

6.5: Periodic Variations in Element Properties

Learning Objectives

- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of Group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

6.5.1: Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure 6.5.1), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity).

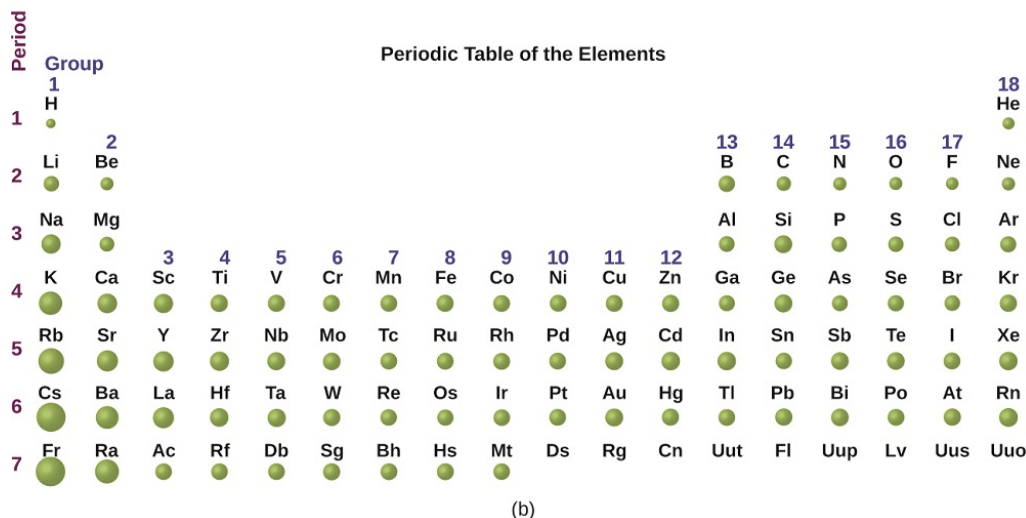
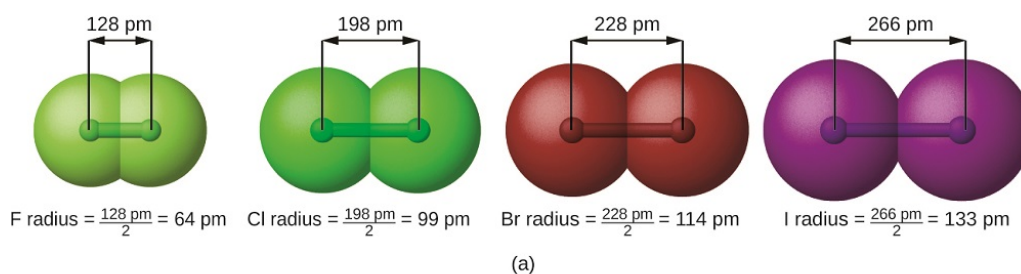


Figure 6.5.1: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as n increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

This figure has two parts: a and b. In figure a, 4 diatomic molecules are shown to illustrate the method of determining the atomic radius of an atom. The first model, in light green, is used to find the F atom radius. Two spheres are pushed very tightly together. The distance between the centers of the two atoms is indicated above the diagram with a double headed arrow labeled, “128 p m.” The endpoints of this arrow connect to line segments that extend to the atomic radii below. Beneath the molecule is the label, “F radius equals 128 p m divided by 2 equals 64 p m.” The next three models are similarly used to show the atomic radii of additional atoms. The second diatomic molecule is in a darker shade of green. The distance between the radii is 198 p m. Beneath the molecule is the label, “C l radius equals 198 p m divided by 2 equals 99 p m.” The third diatomic molecule is in red. The distance between the radii is 228 p m. Beneath the molecule is the label, “B r radius equals 228 p m divided by 2 equals 114 p m.” The fourth diatomic molecule is in purple. The distance between the radii is 266 p m. Beneath the molecule is the label, “I radius equals 266 p m divided by 2 equals 133 p m.” In figure b, a periodic table layout is used to compare relative sizes of atoms using green spheres. No spheres are provided for the noble or inert gas, group 18 elements. General trends noted are increasing circle size moving from top to bottom in a group, with a general tendency toward increasing atomic radii toward the lower left corner of the periodic table.

We know that as we scan down a group, the principal quantum number, n , increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table 6.5.1 and Figure 6.5.1. The trends for the entire periodic table can be seen in Figure 6.5.2.

Table 6.5.1: Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53

Atom	Covalent radius (pm)	Nuclear charge
At	148	+85

As shown in Figure 6.5.2, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of effective nuclear charge, Z_{eff} . This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - \text{shielding}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

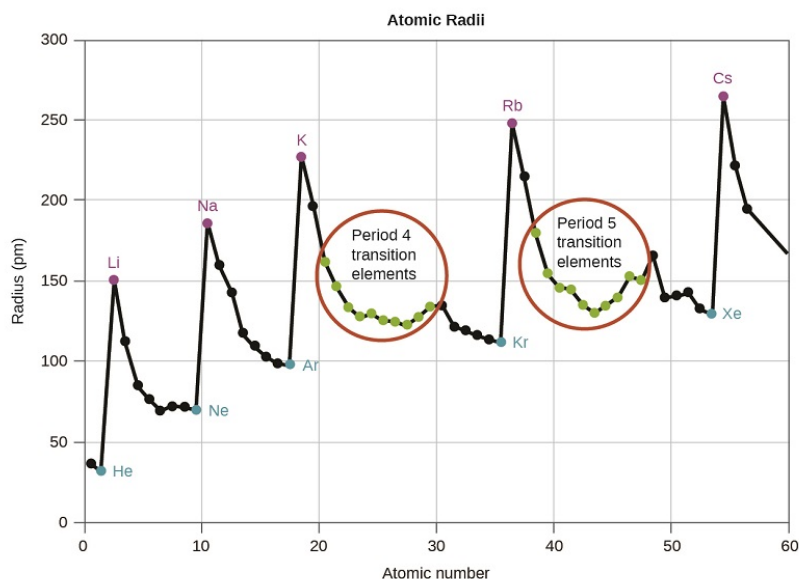


Figure 6.5.2: Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

This graph is labeled Atomic Number on the horizontal axis and Radius (p m) on the vertical axis. A black jagged line connects the radii values for elements with atomic numbers 1 through 60 on the graph. Peaks are evident at the locations of the alkali metals: L i, N a, K, R b, and C s. Similarly, minima exist at the locations of noble or inert gases: H e, N e, A r, K r, X e, and R n. The locations of period 4 and period 5 transition elements are provided with green dots.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the ns or np electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the ns electrons before they begin to lose the $(n - 1)d$ electrons, even though the ns electrons are added first, according to the Aufbau principle.

✓ Example 6.5.1: Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so $\text{Ge} < \text{Fl}$ (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so $\text{Kr} < \text{Br} < \text{Ge}$. Putting the trends together, we obtain $\text{Kr} < \text{Br} < \text{Ge} < \text{Fl}$.

? Exercise 6.5.1

Give an example of an atom whose size is smaller than fluorine.

Answer

Ne or He

6.5.2: Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 6.5.3). For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.



Figure 6.5.3: The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

The figure includes spheres in green to represent the relative sizes of Al and S atoms. Beneath each of these spheres is a red sphere. The red sphere represents the ionic states of aluminum and sulfur respectively. While radius for the aluminum cation is smaller than aluminum, the sulfur anion has a greater radius than sulfur.

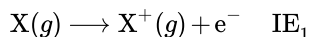
Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, n .

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure 6.5.3). For example, a sulfur atom ($[\text{Ne}]3s^2 3p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[\text{Ne}]3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

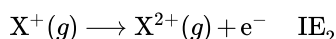
Atoms and ions that have the same electron configuration are said to be isoelectronic. Examples of isoelectronic species are N^{3-} , O^{2-} , F^- , Ne, Na^+ , Mg^{2+} , and Al^{3+} ($1s^2 2s^2 2p^6$). Another isoelectronic series is P^{3-} , S^{2-} , Cl^- , Ar, K^+ , Ca^{2+} , and Sc^{3+} ($[\text{Ne}]3s^2 3p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

6.5.3: Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first ionization energy (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:



The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).



The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

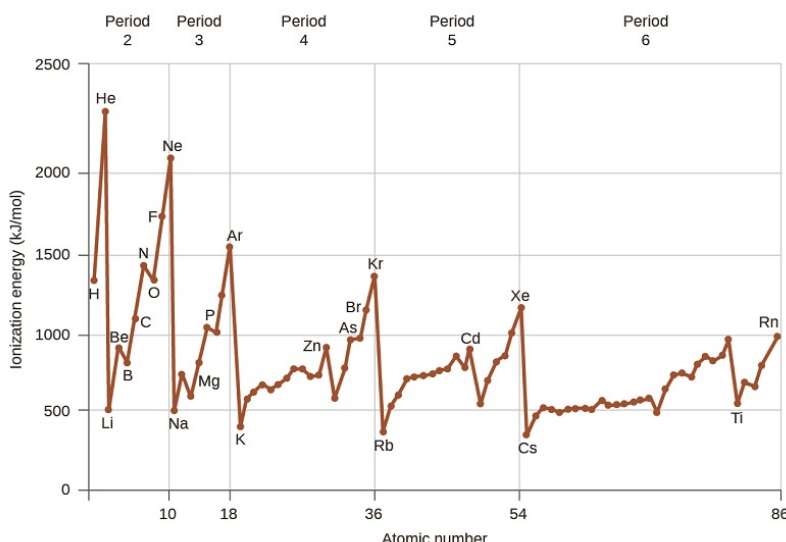


Figure 6.5.4: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

This figure includes Atomic Number on the horizontal axis and, Ionization Energy (kJ divided by mol) on the vertical axis. A red jagged line connects the ionization energies for elements with atomic numbers 1 through 86 on the graph. Peaks are evident at the locations of the noble or inert gases: He, Ne, Ar, Kr, Xe, and Rn. Similarly, minima exist at the locations of the alkali metals: Li, Na, K, Rb, and Cs.

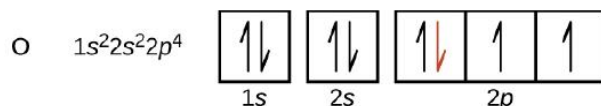
Figure 6.5.4 graphs the relationship between the first ionization energy and the atomic number of several elements. Within a period, the values of first ionization energy for the elements (IE_1) generally increases with increasing Z . Down a group, the IE_1 value generally decreases with increasing Z . There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as l increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the s electrons are lower in energy than the p electrons. This means that an s electron is harder to remove from an atom than a p electron in the same shell. The electron removed during the ionization of beryllium ($[\text{He}]2s^2$) is an s electron, whereas the electron removed during the ionization of boron ($[\text{He}]2s^22p^1$) is a p electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

Period		First Ionization Energies of Some Elements (kJ/mol)																	
Group																			
1	1	H																	He
		1310																	2370
2	2	Li	Be																
		520	900																
3	3	Na	Mg																
		490	730																
4	4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
		420	590	630	660	650	660	710	760	760	730	740	910	580	780	960	950	1140	1350
5	5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
		400	550	620	660	670	680	700	710	720	800	730	870	560	700	830	870	1010	1170
6	6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
		380	500	540	700	760	770	760	840	890	870	890	1000	590	710	800	810	...	1030
7	7	Fr	Ra																
		...	510																

Figure 6.5.5: This version of the periodic table shows the first ionization energy of (IE_1), in kJ/mol, of selected elements.

The trends for first ionization energies across periods and down groups are shown in this version of the periodic table.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the 2p orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 6.5.4).



The electronic configuration for oxygen is 1s superscript 2, 2s superscript 2, 2p superscript 4. An orbital diagram shows 2 squares each filled with a pair of opposite pointing arrows to represent the 1s and 2s orbitals. Each of the three connected squares which represents the 2p orbitals are filled with one arrow respectively with the addition of 1 red arrow in the first of the three squares.

Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table 6.5.2, there is a large increase in the ionization energies (color change) for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Table 6.5.2: Successive Ionization Energies for Selected Elements (kJ/mol)

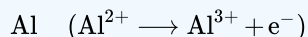
Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

✓ Example 6.5.2: Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher n orbital is farther from the nucleus, so $IE_1(\text{Tl}) < IE_1(\text{Al})$. Ionizing the third electron from



requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(\text{Al}) < IE_3(\text{Al})$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain:

$$IE_1(\text{Tl}) < IE_1(\text{Al}) < IE_3(\text{Al}) < IE_2(\text{Na}).$$

? Exercise 6.5.2

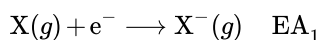
Which has the lowest value for IE_1 : O, Po, Pb, or Ba?

Answer

Ba

6.5.4: Variation in Electron Affinities

The electron affinity [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).



This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 6.5.6. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a -2 ion, and so on.

Period		Electron Affinity Values for Selected Elements (kJ/mol)																	
1	Group 1	2											13	14	15	16	17	18	
1	H																	He	
2	Li	Be											B	C	N	O	F	Ne	
3	Na	Mg											Al	Si	P	S	Cl	Ar	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
7	Fr	Ra																	

Figure 6.5.6: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.:

The trend for electron affinity values across periods and down groups is shown in this version of the periodic table. Values are not shown for groups 3 to 12 as well as period 7.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher n level, which is more difficult to do. Group 2 (2A) has a filled ns subshell, and so the next electron added goes into the higher energy np , so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled np subshell and the next electron must be paired with an existing np electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the second element in the group most often has the greatest EA. The reduction of the EA of the first member can be attributed to the small size of the $n = 2$ shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of -348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is -322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^{-}), we add an electron to the $n = 2$ shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the $n = 3$ shell, it occupies a considerably larger region of space and the electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a

large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Summary

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the n level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

Glossary

covalent radius

one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

effective nuclear charge

charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

electron affinity

energy required to add an electron to a gaseous atom to form an anion

ionization energy

energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

isoelectronic

group of ions or atoms that have identical electron configurations

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