

Some Other Periodic Properties.

(1) **Atomic volume:** It is defined as the volume occupied by one gram atom of an element. Mathematically,

$$\text{Atomic volume} = \frac{\text{Gram atomic weight}}{\text{Density in solid state}}$$

Units of atomic volume are c.c./mole. Atomic volume signifies the volume occupied by one mole (Avogadro number) of atoms of the given element in solid state. Lower atomic volume generally leads to higher density, increased hardness and brittleness, higher melting and boiling points, less malleability and ductility.

(i) While descending a group, the atomic volume generally increases which is due to increase in the number of shells though the valence electrons in a given group remains constant.

(ii) While going left to right across a period the atomic volume first decreases to a minimum and then increases. Francium has the highest atomic volume and boron has lowest atomic volume.

(2) **Density:** The density of the elements in solid state varies periodically with their atomic numbers. At first, the density increases gradually in a period and becomes maximum somewhere for the central members and then starts decreasing afterwards gradually.

(3) **Melting and boiling points:** The melting points of the elements exhibit some periodicity with rise of atomic number. It is observed that elements with low values of atomic volumes have high melting points while elements with high values of atomic volumes have low melting points. In general, melting points of elements in any periodic at first increase and become maximum somewhere in the centre and thereafter begins to decrease.

Tungsten has the maximum melting point (3410°C) amongst metals and carbon has the maximum melting point (3727°C) amongst non-metals. Helium has the minimum melting point (−270°C). The metals, *Cs*, *Ga* and Hg are known in liquid state at 30°C.

The boiling points of the elements also show similar trends, however, the regularities are not as striking as noted in the case of melting points.

(4) Oxidation state (Oxidation number, O.N.):Oxidation number of an element in a compound is the total number of electrons it appears to have gained or lost (negative and positive oxidation states respectively) during the formation of that particular compound.

Trend of oxidation states in various groups

(1) Group 1 (ns^1) and group II (ns^2) elements attain the inert gas configuration by the loss of outer s electrons. The group 1 and 2 elements have oxidation states of I and II respectively.

(2) Groups 13 elements (ns^2p^1) can exhibit oxidation states of I (by the loss of the np^1 electron) and III (by the loss of $np^1 + ns^2$ electrons). The stability of the lowest state (I) increases while that of higher state (III) decreases with increase in atomic number. Thus B, Al and Ga show only III oxidation state. In shows both mono and trivalent states while in Tl monovalent state is more stable.

(3) Group 14 elements (ns^2p^2) show oxidation states of II (by the loss of np^2 electrons) and IV (by the loss of ns^2p^2 electrons). The stability of II state increases while that of IV decreases with the increase in atomic number. Certain elements of this group (C, Si and Ge) also show – IV state in which elements attain inert gas configuration (ns^2p^6) by acquiring four elements. This state can exist only with the highly electropositive elements in carbides, silicides and germanides which are covalent.

(4) Group 15 elements (ns^2p^3) show oxidation state of –III (by the gain of three electrons), III (by the loss of np^3 electrons) and V (by the loss of $np^3 + ns^2$ electrons). The stability of –III and V states decreases while that of III state increases with increasing atomic number. Nitrogen is unique in having a large number of oxidation states, including a fractional one (e.g. $-\frac{1}{3}$ in NH_3).

(5) Group 16 elements (ns^2p^4) show mainly – II oxidation state which can be easily achieved by the gain of two electrons short of the next inert gas configuration. Hence the elements of 16 group are electronegative. The stability of – II state decreases down the group. Other important oxidation states of these elements are II, IV and VI (II oxidation state is not very stable). The different oxidation states may be explained as below,

M $ns^2 p_x^2 p_y^1 p_z^1$

M [-II] $ns^2 p_x^2 p_y^2 p_z^2$

M [III] $ns^2 p_x^2$

M [IV] ns^2

M [VI] No electron in the outermost shell of the atom.

(6) Group 17 elements (ns^2p^5) show mainly -I oxidation state and hence the elements are extremely high electronegative. Fluorine is the most electronegative and cannot give a positive oxidation state. Other members can show the oxidation states of I, III, V and VII; the stability of these states decreases in the order: V > VII > III > I. Moreover, chlorine shows oxidation states of IV (in ClO_2) and VI (in ClO_3).

(7) Group zero elements (ns^2p^6) are stable. However, after 1962 compounds of inert gases with F and O (most reactive elements) have been characterised. In these compounds inert gases show oxidation states of IV, VI, II and VIII (in order of decreasing stability).

(8) **Oxidation states in transition elements:** The general electronic configuration $(n - 1) d^x ns^2$ of the transition elements suggests,

(i) II (achieved by the loss of ns^2 electrons) as the lowest common oxidation state, and

(ii) $2 + x$ [achieved by the loss of $ns^2 + (n - 1) d^x$ electrons] as the maximum oxidation state of these elements.

(a) In the 3d series, the Ti (II) is unstable and strongly reducing. The stability of II state increases (with a decrease in reducing character) with the addition of electrons in $(n-1)$ d orbital. In 4d and 5d series, II state is unstable except for Pt (II) and Pd (II).

(b) In the 3d series, the highest oxidation state increases from III in Sc to VII in Mn. beyond Mn (d^5 in the ground state), electron pairing commences in the d orbitals and the highest oxidation state for the subsequent members does not exceed VI. In the 4d and 5d series, the higher states are more stable and less oxidizing than those in the d series. Thus Nb (V), Ta (V), Mo (VI), W (VI), Tc (VII) and Re (VII) are almost non-oxidizing. In general, the stability of the higher states is in the order, $3d \ll 4d < 5d$

(5) **Oxidizing and Reducing Power** : Tendency to lose electrons and reducing power are directly related to each other; while tendency to gain electrons and oxidizing power are directly related to each other.

(i) In a group, the reducing character generally increases. Thus among alkali metals (except francium), cesium is the most powerful reducing element (in absence of water).

(ii) The reducing character decreases and oxidizing character increases along the period from left to right. Thus alkali metals are strong reducing agents while halogens are oxidizing agents among halogens, fluorine is the most powerful oxidizing agent; the oxidizing property decreases from F to I and actually iodine shows reducing properties.

(iii) Inert gases are neither oxidizing nor reducing agents. (iv) Generally, metals are reducing agents and non-metals are oxidizing agents.

(6) **Paramagnetism, Diamagnetism, and Ferromagnetism**: Magnetic properties of matter depend on the properties of the individual atoms. A substance (atom, ion or compound) capable of being attracted into a magnetic field is known as paramagnetic. The paramagnetic substances have a net magnetic moment which in turn is due to the presence of unpaired electron(s) in atoms, ions or molecules. Since most of the transition metal ions have unpaired d-electrons, they show paramagnetic behaviour. The exceptions are Sc^{3+} , Ti^{4+} , Zn^{2+} , Cu^+ , etc. which do not contain any unpaired electron and hence are diamagnetic.

On the other hand, **a substance which is repelled by a magnetic field is known as diamagnetic**. Such substances do not have any net magnetic moment because they do not have any unpaired electron. Electrons determine the magnetic properties of matter in two ways,

(i) Each electron can be treated as a small sphere of negative charge spinning on its axis. The spinning of charge produces magnetic moment.

(ii) An electron travelling in closed path around a nucleus will also produce magnetic moment just as does electric current travelling in a loop of wire.

The observed magnetic moment is therefore the sum of the two moments: the spin moment and the orbital moment. It is expressed in units called Bohr Magnetons (BM). In terms of n (number of unpaired electron), magnetic moment is given by the formula, $\mu = \sqrt{n(n+2)}$

Thus when $n = 1$ $\mu = \sqrt{1 \times 3} = 1.73 \text{ BM}$

$n = 2$ $\mu = \sqrt{2 \times 4} = 2.83 \text{ BM}$

$n = 3$ $\mu = 3.87 \text{ BM}$

$n = 4$ $\mu = 4.90 \text{ BM}$

$n = 5$ $\mu = 5.92 \text{ BM}$

Thus greater the number of unpaired electrons in a substance, the greater is the magnetic moment of the substance. The value of magnetic moment has been used to calculate the number of unpaired electrons in an ion. In some cases, even the structure of the molecule or complex is indicated by its magnetic moment.

Paramagnetism is generally measured by a simple device known as Guoy's balance which involves weighing the species in presence of a magnetic field. Diamagnetic substances show a decrease in weight whereas paramagnetic substances show increase in weight. The larger the number of unpaired electrons in a substance, the greater is the increase in its weight in a magnetic field.

Ferromagnetism is a special property observed in some substances in the solid state (not in solution). Such substances are strongly attracted to magnetic field and may retain the magnetic properties for some time even after the removal of the field. The most common example is of Fe followed by Co and Ni.

(7) Hydration and hydration energy

(i) Hydration energy is the enthalpy change that accompanies the dissolving of 1 mol of gaseous ions in water.

(ii) Size of ions and its charge determines extent of hydration. Greater the charge smaller the size of the ion, greater the attraction for the lone pair of O of H_2O , hence greater the extent of hydration energy.

(a) Size of the hydration ion increases.

(b) Ionic mobility decreases i.e. heavier (hydrated) ions moves slower.

(8) Acid-base-character of oxides

(i) On moving across a period, the basic character of the oxides gradually changes first into amphoteric and finally into acidic character.

(ii) On moving down a group, reverse behaviour is observed i.e., from more acidic to more basic.

(iii) Stability of oxides decreases across a period.

(9) Hydrides

(i) Hydrogen combines with a number of other elements including metals and non-metals to form compounds called hydrides (with H^-).

(ii) Covalent nature of hydrides increases across a period and decreases down the group.

(iii) Ionic hydride are better reducing agents than covalent hydride and reducing nature of hydride decreases across a period and increases down the group.

(iv) Covalent and ionic hydrides are classified as follows,



