Electronic Structure and Chemical Periodicity

Periodic Law

The periodic law was discovered independently in the mid 1800's by Dimitri I. Mendeleev of Russia and Lothar Mayer of Germany. The **periodic law states that when the elements are arranged in order of increasing atomic number** (the original used atomic mass)**, the properties repeat at "regular" intervals**. If we look at the periodic table, this means that all of the elements in a given column have similar chemical properties. For example, all of the group IA elements react with water to produce a metal hydroxide and hydrogen gas. The chemical reactions are very similar, there are different amounts of energy released in each reaction but the over chemical equation is pretty much the same. Mendeleev used the periodic law to predict the existence of a couple of elements. He predicted the atomic mass and the chemical formula of the oxide of the element. All of this from knowing the properties of the element that would be above it in the periodic table.

The Periodic Table

The **periodic table** is a chart representing the elements that are known. Each element occupies a single spot in the table. It can be thought of as a graphical representation of the periodic law.

The periodic table is divided into two main sections. The division is shown as a stair-step line on the right half of the table. This line divides the metals from the non-metals. The shorter columns are called the transition metals and the last two rows are the inner transition metals. The first group is known as the alkali metals, the second is called the alkaline earth metals. The last group is known as the noble gases. Group VII A is called the halogens.

The periodic table has rows, which are called **periods**, and columns, which are called **groups**. Some of the groups have special names:

Group	Name
I A	Alkali metals
II A	Alkaline Earth Metals
VII A	Halogens
VIII A	Noble gases

The noble gases on some older periodic tables are called the inert gases because, at the time, it was thought that they did not form compounds.

The Energy of an Electron

When we talk about the energy of an electron in an atom, we need to resort to the branch of physics called **quantum mechanics**. Quantum mechanics deals with the way in which very small objects behave. With this theory, we can determine the motion or energy of a particle. In quantum mechanics, we find that the energy of an electron is a **quantized property**. In other words, it can have only certain, discreet values. An electron cannot have just any energy. It can only have an energy that it is allowed to have. This is a fundamental restriction by nature. It is not imposed by anything. It is just the way it is.

Electrons are found to have energies that place the electrons in **shells** around the nucleus. A shell is a mathematical construct that allows us to understand the behavior of the electrons. It is the region around the nucleus where the electrons have approximately the same energy and are approximately the same distance from the nucleus. The shell number, **n**, tells us in which shell the electrons are. The lowest shell number is 1. There is no highest shell number. The number of electrons a shell can hold is given by the formula, $2n^2$. The first shell can hold 2 electrons $(2(1)^2 = 2)$. The second can hold 8 $(2(2)^2 = 8)$, and so on.

Within each shell there are one or more sub-shells. The number of sub-shells is given by the shell number. The first shell has one sub-shell and so on. The sub-shells are given labels of s for the first sub-shell in a shell, p for the second, d for the third and f for the fourth. The sub-shells can hold a number of electrons based on the kind of sub-shell it is:

Sub-shell	# of electrons
s	2
p	6
d	10
f	14

All of the electrons in a given sub-shell have the same energy. Electrons in different sub-shells in the same energy level have slightly different energies.

Each of the sub-shells is further divided into **orbitals**. Each orbital, which again is a mathematical construct, can hold, at most, 2 electrons. The number of orbitals in a sub-

shell is 1 orbital in an s sub-shell, 3 orbitals in a p sub-shell, 5 orbitals in a d sub-shell and 7 in an f sub-shell. All of the orbitals in a given sub-shell have the same name as the sub-shell. For instance, the orbitals in a 3p sub-shell (the second sub-shell in the third energy level) are called 3p orbitals.

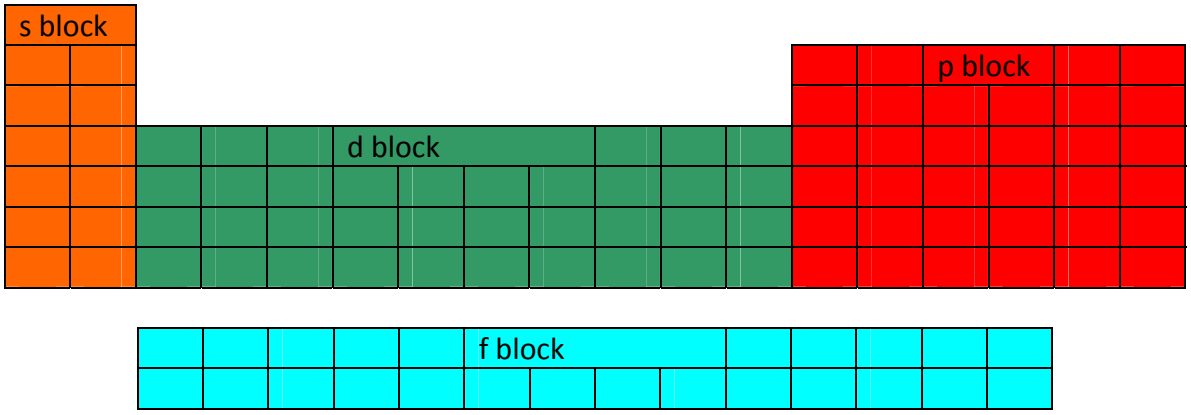
The orbitals have a shape depending on the kind of orbital. All p orbitals have the same shape. The three different p orbitals point in different directions. The p orbitals in the 3^{rd} energy level had the same shape as those in the 4^{th} but have a different size.

Electron configurations

With all of the above in mind, we can start to write **electron configurations,** for elements. An electron configuration just tells us which energy levels and sub-shells all of the electrons are. Some textbooks, yours included, show, initially, a zigzag diagram for learning how to do electron configurations. This is needless and just one more thing to memorize. I would prefer that you use the periodic table to write electron configurations. To do this, realize that the periodic table is "naturally" divided into sections. The first two tall columns (plus Helium) correspond to electrons placed into s orbitals. The last six tall columns correspond to electrons placed into p orbitals. The middle set of ten shorter columns corresponds to electrons placed into d orbitals. The last two rows at the bottom of the table (14 columns) correspond to electrons placed into f orbitals. We can now decide which kind of orbital the electrons are in; we need to decide which energy level they are in. For s and p electrons the energy level is the same as the row number (n). For d electrons the energy levels is equal to the row number minus 1 (n-1). For f electrons it's the row number minus 2 (n-2). This will allow us to construct electron configurations, and later orbital diagrams, for any element. For instance, the simplest element, Hydrogen, has an electron configuration of $1s^1$. The preceding 1 means the electron is in the first energy level, the s means the s orbital and the super-script 1 means one electron in that orbital. The electron configuration for iron is:

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6.$$

To get this, we just read across the periodic table until we get to the element we want. Keep in mind that the blocks in the table correspond to particular sub-levels. See the table below.



There is a short-hand way of doing this. We can recognize that the electron configuration of Argon is:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$,

which is the same as the beginning of the electron configuration of iron. We can, therefore, write the electron configuration of iron as:

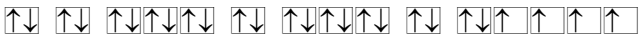
$[Ar]\ 4s^2\ 3d^6$.

This notation means that we use the configuration of Argon and add the rest to it. The element in brackets must be a noble gas that comes before the element in the table.

When we have the electron configuration of an element we can then show the orbital diagram of that element. An orbital diagram shows us in which orbital the electrons are. We need to remember from earlier that the s sub-level has one orbital and so on. We also need to remember Hund's Rule, which states that when electrons are placed into orbitals of the same energy (in the same sub-level), they will go in one at a time until each orbital has one. Then they will pair up with opposite spins. Now we can write an orbital diagram for Hydrogen. It will be:

1s

This shows us the 1 electron in a 1s orbital in Hydrogen. For iron, the orbital diagram would be:



1s 2s 2p 3s 3p 4s 3d

Here we see the electrons, with opposite spins, in the individual orbitals of each of the sub-levels.

Periodic trends

There are two trends we will look at: metallic character and atomic radius.

Metallic character tends to increase as we move down a column. Look a group IV A. It starts with a non-metal, carbon, and ends with a metal, lead. This group is a good indicator of this trend. As we move across the periodic table, the metallic character decreases. In any period we start with metals and end with non-metals.

Atomic radius increases down a group. This is because of the electron in higher energy levels. The radius decreases across a period. This is because of the increased pull from the nucleus on each of the electrons in the outer energy level.