# 6.2 Periodic Trends — Regular Changes in Elemental Properties

## Warm Up

1. What attractive force is responsible for holding the cloud of electrons in place in atoms?
______________________________
2. What effect would a strengthening of that force have on the sizes of atoms?
______________________________
3. What might cause a strengthening of that force?
______________________________
4. What might contribute to a weakening of that force?
______________________________

### Periodic Trends

All of the chemical and physical behaviour of the elements is really a result of their electron configurations. In the last section, we discussed how similar outer-electron configurations explained the similar properties of elements within the chemical families of the periodic table. We will now concentrate on a second key concept associated with the organization of the elements in the table.

As we move across a period or down a chemical family, there are regular changes in elemental properties.

These consistent and predictable changes in elemental properties are known as **periodic trends.** Identifying and explaining them can be a great benefit when describing chemical interactions between atoms.

### Periodic Trends in Atomic Size

In the quantum mechanical model, the outer boundaries of an atom depend on the size of a charge cloud in which electrons spend approximately 90% of their time. This means that the sizes of individual atoms cannot be determined in the same way as we might, for example, measure the size of objects such as marbles or grapefruits. In these cases, the object's boundaries are hard and definite, unlike those of atoms.

However, we can estimate the sizes of atoms based on how close they get to one another when bonds form between them. This can be done by measuring the distance between the nuclei of identical adjacent atoms in an element sample and dividing that distance by two.

The two common definitions of atomic size stem from the classification of elements into metals and non-metals. Non-metal elements commonly occur as diatomic molecules. For these elements, atomic size is defined as the **covalent radius**, which represents one half the distance between the two identical nuclei in the molecule.

Although the nature of bonding between metal atoms is beyond the scope of this course, the process of estimating their atomic size is very similar to that for non-metals. Metal atoms pack together in the solid state to form a crystal lattice much like ions in a

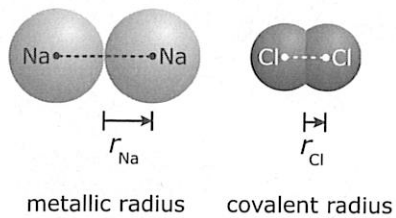


**Figure 6.2.1** *Estimating atomic size involves determining bond length.*

salt. In a sample of a metal element, half the distance between the identical nuclei of adjacent metal atoms in the crystal is defined as the **metallic radius**.

Both of the above techniques for estimating atomic size involve determining half the bond length between identical atoms in element samples as shown in Figure 6.2.1.

## Factors Influencing Atomic and Ionic Size

Let's consider for a moment what might influence the size of an atom. Because an atom's volume is really the result of a cloud of electrons, this question is really the same as asking: What affects the size of an atom's electron cloud? Seen from that perspective, it makes sense that two opposing factors influence atomic size:

1. The number of energy levels present. As the number of energy levels (n) increases, the probability that outer electrons will spend more time further from the nucleus increases and so the atoms become larger.
2. The amount of nuclear charge "felt" or "seen" by the outer electrons. As this effective nuclear charge increases, the outer electron cloud is pulled closer to the nucleus and the atom becomes smaller. Chemists use the symbol "$Z_{eff}$" to refer to the effective nuclear charge.

Of these two opposing factors, the one that predominates as we move across a period or down a chemical family will most influence how the sizes of those atoms change.

Consider Figure 6.2.2, showing the relative atomic radii of the elements. The **atomic radius** of an atom is the distance from the nucleus to the boundary of the surrounding cloud of electrons. The actual sizes range from the smallest, helium, at 31 pm to the largest, cesium, at 270 pm. How those sizes change across periods and down families shows a clear pattern.

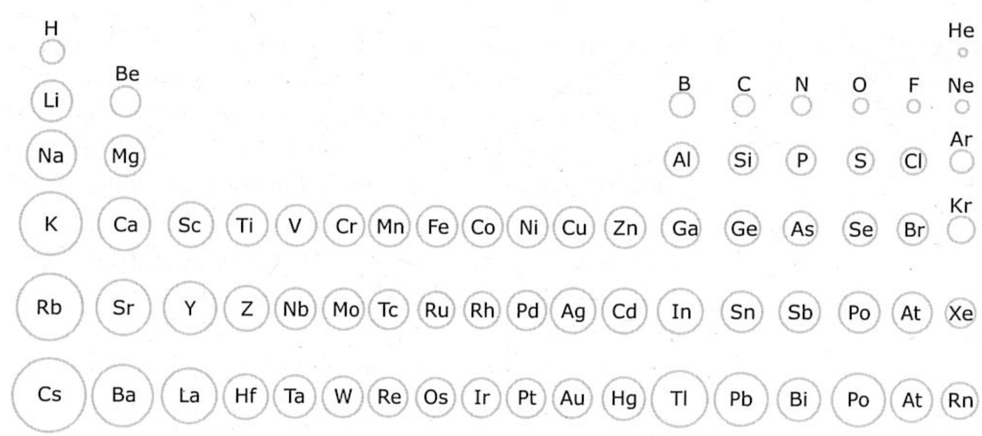


**Figure 6.2.2** *Periodic table showing atomic radii*


 ISBN 978-0-9864778-2-9

Two definite periodic trends are evident:

As we move down a family or group, the sizes of the atoms generally increase.
As we move across a period, the sizes of the atoms generally decrease.

As we move down a chemical family and the value of *n* increases for each new element, a new inner electron level is added between the nucleus and the atom's outer electron cloud. Even though the positive charge on the nucleus is increasing, each additional inner level of electrons *effectively shields* the outer cloud from the attractive force of that nucleus, and the electron cloud increases in size. The additional inner electron clouds also repel each other, which further contributes to the increasing size of atoms as the group as we move lower in the table. This clearly shows that as the number of energy levels present in the atom increases, the size of the atom also increases.

As we move left-to-right across a period, the electrons are being added to the same outer level. This means that the level of shielding by the inner electrons remains the same. It also means that the added electrons are *ineffective at shielding each other* from the increasing positive charge on the nucleus. The result is that $Z_{eff}$ on those outer electrons increases and the charge cloud is pulled closer and closer to the nucleus so the size of the atom decreases.

Consider Figure 6.2.3, which shows the periodic changes in atomic radii as we move from period 1 through period 6. The alkali metals are the largest members of each period and then the radii generally decrease to a minimum at the noble gases. Down each family, the atomic radii generally increase.

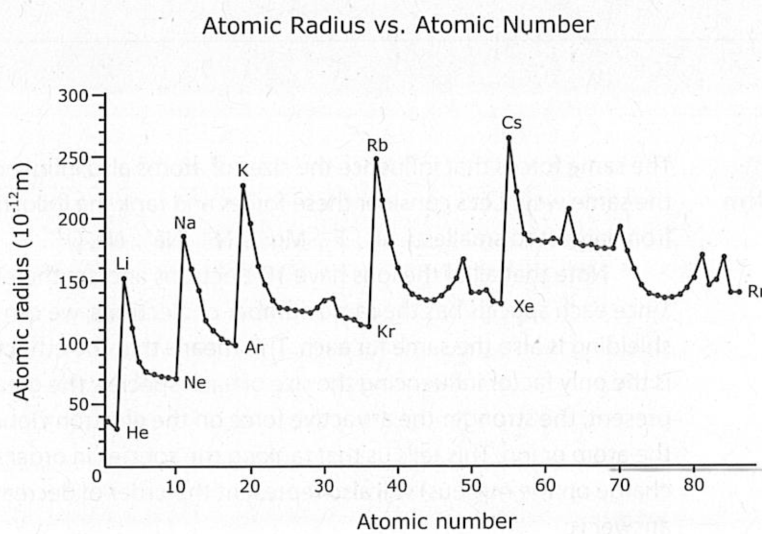


**Figure 6.2.3** *Periodic changes in atomic radii as we move from period 1 through period 6*

There are exceptions to the general trends stated above and they can be explained by considering the electron configurations of the atoms and the electron sublevels being filled in each case.

For example, as we move across period 4, we start filling the 4th energy level at potassium and the atomic sizes shrink as expected for the first two elements. But when we arrive at the transition elements and begin filling the 3d sublevel, the sizes remain relatively constant as we move across to zinc.

To understand this, remember that $n = 3$ electrons spend most of their time *closer to the nucleus* than those electrons in the $n = 4$ charge cloud. We would therefore expect electrons in the 3d sublevel to be capable of shielding the outer 4s electrons from the increasing nuclear charge as we move across the period. This would reduce $Z_{eff}$. Consider the elements vanadium and zinc. The electron configuration for V is $[Ar]3d^3 4s^2$ and the electron configuration for Zn is $[Ar]3d^{10} 4s^2$. Even though zinc has a nucleus with 7 more protons than vanadium, the extra shielding provided by zinc's 10 electrons in the 3d sublevel is such that zinc's atomic radius is equal to vanadium's!

This shows how effective inner electrons can be at shielding outer electrons from the "pull" of an increasingly positive nucleus and significantly influence atomic size. A number of other examples can be found throughout the periodic table.

## Quick Check

1. Which of the two opposing factors that influence atomic size predominates as we move across a chemical period? What is the general result?

___

2. Which of the two opposing factors that influence atomic size predominates as we move down a chemical family? What is the general result?

___

3. In general, is "effective shielding" most evident going across a period or down a family? How can you tell?

___

## Forces Affecting Ion Size

The same forces that influence the sizes of atoms also influence the sizes of ions and in the same way. Let's consider these forces and rank the following species in order of size from largest to smallest: $Al^3$, $F^-$, $Mg^{2+}$, $N^{3-}$, $Na^+$, Ne, $O^{2-}$.

Note that all of the ions have 10 electrons and are therefore isoelectronic with neon. Since each species has the same number of electrons, we can assume that the amount of shielding is also the same for each. This means that the attractive force from each nucleus is the only factor influencing the size of each species. The greater the number of protons present, the stronger the attractive force on the electron cloud and therefore the smaller the atom or ion. This tells us that ranking the species in order of atomic number (positive charge on the nucleus) will also represent the order of decreasing size. Therefore, the answer is:

$$N^{3-} > O^{2-} > F^- > Ne > Na^+ > Mg^{2+} > Al^{3+}$$

## Periodic Trends in Ionization Energy

**Ionization energy** (*IE*) is defined as the minimum energy required to remove an electron from a gaseous atom or ion. The term is often used to mean the "first" ionization energy ($IE_1$) whereby a neutral atom becomes a $1^+$ cation according to the following equation:

$$\text{atom}\,(g) \; + \; IE_1 \; \rightarrow \; \text{ion}^+\,(g) \; + \; e^-$$

Ionization energy tells us how strongly an atom holds onto its outermost electrons. This is an important property because an element with a low $IE_1$ will be more likely to lose


 ISBN 978-0-9864778-2-9

electrons and form cations during chemical changes. A high $IE_1$ might signal an element's tendency to gain electrons and form anions or perhaps not forms ions at all.

We might expect that a large atom, whose outer electrons are held less tightly, would have a lower $IE_1$ than a smaller atom whose outer electrons are held much more strongly. Said another way, as atomic size decreases, ionization energy should increase. This is, in fact, the general trend, as shown in Figure 6.2.4.

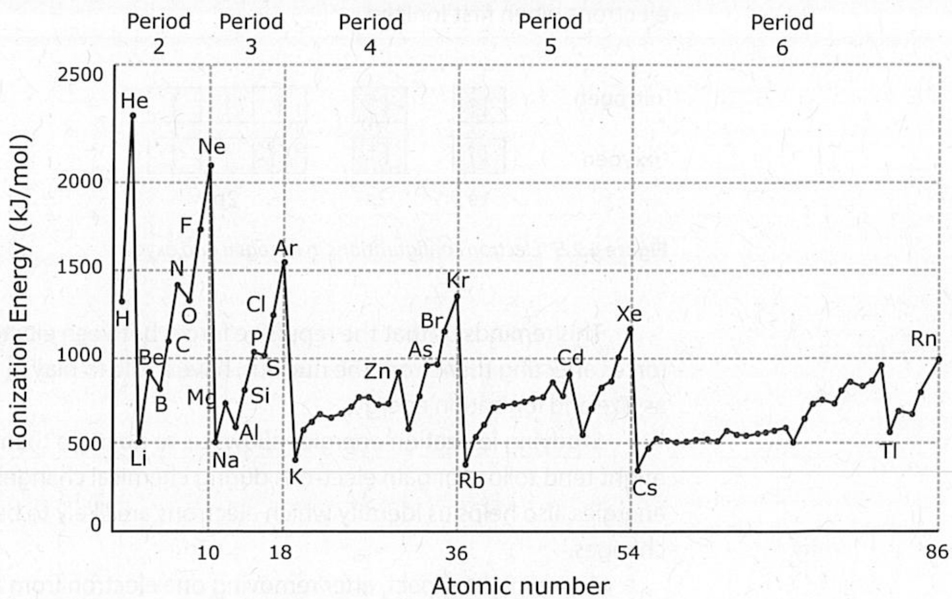


**Figure 6.2.4** *As atomic size decreases, ionization energy increases.*

We can see that the lowest $IE_1$ values are associated with the largest atoms, which are located in the lower left corner of the periodic table. Conversely, the highest $IE_1$ numbers correspond to the smallest atoms, located in the upper right portion of the table.

At the beginning of each period, the largest atoms are the alkali metals, which have the lowest ionization energies. As we progress across the period and the sizes of the atoms decrease, we see a corresponding general increase in ionization energy until we reach the maximum value at each noble gas. At the beginning of the next period, the dramatic drop in ionization energy reflects the significant increase in size of that next alkali metal. As we move down a chemical family, the increase in atomic size results in a general decrease in ionization energy. The periodic trends are clearly evident up to the end of the 6th period.

The diagram shows that lower ionization energies are associated with elements nearer the left side of the periodic table, namely the metals. This tells us that metals generally tend to lose electrons when they are involved in chemical reactions. Non-metals, on the other hand, with relatively high ionization energies, have a tendency to gain or even share electrons rather than lose them. Of course, noble gases do neither of the above.

## Exceptions to Ionization Energy Trends — One Example

As with atomic radii, there are several exceptions to the general trends in ionization energy, which we can explain by analyzing electron configurations. One example of this occurs with nitrogen and oxygen. Even though oxygen is a smaller atom than nitrogen, oxygen has a lower first ionization energy. Nitrogen has a single electron in each of its three 2p orbitals and a half-filled p sublevel that is quite stable. Oxygen, however, has a pair of electrons in one of its 2p orbitals (Figure 6.2.5). The increased electron-electron repulsion associated with that pairing makes it easier for oxygen to lose one of those electrons when first ionized.

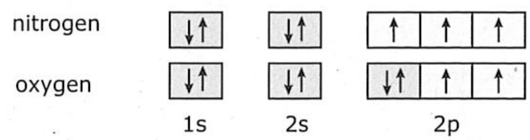


**Figure 6.2.5** *Electron configurations in nitrogen and oxygen*

This reminds us that the repulsive forces between electrons, as well as the attractive forces affecting them from the nucleus, have a role to play in determining properties such as size and ionization energy.

Studying ionization energies allows us to do more than predict which elements might tend to lose or gain electrons during chemical changes. Investigating ionization energies also helps us identify which electrons are likely to be associated with those changes.

As we might expect, after removing one electron from an atom, further ionization energies increase. This occurs because each successive electron removed is being separated from an increasingly positive ion. However, those increases are *not regular*. Whenever the last outer or valence electron is removed, the next ionization requires significantly more energy because inner or "core electrons" are now involved. This can be seen using beryllium as an example. The atom has two valence electrons and the electron configuration is $1s^2 2s^2$. Table 6.2.1 shows the first three ionization energies for beryllium.

**Table 6.2.1** *First Three Ionization Energies of Beryllium*

| Species | Electron Configuration | Ionization Energy (kJ/mol) |
|---|---|---|
| $Be^{o}$ | $1s^2 2s^2$ | $IE_1 = 900$ |
| $Be^{1+}$ | $1s^2 2s^1$ | $IE_2 = 1\,756$ |
| $Be^{2+}$ | $1s^2$ | $IE_3 = 14\,860$ |

After the second (and last valence) electron is removed, the dramatic increase in energy required to remove the third electron reflects the fact that it is an inner or "core" electron. This shows us that core electrons are bound much more tightly to the nucleus, and thus do not take part in chemical reactions. This holds true for all of the elements in the periodic table.

  ISBN 978-0-9864778-2-9

## Sample Problem – Trends in Ionization Energy

Using only the periodic table, rank each of the following alphabetical lists of elements in order of increasing first ionization energies. (a) argon chlorine phosphorus sodium sulphur
(b) antimony arsenic bismuth nitrogen phosphorus

| What to Think about | How to Do It |
|---|---|
| 1. Ionization energy increases left-to-right across a period and moving up a chemical group. | |
| 2. The elements listed in (a) are members of period 3. List the elements in the order they appear from left-to-right in period 3. | Na < P < S < Cl < Ar |
| 3. The elements listed in (b) belong to group 15 of the periodic table. List the elements in the order they appear from bottom-to-top in group 15. | Bi < Sb < As < P < N |

## Practice Problems — Trends in Ionization Energy

1. Using only the periodic table, rank the following alphabetical list of elements in order of decreasing first ionization energy.

   aluminum argon cesium magnesium rubidium silicon sodium sulphur

2. Using the periodic table, write the correct number in the space after each statement below:

   Members of this chemical family have the highest $IE_1$ in their period. ________

   Members of this chemical family have the lowest $IE_1$ in their period. ________

   Members of this chemical period have the highest $IE_1$ in their family. ________

   Members of this chemical period have the lowest $IE_1$ in their family. ________

3. Extension: The nature of the 2s sublevel is such that 2s electrons have a higher probability of being found closer to the nucleus than electrons in the 2p sublevel. Consider this and the following electron configurations:

   beryllium: $1s^2 2s^2$ boron: $1s^2 2s^2 2p^1$

   Suggest a reason why boron's first ionization energy is less than beryllium's, even though boron is a smaller atom.

   ______________________________________________

## An Introduction to Electronegativity

Our discussions so far have focused on the electron configurations, properties, and periodic trends associated with *individual atoms* of the elements. This has been directed towards an eventual understanding of how these atoms behave when they form chemical bonds.

Chemical bonding begins when the valence electrons in a region of space between two atoms are attracted by or "shared" between the adjacent nuclei. Each nucleus exerts an influence on those electrons, which ultimately determine the nature of the resulting bond.

To begin to describe this effect and the nature of the resulting bonds, let's look at an elemental property associated with bonded atoms. It is one of the most important properties in chemical bonding.

**Electronegativity** is defined as the relative ability of a bonded atom to attract shared electrons to itself. Atoms with relatively high electronegativities (EN) tend to pull bonded electrons closer to their nuclei. Atoms with lower EN values have their bonded electrons pulled further away. As we'll see in section 6.3, this will dictate not only the nature of the chemical bonds that form, but also the properties of the compounds containing those bonds.

We might expect that smaller atoms would have higher EN values since their nuclei would be closer to bonded electrons than the nuclei of larger atoms. We might also expect that larger atoms would therefore tend to have lower EN values. This is indeed the case, and because atomic size shows periodic trends, we shouldn't be surprised that electronegativity does as well. In fact, the general trends in electronegativity are similar to those seen in ionization energy.

We can see a clear resemblance to the trends in ionization energy, namely that EN increases going across a period and increases moving up a group (Figure 6.2.6). (The noble gases don't have EN values because they don't generally form chemical bonds.)

Increasing EN

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H 2.1 | | | | | | | | | | | | | | | | | He |
| Li 1.0 | Be 1.5 | | | | | | | | | | | B 2.0 | C 2.5 | N 3.0 | O 3.5 | F 4.0 | Ne |
| Na 0.9 | Mg 1.2 | | | | | | | | | | | Al 1.5 | Si 1.8 | P 2.1 | S 2.5 | Cl 3.0 | Ar |
| K 0.8 | Ca 1.0 | Sc 1.3 | Ti 1.5 | V 1.6 | Cr 1.6 | Mn 1.5 | Fe 1.8 | Co 1.8 | Ni 1.8 | Cu 1.9 | Zn 1.6 | Ga 1.6 | Ge 1.8 | As 2.0 | Se 2.4 | Br 2.8 | Kr |
| Rb 0.8 | Sr 1.0 | Y 1.3 | Zr 1.4 | Nb 1.6 | Mo 1.8 | Tc | Ru 2.2 | Rh 2.2 | Pd 2.2 | Ag 1.9 | Cd 1.7 | In 1.7 | Sn 1.8 | Sb 1.9 | Te 2.1 | I 2.5 | Xe |
| Cs 0.7 | Ba 0.9 | La 1.1 | Hf 1.3 | Ta 1.5 | W 1.7 | Re 1.9 | Os 2.2 | Ir 2.2 | Pt 2.2 | Au 2.4 | Hg 1.9 | Tl 1.8 | Pb 1.8 | Bi 1.9 | Po 2.0 | At 2.2 | Rn |
| Fr 0.7 | Ra 0.9 | Ac 1.1 | | | | | | | | | | | | | | | |

Increasing EN

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ce 1.1 | Pr 1,1 | Nd 1.2 | Pm | Sm 1.2 | Eu 1.2 | Gd 1.1 | Tb 1.2 | Dy 1.2 | Ho 1.2 | Er 1.2 | Tm 1.2 | Yb 1.1 | Lu 1.2 |
| Th 1.3 | Pa 1.5 | U 1.7 | | | | | | | | | | | |

**Figure 6.2.6** *Periodic table showing trends in electronegativity*


 ISBN 978-0-9864778-2-9

The electronegativity values are numbers ranging from a low of 0.7 for cesium to 4.0 for fluorine (Figure 6.2.7). The values were determined by the great American chemist Linus Pauling.

For our purposes, we will only be interested in the relative magnitudes of the numbers.

The trends indicate that metal atoms, which are large with low ionization energies, also have relatively low EN values. Smaller non-metal atoms tend to have higher ionization energies and electronegativities. The consequences of these properties with respect to chemical bonding are coming up in the next section, so stay tuned!

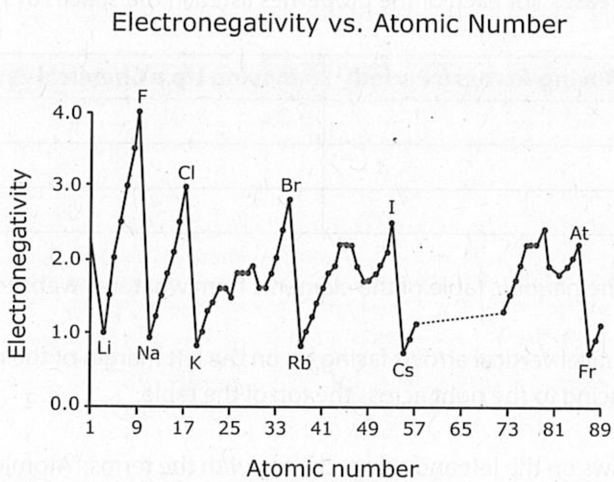


**Figure 6.2.7** *Graph showing electronegativity values*

# 6.2 Activity: A Summary Diagram of Periodic Trends

**Question**

How can we summarize the three periodic trends discussed in this section using one periodic table?

**Materials**

Periodic table, a ruler or straight edge

**Procedure**

1. Consider each of the three periodic trends listed below and complete the following table by writing in either the word "increases" or "decreases" for each of the properties listed in the spaces available.

| | Moving Across a Period | Moving Up a Chemical Family |
|---|---|---|
| Atomic Size | | |
| Ionization Energy | | |
| Electronegativity | | |

2. Print a full page version of the periodic table of the elements from whatever website you wish.

3. Using a ruler, draw three parallel vertical arrows facing up on the left margin of the periodic table. Draw three parallel horizontal arrows facing to the right across the top of the table.

4. Label each of the three arrows on the left and across the top with the terms: "Atomic Size," "Ionization Energy," and "Electronegativity." Next to each term, write the appropriate words from the table that you filled in above.

5. Using a ruler, draw a long diagonal arrow beginning at the bottom left corner of the table and extending and pointing to the top right corner. Along the top side of that arrow, write in how each of the three terms listed above changes as you move from the bottom left corner of the periodic table to the top right corner. Save this table because we will refer to it in Section 6.3.



ISBN 978-0-9864778-2-9