2 ELEMENTAL AND ENVIRONMENTAL CHEMISTRY

'Elemental and Environmental Chemistry' contains the following subtopics:

SUBTOPIC 2.1: The Periodic Table

2.1.1 Subshells

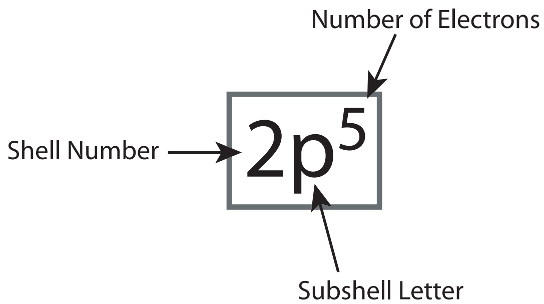
Previously you were taught that electrons orbit the nucleus of an atom in energy levels called shells. These shells are in fact further divided into <u>distinct energy levels</u> called subshells; each subshell corresponds to a particular energy level. There are four types of subshells, known as s, p, d and f.

The electrons in each subshell are represented by:

- The number of the parent shell,
- The letter of the subshell and
- The number of electrons in the subshell.

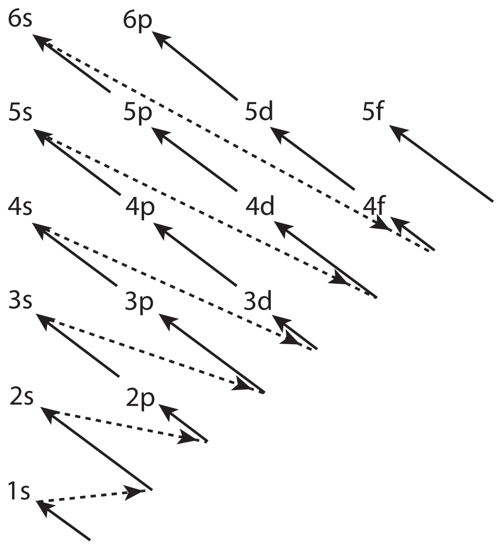
Maximum Number of Electrons per Subshell

Subshell	Maximum Electrons
s	2
p	6
d	10
f	14



Electrons will always try to fill the subshells with the lowest possible energy level. In some cases, *shells* overlap – i.e. the low energy subshells from a higher shell may have less energy than the high energy subshells from a lower shell. For example, the 4s subshell has a lower energy than the 3d subshell, so it is filled first.

THE ORDER IN WHICH SUBSHELLS ARE FILLED



Examples:

$_{38}Sr\ 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$

$_{11}Na\ 1s^2 2s^2 2p^6 3s^1$

$_{17}Cl\ 1s^2 2s^2 2p^6 3s^2 3p^5$

Exceptions (chromium and copper):

For chromium, we might expect that the electron configuration is:

$_{24}Cr\ 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$

However, this is incorrect and the electron configuration of chromium is actually:

$_{24}Cr\ 1s^2 2s^2 2p^6 3s^2 3p^6 \boxed{4s^1 3d^5}$

This is because a half-filled 3d subshell is more stable as it takes less energy to maintain.

Similarly, for copper, we might expect that the electron configuration is:

$_{29}Cu\ 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$

However, the actual electron configuration is:

$_{29}Cu\ 1s^2 2s^2 2p^6 3s^2 3p^6 \boxed{4s^1 3d^{10}}$

This is because a filled 3d subshell is more stable.

Subshell notation for monatomic ions

$_{11}Na\ 1s^2 2s^2 2p^6 3s^1 \rightarrow\ _{11}Na^+ 1s^2 2s^2 2p^6 + 1e^-$ [a loss of $1e^-$]

$_{17}Cl\ 1s^2 2s^2 2p^6 3s^2 3p^5 + 1e^- \rightarrow\ _{17}Cl^-\ 1s^2 2s^2 2p^6 3s^2 3p^6$ [a gain of $1e^-$]

However, during ion formation in <u>transition metals</u> (which all have electrons in the 4s subshell), electrons from this subshell are lost first.

$_{26}Fe\ 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6 \rightarrow\ _{26}Fe^{2+} 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 + 2e^-$ [a loss of $2e^-$]

Extra note:

In the example above, Fe^{2+} normally then undergoes a spontaneous reaction in which a further single electron is lost, forming Fe^{3+}:

$_{26}Fe^{2+} 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 \rightarrow\ _{26}Fe^{3+} 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 + 1e^-$ [a loss of $1e^-$]

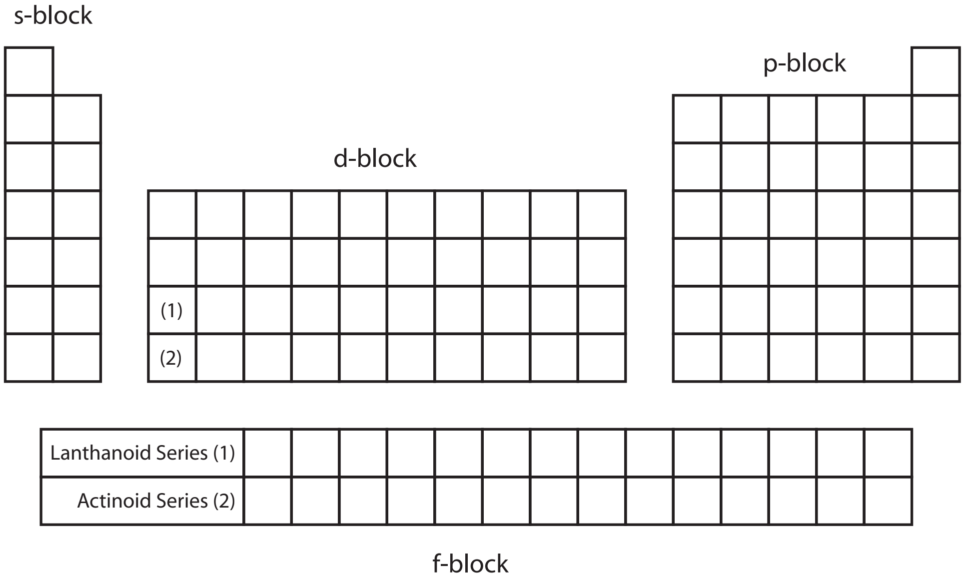
This is because a half-filled 3d subshell is more stable.

Subshell sections of the periodic table

- The period number of an element can be found from the <u>highest shell number</u> in that element's electron configuration. For example, Sodium is in Period 3 as its highest shell number is 3 ($_{11}Na\ 1s^2 2s^2 2p^6 3s^1$).

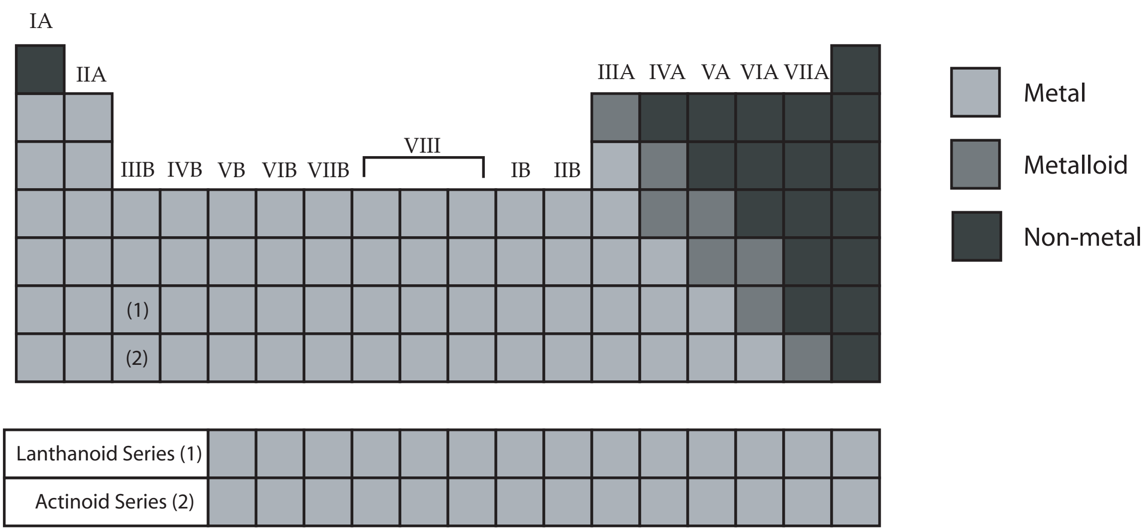
- The group number of an element can be derived from the sum of all the electrons in the outer shell. For example, Bromine is in Group 7 ($_{35}Br$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$) as the sum of all the electrons in the outer 4^{th} shell is 7.

  The periodic table can be broken into 4 blocks, called the s, p, d and f blocks. The letter ascribed to the outermost subshell of any element defines the block that it is placed in.



2.1.2 Properties of Elements in the Periodic Table

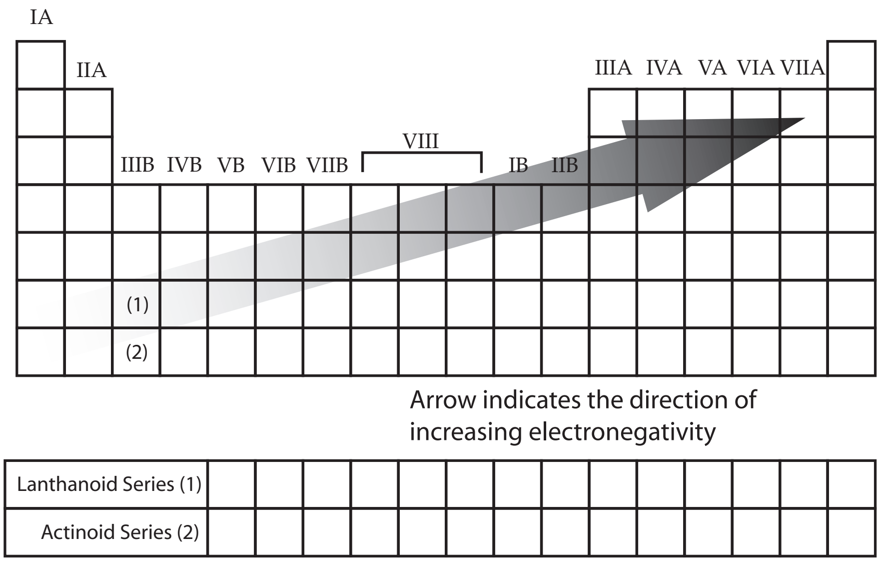
The distribution of metals, non-metals and metalloids (you only need to know the first 38 elements):



Electronegativity is the ability of an atom to attract electrons. Electronegativity increases from left to right across a period and decreases from top to bottom down a group. Non-metals have a high electronegativity while metals have a low electronegativity.

- The most stable electron configuration that can be achieved is a noble gas (octet) electron configuration of 8 outermost shell electrons (in the case of H and He, this number becomes 2).
    - Metals have lower electronegativities, therefore they have less power to attract electrons. As a result, they are more likely to lose the electrons in their outermost shell. They do this to achieve a stable noble gas electron configuration.
    - Non-metals have higher electronegativities, therefore they have greater power to attract electrons. As a result, they are more likely to gain electrons to fill their outermost shell. They do this to achieve a stable noble gas electron configuration.

Note: larger elements with 3 or more shells can hold more than 8 electrons in their outermost shell. However, having 8 electrons in the outermost shell is the most stable configuration.



Oxidation Number Calculations (Rules)

1. All elements have an oxidation number of 0 in their elemental state. For example, in H_2, hydrogen has an oxidation number of 0.

2. Hydrogen has an oxidation number of +1 when it bonds with non-metals and –1 when it bonds with metals (in compounds called hydrides). For example, in H_2O, hydrogen has an oxidation number of +1, and in NaH, hydrogen has an oxidation number of –1.

3. Oxygen has an oxidation number of –2 in compounds except in peroxides such as hydrogen peroxide (H_2O_2) where it has an oxidation number of –1.

4. Monatomic ions have an oxidation number equal to their charge. For example in Ca^{2+}, calcium has an oxidation number of +2.

5. The sum of the oxidation numbers in a compound equals 0. For example, in Na_2O oxygen must have an oxidation number of -2. Hence, sodium must have an oxidation number of +1 $\left[2\times(+1)+(-2)=0\right]$.

6. The sum of the oxidation numbers in a polyatomic ion equals the charge on the ion. For example, in NH_4^+, hydrogen has an oxidation number of +1, so nitrogen must have an oxidation number of -3 $\left[-3+4\times(+1)=+1\right]$.

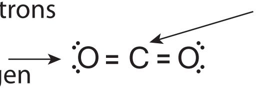
Note: Oxidation numbers always start with a plus (+) or minus (-) sign, followed by a number. Charge is written in the opposite way. For example, Fe^{2+} has a 2+ charge, and an oxidation number of +2.

2.1.2 Covalent Bonding

A covalent bond is formed by the sharing of valence electrons between two atoms. The shared electrons orbit both atoms, and are considered part of each atom's valence shell. By sharing electrons, the atoms are able to increase the number of electrons in their outer shell and thus form a more stable electron configuration.

A single covalent bond consists of two electrons, usually one from each atom. For example, in carbon dioxide (CO_2), as shown below, carbon makes 4 covalent bonds, each consisting of a pair of shared electrons. Thus in CO_2, carbon is said to have 8 electrons in its outermost shell, of which it contributes 4.

By sharing two of its electrons with carbon to form two covalent bonds, this oxygen atom gains an extra two electrons. It has 8 electrons in its outermost shell.

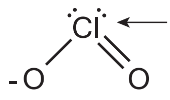


In carbon dioxide, carbon has 8 electrons in its outermost shell - 4 to begin with and another 4 from sharing electrons with the two oxygen atoms.

Octet Expansion

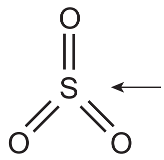
The third shell can hold more than eight electrons because it contains a d subshell as well as s and p subshells. Period 3 elements such as P, S and Cl can access this subshell. When these elements form covalent bonds, the first eight electrons in the third shell reside in the 3s and 3p subshells, while the extra electrons occupy the free space in the 3d subshell. This process is known as the "expansion of the octet". Examples of this are shown on the next diagram:

ClO_2^-



In ClO_2^-, Cl has 10 electrons in its outermost shell

SO_3



In SO_3, sulphur has 12 electrons in its outermost shell

2.1.3 Acidic, Basic and Amphoteric

1. The oxides of non-metals are acidic. That is, they will react with OH^- ions (basic) to form an oxyanion and water, or react with water (if the oxide is soluble) to form an acid.

   Non-metal (acidic) oxide + $OH^-_{(aq)} \rightleftharpoons$ oxyanion $_{(aq)}$ + $H_2O_{(l)}$

   e.g. $CO_{2\,(g)} + 2OH^-_{(aq)} \rightleftharpoons CO_3^{2-}{}_{(aq)} + H_2O_{(l)}$

   Non-metal (acidic) oxide + water$_{(l)} \rightleftharpoons$ oxyacid $_{(aq)}$ (if soluble)

   e.g. $CO_{2\,(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3\,(aq)}$

   $SiO_{2\,(s)} + H_2O_{(l)} \rightleftharpoons$ no reaction as SiO_2 is not soluble

2. The oxides of metals are basic. That is, they will react with an acid (H^+ ions) to form a metal cation and water, or react with water (if the oxide is soluble) to form a base. In both cases, one of the products is a metal cation.

   Metal (basic) oxide + acid$_{(aq)} \rightleftharpoons$ metal cation$_{(aq)}$ + $H_2O_{(l)}$

   e.g. $MgO_{(s)} + 2H^+_{(aq)} \rightleftharpoons Mg^{2+}_{(aq)} + H_2O_{(l)}$

   Metal (basic) oxide + water$_{(l)} \rightleftharpoons$ base$_{(aq)}$ (if soluble)

   e.g. $MgO_{(s)} + H_2O_{(l)} \rightleftharpoons Mg(OH)_{2\,(aq)}$

   $CuO_{(s)} + H_2O_{(l)} \rightleftharpoons$ no reaction as CuO is not soluble

3. "Metalloids form amphoteric oxides. Amphoteric oxides can display basic character by reaction with H^+ ions and acidic character by reaction with OH^- ions" (Adapted from SACE Stage 2 Chemistry Curriculum Statement, Subtopic 2.1).

   Metalloid oxide + $H^+_{(aq)} \rightleftharpoons$ metalloid cation$_{(aq)}$ + $H_2O_{(l)}$

   e.g. $GeO_{2\,(s)} + 4H^+_{(aq)} \rightleftharpoons Ge^{4+}_{(aq)} + 2H_2O_{(l)}$

   Metalloid oxide + $OH^-_{(aq)} \rightleftharpoons$ metalloid oxyanion$_{(aq)}$ + $H_2O_{(l)}$

   e.g. $GeO_{2\,(s)} + 4OH^-_{(aq)} \rightleftharpoons GeO_4^{4-}{}_{(aq)} + 2H_2O_{(l)}$

   In addition, some metals (including zinc, tin, lead, aluminium and beryllium) can also form amphoteric oxides. You will be expected to be able to write the following equations involving Al_2O_3 and ZnO: