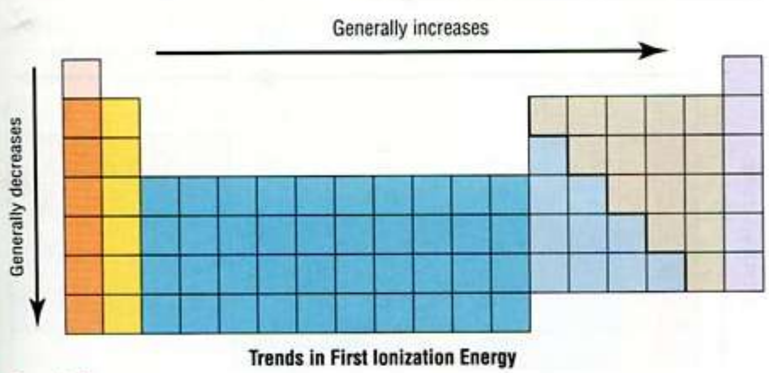


Figure 14.13

First ionization energies generally increase across periods and decrease down groups.

Trends in Electronegativity

The **electronegativity** of an element is the tendency for the atoms of the element to attract electrons when they are chemically combined with atoms of another element. Electronegativities have been calculated for the elements and are expressed in arbitrary units on the Pauling electronegativity scale. This numerical scale is based on a number of factors, including the ionization energies of the elements.

The electronegativities of selected elements, arranged in the form of the periodic table, are presented in **Table 14.2.** Note that the noble gases are omitted because they do not form many compounds. With their exception, each element is assigned an electronegativity number in units of Paulings. As you can see, electronegativity generally decreases as you move down a group. As you go across a period from left to right, the electronegativity of the representative elements increases. The metallic elements at the far left of the periodic table have low electronegativities. By contrast, the nonmetallic elements at the far right (excluding the noble gases) have high electronegativities. The trends in electronegativities among the transition metals are not so regular; these numbers are not included in the table.

The electronegativity of cesium, the least electronegative element, is 0.7; the electronegativity of fluorine, the most electronegative element, is 4.0. Because fluorine has such a strong tendency to attract electrons, when it is chemically bonded to any other element it either attracts the shared electrons or forms a negative ion. In contrast, cesium has the least tendency to attract electrons. It loses the electron "tug-of-war" and forms a positive ion.

As you will learn in the following chapters on ionic bonding and covalent bonding, electronegativity values help predict the type of bonding that can exist between atoms in compounds.

Table 14.2

Electronegativity Values for Atoms of Selected Elements

H 2.1						
Li 1.0	**Be** 1.5	**B** 2.0	**C** 2.5	**N** 3.0	**O** 3.5	**F** 4.0
Na 0.9	**Mg** 1.2	**Al** 1.5	**Si** 1.8	**P** 2.1	**S** 2.5	**Cl** 3.0
K 0.8	**Ca** 1.0	**Ga** 1.6	**Ge** 1.8	**As** 2.0	**Se** 2.4	**Br** 2.8
Rb 0.8	**Sr** 1.0	**In** 1.7	**Sn** 1.8	**Sb** 1.9	**Te** 2.1	**I** 2.5
Cs 0.7	**Ba** 0.9	**Tl** 1.8	**Pb** 1.9	**Bi** 1.9		

LINK TO MUSIC

Newlands's Octaves

Mendeleev's publication of his first periodic table in 1869 was far from the first attempt to organize the elements according to their properties. In 1863, John Newlands (1838–1898), an English chemist, arranged the elements in order of increasing atomic masses. He noted that the properties of the elements repeated when the elements were arranged by increasing atomic mass in groups of eight. For example, the chemical properties of lithium and sodium are very similar. Newlands referred to his arrangement as the law of octaves. This is similar to the musical scale, which repeats every eighth tone. Although the law of octaves fails for elements beyond calcium, Newlands's work was a step in the right direction in the classification of the elements.

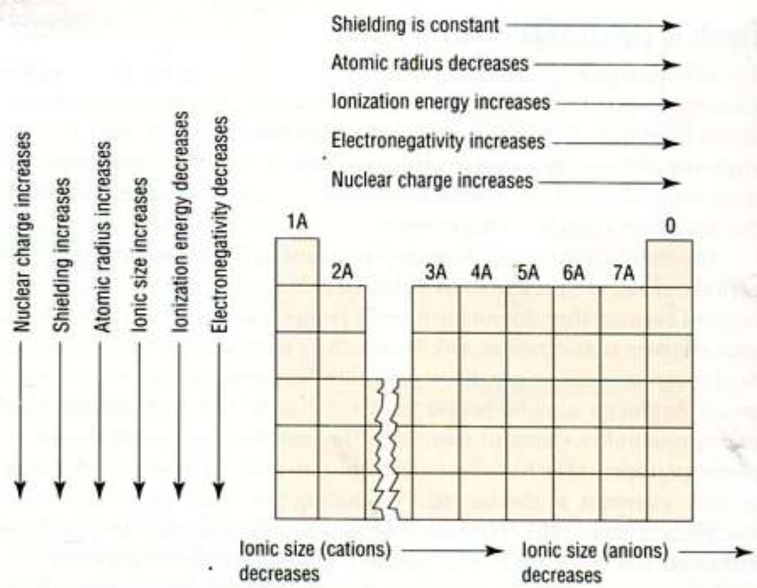


Figure 14.16
Periodic trends vary as you move across and down the periodic table. Properties that show periodic trends include atomic radius, ionic size, ionization energy, nuclear charge, shielding effect, and electronegativity of the elements.

Summary of Periodic Trends

You have now seen that a number of periodic trends exist among the elements and that these trends can be explained by looking at variations in atomic structure. Remember, trends occur within groups and within periods. **Figure 14.16** summarizes the trends in atomic radius, ionization energy, ionic size, and electronegativity that you have just learned about. Which is the only property that shows a decreasing trend as you move from left to right across the periodic table?

section review 14.2

6. For which of these properties does lithium have a larger value than potassium?

a. first ionization energy

b. atomic radius

c. electronegativity

d. ionic radius

7. Arrange these elements in order of decreasing atomic size: sulfur, chlorine, aluminum, and sodium. Does your arrangement demonstrate a periodic trend or a group trend?

8. How does the ionic radius of a typical anion compare with the radius for the corresponding neutral atom?

9. Which element in each pair has the larger ionization energy?

a. sodium, potassium

b. magnesium, phosphorus

Chem ASAP! Assessment 14.2 Check your understanding of the important ideas and concepts in Section 14.2.