Inorganic Chemistry

M.S.C. / First Semester

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The References:-

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2- Concise Inorganic Chemistry by J.D.Lee ; Fifth Edition 2011

3-Introduction to Coordination Chemistry by Geoffrey A. Lawrance ; First Edition 2009

4- Inorganic Chemistry principles of structure and reactivity by James E. Huheey , Ellen A. Keiter , Richard L. Keiter , Okhil K. Medhi ; Fourth Edition 2006

Chemical Bonding:-

From the small number of elements there are derived millions of known compounds, and there are an infinite number possible. This is because there are so many possible ways in which atoms combine to form molecules.

Most of the substances are found in nature in the form of clusters or aggregates of atoms. Any such aggregation, in which atoms are held together and which is electrically neutral is called a molecule. The molecules are made of two or more atoms joined together by some force acting between them. The force is termed as a **chemical bond**. Thus, a **chemical bond is defined as a force that acts between two or more atoms to hold them together as a stable molecule or as a force that holds group of two or more atoms together and makes them function as a unit**. For example, in water the fundamental unit is the H-O-H molecule, which is described as being held together by the two O-H bonds.

The beginning of our modern theory of bonding can be treated to the concept of valency introduced in 1850. The term valency has been derived from the Latin word 'valentia' which means capacity. **Each element was said to have a valency equal to its combining capacity. The number of hydrogen or chlorine atoms with which another atom combines is called its combining capacity.** The valency of these two elements was set as, one. Therefore, oxygen which reacts with hydrogen to form H_2O, was said to have a valency of two. Mg combines with chlorine to form $MgCl_2$, Mg was said to have a valency of two. By using this definition, it is found that elements may have multiple valencies and fractional valencies in certain compounds. For example, nitrogen forms a number of compounds with hydrogen such as NH_3, N_2H_4, N_3H in which valencies of nitrogen come to 3, 2 and 1/3 respectively.

Thus, the concept of valency as a mere number was very confusing. Later on, the definition of valency was changed. **Valency was termed as the number of chemical bonds formed by an atom in a molecule.**

The modern concept of valency deals with the interactions between atoms in light of the structure of atoms, i.e., electronic configurations of atoms. The modern concept believes that **electrons are responsible for chemical combination**. It provides tools to find out the answers to the following questions :

(i) Why do atoms combine?

(ii) How do atoms combine together?

(iii) How can the properties of compounds be understood in terms of chemical bonds?

Cause of Chemical Combination:-

The atoms interact with each other on account of the following reasons:

(i) Decrease in energy : It is a fundamental truth that all natural systems tend to lose potential energy and become more stable. Other things being equal, a system that has stored potential energy is less stable than a system that has none. It is an observed fact that a bonded state is more stable than unbonded state. This is due to the fact that the bonded It is a fundamental truth that state has lower potential energy than unbonded state. Hence, when two atoms approach each other, they combine only under the condition that there is a decrease in potential energy.

When two atoms approach each other, new forces of attraction and repulsion come into play. These forces are :

(a) Electrons and nuclei attract one another. Attractive forces are energetically favourable, so an electron attracted to a nucleus is of lower energy and therefore more stable than a free electron.

(b) Electrons repel each other ,raising the energy and reducing the stability.

(c) Nuclei repel each other , so reducing the stability also.

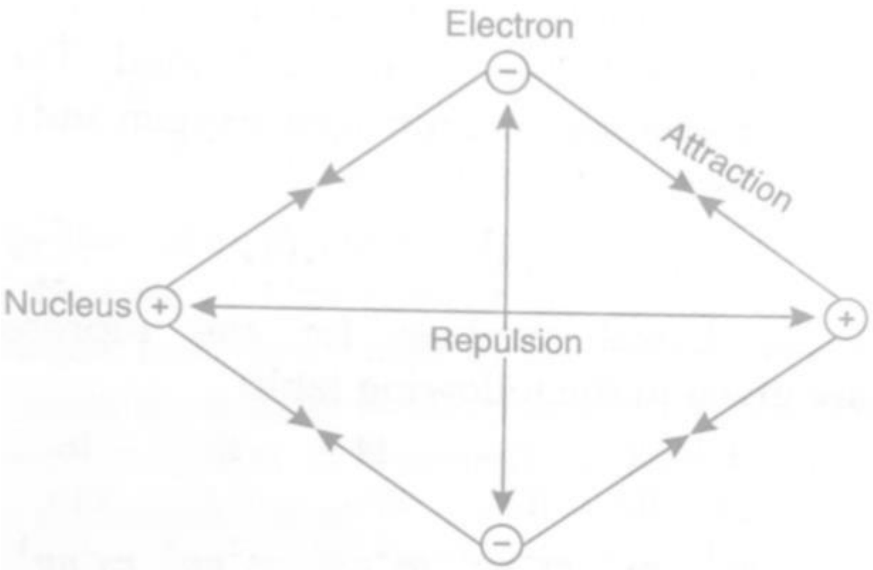


Fig. Electrostatic forces in hydrogen molecule

If the net result is attraction, the total potential energy of the system decreases and a chemical bond results. No chemical bonding is possible if net result is repulsion.

(ii) Lewis octet rule : The noble gases are known for their lack of chemical activity. There are no known compounds of helium, neon and argon. Why are these elements so unreactive towards other elements? All these elements have electronic structures that consist of filled outermost shells. Except for helium, whose electronic configuration is $1S^2$ the s-and p-subshells of the highest energy level contain a total of eight electrons. It is, therefore, concluded that S^2P^6 configuration in the outer energy level constitutes a structure of maximum stability and therefore, of minimum energy.

The atoms of all elements when enter into chemical combination try to attain noble gas configuration, i.e., they try to attain either 2 electrons (when only one energy shell) or 8 electrons in their outermost energy level which is of maximum stability and hence of minimum energy. The tendency of atoms to achieve eight electrons in their outermost shell is known as **Lewis octet rule**. Octet rule was the basis of electronic theory of valency.

Lewis Symbols of Elements:-

Chemical bonding mainly depends on the number of electrons present in the outermost energy level. These electrons are termed as valency electrons. The electronic configuration of sodium (Na) is 2,8,1 and that of Sulphur has (S) 2,8,6. Thus, sodium has one valency electron while Sulphur has six valency electrons. In the case of representative elements, the group number (Modern Mendeleev's periodic table) is equal to the number of valency electrons.

The valency electrons in atoms are shown in terms of Lewis symbols. To write Lewis symbol for an element, we write down its symbol surrounded by a number of dots or crosses equal to the number of valency electrons. Paired and unpaired valency electrons are also indicated.

Generalised , Lewis symbols for the representative elements are given in the following table

Group	1 IA ns^1	2 IIA ns^2	13 IIIA ns^2np^1	14 IVA ns^2np^2	15 VA ns^2np^3	16 VIA ns^2np^4	17 VIIA ns^2np^5
Lewis symbol	X•	•X•	•Ẋ•	•Ẋ̣•	•Ẋ̤•	•Ẍ̤•	:Ẍ̤•
Second period	Li•	•Be•	•Ḃ•	•Ċ̣•	•Ṅ̤•	•Ö̤•	:F̤̈•
Third period	Na•	•Mg•	•Ȧl•	•Ṡịi•	•Ṗ̤•	•S̤̈•	:C̤̈l•

Electronic Theory of Valency :-

The electronic theory of valency owes its rise to the recognition of the existence of electrons in an atom. It was suggested that electrons themselves are responsible for chemical combination. Kossel and Lewis formulated a comprehensive statement which Langmuir and called electronic theory of valency. The main points of the theory are:

(i) Valency of an atom depends mainly on the number of electrons present in the outermost orbit. These electrons are termed as valency electrons.

(ii) Electronic configuration of noble gases is stable, i.e., eight electrons are present in the outermost orbit (except helium having 2 electrons). These gases are chemically inert and do not form any compound.

(iii) Atoms having less than 8 electrons in the outermost orbit are chemically active. It is the tendency of these atoms to achieve 8 electrons in the outermost orbit. [Hydrogen, lithium, beryllium try to achieve helium configuration.] The number of electrons which take part determines the valency of the atom.

(iv) There are two ways by which the atoms can acquire noble gas configuration or 8 electrons in the outermost energy level.

(a) By losing or accepting electrons.

(b) By sharing electrons. Sharing may be of two types:

1. Equal contribution of electrons is made by two atoms and these electrons are then shared equally to form covalent bond, or

2. Contribution of an electron pair is made by one atom and both the electrons are shared equally by the two atoms to form coordinate bond. The theory may be summarised in the following way. "The union of two or more atoms involving redistribution of electrons in their outer shelis (either by transference or sharing) in such a way so that all the atoms acquire the stable noble gas configuration of minimum energy is known as electronic theory of valency."

different types of bonds are formed giving to rise to different properties in compounds. The strength of chemical bonds varies considerably leading to the formation of either strong or primary bonds and weak or secondary bonds.

♣ Strong bonds include ionic or electrovalent bonds, covalent bonds and co-ordinate covalent or dative bonds.

♣ Weak bonds include dipole-dipole interaction and hydrogen bonds. The three main types of atomic bonds are:

1. Ionic Bonds: They are formed because of non-directional interatomic forces and electron transfer. They give structures of high coordination and there is electrical conductivity at low temperatures.

2. Covalent Bonds: They are formed because of localised (directional) large interatomic forces and electron sharing. They help form structures of low coordination and low conductivity at low temperature (for pure crystals).

3. Metallic Bonds: They are formed due to non-directional large interatomic forces.

Ionic or Electrovalent Bond:-

Ionic bonding is the complete transfer of valence electron between atoms. Ionic bonds occur between metals (electron donors) and non-metals (electron acceptors) because of the electrostatic force of attraction between positive and negative ions. Ionic or electrovalent bonds are formed under the conditions of low ionization energy, high electron affinity and high lattice energy.

Why does ionic bonding occur?

♣ It occurs in metals because metals have few valence electrons and metals tend to lose electrons to attain octet configuration and achieve noble gas configuration.

♣ It occurs in non-metals since non-metals readily accept electrons to achieve noble gas configuration.

Characteristics of ionic bonds:

♣ Ionic compounds have high melting and boiling points.

♣ They are dense because their crystalline forms contain crystal lattices of tightly packed molecules.

♣ Their crystalline forms are always soluble in water.

♣ Crystals cannot conduct electricity in the solid state.

♣ The chemical bond generates two oppositely charged ions.

♣ Metals lose electrons to become a positively charged cations while non-metals accept those electrons to become a negatively charged anions.

♣ The charges on the anion and cation correspond to the number of electrons donated or received.

♣ The net charge of the compound is zero.

Ionic Bond Properties

Due to the presence of a strong force of attraction between cations and anions in ionic bonded molecules, the following properties are observed:

1. The ionic bonds are the strongest of all the bonds.
2. The ionic bond has charge separation, and so they are the most reactive of all the bonds in the proper medium.
3. The ionic bonded molecules have high melting and boiling point.
4. The ionic bonded molecules in their aqueous solutions or in the molten state are good conductors of electricity. This is due to the presence of ions which acts as charge carriers.

Examples of Ionic Bonds

The following table shows the elements and the ions formed by them when they lose or gain e^-.

Element	**Electronic config.**	**Reaction**	**Formed ion**
Na(11)	2,8,1	$Na \rightarrow Na^+ + e^-$ …………………… Reaction 1	Na^+
Ca(20)	2,8,8,2	$Ca \rightarrow Ca^{2+} + 2e^-$……………….. Reaction 2	Ca^{2+}
Cl(17)	2,8,7	$Cl + e^- \rightarrow Cl^-$ …………………….…. Reaction 3	Cl^-
O(8)	2,6	$O + 2e^- \rightarrow O^{2-}$…………………… Reaction 4	O^{2-}

- Now when Na reacts with Cl, reaction 1 and reaction 3 will take place and the resultant compound will be NaCl.
- When Na reacts with O, reaction 1 and reaction 4 will take place and the resultant compound will be Na_2
- When Ca reacts with Cl, reaction 2 and reaction 3 will take place and the resultant compound will be $CaCl_2$.
- When Ca reacts with O, reaction 2 and reaction 4 will take place and the resultant compound will be CaO.

Method of Writing Formula of an Ionic Compound:-

In order to write the formula of an ionic compound which is made up of two ions (simple or polyatomic) having electro- valencies x and y respectively, the following points are followed:

(i) Write the symbol of the ions side by side in such a way that positive ion is at the left and negative ion at the right as AB.

(ii) Write their electrovalencies in figures on the top of each symbol as A^xB^y.

(iii) Divide their valencies by H.C.F.

(iv) Now apply criss cross rule as $\overset{X}{A} \times \overset{Y}{B}$, i.e., formula A_yB_x.

Examples:

Calcium chloride	$\overset{2}{Ca} \times \overset{1}{Cl} = CaCl_2$;
Aluminium oxide	$\overset{3}{Al} \times \overset{2}{O} = Al_2O_3$;
Potassium phosphate	$\overset{1}{K} \times \overset{3}{PO_4} = K_3PO_4$;
Magnesium nitride	$\overset{2}{Mg} \times \overset{3}{N} = Mg_3N_2$;
Calcium oxide $\overset{2\ 2}{CaO}$ or	$\overset{1}{Ca} \times \overset{1}{O} = CaO$;
Ammonium sulphate	$\overset{1}{NH_4} \times \overset{2}{SO_4} = (NH_4)_2SO_4$

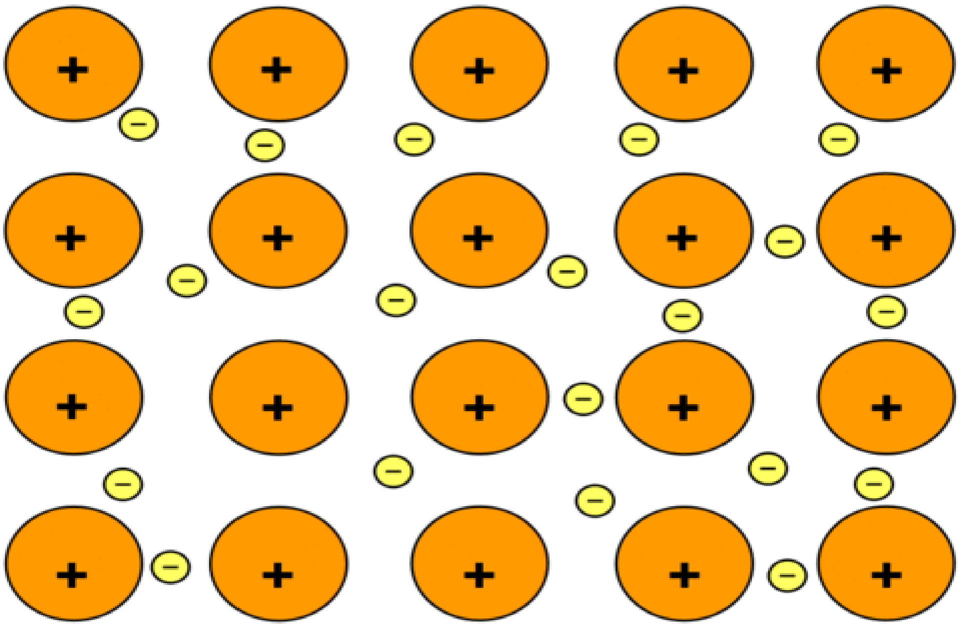
<u>Metallic bond:-</u>

In the early 1900's, Paul Drüde came up with the "sea of electrons" metallic bonding theory by modeling metals as a mixture of atomic cores (atomic cores = positive nuclei + inner shell of electrons) and valence electrons. Metallic bonds occur among metal atoms. Whereas ionic bonds join metals to non-metals, metallic bonding joins a bulk of metal atoms. A sheet of aluminum foil and a copper wire are both places where you can see metallic bonding in action.

Metals tend to have high melting points and boiling points suggesting strong bonds between the atoms. Even a soft metal like sodium (melting point 97.8°C) melts at a considerably higher temperature than the element (neon) which precedes it in the Periodic Table. Sodium has the electronic structure 1s22s22p63s1. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighboring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms - and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. Each of these eight is in turn being touched by eight sodium atoms, which in turn are touched by eight atoms - and so on and so on, until you have taken in all the atoms in that lump of sodium. All of the 3s orbitals on all of the atoms overlap to give a vast number of molecular orbitals that extend over the whole piece of metal. There have to be huge numbers of molecular orbitals, of course, because any orbital can only hold two electrons.

The electrons can move freely within these molecular orbitals, and so each electron becomes detached from its parent atom. The electrons are said to be delocalized. The metal is held together by the strong forces of attraction between the positive nuclei and the delocalized electrons (Figure below).



This is sometimes described as "an array of positive ions in a sea of electrons". If you are going to use this view, beware! Is a metal made up of atoms or ions? It is made of atoms**.** Each positive center in the diagram represents all the rest of the atom apart from the outer electron, but that electron has not been lost - it may no longer have an attachment to a particular atom, but it's still there in the structure. Sodium metal is therefore written as Na, not Na^+.

So Metallic Bond ,force that holds atoms together in a metallic substance. Such a solid consists of closely packed atoms. In most cases, the outermost electron shell of each of the metal atoms overlaps with a large number of neighbouring atoms. As a consequence, the valence electrons continually move from one atom to another and are not associated with any specific pair of atoms. In short, the valence electrons in metals, unlike those in covalently bonded substances, are nonlocalized, capable of wandering relatively freely throughout the entire crystal. The atoms that the electrons leave behind become positive ions, and the interaction between such ions and valence electrons gives rise to the cohesive or binding force that holds the metallic crystal together.

Many of the characteristic properties of metals are attributable to the non-localized or free-electron character of the valence electrons. This condition, for example, is responsible for the high electrical conductivity of metals. The valence electrons are always free to move when an electrical field is applied. The presence of the mobile valence electrons, as well as the nondirectionality of the binding force between metal ions, account for the malleability and ductility of most metals. When a metal is shaped or drawn, it does not fracture, because the ions in its crystal structure are quite easily displaced with respect to one another. Moreover, the nonlocalized valence electrons act as a buffer between the ions of like charge and thereby prevent them from coming together and generating strong repulsive forces that can cause the crystal to fracture.