Periodicity

Periodic Properties

The periodic table gets it name from the fact that it is built on the periodic nature of a number of properties. In other words these properties demonstrate a cyclic nature, they rise and then fall, rise and then fall repeatedly and predictably. By understanding these properties we can begin to appreciate the remarkable document that is the periodic table.

We will be looking at five properties in this chapter. They are ionization energy (also known as ionization potential), electron affinity, electronegativity, atomic radius and ionic radius. We will begin by looking at each of these properties individually. We will then look at the periodic table and the things we already know atomic number and electron configurations. Lastly we will put the two together to understand how the structure of the atoms is related to the five properties and how that changing atomic structure creates periodic patterns in those properties.

Ionization Energy is defined as the energy required to remove an electron from an neutral atom. This energy is sometimes measured in terms of the voltage necessary to remove the electron which is why it is sometimes called ionization potential (potential is the fancy physics term for voltage). This process results in a positive ion.

Electron Affinity is the amount of energy released when an electron is added to a neutral atom, making a negative ion. If it is not immediately obvious why adding an electron should release energy, remember the definition of potential energy; potential energy involves an attractive force and a distance. When the electron enters the atom it is coming from far away and the distance to the nucleus is getting smaller. As the distance gets smaller, the potential energy gets smaller. Since energy can't be destroyed, it must be leaving. This is essentially the same explanation that Bohr gave for how the Hydrogen tube gave off light, only in a much more extreme version; here the electron is falling, not from an upper level of the atom, but from completely outside the atom.

Electronegativity is the force with which one atom pulls on the electrons of another atom in a covalent bond. To understand this we need to understand what a covalent bond is and what it is not. Many books (chemistry, physical science, biology, etc.) state that a covalent bond is formed when two atoms share electrons. This is <u>not</u> true. Sharing is a mature rational act done for mutual benefit. Atoms are not mature nor rational.

Atoms are much more like two-year-olds in behavior. When two-year-old children play together, conflict is nearly inevitable, especially if the number of toys is less than the number of children. Even when there is a toy for each child when one child wants more than one, conflict is inevitable. In the same way, when two atoms come together there is a nearly inevitable conflict over their toys, that is their electrons.

As the atoms approach, the nucleus of atom A (for lack of a better name) pulls on the electrons of atoms B. The nucleus of atom B, being positively charged, of course resists this. At the same time, the nucleus of atom B, pulls on the electrons of atom A. If both atoms are similar in strength, then the two will end up locked in a constant tug-of-war without a victor. Because this fight does not involve muscles, neither ever tires and until something else comes along, the atoms will remain locked together. This state of eternal tug-of-war is a covalent bond and electronegativity is the ability of an atom to pull on another atom's electrons in that tug-of-war.

Atomic radius is the radius an an atom. This can be measured in various ways and is sometimes described as the covalent radius (half of the distance between two nuclei in a covalent bond). For our purposes, it is simple a measure of how big the atom is.

Ionic radius is the radius of the ion that is isoelectronic with the nearest noble gas. This means that as you go across the periodic table from the left to the right the ions start with positive charges and then in the middle of the table (around C in the second row) switch to negative ions. Ionic radius is simply a measure of the size of these ions.

What Matters as You Move Across the Table

To understand the periodic properties we need to appreciate the structure of the table itself. As you move from the left side of the table to the right (in a single row) what changes is the number of protons (represented by the atomic number) The further to the right you go, the more protons can be found in the nucleus. This makes the nuclear charge greater and the nucleus' attraction for electrons stronger.

It is also true that as you move from the left to the right on the periodic table, each atom also has more electrons. Since electrons are all negative, this would imply that each electron is increasingly repelled. It is even tempting to imagine that this additional repulsion balances out the additional attraction caused by the extra protons. Life (and atoms) however are not that simple.

As electrons are added in a single energy level they are placed in orbitals that are spatially oriented to avoid repulsion. As a specific example, Boron has 5 protons in the nucleus and 5 electrons. Carbon has an additional proton and an additional electron. All 6 of the electrons feel the extra attractive force of the extra proton. However, the new electron will go into an empty orbital. Assuming that the first p electron went into the p_x orbital, the next will either go into the p_y or the $p_{z.}$ These orbitals are oriented along different axes so that the repulsion gained from adding an electron is not as great as the attraction gained from the proton.

What Matters as You Move Down the Table

As you move down the table in a single column, or **family**, the number of protons increases as does the number of electrons. In addition, the size of the outermost orbital gets bigger; a 2s is bigger than a 1s, etc. Despite the additional electrons and protons, it is, in fact, only the size of the orbital that matters when looking at periodic properties.

To understand why the number of protons and electrons is irrelevant, we need to relate the electron configuration of the elements to the properties themselves. Each of the five properties depends on the outermost electron, whether we are stealing it (ionization energy), adding it (electron affinity), pulling on it (electronegativity), or measuring the outer edge (both atomic and ionic radius).

The outermost electron is attracted by all of the protons in the nucleus and is repelled by the electrons on lower energy levels; as described above, the electrons on the same level largely ignore each other. If we think about a lithium atom the outermost electron (the third) is attracted by 3 protons and repelled by 2 electrons. So, as the outer electron “looks” toward the nucleus it “feels” the proportional pull of one proton (3 positive attractions – 2 negative repulsions = 1 positive attraction). This is called the effective nuclear charge. (There are, not surprisingly some additional details, but this is a pretty good approximation and is certainly good enough for our purposes here.) If we then calculate the effective nuclear charge on sodium's outermost electron we find the same answer of +1. (11 positive attractive protons – 10 negative repulsive electrons = 1 positive attraction.)

Thus, the outer electron in sodium feels the same effective pull from the nucleus as the outer electron in lithium, but it is further away. Absence may make the heart grow fonder in poetry, but in chemistry distance makes the attraction weaker.

The General Trends

Ionization Energy increases as you move across the chart from left to right and decreases as you move down the chart. In other words the highest electronegativities are found in the top right hand corner of the chart and the lowest in the bottom left corner.

Why? As you move across the chart the nucleus becomes more positive and pulls harder on electrons. As a result, it is harder to steal an electron (it take more energy to do so). As you move down the chart, the electron that is being stolen is further from the nucleus and is thus not held as strongly. As a result it is easier to steal (it takes less energy).

Electron Affinity increases as you move across the chart from left to right and decreases as you move down the chart. In other words the largest amounts of energy are released by those atoms in the upper right hand corner of the chart and the least amount of energy is released by those atoms in the bottom left hand corner of the chart when they gain an electron.

Why? As you move across the chart the nucleus becomes more positive and pulls harder on electrons. As a result the electron is pulled into the atom harder and the change in potential energy is greater. In human terms this is similar to falling on earth versus falling on the moon. Earth's gravity is bigger so you fall faster and hit the ground harder. You make more noise, do more damage to yourself and more heat is dissipated to the ground. On the moon, the gravity is weaker, you fall more slowly, hit the ground with less force and release less heat to the ground. As the attraction gets weaker, the amount of energy lost gets smaller and vice versa.

As you move down the chart, the electron being added is joining a higher energy level. In a lithium atom the electron would be added to the 2s orbital. In sodium it would be added to the 3s orbital. This means that an electron falling into the 3rd energy level won't fall “as far” as one falling into the 2nd. Falling less distance equates to losing less energy. Again in human terms, imagine falling down some stairs. If you fall down a single stair, you will not do as much damage to yourself, be moving as fast when you land or dissipate as much heat at the bottom as you would if you fell down an entire flight of stairs. The bigger the fall the more energy is released.

Electronegativity increases as you move from the left side of the table to the right and decreases as you move from the top of the chart to the bottom. So the atoms in the top right corner of the table have the highest electronegativities and those in the bottom left corner have the lowest. There is one exception to this. The noble gases (those elements in the last column on the right: He, Ne, Ar, Kr, Xe, Rn) do not have electronegativity values. This is because the definition of electronegativity states that the property is demonstrated in a covalent bond. These elements, do not form covalent bonds (with a few rare exceptions) and therefore do not have measured electronegativities. Therefore, Fluorine has the highest electronegativity.

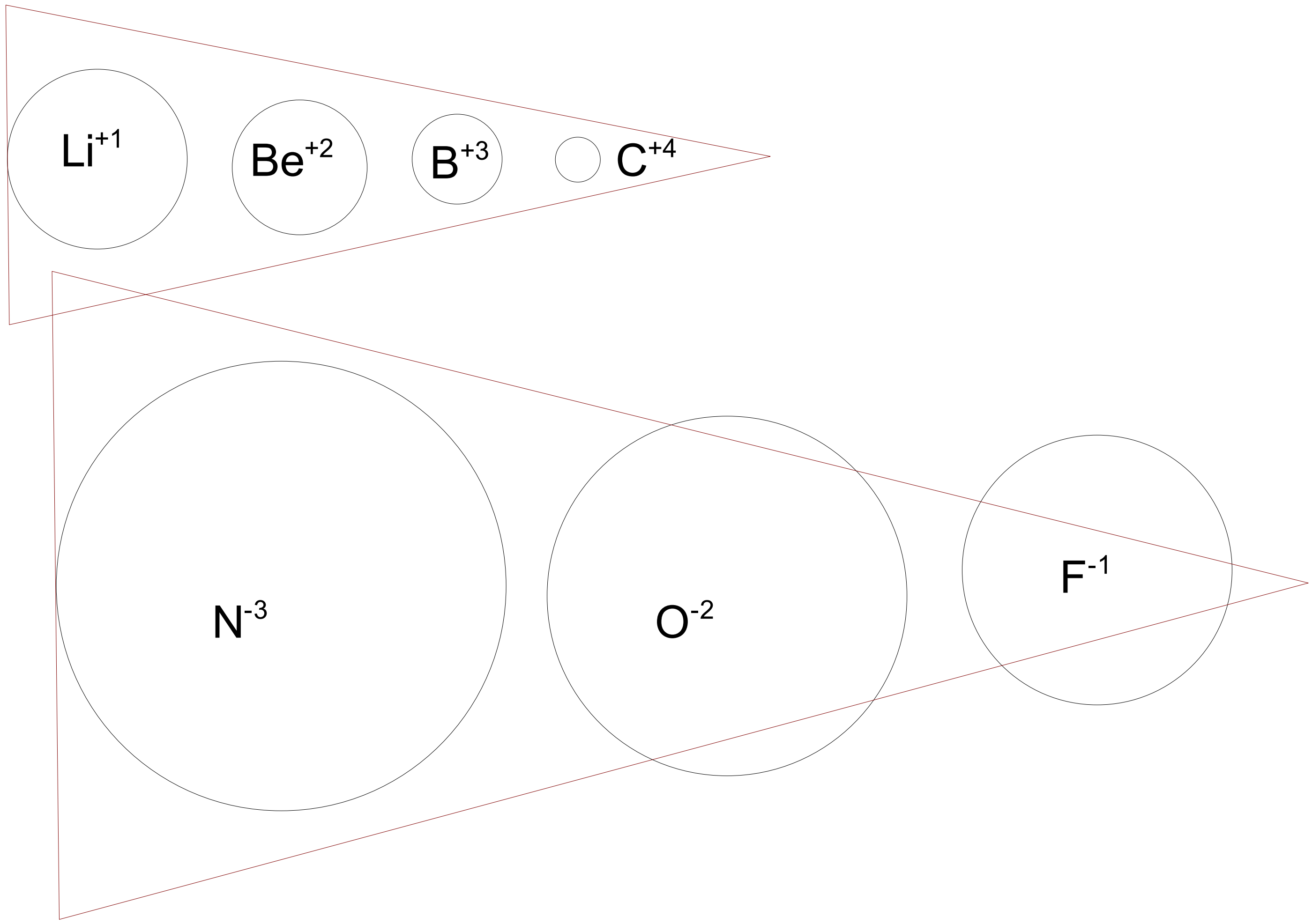
Why? As you move across the chart from the left to the right the nucleus becomes more positive. This more positive nucleus can pull harder on electrons. It makes no difference to the positive charge on which electrons it is pulling. As you move down the chart the edge of the atom gets further from the nucleus. Since another atom's electrons are limited in their approach by those electrons they electrons are further from the nucleus and the pull is weaker.

Atomic radius decreases as you move from the left side of the chart to the right and increases as you move down the table. Thus the smallest atoms are in the top right hand corner of the table and the biggest are in the bottom left hand corner.

Why? As you move from the left side of the table the right the nucleus becomes more positive which pulls the electrons in tighter resulting in a smaller radius. As you move down the chart the effective nuclear charge stays the same, but the orbitals get bigger.

Ionic radius has a more interesting trend. As you move across the table from the left to the right the ions get smaller and then much larger and then smaller again. As you move down the table the ions get bigger.

Why? The vertical trend occurs for exactly the reason described above under atomic radius. The horizontal trend requires some more careful thought. The diagram below shows the relative sizes of the ions on the second row of the table.



Note that within the positive ions, the trend matches the trend for atomic radius (as does the reason). The same is true within the negative ions. The discrepancy is between the positive ions and the negative ions.

To understand the change in size from the small positive ions to the larger negative ions we need to look at the electron configurations of the ions. The electron configurations for the ions above are listed below.

Li^{+1}	$1s^2$
Be^{+2}	$1s^2$
B^{+3}	$1s^2$
C^{+4}	$1s^2$
N^{-3}	$1s^2 2s^2 2p^6$
O^{-2}	$1s^2 2s^2 2p^6$
F^{-1}	$1s^2 2s^2 2p^6$

Note that all of the positive ions have exactly the same electron configuration, that is they are isoelectronic. All of the negative ions are also isoelectronic. What matters here is that the negative ions all contain 8 more electrons, and an entire extra energy level relative to the positive ions. As energy levels get larger, so do the orbitals themselves. It is therefore, no surprise that all of the negative ions are bigger than any of the positive ions.

The Bumps in the Trends

Unfortunately, the picture is not quite as clear as I have described. Specifically, the trends for ionization energy and electron affinity have inconsistencies. Both of these inconsistencies can be understood by looking at the electron configurations of the atoms before and the ions created after the loss or gain of an electron. We will use the second row of the periodic table to explain these inconsistencies.

Ionization Energy, as stated before increases as you move across the chart from the left to the right. This is because each element has one more proton in the nucleus than the previous one and therefore the nucleus pulls harder. However the ionization energy of boron is actually less than that of Beryllium, and the ionization energy of oxygen is less than that of nitrogen. Both of these can be explained by examining the electron configurations of the atoms involved. Beryllium has a configuration of $1s^2 2s^2$, a stable structure (all orbitals are filled or empty), while Boron has a configuration of $1s^2 2s^2 2p^1$, which is not stable due to the single electron in the 2p. If Beryllium loses an electron it will remain stable (the 2s will then be half filled), however, if Boron loses an electron it goes from an unstable structure to a stable one (emptying the 2p). As a result, nature resists the change to Boron less and it is easier to remove the electron.

The situation with oxygen and nitrogen is even more extreme. Nitrogen ($1s^2 2s^2 2p^3$) is stable, while oxygen ($1s^2 2s^2 2p^4$) is not. If a nitrogen loses an electron it becomes unstable ($2p^2$) while if oxygen loses an electron it becomes stable ($2p^3$). As a result there is a great deal of resistance to nitrogen losing an electron, while much less resistance for oxygen to lose an electron.

Electron Affinity, as stated above increases as you move across the chart from left to right, but it also has some “bumps.” The electron affinity of carbon is higher than that of nitrogen and the electron affinity of fluorine is higher than that of neon. Again, the answer can be found in the electron configuration, and in the understanding of one additional fact. Stability is actually a measure of energy. When we say that something is stable we are saying that it is lower in energy. An easy example of this is that rocks are more stable at the bottom of a hill than on the side of the hill or at the top. The point where they have the lowest potential energy is the point where they are most likely to stay. Likewise when we say that an atom has a stable electron configuration, what we are really saying is that the energy of that configuration is lower than the energy of a different configuation.

Carbon has the configuration 1s22s22p2, which is unstable. However, when it gains an electron it will become stable (p3). Since the atom becomes more stable, and therefore lower in energy the excess energy must be given off in some way. If electron affinity is the amount of energy given off when an atom gains an electron, then for carbon the atom gives off the energy we expect for the addition of the electron and then gives off an additional amount for the gain in stability. Therefore the total amount of energy given off is more than expected.

Fluorine undergoes the same process. As an atom (1s22s22p5) it is unstable. When an electron is added energy is given off for the addition of the electron and then an additional amount of energy is given off for the creation of a stable electron structure (p6). Thus the amount of energy given off when a fluorine atom gains an electron is greater than expected.

Neon provides and excellent counter example. Neon is stable as a neutral atom (1s22s22p6). When an electron is added to Neon, some energy is given off, but there is a huge loss of stability; not only do we add an electron to a stable structure but that electron is added to a new energy level and is therefore not as close to the nucleus and not as strongly held. The DECREASE in stability causes a smaller amount of energy to be given off. In fact most noble gases actually require energy to be added in order for them to take in an extra electron.

An Annoying Issue with Electron Affinity It is important to note that when dealing with electron affinity numerically, rather than theoretically you must take into account the sign of the measurement. Processes the give off energy (called exothermic or exo-energetic processes) have a negative sign on the energy measured. This is because the elements or compounds that give off the energy will then have LESS, hence the negative sign. For us, what that means is that electron affinities are generally negative numbers and when we think about the electron affinity getting larger, we actually mean that the number becomes more negative. Again, this ONLY matters if you are looking at the numbers. The theory is easier and is exactly as described above.