

Chapter 9: Periodic Table and Atomic properties

Periodic Law:

There are a lot of elements in chemistry. How do you organize all these elements? This became the central question during the 19th century.

Some people choose to arrange elements in terms of their atomic mass. They would line the elements up by having the elements with the lowest atomic mass on the left and those with the greatest atomic mass on the right. It is a good start and this method was rather successful because it showed something!

Well, what did it show? It showed that for every once in a while, you get elements with similar properties. Hmm, this is very interesting. This observation was made into the **periodic law**. The law states that if we arrange elements by atomic mass or volume, we would see that certain sets of property occur periodically.

There are two people that are really famous for working with this periodic law. The one we are going to talk about is Medeleev, the Russian dude that became the father of periodic table.

Medeleev created a table that contained all the elements known at his time. He divided them into groups based on similar chemical and physical properties. He also purposely left a number of blanks in his table for the elements that he predicts would be there. His predictions were right and all the corresponding elements were eventually discovered.

Periodic Law, redefined:

Medeleev's periodic table good but not perfect. In his arrangement of elements based on their atomic mass, he made a number of exceptions in the table in order to fit elements with similar properties together. (Exceptions means that when atomic mass dictates Element X will be placed next on the periodic table, this is not obeyed. Instead, element X is placed around where it is suppose to be in order to fit into the group that it has similar characteristics with.)

There were a lot of exceptions and there were really no explanation for them. What do we do? Here is where Mr. Moseley come along.

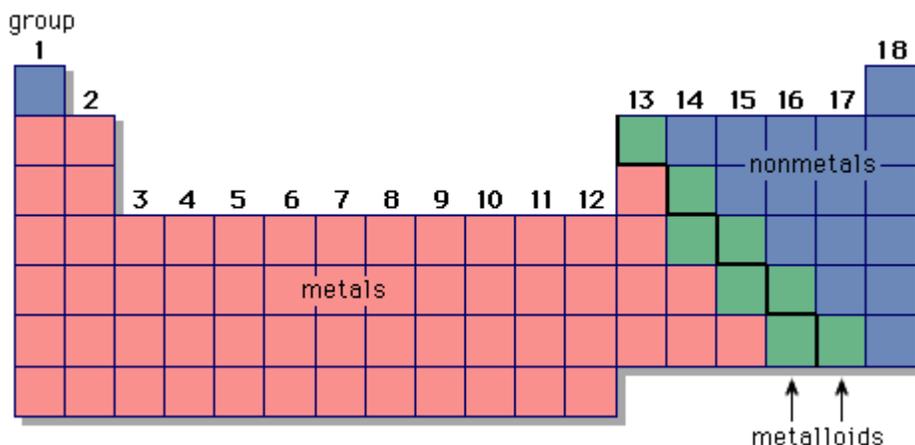
Moseley is famous because he discovered the concept of atomic numbers. He played around with the x-rays emitted from each element. After some fooling around, he discovers that each element emitted x-ray of a unique frequency. He took these frequencies and ordered them from the lowest to the highest. He then assigned unique whole numbers to each frequency. His reasoning was that energy of the electron orbits depends on the nuclear charge. Thus, the x rays that are emitted as the results of electrons falling to the orbits closest to the nucleus should depend on the nuclear charge of the atom. These unique whole numbers became atomic numbers and came to represent the number of protons in the atom of an element.

If we arrange the atoms in terms of increasing atomic numbers rather than increasing mass, we would obtain a much better table with few exceptions. Thus, the periodic law was restated as

similar properties occur periodically when elements are arranged according to increasing atomic number.

Lets talk about the periodic table:

Lets take a tour. The periodic table is arbitrarily divided into three sections, metals, metalloids and non metals. Metalloids are elements that look like metals and behave like metals. However, they also have non metal characteristics.



The table can also be divided into main groups and transitional groups. In this division, we have main group metals in the s-block that are available to form noble gas configuration by losing 1 or 2 electrons. (Noble gas configuration is very stable and most elements try to achieve it by adding/removing electrons so that they look like the closest noble gas) We also have main group non metals in group 16 and 17 mostly. These main group non metals acquire stable noble gas configuration by gaining the appropriate number of electrons.

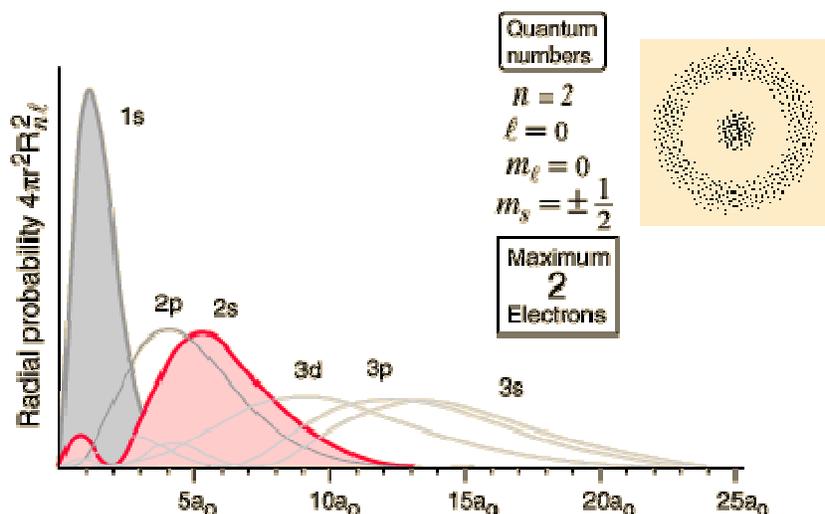
Between the main group metals and main group non metals are the transitional metals. These are the elements in which the $(n-1)$ d subshell are filled up. Most of them do not try to achieve noble gas configurations but rather half filled or filled d orbitals for stability.

Valence electrons are electrons at the outmost principal quantum (n) level of an atom. Non valence electrons are known as core electrons. Physical and chemical properties of an element is determined by its electron configuration, especially the configuration of the valence electrons. Elements with the same valence electron configuration tend to share similar physical and chemical properties.

Screening and penetration:

Lets define those terms first. Penetration is how close an electron can get to the nucleus. Screening/shielding reflects how an outer electron is blocked from nuclear charge by inner electrons. You must be thinking. Whoa.. hold your horse there. Lets take a look at them in detail.

Penetration, as the term applies, is really penetration. It tells you how close an electron can penetrate the atom's "defences" to reach the nucleus. If you are an electron, you get different penetration abilities depending on the sublevel you are on. In general, s sublevel can penetrate better than the p, the p better than the d, and so on. To explain why this happens requires the discussion of Schrodinger's equation, which I am pretty sure that you don't want to hear. However, we can discuss the results and how it connects to penetration.

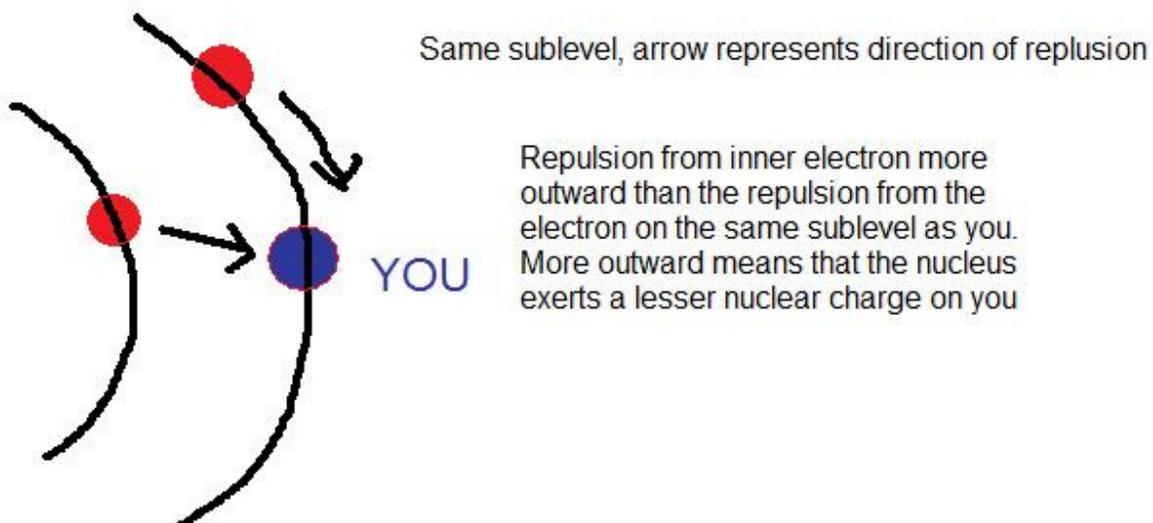


What you see here is a radial probability density graph obtained from Schrodinger's equation. The y axis represents the likelihood of an electron to exist there while the x axis represents the distance from the nucleus. As you can see, the 2s orbital have a much greater density (y value) near the nucleus than the 2p orbital. This means that there a better chance of finding a 2s electron there. Thus, the 2s electrons can penetrate better than the 2p electrons. (Able to get to the nucleus closer)

Generally, $s > p > d > f$ in terms of who has better penetration.

Screening is caused by the repulsion of electrons. Electrons are all negatively charged and don't like to get together. When an electron is in an inner orbital than you, it tries to get away from you by pushing you outwards. This creates what's the called the screening effect as the nuclear charge exerted on you is significantly reduced by the repulsion from the inner electron. Screen also occurs with electrons in the same orbital. However, this effect is more reduced since the electron cannot push you out as much as the electron in the inner orbital. Thus, if you are screen, the nuclear attraction you experiences, Z_{eff} is less than the true nuclear attraction by a factor of S, where S is the charge that is screened by the electrons on an inner level than you.

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



Generally, penetration depends on sublevel more. (s, p, d, f, all have different penetration values) while screening depends on principal quantum number (n) more. (if an electron is below you, it is going to have 1 less n than you most of the time. Thus, it doesn't matter what the sublevel the electron is on since a 2p will screen you just as well as a 2s electron. (if you are on the n=3 level))

Please keep in mind that penetration and shielding only applies for multielectron atoms. It does not apply for hydrogen like atoms since they only got electron and you can't penetrate/shield with one electron.

Atomic radius:

First of all, what is the atomic radius? Atomic radius is the radius of an atom. By finding out the atomic radius of that atom, you have figured out how large that atom is. The atomic radius can be found by using the distance between the two nuclei of atoms joined by a bond. (Also known as bond distance) Keep in mind that atomic radius is not the distance between two nuclei of atoms in a bond, the distance between two nuclei in a bond is used to find the radius. Now, this bond could be either covalent bond, ionic bond or metallic bond.

If we have a covalent bond, we can find the atomic radius by using $\frac{1}{2}$ of the bond distance. This is valid because most of the covalent bonds are joined formed by 2 atoms of the same element. Thus, the electron is equally shared and atomic radius is simply $\frac{1}{2}$ the distance between their nuclei.

If we have a metallic bond (bonding between metals). We can use the same strategy since metallic bonds are joined by two atoms of the same element as well.

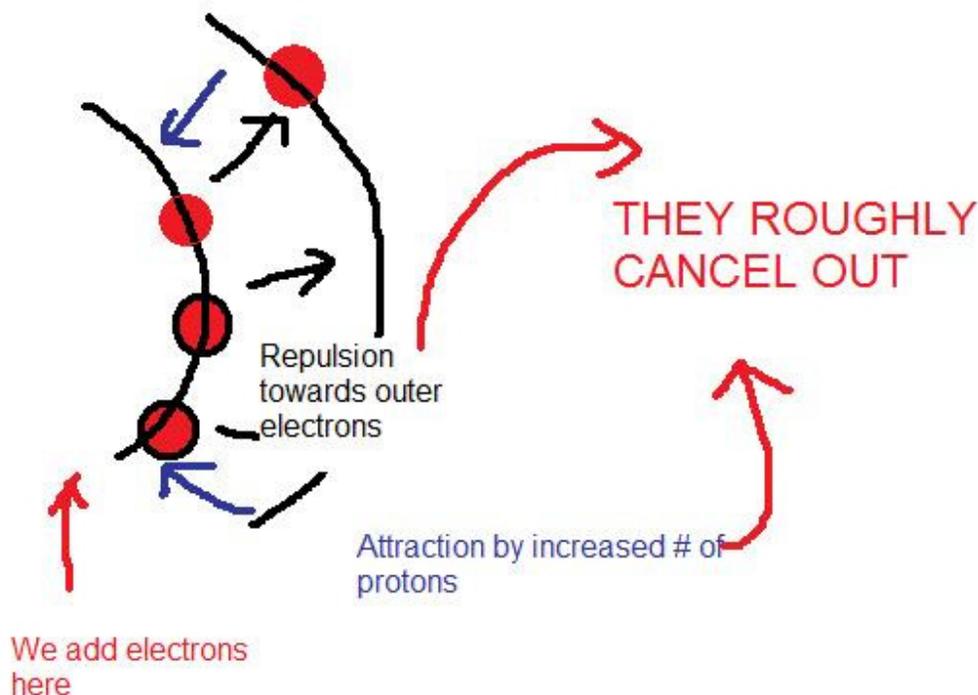
However, if we have an ionic bond, we have atoms from two different elements. Thus, we cannot simply use $\frac{1}{2}$ bond distance. We must somehow determine the atomic radius via some other means and then use (bond distance – known atomic radius of one) to figure the bond distance of the other.

Armed with the knowledge of screening and penetration, the trend in atomic radius becomes a lot easier to explain. Let me state the trend and then explain it. Generally, atomic radius increases as you go down a group (vertical) and decreases as you go from left to right in a period (horizontal). The reason is as follows.

When you go from left to right in a period, you are adding both protons (increase in atomic number) and electrons. The electrons you are adding are all on the same principal quantum level (n) and some are added to the same sublevel. Thus, although the increased # of electrons increase the repulsion between electrons, it is not greater as the increased nuclear charge provided by the increase in the # of protons.

Effect of increase in #protons > effect of increase in #electrons as you go from left to right

Now, you must be wondering, why is this *not* true for transitional metals? Well, let's take a look. When we are adding electrons in the transitional metal section, we are adding electrons to the $(n-1)$ d orbital. This means that we are inputting electrons in the inner orbital since we already have the ns orbitals filled in. As I have explained before, electrons on an inner level than you will screen you better than the electron on the same level as you. Thus, by adding electrons to the $(n-1)$ d level, you are increasing the repulsion to electrons on the ns level and thus significantly increase the radius as a result. This increased radius roughly cancel out the increased nuclear attraction brought on by the increased # of protons. As a result, the radius stays relatively constant as you go from left to right in a period of transitional metals. The figure below illustrates the situation.



Each time you go down a group, you are adding electrons to a new principal quantum level (n). Because you start on a new principal quantum level, you are going to be repulsed by all the core electrons. Thus, each time you go down, you are getting increase in atomic radius. Yes, your # of protons increases as well but that increase is nowhere as dramatic as adding electron to a new principal level.

Ionic Radius:

Metals lose electrons to form positive ions known as cations. (Electrons are negative, thus, losing electrons make you positive) Non metal gain one or more electrons to form negative ions known as anions. Cations are generally smaller than the atom from which it was formed. This is due to the fact that losing one electron = less repulsion between the remaining electrons. With reduced repulsion, the nuclear core can grab on to the electrons tighter and thereby reducing the radius significantly. Anions are generally larger than the atom from which it was formed. This is caused by the fact that you are adding more electrons in, which causes increased repulsion between electrons within that atom. With increased repulsion between electrons, the nuclear core cannot grab on to them as well and thus the radius expands as a result.

$\text{Radius of Cations} < \text{Radius of atom} \mid \text{Radius of Anions} > \text{Radius of atom}$

Ionic radius becomes useful when trying to distinguish size of isoelectronic (having the same number of electron) atoms/ions. For example, between Br^- , Cs^+ and Kr. They all have the same number of electrons but different number of protons. This allows us to use the following rule:

1. List the ions/atoms in terms of increasing atomic number
2. With increased atomic number, the nuclear charge increases, which implies that the ionic/atomic radius decreases.

For the example we have above, we would line them up in terms of increasing atomic number, which is.. Br^- , Kr, Cs^+ . Since Cs^+ have the largest atomic number, it will have the biggest nuclear charge and thus smallest ionic radius. On the contrary, Br^- would have the largest radius.

Ionization energy:

First of all, what is ionization energy? Ionization energy is the amount of energy that is required to pull out an electron from an atom in the gaseous state. Yes, gaseous state, remember that! Ionization energy is ALWAYS positive because it takes energy to pull electron out. Atoms do not eject electrons by themselves, energy must be put in to get it. A useful analogy is the one involving no free lunch. There is no such thing as a free lunch, you must put some money (energy) in to get it.

Ionization energy is denoted by the symbol I . The first ionization energy, I_1 is the energy required to pull an electron that is the most loosely held in neutral atom. The second ionization energy, I_2 is the energy required to pull a second electron from the same atom (which is an ion by now). Each succeeding ionization is larger than the previous one because it gets harder to pull electrons. (The nuclear charge pulls more closely on the remaining electrons due to the lessened repulsion between the remaining electron) There is a huge a jump in ionization energy when we get to a noble gas configuration through the pulling of successive electrons. When we want pull an electron off from that noble gas configuration, the energy required will be enormous. This is caused by the fact that the noble gas configuration is more stable than any other forms.

Generally, ionization energy decreases as atomic radius increases. (Atomic radius increases due to weakened nuclear charge, which means that it is easier to pull off an electron, hence less ionization energy). However, exceptions can sometimes occur. For example, in comparing the ionization energy of Al and Mg, we would expect Mg to have a smaller ionization energy since it has a bigger atomic radius (it is to the left of Al). However, experimental results show that Al have a smaller ionization energy. How to explain this?

Well, when we pull electrons from Al, we are pulling from the 3p orbital. Whereas with Mg, we are pulling from the 3s orbital. Since 3p orbital is higher than the 3s orbital in energy and distance from the nucleus, it is easier to pull electron from the Al atom and hence lesser ionization energy.

Electron Affinity:

Electron affinity is the measure of energy change that occurs when a gaseous atom gains an electron. Electron Affinity could be either negative or positive. If EA is negative, it means that energy is given off as an electron is inserted into the atom. Thus, it would be an exothermic process. If EA is positive, it means that energy must be added to force that electron into that atom. For elements in Group 2, 12 and Noble Gases, EA is usually positive since these elements have no tendency to gain electrons. The reason is that adding electrons to Group 2 and 12 is same as adding electrons to the new p orbital, which we don't really want to do.

Generally, as we go from left to right across a period, the EA becomes larger negatively (More energy is given off since the nuclear charge increases and thus more likely to attract an electron and will "trade" more energy for it)

As we go down a group, EA tends to be less negative since nuclear charge are reduced each time we go down.

Magnetic Properties:

A spinning electron is an electric field in motion. Diamagnetic atoms have all the electrons paired and individual magnetic effects cancelled out. (Hint: Think di as two, therefore paired electron, which exhibit no magnetic effects) It is WEAKLY repelled by magnetic field.

Paramagnetic atoms have unpaired electrons. Thus, individual magnetic effects do not cancel out and this cause paramagnetic atoms to be attracted/repelled to an external magnetic field. In general, the more unpaired electrons present, the stronger the paramagnetism. Keep in mind that all the unpaired electrons in an atom must have parallel spins (Hund's Rule). Thus, paramagnetism is never "cancelled" out.

Reduction and Oxidization:

LEO the lion says GER

Group 1 and 2 are Reducing agents (reducing = gaining electron) since they cause non metals to gain electron.

Group 17 (Halogens) are oxidizing agents since they cause metals to lose electrons. Fluorine is the strongest oxidizing agent.