CHEMICAL BONDING AND MOLECULAR STRUCTURE

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Molecules and chemical bond: Atoms are usually not capable of free existence but groups of atoms of the same or different elements exist as one species, e.g., H_2, O_2, H_2O, P_4

"A group of atoms existing together as one species and having characteristic properties is called a molecule." Obviously, there must be some force which holds these atoms together within the molecules. "This force which holds the atoms together within a molecule is called a chemical bond.

A number of questions now arise: (i) Why do atoms combine? (ii) Why are only certain combinations possible, e.g., hydrogen exists as H_2 and not as H_3? (iii) Why do some atoms combine while certain others do not, e.g., two H-atoms combine to form H_2 but two helium atoms do not combine to form He_2? (iv) Why do molecules possess definite shape, e.g., CO_2 is linear but H_2O is a bent molecule (V-shape)? Similarly, BF_3 is planar but NH_3 is pyramidal. To answer such questions different theories and concepts have been put forward from time to time. These are:

1. Kossel-Lewis approach
2. Valence shell electron pair repulsion (VSEPR) theory
3. Valence bond theory
4. Molecular orbital theory

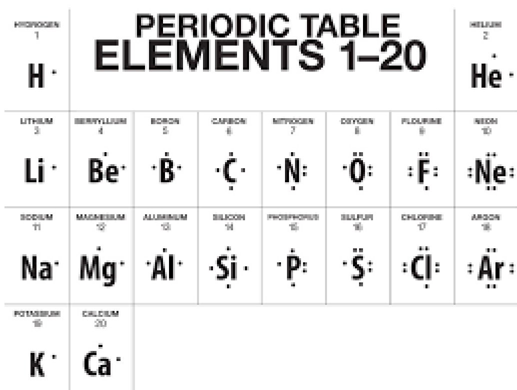
Why do atoms combine?-Kossel-Lewis approach to chemical bonding: In order to explain the formation of chemical bond in terms of electrons, a number of attempts were made, but it was only in 1916 when Kossel and Lewis succeeded independently in giving a satisfactory explanation. They were the first to provide some logical explanation of valence which was based on the inertness of noble gases.

The study of noble gases, earlier called inert gases, (group 18 elements) suggests that neither they combine chemically with any other element nor among themselves, i.e., they are chemically inactive. Further, their electronic configurations are as follows:

From the study of electronic configurations of the noble gases, it is clear that they have 8 electrons in their outermost orbit except in case of helium which has 2. Thus, noble gases are inactive or stable because they have 8 electrons in the outermost shell (called octet) or 2 electrons in case of helium (called duplet). Hence, it was suggested that they possess stable electronic configurations. In case of all other elements, the number of electrons in their outermost shell is less than 8 and hence they are chemically reactive. This led to the following conclusion, called octet rule: The atoms of different elements combine with each other in order outermost shell having 2 electrons) in case of H, Li, and Be to attain stable nearest noble gas configuration.

Noble Gas	Atomic Number	Electronic Configuration
Helium	2	2
Neon	10	2, 8
Argon	18	2, 8, 8
Krypton	36	2, 8, 18, 8
Xenon	54	2, 8, 18, 18, 8
Radon	86	2, 8, 18, 32, 18, 8

Lewis Symbols- Representing the valence electrons: In the formation of a molecule, only the outer shell electrons are involved and they are known as valence electrons. The inner shell electrons are well protected and are generally not involved in the combination process. It is, therefore, quite reasonable to consider the outer shell electrons, i.e., valence shell electrons while discussing chemical bonds. G.N. Lewis introduced simple symbols to denote the valence shell electrons in an atom. The outer shell electrons are shown as dots surrounding the symbol of the atom. These symbols are known as Lewis symbols or electron dot symbols. These symbols ignore the inner shell electrons. A few examples are given below:



Significance of Lewis symbols: The number of dots around the symbol gives the number of electrons present in the outermost shell. This number of electrons helps to calculate the common valency of the element. That is why these electrons are called valence shell electrons. The common valency of the element is either equal to the number of dots in the Lewis symbol (if these are ≤ 4) or 8 minus the number of dots (if these are > 4). For example, Li, Be, B and C have valencies 1, 2, 3, and 4 respectively, i.e., equal to the number of dots whereas valencies of N, O, F and Ne are 3, 2, 1 and 0 respectively, i.e., 8 minus the number of dots.

How do atoms combination? (Modes of chemical combination): As discussed above, atoms combine together in order to complete their respective octets so as to acquire the stable inert gas configuration. This can occur in two ways:

1. By complete transference of one or more electrons from one atom to another. This process is referred to as electrovalency and the chemical bond formed is termed as electrovalent bond or ionic bond.
2. By sharing of electrons. This can occur in two ways as follows: (a) When the shared electrons are contributed by the two combining atoms equally, the bond formed is called covalent bond.
   (b) When these electrons are contributed entirely by one of the atoms but shared by both, the bond formed is known as a coordinate bond, also called dative bond.

Electrovalent or Ionic Bond: " When a bond is formed by complete transference of electrons from one atom to another so as to complete their outermost orbits by acquiring 8 electrons (i.e., octet) or 2 electrons (i.e., duplet) in case of hydrogen, lithium etc. and hence acquire the stable nearest noble gas configuration, the bond formed is called ionic bond or electrovalent bond".

Explanation of the formation of ionic bond- Atoms are electrically neutral. Therefore, they possess equal number of protons and electrons. On losing an electron, an atom becomes positively charged since now the number of protons exceeds the number of electrons.

$$A \rightarrow A^+ + e^-$$

On the other hand, in case of atom, gaining the electron, the number of electrons exceeds the number of protons and thus the atom becomes negatively charged.

$$B + e^- \rightarrow B^-$$

The oppositely charged particles formed above attract each other by electrostatic forces of attraction. The bond thus formed is known as electrovalent or ionic bond. Such a type of bond is formed only when one of the atoms can easily lose electrons while the other can gain electrons and thus each acquires the stable electronic arrangement of the nearest noble gas.

Examples:

1. Formation of sodium chloride. Sodium (atomic number = 11) has electronic configuration 2, 8, 1. By losing one electron of its outermost shell it acquires the inert gas configuration of neon and changes into ion.

$Na \rightarrow Na^+ + e^-$

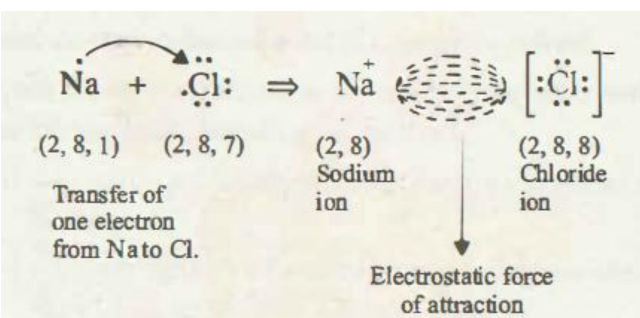
2,8, 1   2, 8

On the other hand, chlorine (atomic number = 17) having electronic configuration 2, 8, 7 , accepts one electron released by sodium to complete its octet by attaining stable configuration of argon. In this process, chlorine is converted into chloride ion.

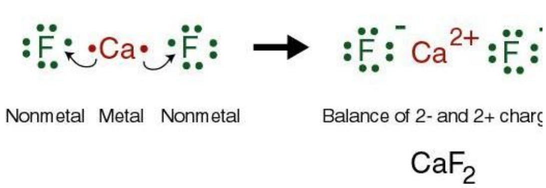
$Cl + e^- \rightarrow Cl^-$

(2, 8, 7)   (2, 8, 8)

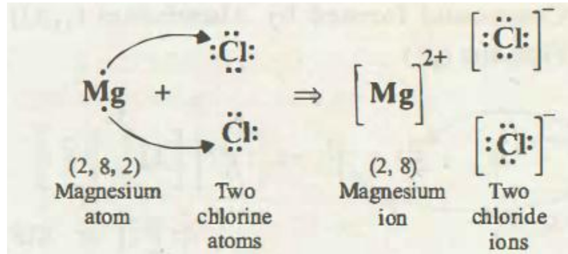
Now, we have two species, one is positively charged sodium ion and the other is negatively charged chloride ion. As they approach each other, they are held together by strong electrostatic forces of attraction. Thus formation of sodium chloride takes place.



2. Formation of calcium fluoride (CaF_2)



3. Formation of magnesium chloride ($MgCl_2$)



When the structures of atoms or ions are written in such a way that the electrons present in the outermost shell are represented by dots (.) around the symbol of the element, as in the example above, these structures are called Lewis dot structures.

"The number of electrons lost or gained during the formation of an electrovalent linkage is termed as the electrovalency of the element."

For example, sodium and calcium lose 1 and 2 electron respectively and so their valencies are 1 and 2. Similarly, chlorine and two fluorine atoms gain 1 and 2 electrons respectively, so they

Factors governing the formation of ionic bonds: The formation of ionic bond involves, (i) the formation of a positive ion by loss of electrons from one kind of atoms. (ii) The formation of a negative ion by gain of electrons from another kind of atoms. (ii) Holding the positive and negative ions by electrostatic forces of attraction.

The formation of ionic bond depends upon the following factors:

(i) Ionization Enthalpy: Ionization enthalpy of any element is the amount of energy required to remove an electron from the outermost shell of an isolated atom in gaseous phase so as to convert it into a gaseous positive ion.
It is clear that lesser the ionization enthalpy, easier will be the removal of an electron, i.e., formation of a positive ion and hence greater the chances of formation of an ionic bond.

Ionization enthalpy of alkali metals is low, hence they have more tendency to form to positive ions. $Na (g) \rightarrow Na^+ (g) + e^-$ I.E = – 495kJ mol^{-1}

(ii) Electron Gain Enthalpy:" Electron gain enthalpy (electron affinity) of an element is the enthalpy change that takes place when an extra electron is added to an isolated atom in the gaseous phase to form a gaseous negative ion.

Higher is the electron affinity, more is the energy released and stable will be the negative ion produced. Consequently, the probability of formation of ionic bond will be enhanced. Halogens possess high electron affinity. So the formation of their negative ions is very common, e.g., in case of chlorine, electron affinity is +348 $kJmol^{-1}$.

(iii) Lattice enthalpy: In the formation of ionic compounds, the positively charged ions combine with negatively charged ions to form the compound.

$$A^+ (g) + B^- (g) \rightarrow A^+B^- (s)$$

The energy released when the requisite numbers of gaseous positive and negative ions combine to form one mole of the ionic compound is called lattice enthalpy.

The higher the value of lattice enthalpy of the resulting ionic compound, the greater will be the stability of the compound and hence greater will be the ease of its formation. We know that the force of attraction between the oppositely charged ions is directly proportional to the magnitude of the charges (q_1, q_2) and inversely proportional to the square of the distance 'd' between them, i.e., force of attraction $\alpha\ q_1 q_2 / d^2$

Hence, the value of lattice enthalpy depends upon the following two factors:

(a) *Charge on the ions:* The higher the charge on the ions, greater is the force of attraction and hence larger is the amount of energy released. For example, lattice enthalpies of some ionic compounds are in the order:

$NaCl$ < $CaCl_2$ < MgO

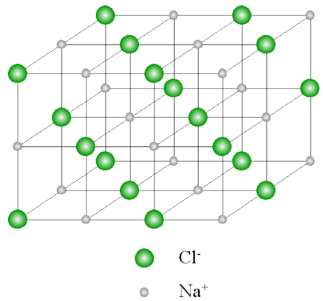
(– 758kJ mol^{-1}) (– 2254kJ mol^{-1}) (– 3932kJ mol^{-1})

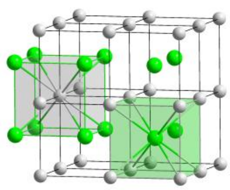
(b) *Size of the ions:* Smaller the size of the ions, lesser is the internuclear distance. Consequently, the interionic attractions will be high and the lattice enthalpy will also be large. For example, ionic radius of K^+ (133 pm) is larger than that of Na^+ (95 pm), therefore, the lattice enthalpy of NaCl (758.7 kJ mol^{-1}) is greater than that of KCl (681.4kJ mol^{-1}).

Net effect: If lattice enthalpy + electron gain enthalpy > ionization enthalpy, the net effect will be the release of energy and hence an ionic bond is formed.

General characteristics of ionic compounds:

1. *Physical State:* These compounds usually exist in the solid state.
2. *Crystal Structure:* X- ray analysis of the ionic compounds shows that they exist as ions and not as molecules. These ions are arranged in a regular pattern in the three dimensional space to form a lattice. The pattern of arrangement, however, depends upon the size and charges of the ions. For example, in case of sodium chloride, each sodium ion is surrounded by six chloride ions and each chloride ion by six sodium ions, thus giving rise to a three dimensional octahedral crystal structure. The formula of an ionic compound merely indicates the relative number of ions present.





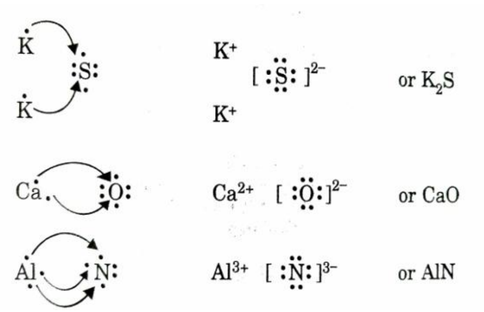
Crystal structure of NaCl

3. *High Melting and Boiling Point:* Ionic compounds possess high melting and boiling points. This is because ions are tightly held together by strong electrostatic force of attraction and hence a huge amount of energy is required to break the crystal lattice.
4. *Solubility:* Electrovalent compounds are soluble in solvents like water which are polar in nature and have high dielectric constant. It is due to the reason that the polar solvent interacts with the ions of the crystals and further the high dielectric constant of the solvent (i.e., capacity of the solvent to weaken the forces of attraction) cuts off the force of attraction between these ions. Furthermore, the ions may combine with the solvent to liberate energy called the hydration enthalpy which is sufficient to overcome the attractive forces between the ions. Non – polar solvents like carbon tetrachloride, benzene etc. having low dielectric constants are not capable of dissolving ionic solids. Hence, ionic solids are soluble in polar solvents and insoluble in non-polar solvents.
5. *Electrical Conductivity:* Ionic compounds are good conductors of electricity in solution or in the molten state. In solution or molten state, their ions are free to move. As the ions are charged, they are attracted towards electrodes and thus act as carrier of electric current.
6. *Ionic reaction:* The reactions of the ionic compounds are, in fact, the reactions between the ions produced in solution. As the oppositely charged ions combine quickly, these reactions are, therefore, quite fast.

$$Na^+ Cl^- (aq) + Ag^+ NO_3^- (aq) \rightarrow AgCl (s) + NaNO_3 (aq)$$

Example: Use of Lewis symbols to show electron transfer between the following atoms to form cations and anions.(i) K and S (ii) Ca and O (iii) Al and N

Solution:



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