

Topic: S – Block Elements

STUDY MATERIAL

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(1st Semester)
Students***

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Electronegativity is defined as the relative electron attracting tendency of an atom for a shared pair of electron in a chemical bond. Being relative in nature, electronegativity has no specific units and its value is also not constant. It simply depends on the nature of the atom with which a particular atom is linked. Different scales of comparison have been designed for this purpose such as *Pauling scale*, *Mulliken-Jaffe scale*, *Allred-Rochow scale* etc. Among these scales *Pauling scale* is most widely accepted electronegativity scale. Electronegativity cannot be directly measured. Electronegativity is not a property of an atom alone, but rather a property of an atom in a molecule.

- ❖ Both Pauling and Mulliken electronegativity is a measure of electron attraction tendency of an atom in a molecule. According to the Pauling formulation, electronegativity is considered as a thermodynamic property, which relate to the bond energy of the molecule. The difference in the bond energy of any molecule, A-B from the average of A-A and B-B bond energies is a measure of the electronegativity difference between A and B. In other words, if $\chi_A - \chi_B$, are the electronegativity of atom A and B, then

$$[\chi_A - \chi_B] = (\text{eV})^{-1/2} \mathbf{0.102} (\Delta E)^{1/2}$$

$$\Delta E = B_{A-A} - 1/2 (B_{A-A} + B_{B-B})$$

ΔE is in KJ/mol

The factor 0.102 is a conversion factor between KJ/mol and eV. The factor $(\text{eV})^{-1/2}$ is added just to make electronegativity a dimensionless quantity. Pauling arbitrarily chooses a value of 2.1 for the electronegativity of H-atom. The electronegativity values for other atoms were established relative to hydrogen atom. Thus Pauling scale is not an absolute scale of electronegativity.

- ❖ Another scale which was introduced by Mulliken is based on the properties of atoms. An atom with high ionisation energy and high electron affinity is less likely to lose an electron, while it is bonded to another atom, whereas it is more probable that it will gain electrons and hence will be called highly electronegative. Thus Mulliken expressed electronegativity as the average of ionisation energy (IE) and electron affinity (EA). In the actual calculations, IE and EA are replaced by IE_v and EA_v , thus Mulliken Electronegativity (χ_m) can be expressed as,

$$\chi_m = IE_v + EA_v/2$$

- ❖ If both EA and IE are in eV units then Pauling's electronegativity $(EN)_P$ is related to Mulliken's electronegativity $(EN)_M$ by the equation:

$$(EN)_P = \mathbf{0.336} [(EN)_M - \mathbf{0.615}]$$

- ❖ If EA and IE are in eV then EN in eV is given by $\mathbf{0.187 (IE+EA) + 0.17}$
- ❖ Mulliken's values were found to be about 2.8 times larger than the Pauling's values. Among all elements Cesium is least electronegative element (0.79) while Fluorine is the most electronegative element (3.98). Greater the electronegativity difference between the two bonded atoms, more the electron density will be drifted toward the more electronegative atom.

- ❖ Allred and Rochow defined electronegativity as the force exerted by the nucleus of an atom on its valence electrons.

$$(EN)_{A-R} = \mathbf{0.359} \times Z_{eff} / r^2 + \mathbf{0.744}$$

where Z_{eff} is the effective nuclear charge and r is the covalent radius (\AA)

Factors Affecting Electronegativity

(i) Size of an Atom

A greater atomic size will result in less value of electronegativity, this happens because electrons being far away from the nucleus will experience a lesser force of attraction.

(ii) Nuclear Charge

A greater value of nuclear charge will result in a greater value of electronegativity. This happens because an increase in nuclear charge causes electron attraction with greater force.

(iii) Effect of Substituent

The electronegativity of an atom depends upon the nature of substituent attached to that atom. For example, the carbon atom in CF_3I acquires a greater positive charge than CH_3I . Therefore, carbon atom in CF_3I is more electronegative than in CH_3I .

(iv) Number of inner shells

The atom with greater no. of inner shells has less value of electronegativity than the atom with smaller no. of inner shells. For example, electronegativity values of halogens decrease from Fluorine to Iodine as the number of inner shells increases from Fluorine to iodine.

(v) Charge on ion

Electronegativity is a variable quantity. It varies with the change in the oxidation state of the element. The element in higher oxidation state has more value of electronegativity than in the lower oxidation state. Thus the value of electronegativity of Fe^{3+} is higher than Fe^{2+} .

(vi) Type of hybridization

The magnitude of electronegativity of an atom also depends on the type of hybridization which the atom undergoes in the formation of different bonds in the molecule. The magnitude of electronegativity increases as the s-character in the hybrid orbital increases.

(vii) Nature of atoms to which the atom is bonded

Since the electronegativity of an atom is not the property of isolated atom, it depends on the no. and nature of the atoms to which the atom is bonded. Therefore the electronegativity value of an atom is not constant. For example, electronegativity value of Phosphorous atom in PCl_3 molecule is different from that in PF_5 molecule in which the no. and nature of the atom both to which Phosphorous atom is bonded change.

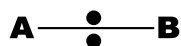
Difference between Electronegativity and Electron Affinity

Serial No.	Electronegativity	Electron Affinity
1.	It is ability of an atoms to attract a shared pair of electron	The amount of energy liberated when a molecule or neutral atom acquires an electron from outside
2.	It is relative electron attracting tendency of an atom	It is absolute electron attracting tendency of an atom
3.	Property of bonded atom	Property of an isolated atom
4.	It has no units	It has specific units i.e; KJmol^{-1} , eV/atom

Applications of Electronegativity

Electronegativity predicts us how strongly an atom of an element attracts the shared electrons in a bond. Fluorine, for example, has an electronegativity of 3.98 and attracts bonding electrons more strongly than any other element in the periodic table. The alkali metals have very low electronegativity, so they very weakly attract bonding electrons. By comparing the electronegativities of two elements in a bond we can make a well-informed guess regarding the nature of the bond. Larger difference in electronegativity between the elements the more ionic the bond becomes (greater ionic character). A difference in electronegativity of 1.7 results in a bond with 51% ionic character. This tells us that as the difference in electronegativity between any two elements gets increasingly larger than 1.7, a bond between these two elements is more likely to be ionic. Similarly, as the difference in electronegativity between any two elements approaches zero, the less ionic and more covalent the bond becomes. As a difference of electronegativity exceeds zero and approaches 1.7, the bond becomes more polar covalent.

Consider a bond between two atoms, A and B. If both the atoms are equally electronegative, then the electron cloud between these two atoms will be exactly half way. This type of electron density exactly is found in homo-nuclear molecules in which both the bonded atoms are same such as, H₂, Cl₂, etc.



If atom B is slightly more electronegative than atom A, then B will attract the electron pair rather more than atom A does. As a result B end of the bond has slightly more electron density and acquire slightly negative charge. At the same time A end of the bond will be slightly electron deficient and will attain slightly positive charge. This situation arise in hetero-nuclear molecules where a bond is between two different electronegative atoms such as, HCl, HF, O-H bond (H₂O), N-H bond (NH₃) etc.



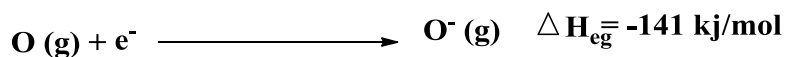
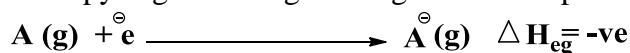
The implication of all this is that there is no clear cut division between covalent and ionic bonds. In a pure covalent bond, the electrons are held on average exactly half way between the atoms. In a polar bond, the electrons have been dragged slightly towards one end. How far does this dragging have to go before the bond becomes purely ionic? There is no real answer to this question.

Conclusions:

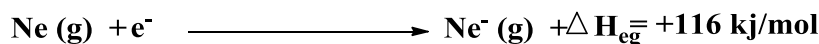
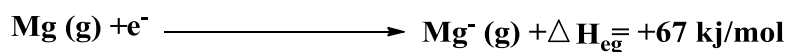
- ❖ $(\chi_X - \chi_H) = 1.7$ {50% ionic}
- ❖ $(\chi_X - \chi_H) > 1.7$ {predominantly ionic}
- ❖ $(\chi_X - \chi_H) < 1.7$ {predominantly covalent}

Electron Gain Enthalpy or Electron Affinity

Electron gain enthalpy is defined as the change in enthalpy which takes place when a gaseous atom gains an extra electron to form monovalent anion in the gaseous state. When an electron is added to an isolated atom energy is released during the process, therefore electron gain enthalpy is given a negative sign. For example



In many cases, the atoms have already symmetrical electronic configurations e.g; Noble gases and alkaline earth metals of group 2. These atoms don't have any urge to gain extra electron and energy has to be supplied in such cases. This means that the electron gain enthalpy will be positive. For example



Similarly, when an electron is added to an anion, energy is required to overcome the repulsions between anion and the incoming electron and thus electron gain enthalpy will be positive.

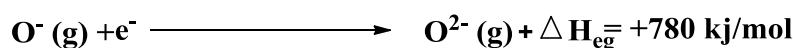
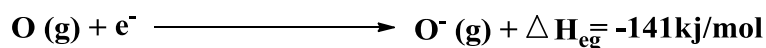


Conclusions:

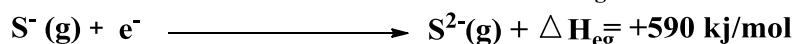
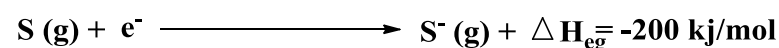
- ❖ Elements have normally negative electron gain enthalpy
- ❖ Elements with symmetrical electronic configuration have positive electron gain enthalpy
- ❖ Anions have positive electron gain enthalpy

Successive Electron Gain Enthalpies

Atom gains electrons in a successive manner i.e; one after the other. When an electron is added to a neutral isolated gaseous atom it acquires negative charge. In case the anion so formed is to gain another electron, energy will be required to overcome the the repulsions between the anion and the incoming electron. As a result, electron gain enthalpy will be positive. For example



Similarly for sulphur atom,



Factors Affecting Electron Gain Enthalpy

(i) Atomic Size

As the size of an atom increases, the distance between its nucleus and the incoming electron also increases. Consequently the incoming electron experiences less attraction towards the nucleus of the atom. Therefore the electron gain enthalpy becomes less negative down the group.

(ii) Nuclear charge

With the increase in nuclear charge force of attraction between the nucleus and the incoming electron increases thereby increasing the value of electron gain enthalpy. Thus the electron gain enthalpy becomes more negative with increase in nuclear charge.

(iii) Symmetry of the electronic configuration

The symmetry of the electronic configuration has a very vital role to play. The atoms with symmetrical electronic configuration (having filled or half filled orbitals in the same sub-shell) don't have any urge to gain an extra electron because their configuration will become

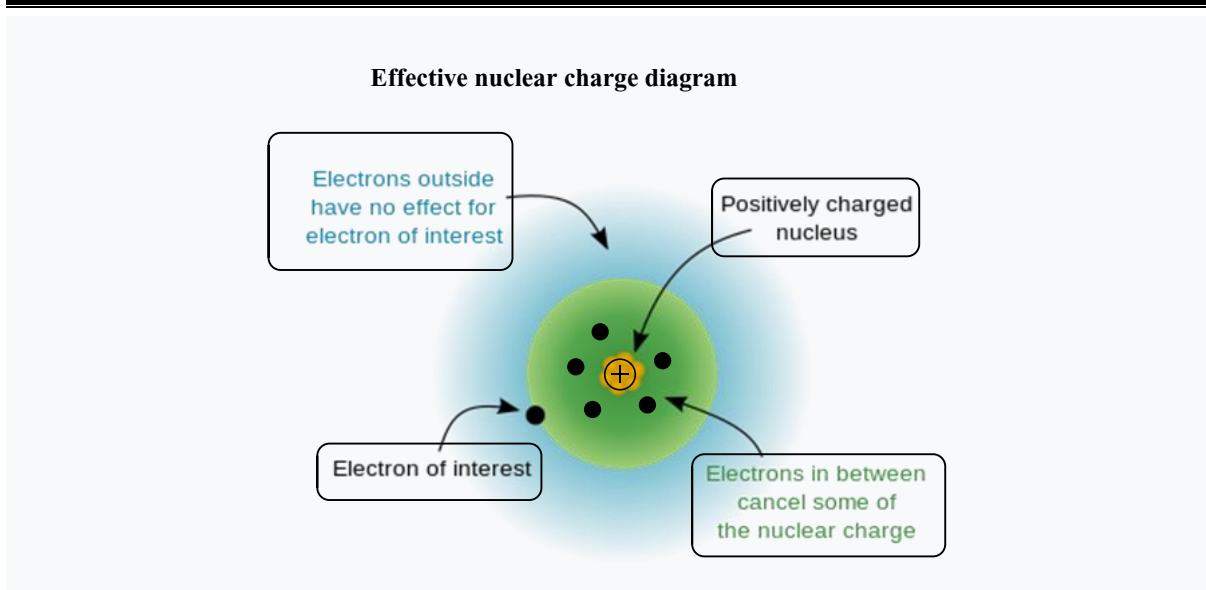
unsymmetrical or less stable. In case these are still made to accept electrons, energy will be required and electron gain enthalpy will be positive. For example noble gas elements have positive electron gain enthalpies.

Some Typical Trends in the Electron Gain Enthalpy

(i) **Halogens have the maximum negative electron gain enthalpies in their respective periods.** The negative electron gain enthalpy of Fluorine is less than that of Chlorine whereas it is expected to be more. The exceptionally low electron gain enthalpy of Fluorine is because of its very small atomic size and the presence of nine electrons. Thus the electrons crowd the small space around the nucleus and the electron-electron repulsions are quite high therefore, the incoming electron is not easily accepted with same ease as in case of chlorine in which the atomic size is bigger and the electron crowding comparatively is less. As a result the negative electron gain enthalpy of fluorine is lower as compared to chlorine.

(ii) **Noble gas elements have positive electron gain enthalpy.** The members of the noble gas family have highly symmetrical electronic configuration and have completely filled orbitals. Therefore, their atoms have hardly any urge to take up extra electron. In case they are forced to gain an extra electron energy will be needed and their electron gain enthalpies will be positive.

Effective Nuclear Charge



The effective nuclear charge (often symbolized as (Z_{eff} or Z^*)) is the net positive charge experienced by a valence electron in a polyelectronic atom. The term "effective" is used because the shielding effect of negatively charged electrons prevents higher orbital electrons from experiencing the full nuclear charge of the nucleus due to the repelling effect of inner-layer electrons. The effective nuclear charge experienced by the electron is also called the core charge. The combined effect of this attractive and repulsive forces acting on the valence electron is that the valence-electron experiences less attraction from the nucleus. As the size of the atom increases the no of shells increase which reduces the force of attraction between valence shell electron and nucleus. This is called **Shielding effect** or **Screening Effect**.

Effective nuclear charge (Z^*) = Nuclear charge - Shielding effect

$$Z^* = Z - \sigma$$

where Z is atomic number and σ is Slater's screening constant

Slater's Rules

In quantum chemistry, Slater's rules provide numerical values for the effective nuclear charge in a polyelectron atoms. Each electron is said to experience less attraction than the actual nuclear charge, because of shielding or screening by the inner electrons. For each electron in an atom, Slater's rules provide a value for the screening constant, denoted by S or σ . The rules were devised semi-empirically by John C. Slater and published in 1930. Revised values of screening constants based on computations of atomic structure by the Hartree-Fock method were obtained by Enrico Clementi *et al* in the 1960. **“According to J. C. Slater, effective nuclear charge (Z^*) is the net force of attraction that the nucleus exerts on an electron in an atom and depends on the type of orbital in which the electron is housed and on the ability of the other electrons in more penetrating orbitals to screen or shield the electron in question from the nucleus”**

- ❖ The relative extent to which the various orbitals penetrate the electron clouds of the other orbitals is $s > p > d > f$. Thus for any given principal quantum number n , an electron will experience the greatest effective nuclear charge when in an s orbital than a p orbital and so on.
- ❖ The electron is more stable in the more penetrating orbital

Postulates

The electrons have been arranged into a sequence of groups in order of increasing principal quantum number n and in order of increasing azimuthal quantum number l , except that s - and p - orbitals are kept together. [1s] [2s,2p] [3s,3p] [3d] [4s,4p] [4d] [4f] [5s, 5p] [5d] etc.

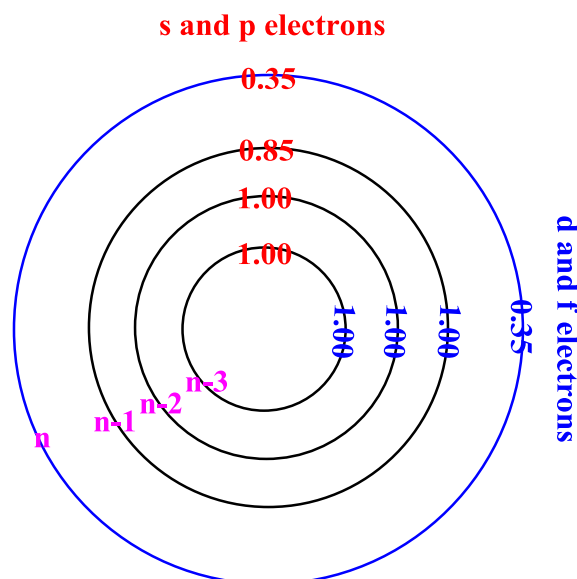
Each group is given a different shielding constant which depends upon the number and types of electrons in those groups preceding it.

The shielding constant for each group is formed as the sum of the following contributions:

- (i) An amount of 0.35 from each other electron within the same group except for the [1s] group, where the other electron contributes only 0.30.
- (ii) If the group is of the [ns, np] type, an amount of 0.85 from each electron with principal quantum number $(n-1)$, and an amount of 1.00 for each electron with principal quantum number $(n-2)$ or less.
- (iii) Shielding experienced by (nd) or (nf) valence electrons, electrons within same group shield 0.3, electrons within the lower groups shield 1.00
- (iv) One electron system will have $\sigma = 0$ and thus $Z^* = Z$, thus in case of H, He^+ , Li^{2+} , Be^{3+} etc; with one electron $Z^* = \text{Atomic number}$

Examples:

- ☞ For H-atom ($Z = 1$), there is no screening, being one electron system. Thus, $\sigma = 0$ and $Z^* = Z = 1$
- ☞ For He-atom ($Z = 2$), there is screening by one electron on the other electron
 $\sigma = 0.30$ thus $Z^* = 2 - 0.30 = 1.70$
- ☞ For Lithium atom ($Z = 3$), there is screening of valence electron by two electrons in 1s orbital $(n-1)$, thus the σ for two electrons will be, $\sigma = 2 \times 0.85 = 1.70$, thus $Z^* = 3 - 1.70 = 1.3$



Graphical representation of Slater's rules with shielding constants indicated

Position of Hydrogen in the Periodic Table

- ❖ Position of hydrogen has always been a debate.
- ❖ It acts as both a metal as well as non-metal.

In general, we consider it to be a group I element but sometimes it is also shown on the top of group 17 as it acts as a non metal. This is because hydrogen is one electron short to attain the nearest noble gas configuration just like halogens. But in the end, hydrogen is the lightest element among all so it is placed at the top of group 1 with the alkali metals. It took chemists years and many attempts to arrive at our current periodic table and one main point of contention in the previous attempts was the position of hydrogen in the periodic table.

If we glance at the periodic table, hydrogen is the first element of the periodic table. It is the smallest element in the table and has atomic number one, which means it has only one electron orbiting its shell. In fact, Hydrogen has only one shell. It is also the lightest element in the periodic table. Now we know that the position of elements in the periodic table largely depends on their electronic configuration. Hydrogen has the electronic configuration of $1s^1$. It can gain one electron to attain noble gas configuration equivalent to Helium. This characteristic of hydrogen matches with those of Halogens.

Resemblance with Alkali Metals

Hydrogen shares many similarities with alkali metals, i.e. elements in group I-A. This is one of the factors that dictate the position of hydrogen in the periodic table. Let us take a look at the similarities with alkali metals.

(i) Electronic Configuration

Like all the elements of the group I-A, Hydrogen also has one electron in its last shell, the valence shell. Let us take a look at the composition of valence shells of a few of these alkali metals.

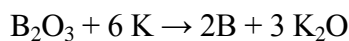
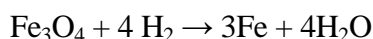
H (Z = 1) $1s^1$

Li (Z = 3) $1s^2, 2s^1$

Na (Z = 11) $1s^2, 2s^2, 2p^6, 3s^1$.

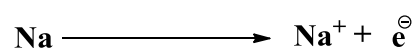
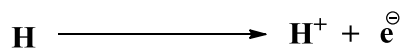
(ii) Strong Reducing Agents

Hydrogen is a strong reducing agent like all the other alkali metals.



(iii) Electropositive character

Both hydrogen and alkali metals form monovalent cations by losing an electron in the valence shell.



(iv) Oxidation state

Both hydrogen and alkali metals show +1 oxidation state in their compounds. For example, HCl and NaCl

(v) Affinity for Electronegative Elements

Both hydrogen and alkali metals are electropositive in nature and thus are expected to have high affinity for electronegative elements and readily combine them.

For example, Na₂O, NaCl, Na₂S are compounds of sodium

H₂O, HCl, HF, H₂S are compounds of hydrogen

Differences from Alkali Metals

- (i)** Alkali metals are typical metals while hydrogen is a non-metal
- (ii)** Although hydrogen has only one electron in its outer shell, hydrogen cannot easily lose this electron to gain electropositivity. However all other alkali metals can do this with ease.
- (iii)** At room temperatures all alkali metals exist in the solid state, hydrogen is a gas.
- (iv)** The H⁺ ion of hydrogen is much smaller than ions of alkali metals.
- (v)** Hydrogen is diatomic (H₂) while the alkali metals are monoatomic in nature
- (vi)** Ionization enthalpy of hydrogen is 1312 kJ mol⁻¹ which is very high as compared to alkali metal
- (vii)** Compounds of hydrogen are mainly covalent in nature (HCl, H₂O etc.) while those of alkali metals are ionic in nature (NaCl, KF etc.)

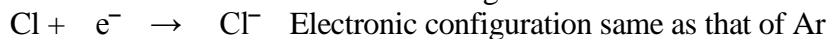
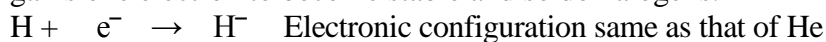
Resemblance with Halogens

(i) Noble Gas Configuration

Hydrogen can gain one electron to acquire noble gas configuration equivalent to Helium. Halogens also have seven electrons in their last shell and can gain one electron to gain noble gas configuration.

(ii) Electronegativity

Both hydrogen and halogens share the same electronegative nature. Hydrogen also gains one electron to become stable and so do halogens.



(iii) Diatomic Molecules

Both hydrogen and halogens form diatomic molecules. Hydrogen forms H_2 and halogens form Cl_2 , F_2 etc

(iv) Oxidation State

Halogens show -1 oxidation state in their compounds. Hydrogen also exhibits -1 oxidation state in compounds with metals. For example, NaH, NaF

(v) Nature of Compounds

Most of the compounds of hydrogen as well as halogens are covalent in nature. For example, CH_4 , SiH_4 , GeH_4 are covalent compounds of hydrogen
 CCl_4 , $SiCl_4$, $GeCl_4$ are compounds of chlorine

Difference from Halogens

- (i)** Hydrogen has only one electron in its outer shell while as, all halogens have seven electrons in their outer shell
- (ii)** Halogens readily form halide ions but hydrogen forms hydride ion H^- only in compounds with alkali and alkaline earth metals.
- (iii)** In the molecular form, the H atoms don't have any unshared electron pair while halogen atoms have three such pairs.
- (iv)** The oxides of halogens are generally acidic (Cl_2O_7) while that of hydrogen is neutral (H_2O)

Isotopes of Hydrogen

Hydrogen exists in the form of three main isotopes; protium (1H), Deuterium (2H) and tritium (3H). The isotopes of Hydrogen have only one proton in nucleus and one electron in the only K-shell. They differ in the no. of neutrons. Protium is ordinary hydrogen (H) and is the most abundant form of hydrogen. Deuterium is heavy hydrogen (D) and is obtained by the electrolysis of heavy water (D_2O) Protium and Deuterium are stable. Tritium is radioactive and has a half-life of about 12 years. Scientists have created four other hydrogen isotopes (4H to 7H), but these isotopes are very unstable and do not exist naturally. Deuterium and Tritium sometimes get their own symbols, D and T. However, the International Union of Pure and Applied Chemistry (IUPAC) do not like these names very much, even though they are often used. There are other isotopes that had their own names when scientists studied radioactivity but their names are no longer used today.

(i) Protium (1H)

It is one of the common isotopes of hydrogen. It is ample in nature with an abundance of 99.98%. It is not radioactive in nature.

(ii) Deuterium (2H)

It consists of one proton and one neutron in its nucleus. The nucleus of 2H is termed as Deuterium. It is not radioactive. Heavy water is extremely useful in nuclear reactors to slow the speed of neutrons. In India, plants for the manufacture of heavy water are located in Barodra (*Gujrat*), Kota (*Rajasthan*), Nangal (*Punjab*) and Thane (*Rajasthan*).

Applications of Deuterium

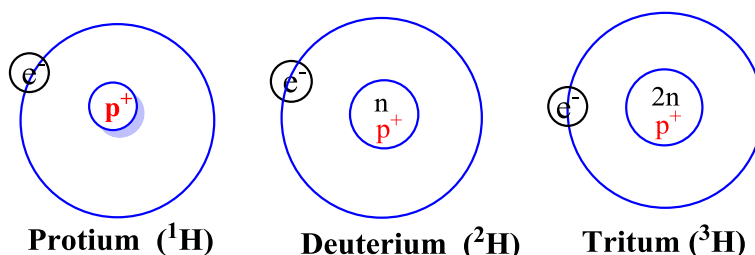
- Drugs
- Nuclear weapons
- Tracing
- NMR spectroscopy
- Nuclear reactors and Nuclear Power Plants

(iii) Tritium (${}^3\text{H}$)

It comprises of two neutrons and one proton in its nucleus. They are also released in small amounts at the time of nuclear weapons tests. It is extremely unstable and radioactive in nature.

Applications of Tritium

- Analytical chemistry
- Controlled nuclear fusion
- Neutron initiator
- Nuclear weapons
- Self-powered lighting
- Used as an oceanic transient tracer



(iv) Hydrogen-4 or ${}^4\text{H}$

It comprises of one proton and three neutrons in its nucleus. Hydrogen-4 is highly unstable isotope of hydrogen. It is incorporated in laboratories by bombarding Tritium with fast-moving Deuterium nuclei. Its atomic mass is 4.02781 ± 0.00011 .

(v) Hydrogen-5 or ${}^5\text{H}$

It comprises of four neutrons and one proton in its nucleus. Hydrogen-5 is a highly unstable isotope of hydrogen. It has been incorporated in the laboratory by bombarding Tritium with fast moving Tritium nuclei.

(vi) Hydrogen-6 or ${}^6\text{H}$

It consists of five neutrons and one proton in its nucleus. It decays through triple neutron emission into ${}^3\text{H}$.

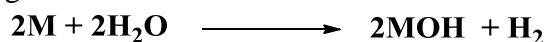
(vii) Hydrogen-7 or ${}^7\text{H}$

It is comprised of six neutrons and one proton. It has a half-life of 23 yoctosecond.

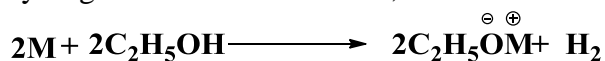
Chemical Reactivity of

S-Block Elements towards Water, Oxygen, Nitrogen and Halogens

- ❖ Alkali metals react with water liberating Hydrogen gas and forming their hydroxides. The metal hydroxides (MOH) formed are strong bases. The reaction becomes more and more violent as we move down in a group. Lithium reacts gently, sodium reacts rapidly with evolution of heat. Thus Sodium and Potassium metals are generally placed in kerosene. Potassium melts and catches fire and so are Rb and Cs. The general reaction can be shown as:

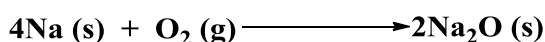
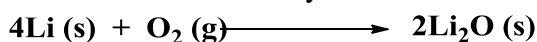


Because of large negative reduction potential of alkali metals they behave as strong reducing agents than hydrogen. They react with compounds containing acidic hydrogen atoms such as water, alcohol and acetylene liberating H_2 gas.



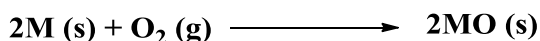
Among alkaline earth metals Ca, Sr and Ba readily react with cold water to form hydroxides and H₂ gas. However Be and Mg are passivated by the formation of an impervious layer of oxide on their surface.

- ❖ When alkali metals are cut, they initially appear shiny but quickly become dull and white as they react with oxygen in air. This phenomenon is known as Tarnishing. Lithium tarnishes slowly than sodium due to its relatively slow reaction with oxygen.

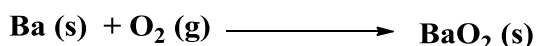


Other alkali metals such as K, Rb and Cs react with oxygen to form superoxides of the formula MO₂ where M = K, Rb and Cs. The reactivity of alkali metals with oxygen increases down the group. The increasing stability of peroxides or superoxides is due to the stabilization of larger anion by the larger cations through higher lattice enthalpy.

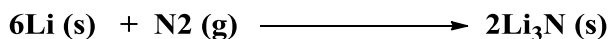
Alkaline earth metals generally react with oxygen to form metal oxides. Beryllium is reluctant to react with oxygen unless it is in the form of powder. Beryllium has a very strong layer of beryllium oxide on its surface and this prevents any new oxygen to react with it.



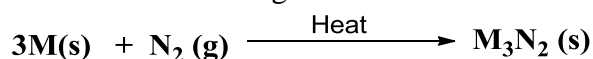
Thus all alkaline earth metals form normal oxides. However Barium form peroxide.



- ❖ Although the alkali metals possess a high chemical reactivity, lithium is the only element of the alkali metals to react with nitrogen gas at room temperature to give Lithium nitride (Li₃N)



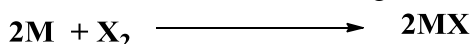
The heavier alkali metals are seen to be chemically inactive towards nitrogen upon heating or under ambient states. All alkaline earth metals are competent to give nitrides on reaction with nitrogen. The basic structure of reactions with an alkaline earth metal and nitrogen are as follows:



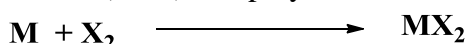
M = Be, Mg, Ca, Sr, Ba

Nitrides of alkaline earth metals are ionic and solid in nature except for beryllium nitride (Be₃N₂) which is covalent in nature.

- ❖ Alkali metals react with halogens directly to form metal halides.



Lithium halides are somewhat covalent in nature, the rest of the metals halides are ionic in nature and have high melting and boiling points. all alkaline earth metals combine directly with halogens at appropriate temperature to form corresponding halides (MX₂). No polyhalides are formed.



Anomalous behaviour of Lithium

An interesting feature of the representative elements (S-block) is that the first member of each group differs from rest of the elements in the same group also known as Congeners in

many characteristics. Lithium is no exception. The main reasons for such behaviour are as follows:

- (i) Small size of Li atom and Li^+ ion.
- (ii) High ionisation enthalpy and low electropositive character as compared to rest of members.
- (iii) High polarising power of Li^+ ion resulting in covalent character of its compounds
- (iv) Non-availability of d-electrons in its valence shell.
- (v) Strong intermetallic bonding due to its small size.

Distinction Between Lithium and other Alkali Metals

The anomalous behaviour of Lithium with respect to the rest of the members is illustrated by the following features:

- (i) Lithium is quite hard while other alkali metals are soft.
- (ii) Lithium is not easily affected by the action of air while rest of the elements get their surfaces tarnished on exposure to air.
- (iii) Lithium reacts with water slowly whereas other alkali metals react violently and even catch fire.
- (iv) Lithium hydroxide is very weak base and sparingly soluble in water. Hydroxides of its congeners are strong bases and are highly soluble in water.
- (v) On heating lithium hydroxide decomposes to lithium oxide while the hydroxides of other alkali metals fail to decompose even on strong heating. However they do sublime on heating.
- (vi) Li_2CO_3 decomposes on heating to release CO_2 while carbonates of other alkali metals are stable to heat.
- (vii) Lithium is the only alkali metal which combines with nitrogen to form Li_3N .
- (viii) Lithium forms monoxide (Li_2O) with oxygen while sodium forms peroxide (Na_2O_2) and the other alkali metals give superoxides (KO_2) with oxygen.

Anomalous behaviour of Beryllium

Beryllium which is the first member of the alkaline earth metals differs from the rest of the members in many characteristics although it has the same valence shell configuration (ns^2). Thus it is anomalous in behaviour mainly due to the following reasons:

- (i) Small size of Be atom and Be^{2+} ion
- (ii) High polarising power on anions associated with it resulting in covalent character of its compounds.
- (iii) High ionisation enthalpy and electronegativity compared to its other members.
- (iv) Non-availability of d electrons in its valence shell.

Distinction Between Beryllium and other Alkaline Earth Metals

The anomalous behaviour of Beryllium with respect to the rest of its members is illustrated by the following features:

- (i) Beryllium is hard while rest of its members are comparatively soft in nature
- (ii) Beryllium reacts with oxygen only at high temperature while rest of members react at low temperature
- (iii) BeO is of amphoteric nature while as oxides of magnesium and other members are basic in nature
- (iv) Compounds of beryllium are mostly covalent in nature while as compounds of other members are mostly ionic
- (v) Except beryllium, rest of members combine with hydrogen to form metal hydrides

- (vi) Beryllium does not liberate hydrogen gas from dilute acids readily while other members release hydrogen gas readily
- (vii) $\text{Be}(\text{OH})_2$ is amphoteric in nature while other members are basic in nature
- (vii) Beryllium does not react with water under any conditions while other members do react upon heating
- (viii) Beryllium carbide (Be_2C) is covalent while carbides of other metals are ionic e.g; calcium carbide (CaC_2)
- (ix) Be_2C reacts with water to evolve methane while other metal carbides evolve acetylene gas

$$\text{Be}_2\text{C} + 4\text{H}_2\text{O} \longrightarrow 2\text{Be}(\text{OH})_2 + \text{CH}_4$$

$$\text{CaC}_2 + 2\text{H}_2\text{O} \longrightarrow 2\text{Ca}(\text{OH})_2 + \text{HC}\equiv\text{CH}$$
- (x) Both Be and Mg do not impart any colour to the flame while the other members do impart characteristic colours to the flame when volatile salts (chlorides) are burnt on the tip of a platinum wire

Similarity in Lithium and Magnesium (Diagonal Relationship)

Lithium the first member of the family differs from the rest of its members in most of the characteristics. However, it has some resemblance with magnesium, the second element of alkaline earth metals (Group – 2) to which it is linked diagonally. In other words, Lithium and magnesium exhibit diagonal resemblance or diagonal relationship. In fact, the first three elements of second period (Li, Be, B) show diagonal similarity with the elements (Mg, Al, Si) of third period placed on the right hand side.

Diagonal Relationship				
Group	1	2	3	4
Second Period	Li	Be	B	C
Third Period	Na	Mg	Al	Si

Cause of Diagonal Relationship

The cause of diagonal relationship is due to the opposing trends in the main periodic properties of the elements along a period and down the group. For example, both atomic and ionic size decreases along a period and increases down the group. Ionisation enthalpy, electron gain enthalpy and electronegativity follow opposing trends i.e; they increase along a period and decrease down the group. On moving diagonally, these opposing trends tend to cancel mutually and as a result, the elements listed above show diagonal similarity or diagonal relationship.

Some of the common characteristics which support the diagonal relationship between Lithium and Magnesium are listed as:

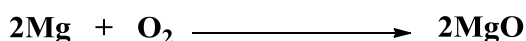
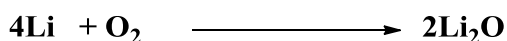
- (i) Both these metals are quite hard and have high melting points than the other metals in their respective groups
- (ii) Both of these evolve hydrogen gas from water

$$2\text{Li} + 2\text{H}_2\text{O} \longrightarrow 2\text{LiOH} + \text{H}_2$$

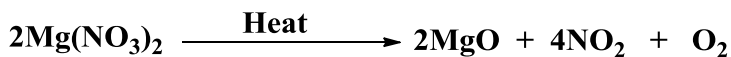
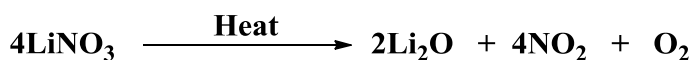
$$\text{Mg} + 2\text{H}_2\text{O} \longrightarrow \text{Mg}(\text{OH})_2 + \text{H}_2$$
- (iii) Both react with nitrogen to form nitrides on heating

$$6\text{Li} + 2\text{N}_2 \longrightarrow 2\text{Li}_3\text{N}_2$$

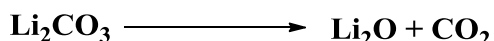
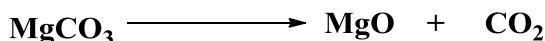
$$3\text{Mg} + \text{N}_2 \longrightarrow \text{Mg}_3\text{N}_2$$
- (iv) Both these metals form their respective monoxides on heating in oxygen



- (v) Nitrates of both these metals evolve NO_2 and O_2 on heating



- (vi) Carbonates of both of them evolve CO_2 gas on heating



- (vii) Halides of both of these metals are sparingly soluble in water and dissolve in organic solvents like alcohol, pyridine etc.

- (viii) Chlorides of both these metals get separated from the aqueous solutions as hydrated salts e.g; $\text{LiCl} \cdot 2\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

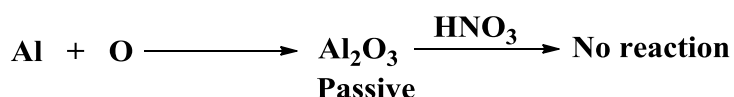
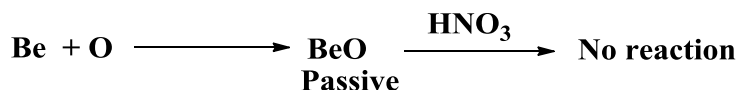
- (ix) Bicarbonates of both these metals do not exist in solid state and exist in solutions

- (x) Both Li_2SO_4 and MgSO_4 do not participate in double salt formation

Similarity in Beryllium and Aluminum (Diagonal Relationship)

Some of the common characteristics which support the diagonal relationship between Beryllium and Aluminium are as follows:

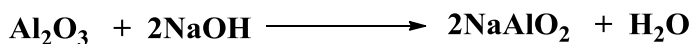
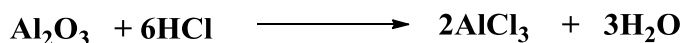
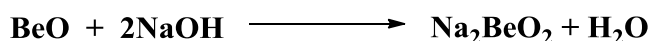
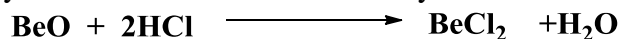
- (i) Chlorides of both Be and Al show chlorine bridged structures in vapour phase
- (ii) Both metals have tendency to form covalent compounds. For example, chlorides of both metals being covalent are soluble in organic solvent
- (iii) Both BeCl_2 and AlCl_3 act as Lewis acids and are used as Friedal-Crafts catalysts
- (iv) Both these two metals possess same value of electronegativity and polarising power i.e; charge/radius ratio of their ions is very similar
- (v) Both Be and Al are resistant to the action of acids due to the formation of protective film of the oxides on their surface



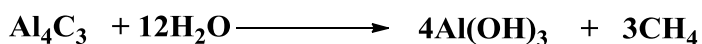
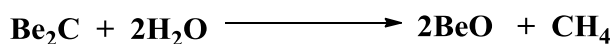
- (vi) Both the metals dissolve in strong alkalies to form soluble complexes, beryllates and aluminates

- (vii) Oxides of both BeO and Al_2O_3 are hardm high melting insoluble solids

- (viii) Oxides and hydroxides of both Be and Al are amphoteric and dissolve in sodium hydroxide solution as well as in hydrochloric acid



- (ix) Carbides of both metals react with water releasing methane gas



- (x) Both have strong tendency to form complexes. Be forms tetrahedral complexes as BeF_4^{2-} and $[\text{Be}(\text{C}_2\text{O}_4)_2]^{2-}$. Aluminium forms octahedral complexes such as AlF_6^{3-} and $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$.

*You can send your feedback/suggestions at haiderchem09@gmail.com
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