| EENS 2110 | Mineralogy |
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## Crystal Chemistry

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As we have been discussing for the last several weeks, crystals, and thus minerals, are made up of a 3-dimensional array of atoms arranged in an orderly fashion.  Now we explore what these atoms are and how they interact with one another to determine the physical and structural properties of crystals.  So, first we explore the properties of the atom.

### Atoms

Atoms make up the chemical elements. Each chemical element has nearly identical atoms. An atom is composed of three different particles:

- *Protons* -- positively charged, reside in the center of the atom called the *nucleus.*

- *Electrons* -- negatively charged, orbit in a cloud around nucleus.

- *Neutrons* -- no charge, reside  in the nucleus.

In a neutrally charged atom, each element has the same number of protons and the same number of electrons.

- Number of protons = Number of electrons.

- Number of protons = *atomic number*.

- Number of protons + Number of neutrons = *atomic weight*.

*Isotopes*  are  atoms of the same element with differing numbers of neutrons. i.e. the number of neutrons may vary within atoms of the same element. Some isotopes are unstable which results in radioactivity.

- Example:  K (potassium) has 19 protons. Every atom of K has 19 protons. The Atomic number of K=19. Some atoms of K have 20 neutrons, others have 21, and others have 22. Thus atomic weight of K can be 39, 40, or 41. $^{40}$K is radioactive and decays to $^{40}$Ar and $^{40}$Ca.

It is the electrons in the atoms that are responsible for the chemical properties of atoms.  The electronic configuration determines the types of atoms that can be bound to one another, the strength of the bonds, and the types of bonds.  Thus, we need to look closely at the electrons and the electronic configuration of atoms.

## Bohr Atom

Electrons orbit around the nucleus in different shells, labeled from the innermost shell as K, L, M, N, etc. Each shell can have a certain number of electrons. The K-shell can have 2 Electrons, the L-shell, 8, the M-shell 18, N-shell 32.

Each shell is associated with a principal quantum number, n, where $n_K = 1$, $n_L = 2$, $n_M = 3$, $n_N = 4$, etc.

The number of electrons in each shell is controlled by this principal quantum number by the following relationship:

$$\text{\# electrons} = 2n^2$$

Thus, the K-shell can contain 2 electrons, the L-shell, 8 electrons, the M-shell, 18 electrons, and the N-shell, 32 electrons.

Electrons in the outermost shells have higher energy than those in the inner shells. This is because the electrons in the outermost shells would release more energy if they were to fall into the inner shells. When such electronic transitions occur, the energy is released as photons, such as X-rays, as we discussed previously.

Planck found that the energy released in the electronic transitions is only released in distinct packets, which he called "*quanta*", and that these packets of energy are related to a constant (now called Planck's constant, and the frequency or wavelength of the radiation released.
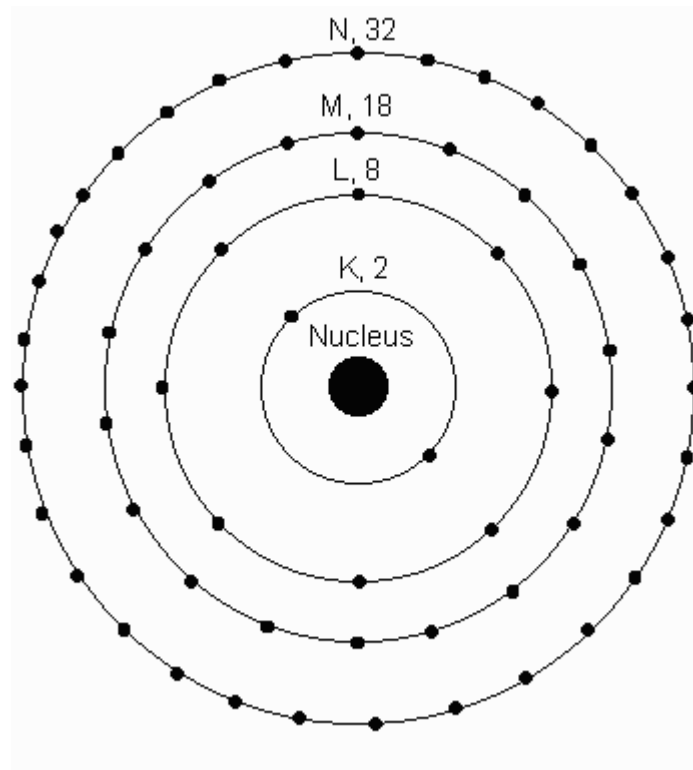
$$E = h\nu = hc/\lambda$$

where

E = energy
h = Planck's constant, $6.62517 \times 10^{-27}$ erg·sec
$\nu$ = frequency
c = velocity of light = $2.99793 \times 10^{10}$ cm/sec
$\lambda$ = wavelength

This led to the quantum mechanical view of the atom.

**Quantum Mechanical View of the Atom**

The quantum mechanical view of the atom suggests that the electrons are located within specific regions of probability. These probability regions are described by the *azimuthal quantum number* or *orbital shape quantum number, l*. A maximum of 2 electrons can be found in each probability region, each electron have a *spin quantum number* with a value of either $+\frac{1}{2}$ or $-\frac{1}{2}$. The orbital shape quantum number has the following values and designations for the shape of the probability region in which the electrons are most probably to be found.

| Value of $l$ | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Sub-shell designation | s | p | d | f |

The sub-shell designations stand for sharp, principal, diffuse, and fundamental. The probability regions described by these sub-shells are as follows:

- **s - orbitals** - are spherical shaped probability regions. The radius of these spherical regions increases with increasing principal quantum number, n. Again, each of these orbitals can contain a maximum of 2 electrons.
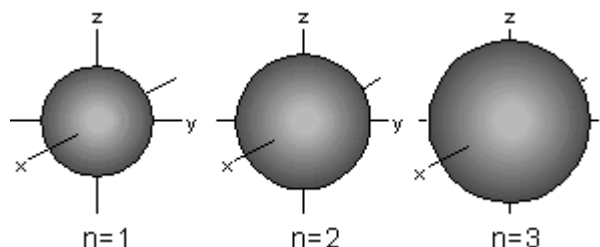
- **p - orbitals** - these can only be present if the principal quantum number is 2 or greater. There are 3 different types of p orbitals, designated $p_x$, $p_y$, and $p_z$. These are approximately peanut shaped orbitals, with the axis oriented vertically ($p_z$) and horizontally ($p_x$ & $p_y$).
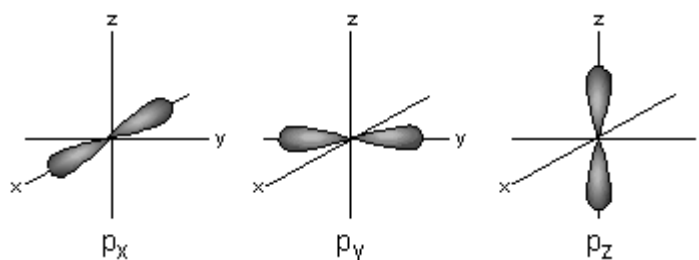
Since 2 electrons can occur in each of the different p orbitals, a maximum of 6 electrons are associated with p-orbitals in each principal shell.

- **d - orbitals** - These can only be present if the principal quantum number is 3 or greater. There are 5 different probability regions of d orbitals. These are seen in the drawings

below, and are designated $d_z2$, $d_x2 - y2$, $d_{xy}$, $d_{yz}$, and $d_{xz}$. Since 2 electrons can occur in each of the different d orbitals, a maximum of 10 electrons can occur in d-orbitals for each principal shell.
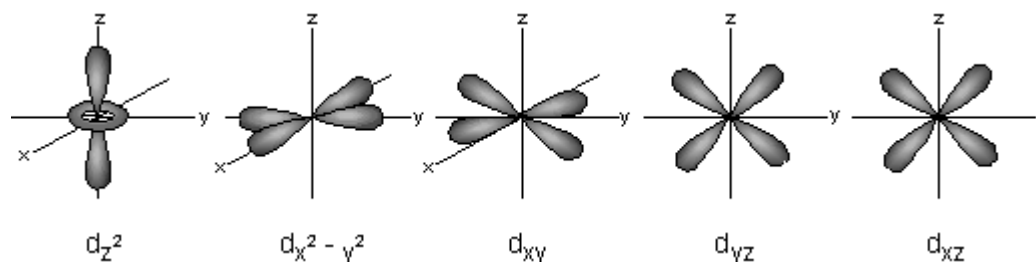


- **f - orbitals -** these are more difficult to describe in a graphical sense, but it turns out there are 7 possible f -orbitals, each being able to contain 2 electrons, for a maximum total of 14 electrons. Only shells with principal quantum numbers of 5 or greater can contain f -orbital electrons.

The *Pauli Exclusion Principal* states that no 2 electrons in an atom can have the same quantum numbers, thus each of the sub-orbitals described above can have a maximum of 2 electrons, and each of these will have opposite values of the spin quantum number.

As the atomic number (number of protons) in an atom increases, the shells and sub-shells with lower energy are filled first. The drawing at the right illustrates qualitatively the energy relationships between the various shells and sub-shells of atoms. Thus 1s sub-shells with the lowest energy are filled first. These are followed by 2s orbitals, then 2p orbitals. As the principal quantum number increases to 3, the 3s, 3p, and 3d orbitals are filled. But, beginning with n = 4, there is overlap between the energies of s and d orbitals, and thus the 4s orbital is filled before the 3d orbitals, and the 4p orbitals do not contain electrons until the 3d orbitals are filled. This overlap continues in a similar way for higher principle quantum number shells.
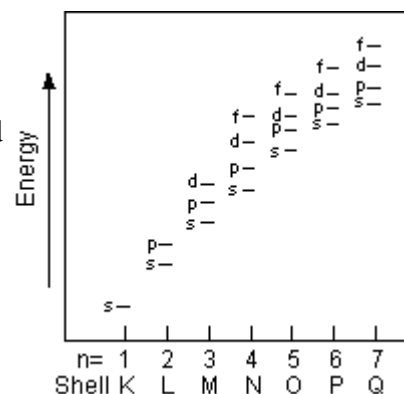


**Electronic Structure of the Atom and the Periodic Table of the Elements**

Based on the energy levels of the various sub-shells, we can begin filling in the electronic structure of atoms as shown in the following table. Note that this table only goes up to atomic number 36. A complete table can found in your textbook on pages 44-46.

| At. # | Elem. | K | L | | M | | | N | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1s | 2s | 2p | 3s | 3p | 3d | 4s | 4p | 4d | 4f |
| 1 | H | 1 | | | | | | | | | |
| 2 | He | 2 | <------ K-shell completely filled | | | | | | | | |
| 3 | Li | 2 | 1 | | | | | | | | |
| 4 | Be | 2 | 2 | | | | | | | | |
| 5 | B | 2 | 2 | 1 | | | | | | | |
| 6 | C | 2 | 2 | 2 | | | | | | | |
| 7 | N | 2 | 2 | 3 | | | | | | | |
| 8 | O | 2 | 2 | 4 | | | | | | | |
| 9 | F | 2 | 2 | 5 | | | | | | | |
| 10 | Ne | 2 | 2 | 6 | <----L-shell completely filled | | | | | | |
| 11 | Na | 2 | 2 | 6 | 1 | | | | | | |
| 12 | Mg | 2 | 2 | 6 | 2 | | | | | | |
| 13 | Al | 2 | 2 | 6 | 2 | 1 | | | | | |
| 14 | Si | 2 | 2 | 6 | 2 | 2 | | | | | |
| 15 | P | 2 | 2 | 6 | 2 | 3 | | | | | |
| 16 | S | 2 | 2 | 6 | 2 | 4 | | | | | |
| 17 | Cl | 2 | 2 | 6 | 2 | 5 | | | | | |
| 18 | Ar | 2 | 2 | 6 | 2 | 6 | <----3p-orbitals completely filled | | | | |
| 19 | K | 2 | 2 | 6 | 2 | 6 | | 1 | | | |
| 20 | Ca | 2 | 2 | 6 | 2 | 6 | | 2 | | | |
| 21 | Sc | 2 | 2 | 6 | 2 | 6 | 1 | 2 | | | |
| 22 | Ti | 2 | 2 | 6 | 2 | 6 | 2 | 2 | | | |
| 23 | V | 2 | 2 | 6 | 2 | 6 | 3 | 2 | | | |
| 24 | Cr | 2 | 2 | 6 | 2 | 6 | 5 | 1 | | | |
| 25 | Mn | 2 | 2 | 6 | 2 | 6 | 5 | 2 | | | |
| 26 | Fe | 2 | 2 | 6 | 2 | 6 | 6 | 2 | | | |
| 27 | Co | 2 | 2 | 6 | 2 | 6 | 7 | 2 | | | |
| 28 | Ni | 2 | 2 | 6 | 2 | 6 | 8 | 2 | | | |
| 29 | Cu | 2 | 2 | 6 | 2 | 6 | 10 | 1 | | | |
| 30 | Zn | 2 | 2 | 6 | 2 | 6 | 10 | 2 | | | |
| 31 | Ga | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 1 | | |
| 32 | Ge | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 2 | | |
| 33 | As | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 3 | | |
| 34 | Se | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 4 | | |
| 35 | Br | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 5 | | |
| 36 | Kr | 2 | 2 | 6 | 2 | 6 | 10 | 2 | 6 | <- 4p orbitals filled | |

This periodic filling of shells and sub-shells forms the basis of the periodic table of the elements. Elements with similar configurations of outer shell electrons (called *valence electrons*) have similar chemical properties. The rows in the table, labeled 1, 2, 3, 4, 5, 6, & 7, correspond to the principal quantum number.

- Column I is a groups of elements that have 1 electron on their outermost shell, which in this case is an s - orbital. Group I elements are called the *alkaline metals*.

- Elements in column II, called the *alkaline - earth metals,* all have 2 electrons in their completely filled outer s-orbital shells.

- Groups III, IV, V, VI, and VII all have the same number of outer shell electrons as the group number. Group VII elements are known as the *halogens*.

- Group VIII elements are all characterized by having completely filled p -orbital shells with 8 electrons total in their outermost s - and p -shells. This group is known as the *Noble Gases* or *Inert Gases,* inert because these elements do not combine with themselves or any other element under normal conditions.





- The *transition metals* occur between the alkaline earths (Group II) and Group III. These are elements with partially filled d - orbitals.

- Note the discontinuity in the table at element 57. Beginning with Ce, 4f -orbitals begin to be filled, and to keep the chart from becoming too wide, elements 58 to 71 (Ce to Lu) are placed at the bottom of the chart. The series from La to Lu is known as the *Lanthanides* and these elements are also commonly called the *Rare Earth Elements*.

- Similarly, another discontinuity occurs at element 89, Ac where the 5f - orbitals begin to

be filled, starting with the element Th.  elements 89 through 103 are referred to as the *Actinides*.

### The Ion

In  a neutral atom, the number of protons and the number of electrons are equal, thus the number of positive charges is the same as the number of negative charges and the atom has no charge.  However, some elements in the Periodic Table tend to loose electrons to become positively charged and some elements tend to gain electrons to become negatively charged. Atoms with an electrical charge are called *ions*.

Elements that tend to loose electrons are called *metals*, while those that tend to gain electrons are *non-metals*.

Metals thus tend to form positively charged ions called *cations*, while non-metals tend to form negatively charged ions called *anions*.

### Ionization Potential

When electrons are either removed or gained by an atom there is a transfer of energy.  The amount of energy required to remove an electron is called the *ionization potential*.  The version of the periodic table shown below gives value of the first ionization potential.  Note that elements with high ionization potential do not like to give up electrons, while those with low ionization potential can give up electrons more readily and tend to become cations.  We can make the following observations:



- The Noble gases all have very high first ionization potentials, indicating that their electronic structure is stable.  A glance at the periodic table showing filling shells (above) indicates that the Noble Gases all have in common completely filled p - orbitals.  It is because these sub-orbital shells are full that these elements do not readily become ions

and do not easily combine with other elements to become compounds.

- Elements in Group I (the alkalies), on the other hand have very low first ionization potentials, and thus it is relatively easy to remove one electron. Since all of these elements have in common an outermost shell containing 1 electron in the s - orbital, these elements tend to become +1 ions (i.e. $Li^{+1}$, $Na^{+1}$, $K^{+1}$, $Rb^{+1}$, $Cs^{+1}$, etc.) Note that removal of this electron will leave the atoms with an electronic configuration of the Noble gases, i.e. they will have completely filled outermost electron shells. Second ionization potentials (the energy required to remove a second electron) is also very high for these elements, again indicating that once they become +1 ions they have a stable electronic configuration.

- Elements in Group II (the alkaline earths) also have relatively low first ionization potentials and have relatively low second ionization potentials. Thus, these elements tend to lose 2 electrons to become +2 ions (i.e. $Be^{+2}$, $Mg^{+2}$, $Ca^{+2}$, $Sr^{+2}$, $Ba^{+2}$, etc.) Once they have lost these two electrons they also have an electronic configuration with completely filled outer electron shells, similar to the Noble Gases.

- Elements in Group VII (the halogens) have very high first ionization potentials. They don't like to give up electrons. But note that if they gain an electron to become a -1 ion, they will also have completely filled outer electron shells similar to the Noble gases. Thus these elements tend to gain electrons to become -1 ions (i.e. $F^{-1}$, $Cl^{-1}$, $Br^{-1}$, etc.).

- Based on similar reasoning, Group III elements tend to lose 3 electrons to become +3 ions (i.e. $B^{+3}$, $Al^{+3}$, $Ga^{+3}$, etc.). Group IV elements tend to lose 4 electrons to become +4 ions (i.e. $C^{+4}$, $Si^{+4}$, $Ge^{+4}$). But Pb, usually only loses 2 electrons to become $Pb^{+2}$.

- Elements in Group V tend to lose 5 electrons to become +5 ions (i.e. $N^{+5}$, $P^{+5}$, $As^{+5}$).

- Group VI tend to gain electrons to become -2 ions (i.e. $O^{-2}$, $S^{-2}$, $Se^{-2}$), but sulfur sometimes loses 6 electrons to become $S^{+6}$.

- The transition elements all have d-orbital electrons in their outermost shells, and because they have low to high first ionization potentials their behavior is somewhat variable. The elements in the third column tend to become +3 ions ($Sc^{+3}$, $Y^{+3}$, $La^{+3}$ ), those in the 4th column tend to become +4 ions ($Ti^{+4}$, $Zr^{+4}$, $Hf^{+4}$), and those in the 5th column tend to become +5 ions ($V^{+5}$, $Nb^{+5}$, $Ta^{+5}$). But the 5th through 11th column show variable ions. For example, Cr is usually $Cr^{+3}$, Mn can be usually $Mn^{+2}$, $Mn^{+3}$, or $Mn^{+4}$, Fe can be either $Fe^{+2}$ (ferrous iron) or $Fe^{+3}$ (ferric iron), Ni, Co, and Zn become +2 ions, and Cu can be either $Cu^{+1}$ or $Cu^{+2}$.

- The rare earth elements tend to become +3 ions, with the exception of Eu, which can be either $Eu^{+2}$, or $Eu^{+3}$. The actinides U and Th tend to become +4 ions.

To summarize, the common valence states of the common elements are listed in the table below for quick reference.

| Valence States of the Common Elements | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H^{+1}$ | | | | | | | | | | | | | | | | | |
| $Li^{+1}$ | $Be^{+2}$ | | | | | | | | | | | $B^{+3}$ | $C^{+4}$ | $N^{+5}$ | $O^{-2}$ | $F^{-1}$ | |
| $Na^{+1}$ | $Mg^{+2}$ | | | | Transition Elements | | | | | | | $Al^{+3}$ | $Si^{+4}$ | $P^{+5}$ | $S^{-2}$ $S^{+6}$ | $Cl^{-1}$ | |
| $K^{+1}$ | $Ca^{+2}$ | $Sc^{+3}$ | $Ti^{+4}$ | $V^{+5}$ | $Cr^{+3}$ | $Mn^{+2}$ $Mn^{+3}$ $Mn^{+4}$ | $Fe^{+2}$ $Fe^{+3}$ | $Co^{+2}$ | $Ni^{+2}$ | $Cu^{+2}$ | $Zn^{+2}$ | $Ga^{+3}$ | $Ge^{+4}$ | $As^{+3}$ $As^{+5}$ | | $Br^{-1}$ | |
| Th+4 REE +3, except Eu sometimes +2 $U^{+4}$ | | | | | | | | | | | | | | | | | |

**Electronegativity**

Another way of looking at the tendency to gain or lose electrons is based on the electronegativity. *Electronegativity* is defined as the ability of an atom in a crystal structure or molecule to attract electrons into its outer shell. Elements with low values of electronegativity are electron donors, and those with high values are electron acceptors. The Noble gases have electronegativity values of zero, because they neither accept or donate electrons. As we will see in our later discussion, electronegativity difference between atoms plays an important role in determining they type of chemical bond that forms between elements.

## Chemical Bonding

The chemical and physical properties of crystals depend almost entirely on the forces that bind the atoms together in a crystal structure.  These forces are known collectively as chemical bonds.  Chemical bonding depends on the electronic structure of the atoms involved, in particular the valence electrons in the outermost shells, and on the size of the ion or atom.

In general we recognize 4 different types of chemical bonds, although as we will see, all bond types are transitional from one type to another.
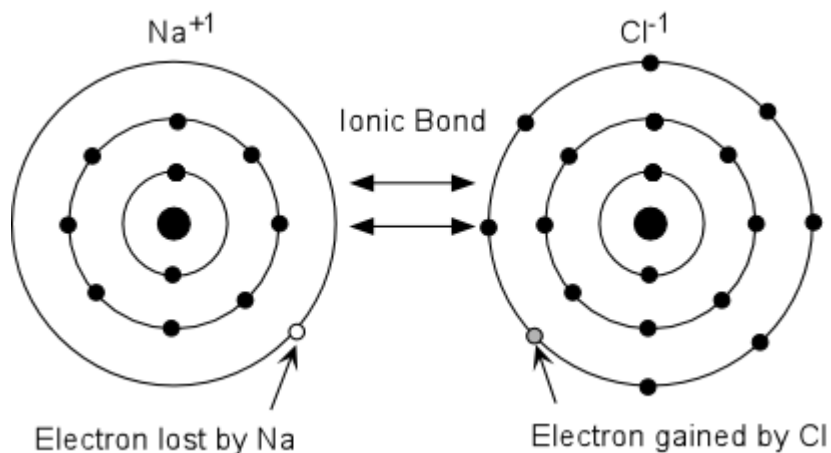
### Ionic Bonds

As we have seen, there is a tendency for atoms to lose or gain electrons and become ions in order to achieve the stable electronic configuration with completely filled outer electron shells. Positively charged ions are called cations and negatively charged ions are called anions.  These ions can achieve various values of electronic charge depending on the number of electrons gained or lost.

- +1    monovalent cations
- +2    divalent cations
- +3    trivalent cations
- +4    tetravalent cations
- +5    pentavalent cations
- -1    monovalent anions
- -2    divalent anions

When atoms become charged ions the force of attraction between oppositely charged ions results in an ionic bond.

For example, Na has one electron in its outermost shell. It will tend to give up this electron to become $Na^{+1}$ ion. Similarly, Cl has 7 electrons in its outermost shell and would like to gain an electron to become $Cl^{-1}$ ion.  Once these atoms become Na+1 and Cl-1, the force of attraction between the oppositely charged ions results in an ionic bond.



Ionic bonds are non-directional in nature, that is the attractive forces occur form all directions. Crystals made of ionically bonded atoms tend to have the following properties:
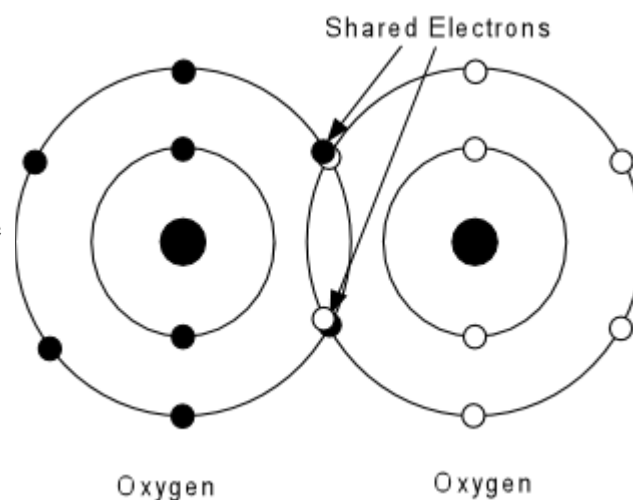
- Dissolve easily in polar solvents like water ($H_2O$ is a polar solvent because the hydrogen ions occur on one side the water molecule and give it a slight positive charge while the other side of the water molecule has a slight negative charge).

- Tend to form crystals with high symmetry.

- Moderate hardness and density.

- High melting temperatures.

- Generally poor conductors of heat and electricity (they are good materials for thermal and electrical insulation).

### Covalent Bonds

Covalent bonds can also be thought of as shared electron bonds. Covalent bonds develop when atoms can achieve the a stable outer shell electron configuration by sharing electrons with another atom. This results in each of the atoms having a stable electronic configuration part of the time.

For example, Oxygen has six electrons in its outer shell, 2 are in s-orbitals and 4 are in p-orbitals. If it can gain two more electrons to fill its p-orbital shells, it would have the stable electronic configuration of a Noble gas. A second Oxygen atom also needs 2 more electrons to achieve the stable configuration. If the two Oxygens each share 2 electrons with each other, then each Oxygen has the stable electronic configuration part of the time. The covalent bond thus formed is a very strong bond. Thus we find oxygen gas is composed of $O_2$ molecules. Similarly, $F_2$ and $Cl_2$ gases are composed of covalently bonded F and Cl pairs.



Covalent bonds are very strong directional bonds, that is they occur along the zone where they electrons are shared. Covalently bonded crystals have the following properties:

- Relatively insoluble in polar solvents like water.

- High melting temperatures.

- Generally form crystals structures of low symmetry.

- Tend to have high hardness.

- Generally poor conductors of heat and electricity.

Elements near the right hand side of the periodic table tend to bond to each other by covalent bonds to form molecules that are found in crystal structures. For example Si and O form an $SiO_4^{-4}$ molecule that can bind to other atoms or molecules either covalently or ionically.

Carbon has four electrons in its outer shell and needs 4 more to achieve the stable electronic configuration. So a Carbon atom can share electrons with 4 other Carbon atoms to form covalent bonds. This results in compounds like diamond or graphite that are held together by strong covalent bonds between Carbon atoms.

In reality, bonding between atoms usually does not take place as pure covalent or pure ionic bonds, but rather as a mixture of bond types. The amount of each type is determined by the electronegativity difference between the atoms involved.

For example, consultation of electronegativity chart above shows Cl with a value of 3.16 and Na with a value of 0.93. The electronegativity difference is 2.3, suggesting that only 80% of the bonding in NaCl is ionic. Even looking a larger electronegativity difference like for NaF, the bonding would by only about 90% ionic. Bonding between Oxygen atoms or between Carbon atoms, where the electronegativity difference is 0, would result in pure covalent bonds.
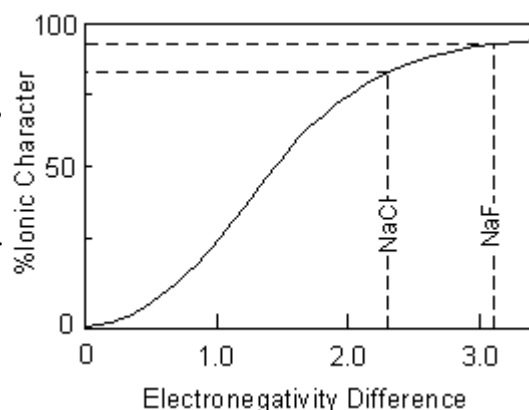
**Metallic Bonds**

None of the bond types discussed so far result in materials that can easily conduct electricity. Pure metals however do conduct electricity easily and therefore must be bonded in a different way.

This is the metallic bond, where positively charge atomic nuclei share electrons in their electron clouds freely. In a sense, each atom is sharing electrons freely with other atoms, and some of the electrons are free to move from atom to atom. Since some of the electrons are free to move, metallically bonded materials have high electrical conductivity.
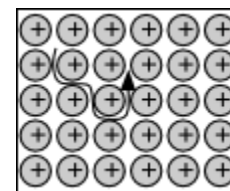
Pure metals appear to bind in this way. When crystals are formed with metallic bonds they have the following properties:

- Low to Moderate hardness.

- Usually very malleable and ductile.

- Good thermal and electrical conductors.

- Soluble only in acids.

- Crystals with high symmetry.

**Residual Bonds**

Residual bonds are weak bonds that involve the attraction of partially charged atoms or molecules. These partial charges are created when electrons become concentrated on one side of an atom or molecule to satisfy ionic or covalent bonds. This sometimes creates a polar atom or molecule which has a concentration of negative charges on one side and a concentration of positive charges on the other side. When residual bonds occur in a crystal structure, they generally form planes or zones of easy cleavage because of the weakness of the residual bond.

Two special cases are discussed here.

- Hydrogen Bonds - These occur in the special case of hydrogen, because H has only one electron. When Hydrogen gives up this electron to become $H^{+1}$ ion or shares its single electron with another atom in a covalent bond, the positively charged nucleus of the hydrogen atom is exposed, giving that end of the H ion a residual +1 charge. This is what causes the $H_2O$ molecule to be a polar molecule seen here.

  Similarly, an $OH^{-1}$ molecule, common in sheet silicate minerals like micas and clay minerals, although possessing a -1 charge will have exposed H nuclei that can bond to other negative residual charges forming a weak hydrogen bond. Layers of $OH^{-1}$ molecules in the sheet silicates result in the easy cleavage along the {001} planes.
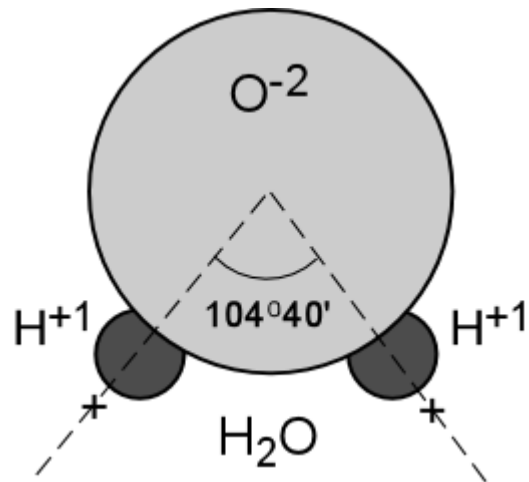
- van der Waals Bonds are also residual bonds that result from polarization of atoms or molecules. In the mineral graphite, the C atoms are held together by strong covalent bonds, that result in concentrations of positive and negative charges at either end of the C atoms. Bonding between sheets takes place as a result of the slight attraction between these residual charges from one sheet to another.
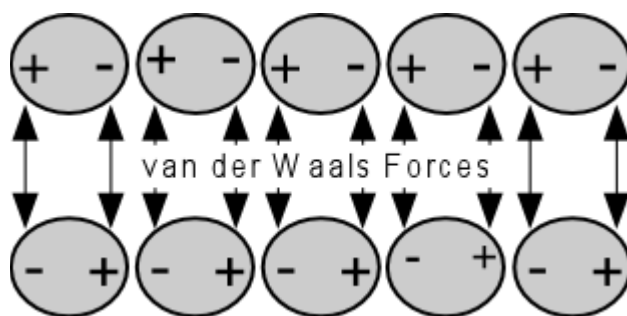
**Mixture of Bonds in Crystals**

Since most crystals are complex mixtures of atoms, there will likely be more than one bond type in complex crystals.  Thus, except in very simple compounds properties such as hardness, cleavage, solution rate, and growth rate may be directional, as discussed in a previous lecture.

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**Examples of questions on this material that could be asked on an exam**

1. Define the following :  (a) atomic number, (b) atomic weight, (c) s-orbitals, (d) p-orbitals, (e) d-orbitals, (f) ion, (g) cation, (h) anion.

2. What are ionic bonds and what physical properties are characteristic of compounds that contain ionic bonds?

3. What are covalent bonds and what physical properties are characteristic of compounds that contain ionic bonds?

4. What are metallic bonds and what physical properties are characteristic of compounds that contain ionic bonds?

5. What are residual bonds and what physical properties are characteristic of compounds that contain ionic bonds?

6. Name several elements in each of the following groups (a) Alkalies, (b) Alkaline Earths, (c) halogens, (d) Nobel Gases, (e) Rare Earths, (f) Actinides

7. What is the common valence state of elements in each of the following groups (a) Alkalies, (b) Alkaline Earths, (c) halogens

8. What is electronegativity and why is it important?

Return to EENS 2110 Page

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