SYNOPSIS

(GENERAL CHEMISTRY)

Introduction

General chemistry is a branch in chemistry to study about matter and energy and how these two are inter-related. The study of general chemistry is essential for meeting our basic needs of food, shelter and clothing, health, energy, clean air, water and soil.

General chemistry teaches us important principles concepts to be used in other parts of chemistry in numerous ways. The study of general chemistry requires analytical skill and mathematical knowledge and understanding. General chemistry is a natural science that covers the elements that make up matter to the compounds composed of atoms, molecules and ions and how the properties and composition, structure of elements and compounds changes during a chemical reaction.

The topics included in the general chemistry course are:

1. **Basic concepts of chemistry** (measurement and units, matter and energy, stoichiometry, mole concept, limiting reagent, empirical and molecular formula, methods of expressing concentration of solution.

2. **Atomic structure** (electronic structure of atoms, hydrogen spectra, particle and wave nature of electron, Quantum mechanical model of an atom)

3. **Periodic table and periodic trends**: Trends in physical and chemistry properties across the period and down the group (atomic and ionic size, ionization enthalpy, electron gain enthalphy, electronegativity, etc.

4. **Chemical bonding and molecular structure** (ionic and covalent bonding, sigma and pi bonds) shapes of molecules, dipole moment, resonance, molecular orbital theory, hybridization.

5. **Redox reactions:** Oxidation, reduction, oxidizing agent and reducing agent, concept of oxidation number, writing and balancing redox reactions using ion-electron method and oxidation number method.

Basic concepts of Chemistry

Chemistry is the study of composition, structure and properties of matter and the reactions by which one form of matter may be converted into another form. On the basis of composition, matter is classified into homogeneous and heterogeneous mixture. A mixture is a simple combination of two or more substances.

All pure substances are classified as either elements or compounds. Chemistry represents elements by symbols. Laws of chemical combinations led to the statement of atomic theory by Dalton.

Laws of combining volume and Avogadro's hypothesis can be used to predict molecular formulae.

Atomic and molecular masses can be determined with high accuracy using mass spectroscopy.

Atomic mass is an average of the masses of isotopes of that element, weighed by their fractural natural abundance. **Molecular masses** of compounds obtained by adding the atomic masses of the constituent elements.

One mole is the amount of substance that contains the number of particles (atoms, molecules, ions or electrons, etc) present in 0.012 kg of carbon. This number is equal to 6.022×10^{23}.

The number 6.022×10^{23} is called Avogadro number. One mole of any gas at STP (273 K, 1 bar pressure) contain 6.022×10^{23} molecules and occupies volume of 22.4 L at STP.

Empirical formula gives the simplest ratio and **molecular formula**, which gives the actual number of atoms of each element in a compound.

Empirical formula is more meaningful in ionic solids and liquids. In such cases formula mass instead of molecular mass is used.

Percentage composition of each element helps in calculation of empirical formula. Molecular formula can be derived if we know molecular mass. The relation between the masses of chemical reactants and products in a balanced chemical equation is called **stoichiometry** of the reaction.

A solution is a homogeneous mixture of two or more substances whose composition can be varied within certain limits.

The concentrations of solutions are expressed in terms of percentage, molality, molarity, mole fraction. Stoichiometry of reaction in solutions is very important as most of the reaction takes place in solution.

In a reaction involves two or more reactants, the reactant that is completely used up first, limiting the amount of product (s) is called limiting reactant or limiting reagent.

Atomic Structure

Atoms are the building blocks of elements. The first atomic theory was proposed by John Dalton regarded atom as the ultimate indivisible particle of matter. But atoms is divisible and consists of three fundamental particles electrons, protons and neutrons.

Thomson model proposed that an atom consists of uniform sphere of positive electricity with electrons embedded into it. But this model was proved wrong by Rutherford alpha ray scattering experiment. Rutherford concluded that atom consists of tiny positively charged nucleus surrounded by electrons in circular orbits.

But Rutherford model could not explain the stability of an atom i.e., why does the electron not fall on the nucleus?

The difficulties of the Rutherford model were overcome by Neil Bohr in the model of the hydrogen atom. Bohr postulated that electron moves around the nucleus in circular orbit. Only certain orbits can exist and each orbit corresponds to specific energy. These orbits are called **stationary orbits**. Bohr calculated

(i) The radius of an atom, $r_n = 0.529\frac{n^2}{Z}\text{Å}$

(ii) energy of an electron in various orbits

$$E_n = -2.18\times10^{-19}\frac{Z^2}{n^2}\ \text{J/atom}$$

Also, Bohr model satisfactorily explained the spectrum of hydrogen atom but failed to explain spectrum of multi electron atoms.

This is because Bohr considered electrons as a particle and completely ignored the wave character of electron. Further an orbit is a clearly defined path and this path can completely be defined only if both the exact position and the exact velocity of the electron at the same time are known. This is not possible according to Heisenberg's uncertainty principle. Bohr model of the hydrogen atom, therefore, not only ignores the dual behavior of electron but also contradicts Heisenberg's uncertainty principle.

Schrodinger proposed an equation called Schrodinger equation to describe the electron distribution in space and the allowed energy levels in atom. This equations incorporates de-Broglie concept of wave particle duality and in consistent with Heisenberg's uncertainty principle. Solving Schrodinger equation for hydrogen atom gives possible energy states the electron can occupy and the corresponding wave function (ψ) of the electron associated with each energy state. These quantized energy states are called orbitals characterized by set of three quantum number (*n*, *l* and *m*).

According to the quantum mechanical model of the atom, the electron distribution of an atom containing a number of electrons is divided into shells. The shells consists of one or more subshells and subshells are associated to be composed of one or more orbitals, which the electron occupy.

The subshells are s, p, d and f. For hydrogen atom and hydrogen atom like species, all the orbitals within a given shell have same energy (depends only on the principal quantum number, *n*) . For multi electron systems, the energy of the orbitals depends on the values of *n* and *l*. The energy of

orbital increases as (n + l) value increases and for the same (n + l) value, energy increases as n increases.

The distribution of electrons into various orbitals and subshells is called **electronic configuration**. According to Aufbau's principle, electrons are filled into various orbitals in order of increasing energy. According to Pauli exclusion principle, an orbital can accommodate a maximum of two electrons with opposite spins. It states that "*No two electrons in atoms can have the same set of four quantum numbers*".

Orbitals having the same energy are called **degenerate orbitals**. According to **Hunds' rule** of **maximum multiplicity** no pairing of electron starts in the orbital having same energy until and unless each orbital is singly filled. This form the basis of electronic structure of atom. We also write the electronic configuration of ions.

Classification of Elements and periodicity in Properties: Mendeleev classified the elements in the periodic table on the basis of atomic masses, Modern periodic table arrange the elements in the order of their atomic numbers and according to their electronic configuration. The elements in the same vertical column exhibit similar chemical properties and constitute a family or a **group**. The horizontal rows are called **periods**. In the modern periodic table, there are 18 group and eight periods.

Modern periodic table has been divided into four blocks: s, p, d and f block depending upon the subshell in which the last electron present. Hydrogen with one electron in the 1s orbital occupies a unique position in the periodic table.

In the periodic table, nearly seventy five percent of the elements are **metals**. There are about twenty **non-metals** which are located at the right of the periodic table. Elements which lie at the borderline between metals and non-metals (Si, Ge, As) are called **metalloids** or **semimetals**.

Metallic character increases as we go down a group. Non-metallic character increases across a period. The physical and chemical properties of elements vary periodically with their atomic numbers. Periodic trends are observed in **atomic sizes, ionization enthalpies, electron gain enthalpies electronegativity** and **valence of elements.**

The first ionization enthalpy is the enthalpy change for the reaction:

$$M_{(g)} \rightarrow M^{+}(g) + e^{-}.$$

Ionization enthalpy depends on the atomic size, electronic configuration, shielding or screening effect and penetration effect. Ionization enthalpy generally increases across the period and decreases down the group.

Electron gain enthalpy is the enthalpy change accompanying the addition of an electron to a gaseous atom of the element represented by the reaction:

$$X(g) + e^{-} \rightarrow X^{-}(g)$$

In general, electron gain enthalpies become more negative (more exothermic) across a period and less negative down the group. In the periodic table, halogen have the most negative electron gain enthalpy.

The atomic or covalent radius is defined as one half the distance between the nuclei of two atoms in a diatomic or polyatomic molecule of an element or between two metal atoms in a metallic solid. The atomic radius decreases from left to right across the period and increases from top to bottom in a group.

Electronegativity is defined as the ability of an atom to attract covalent or shared pair of electrons towards itself in a molecule. Electronegativity increases from left to right in a period and decreases from top to bottom in a group.

Valence can be defined as the number of atoms of hydrogen (or twice the number of oxygen) required by one atom of the element to form a stable compound. There is some periodicity in valence; for example, among representative elements, the valence is either equal to the number of electrons in the outer most orbitals of eight minus this number.

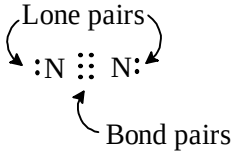
Chemical Bonding

Atoms attains stable octet when chemical bonds are formed. During the formation of positive and negative ions, the ions also attain the electronic configuration of nearest noble gas. Electrostatic attraction between ions is the cause of their stability. This gives the concept of **electrovalency**.

An **ionic bond** is formed by transfer of electrons between the atoms forming the bond. An ionic compound is pictured as a three-dimensional aggregation of positive and negative ions in an ordered arrangement called the **crystal lattice.** The crystal lattice is stabilized by the enthalpy of lattice formation. Infact, lattice enthalpy is taken as a measure of the stability of an ionic solid and its value can be calculated with the help of Born-Haber cycle.

A covalent bond is formed by sharing of electron between atoms. The Lewis dot structure provide the picture of bonding in molecules and ions**. Octet rule** explains the formation of bond by sharing, gain or loss of electrons in order to have eight electrons in the valence shell. There are many exceptions to the Lewis octet rule. There are mainly three exception: hypovalent molecules (less than 8 electron), hypervalent molecules (more than 8 electrons), and odd electron molecules.

A single covalent bond is formed by sharing of an electron pair between two atoms, while multiple bonds result from the sharing of two or three electron pairs. The electron pairs not used in the bonding are called lone pairs of electrons. A Lewis dot structure shows the arrangement of bonded pairs and lone pairs around each atom in a molecule.



Bond enthalpy, bond order, electronegatvity and bond polarity are the important bond parameter and have significant effect on the properties of compounds.

Resonance is a phenomenon in which the molecule or polyatomic ions can be described by more than one Lewis dot structure. The contributing structures or canonical forms taken together constitute the resonance hybrid which represents the molecule or ion.

The **VSEPR** theory is used to predict the geometrical shapes of molecules is based on the assumption that electron pairs repel each other and therefore, tend to remain as far apart as possible. According to this theory, molecular geometry is determined by repulsions between lone pairs and lone pairs; lone pairs and bond pairs and bond pairs and bond pairs. The order of these repulsion is

$$LP - LP > LP - BP > BP - BP$$

The **valence bond theory** (VBT) discussed the bond formation in terms of overlap of orbitals. A single covalent bond is formed in H_2 molecule by the overlap 1s orbitals of the two H atoms which are singly occupied. Because of orbital overlap, the electron density between the nuclei increases which helps in bringing atoms closer, potential energy decreases and stability increases. The internuclear distance when the H_2 molecule has lowest potential energy is called **bond length**. Types of overlap involving s and p orbitals are s-s, s-p and p-p orbital overlaps. The VBT fails to explain the number of valence unpaired electrons in an atom forming the number of bonds and also does not explain the geometry of some molecules.

Hybridisation is the process of mixing and recasting of atomic orbitals of the same atom with comparable energies to form equal number of new orbitals of equal energy, maximum symmetry and definite orientation in space.

s and p- orbitals hybridise to give sp hybridization sp^2 hybridisation and sp^3 hybridisation the types of hybridization between s, p and d orbitals are sp^3d, sp^3d^2 and sp^3d^3.

Sigma (σ) and pi (π) bonds are the two types of covalent bonds. Sigma bond is formed by end-to-end overlapping of atomic orbitals and pi bond is formed by lateral or sideways overlapping of atomic orbitals.

Molecular orbital Theory

The probability of finding electrons in an atom is in the atomic orbitals. Similarly the probability of finding electrons in a molecule are in molecular orbitals. There are two types of molecular orbitals and are called bonding molecular orbitals and antibonding molecular orbitals. These molecular orbitals are formed by linear combination of atomic orbital. The electron placed in bonding molecular orbital tend to decrease the energy of molecule and increase its stability. Whereas the electrons in antibonding molecular orbital try two increase the energy of molecule, hence lowers the stability. For the homonuclear, diatomic molecule, the order of molecular orbitals is

$$\sigma 1s \;\; \sigma^* 1s \;\; \sigma 2s \;\; \sigma^* 2s \;\; \sigma 2p_z \;\; \begin{bmatrix} \pi 2p_x \\ \pi 2p_y \end{bmatrix} \;\; \begin{bmatrix} \pi^* 2p_x \\ \pi^* 2p_y \end{bmatrix} \;\; \sigma^* 2p_z$$

For molecules with less than 16 electrons, $\begin{bmatrix}\pi 2p_x \\ \pi 2p_y\end{bmatrix}$ has a lower energy than $\sigma 2p_z$

MOT is used to calculate the bond order which is defined as

$$\text{bond order} = \frac{(\text{no. of bonding electrons} - \text{no. of antibonding electrons})}{2}$$

$$\text{Bond order} \propto \text{bond strength} \propto \text{bond energy} \propto \frac{1}{\text{bond length}}$$

The molecule is called paramagnetic if one or more unpaired electrons present. If all electrons paired, then the molecule is called diamagnetic. Paramagnetic species are attracted towards the magnetic field.

The dipole moment (μ) is a quantity used to measure polarity of a covalent bond

$$\mu = Q \times d$$

Where Q = charge and d is the internuclear distance. Dipole moment is a vector quantity. All heteronuclear diatomic molecules have a net dipole moment. In polyatomic molecules dipole moment depends upon bond dipole and spatial arrangement of various bonds in the molecules.

The presence of strongly electronegative atom makes the molecule polar. In polar molecules there is hydrogen bonding. The hydrogen bonding may be

(i) intramolecular (within a molecule) or

(ii) intermolecular (between the molecules)

Hydrogen bonding affects melting point, boiling point, solubility and viscosity.

Redox Reactions

Redox reactions form an important class of reactions in which oxidation and reduction takes place simultaneously. Oxidation is less of electron (s) from a species and reduction is a gain of electron(s) by a species.

In redox reactions, one species loses electron(s) and the other species accepts electron(s). Thus, the redox reactions are electron transfer reactions.

Oxidsing agent is an electron acceptor while reducing agent is electron donor. An oxidant is itself reduced and a reductant is itself oxidized.

Oxidation number or oxidation state of an atom or ion is the number of charges it would carry if the electrons were completely transferred. Metallic elements have only positive oxidation number whereas non-metals have either positive or negative oxidation states.

If the oxidation number of an element in a compound increases, then the compound is oxidized and it acts as reducing agent. Similarly, if the oxidation number of an element in a compound decreases the compound is reduced and it acts as an oxidant. This means redox reaction involves simultaneous increase and decrease in an oxidation number. Oxidant lowers its oxidation number and reductant goes to higher oxidation state. This helps is an identifying oxidizing and reducing agents in a reaction and also in balancing the chemical equation corresponding to that reaction.

The redox reaction can be balanced either by oxidation number method or by ion electron (half reaction) method.

The oxidation number method is based on the principle that net change in the total oxidation number is zero. In half reaction method, the redox reaction is divided into oxidation half equation and reduction half equation. The two half equations are separately balanced and then are added together. The ionic equation can be balanced in acidic medium or in basic medium. The combustion of a fuel, bleaching of material and corrosion are all redox reaction. Redox reactions also play an important role in respiration, extraction of metals and batteries.