Chapter 1 "S" and "P" Block Elements

CHAPTER 1

"s" AND "p" BLOCK ELEMENTS

Up till now more than 120 elements has been discovered. The latest discovered elements are Nihonium (Nh¹¹³), Flerovium (Fl¹¹⁴), Moscovium (Mc¹¹⁵), Livermorium (Lv^{116}) , Tennessine (Ts^{117}) and Oganesson (Og^{118}) . The Flerovium and Livermorium elements have been discovered by Flerov and Livermore in Dubna, Russia. Nihonium is the first element discovered in an Asian country Japan. Moscovium has been discovered in Moscov. Tennessine has been discovered in Tennessi USA. Oganesson has been discovered by Yuri Oganesson scientist. These elements will soon be named by IUPAC system and will be placed in the $7th$ period of the periodic table.

Individual study of each element was a difficult job, so need was felt to classify the elements in order to study them easily and systematically.

History of periodic classification

Many Scientists classified the elements on different basis like increasing atomic weight, volume, increasing atomic number, electronic configuration etc. Important contributions from various scientists in the elemental classification are given below.

- 1. Al-Razi classification
- 2. Levisor classification
- 3. Lothar Mayer atomic volume curve
- 4. Spiral arrangement
- 5. Doberinier triads
- 6. Newland octaves
- 7. A.E. Dechancourtois telluric helical classification
- 8. Mendeleev's periodic table
- 9. Languit Huggins arrangement
- 10. Werner classification
- 11. Rang classification
- 12. Burry classification
- 13. Modern periodic table based on modern periodic law
- 14. Stewart periodic table, called chemical galaxy (2005).
- 15. Sayyed Noor Zada in 2015 proposed a new form of the periodic table in which the there is a proper position for Lanthanides and Actinides. It consists of 32 columns and 7 periods. It is the latest and longest periodic

table in the history of periodic classification.

In the modern periodic table, the elements have been arranged on the basis of increasing atomic number (modern periodic law).

The modern periodic table consists of horizontal rows and vertical columns. Horizontal rows are called periods and the vertical columns are called groups or families. There are seven periods and two groups in the modern periodic table.

Periods in modern periodic table

Horizontal rows of elements in the periodic table are called periods. Each period begins with an alkali metal and ends with an inert gas element.

First period: The **first period** is made up of only **2 elements,** namely, *hydrogen* and the noble gas *helium*.

Second period: The **second period** contains 8 elements. It starts with *lithium,* an alkali metal of Group I. The other elements placed in succeeding groups are: *beryllium, boron, carbon, nitrogen, oxygen, fluorine* and lastly, *neon,* a noble gas.

Third period: The **third period** which begins with *sodium* also contains 8 elements. These are: *sodium, magnesium, aluminium, silicon, phosphorus, sulphur, chlorine* and the noble gas *argon.*

Fourth period: The **fourth period** begins, again, with an alkali metal, potassium. This period consists of 18 elements from potassium $(Z = 19)$ to the noble gas, krypton $(Z = 36)$.

Fifth period: The **fifth period,** like the fourth period, also consists of **18 elements** $(Z = 37$ to 54). It begins with rubidium $(Z = 37)$ and ends with xenon $(Z = 54)$ which, again, is a noble gas. Of the 18 elements, eight $(Z = 37, 38, 49, 54)$ are normal elements and the remaining ten $(Z = 39$ to 48) are transition elements.

Sixth period: The **sixth period** is the longest period. It consists of **32 elements** $(Z = 55$ to 86). These include 8 normal elements $(Z = 55, 56$ and 81 to 86), 10 transition elements $(Z = 57$ and 72 to 80) and 14 **rare earth elements** $(Z = 58$ to 71). The **rare earth elements** begin with cerium $(Z = 58)$ and continue up to lutetium $(Z = 58)$ = 71). These are so called because these occur very *rarely.* The rare earths are so similar to one another and also to *lanthanum* that these are called collectively as **lanthanides.** If these elements are placed horizontally in the same group, there will be undue expansion of the table. To avoid this, these are placed as a separate series below the periodic table.

Seventh period: The **seventh period** is an incomplete period. It starts with a radioactive element francium with atomic numbers 87 and ends with unnilbium atomic number 112. It consists of 26 elements. Just as the elements after lanthanum are called lanthanides, similarly, the elements after *actinium, i.e.,* from *thorium* to *lawrencium* $(Z = 90 \text{ to } 103)$ are called **actinides.** These elements, too, are placed as a

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separate series below the periodic table.

Transuranic elements: The elements beyond uranium which have been prepared artificially by nuclear reactions are called **transuranic elements.** The common names of elements with atomic numbers 93 to 105 are: *neptunium, plutonium, americium, curium, berkelium, californium, einstenium, fermium, mendelevium, nobelium, lawrencium, kurchatovium*and *hahnium.*

The IUPAC convention of 1977 has suggested new names for elements having atomic numbers beyond 100. These names are un-nil-unium (Unu, 101), un-nil-bium (Unb, 102), un-nil-trium (Unt, 103), un-nil-quadium (Unq, 104), un-nil-pentium (Unp, 105), un-nil-hexium (Unh, 106), un-nil-septium (Uns, 107), un-nil-octium (Uno, 108), un-nil-annium (Unc, 109), un-un-nilium (Uun, 110), un-un-unium (Uuu, 111), un-un-bium (Uub, 112) etc.

Groups in the modern periodic table

Modern periodic table consists of two main groups. **"A"** group elements are called normal or representative elements while the **"B"** group elements are called transition elements. The "A" group has further been divided into eight sub-groups; similarly the "B" group has also been divided into eight sub-groups. Group "A" consists of the following eight subgroups.

Group IA

The elements, **lithium, sodium, potassium, rubidium, cesium** and **francium,** constitute Group I of the periodic table. They are highly reactive and readily decompose water even at room temperature yielding metal hydroxides which are strong alkalies. These elements are, therefore, known as **alkali metals.**

Group IIA

The elements, **beryllium, magnesium, calicium, strontium,** barium and **radium,** constitute Group II of the periodic table and are called alkaline earth metals. These are present in the earth crust in combined (mineral/ore) forms.

Group IIIA

Group III of the periodic table contains five elements, namely, **boron,aluminium,gallium, indium** and **thallium.** This group is called boron family.

Group IVA

Group IV Contains five elements, namely, **carbon, silicon, germanium, tin** and **lead.** This group is called carbon family.

Group VA

Group V contains five elements, namely **nitrogen, phosphorus, arsenic,**

antimony and **bismuth,** and after the first element of the group, they are known as the **nitrogen family.**

Group VIA

Group VI contains five elements, namely **oxygen, sulphur, selenium, tellurium** and **polonium** and after the first element of the group, they are also named as **oxygen family**. These are also called chalcogens means ore formers.

Group VIIA

Group VII comprises of five elements, namely, **fluorine, chlorine, bromine, iodine** and **astatine.** These are known as halogens means salt formers. **Group VIIIA**

The noble gases comprise of **helium, neon, argon, krypton, xenon** and **radon.** These elements are called inert gases, noble gases, rare gases, airogens or zero group elements.

Group "B" elements are called transition elements. Group "B" consist of eight subgroups IB, IIB, IIIB, IVB, VB, VIB, VIIB and VIIIB.

Remember that elements in a group have the same valence shell electronic configuration and hence has the same chemical properties. Alkali metals have one electron in the valence shell and have the same reactivity while halogens have seven valence electrons. Elements in a period have the same shell in the process of completion. Like all elements of third period have $3rd$ shell in the process of completion.

Blocks in the modern periodic table

On the basis of electronic configuration the elements has been classified into four blocks known as *s, p, d* and *f* blocks. This classification depends upon the type of the orbitals (*s, p, d* or f) into which the last electron of the atoms of the elements enters.

s **Block Elements:***The elements whose atoms receive the last electron in the s orbital of their outermost energy shell* are called *s block elements.* This block consists of elements of Groups I and II in which the *s* orbitals are being progressively filled. The elements of Group I have the general ground state electronic configuration n*s* 1 and are called **alkali metals.**

The elements of Group II have the general ground state electronic configuration n*s* 2 and are called **alkaline earth metals.**

*p***Block Elements:***The elements whose atoms receive the last electron in their p orbitals* are called *p* **block elements.** The atoms of elements of Group III, IV, V, VI, VII and Zero involving one, two, three, four, five and six electrons, respectively, in *p* orbitals (while *s* orbitals are already filled) in the outermost shells, constitute *p block.* The general electronic configuration for the atoms of the elements of this block may

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be written as $ns^2 np^{1-6}$.

d **Block Elements:** The atoms of elements lying between *s* and *p* blocks have the *s* and *p* orbitals (of their outermost principal energy shell) completely filled. The *dorbitals in the penultimate (inner to the outermost) shell, however, are still empty.* The last electron in these elements, therefore, enters the *d* orbitals which, thereby, get progressively filled as we move across a period. Thus, *the elements in which the last electron enters the d orbitals of their last but one (penultimate) energy shells are called d* **block elements.** The general electronic configurations of *d* block elements may be written as $(n - 1)$ ns^{1-2} , d^{1-10} . These elements are also called **transition elements.** This block consists of three rows called *First, Second and Third transition series* which involve the filling of 3*d*, 4*d* and 5*d* orbitals, respectively. The elements from scandium $(Z = 21)$ to zinc $(Z = 30)$ in the fourth period constitute the *First transition series;* from yttrium $(Z = 39)$ to cadmium $(Z = 48)$ in the fifth period constitute *the Second transition series* and from hafnium $(Z = 72)$ to mercury $(Z = 80)$ in the sixth period constitute *the third transition series.*

f **block Elements:***The elements in which the last electron enters the f orbitals of their atoms* are called *f* **block elements.** In these elements, the last electron enters the third to the outermost (ante penultimate), *i.e.*, $(n-2)$ *f* energy shell. It consists of two series of 14 elements each placed at the bottom of the periodic table. The first series follows lanthanum, La $(Z = 57)$ and the other follows actinium, Ac $(Z = 89)$ in the order of increasing atomic numbers. These series are called **lanthanides** (from cerium to lutetium) and **actinides** (from thorium to lawrencium), respectively. In lanthanides, 4*f* orbitals and in actinides, 5*f* orbitals are being progressively filled.

Classes in the periodic table

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Elements in the periodic table have been classified into three classes; (i) Metals (ii) Non-metals

(iii) Metalloids

On the basis of physical states elements can be classified into solids, liquids and gases. Some elements are natural and some are artificial.

There are 89 metals, 17 non-metals and 6 metalloids in total of 112 elements. There are 96 solids, 5 liquids and 11 geseuos elements in the periodic table. There are 14 s-block, 30 p-block, 40 d-block and 28 f-block elements in the periodic table. There are 92 natural and 20 artificial elements in total of 112 elements. $\sqrt{2}$

Elements of the period third (sodium to argon)

Period third consists of eight elements namely sodium, magnesium, aluminium, silicon, phosphorous, sulphur, chlorine and argon. These elements have $3rd$ shell in the process of completion. Their electronic configuration is given below.

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Importance of the elements of period third

Period third consist of metals, metalloid and non metals. The elements of period third are most important in daily life. Sodium is present in the form of table salt (NaCl). It is used in street lights (yellow light). Magnesium is present in the form of dolomite, asbestos, milk of magnesia etc. Aluminium is used in construction of various substances like aeroplanes, ships, bridges etc. due to its lightness and corrosion resistant properties. Silicon is a semiconductor and semiconductor industries are based on Silicon. Phosphorous is a light bearing element found in bones and teeth. It is used in fertilizers and toothpastes. Sulphur is found in combined form as well as in free form. Its compounds like thiols are added to natural gas to impart characteristic smell. Chlorine is used for water purification and bleaching purposes. Argon is used in light bulbs as inert gas. It is used in Lasers and Geiger counters.

Periodic properties

Properties of the elements which repeat again and again at regular intervals in the periodic table across the period and down the group are called periodic properties. These properties are physical and chemical both. There are about 40 periodic properties.

Periodicity: The repetition of properties in the periodic table is called periodicity. Due to periodicity in properties of the elements the elemental table is called periodic table.The periodicity in properties is caused primarily by differences in three characteristics.

- (i) The magnitude of nuclear charge and the number of electrons in the shell, both of which are equal to the atomic number.
- (ii) The number of shells and number of electrons in the shells, particularly in the valence shell.
- (iii) The distance of electrons in various shells from the nucleus.

Trends in periodic properties across the third period

1. Atomic radius

The **radius of an atom** or **an ion** may be taken, in the ordinary sense, as *the distance between the centre of the nucleus and the outermost shell of electrons.* If the atom or the ion is assumed to be spherical, the atomic or ionic radius corresponds to the radius of the sphere. However, the absolute size of an atom is difficult to define because of the following reasons:

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- (i) Atom does not exist free in nature.
- (ii) Theoretically, an electron, at a time, may be very close to the nucleus while at other time it may be far away from the nucleus.
- (iii) The electron probability is never zero even at very large distances from thenucleus.
- (iv) The probability of distribution of electrons in an atom is appreciablyinfluenced by the presence of other atoms in its environment.
- (v) Electron has dual nature, it behave as particle as well as wave. Atomic radius may be of the following four types.
	- *(1) Covalent Radius (2) Ionic Radius*
	- *(3) Metallic Radius (4) Van der Waals' Radius*

Covalent radius

Half of the distance between the nuclei of two covalently bonded atoms of the same element in a molecule, is taken as the **covalent radius***of the atom of that element.* While defining the covalent radius as above, it is assumed that atoms are hard, incompressible spheres which are touching each other in normal covalent bond formation. However, atoms are neither fully incompressible nor do they touch each other in a covalent molecule. Therefore, the covalent radii calculated on the basis of the above definition cannot be regarded as exact.

The distance between the centres of any two neighbouring atoms (*viz.,* the internuclear distance) can be measured by X-ray diffraction or spectroscopic studies.

Covalent radii (Å) of various elements

| \vert Na = 1.54 \vert Mg= 1.30 \vert Al = 1.18 \vert Si = 1.11 \vert P = 1.06 \vert S = 1.02 \vert Cl = 0.99 \vert Ar = 1.74 | | | | Group I Group II Group III Group IV Group V Group VI Group VII Group Zero | |
|--|--|--|--|---|--|
| | | | | | |

The radius for noble argon is only the van der Waals' radius.

Vander Waals' radius: The van der Waals' radius is defined *as one half of the distance between the nuclei of two adjacent identical atoms belonging to two neighbouring molecules of an element in the solid state*.

Periodic trends in covalent radii: Generally speaking, *the covalent radii decrease in moving from left to right in any given***period** and *increase in moving from top to bottom in any given* group.

The variation of covalent radii in a period can be explained easily on the basis of electronic configurations and the effective nuclear charges. The greater the effective nuclear charge, the greater would be the force with which the electron is pulled towards the nucleus. As a consequence, the valenceshell electrons tend to lie closer and closer to the nucleus. Thus, here is more and more contraction and more and more reduction in the covalent radii in moving from left to right across the period.In the case of noble gases, the atomic radii are only the Van der Waals' radii which are, therefore, larger than the covalent radii of other elements.

In moving down a group, the number of the principal shell increases and, therefore, the size of the atom increases. This effect, no doubt, is partly annulled by the drawing in of the electron shells on account of the increasing nuclear charge. But the effect of adding a new shell is so large that it overcomes the contractive effect of the increased nuclear charge. Hence, *the radius of the atom increases in moving from top to bottom in* a **group.**

Ionic Radius: The ionic radius corresponds to the radius of an ion in an ionic crystal. It may be defined as *the distance from the nucleus of an ion up to which it has influence on its electron charge cloud.* The electron charge cloud, no doubt, may extend theoretically up to a very large distance. However, it is important to characterize each ion by some value. For this purpose, the inter-nuclear distance in any ionic compound is determined from X-ray measurements. *This distance is taken as the sum of the radii of the two ions involved.* Knowing the radius of one, that of the other can be calculated.

Half of the distance between the nuclei of two isoelectronic species connected by ionic bond is called ionic radius. Isoelectronic species has same number of electrons and same shells and almost same size. This definition can be applied to NaF, KCl, RbBr and CsI only in which the cations and anions are isoelectronic.

Metallic radius: Half of the distance between the nuclei of two atoms bonded by metallic bond. Metals form metallic bond so their radii are expressed interms of

metallic radius. In the period third, the radii of Na, Mg and Al are metallic, these of Si, P, S and Cl are covalent while that of Argon is Vander Waal's radius.

Trend in atomic radius across the period third

In the period third, Na, Mg and Al are metals so these are always connected by metallic bonds and their radii will be metallic. The atoms of Si, P, S and Cl are connected by covalent bonds so their radii will be covalent. The atoms of noble gas Argon are connected by Vander Waal's forces so its radius is Vander Waal's radius. Atomic radius decreases gradually from left to right upto Chlorine and then increases in case of Argon as its atomic radius is Vander Waal's radius.

2. Ionization energy

The **ionization energy,** *IE,* of an element is defined as *the amount of energy required to remove an electron from the valence shell of an isolated gaseous atom to form a positive ion.* This gives a direct measure of the ease with which an atom can change into a cation, as represented below:

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M_{(g)} + I E \longrightarrow M^+_{(g)} + e^-
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The energy required to bring about the above change is called **ionization energy.** Evidently, *the smaller the ionization energy, the easier it is for the neutral*

atom to change into a positive ion.

Ionization energies are generally measured by spectroscopic techniques. Another method is to have the vapours of the element in a discharge tube and connect it to a source of current. The voltage applied is gradually increased. At a certain voltage there will be a sudden rise in the current passing through the tube. The energy corresponding to this voltage is known as the **first ionization energy** $(IE)_1$. The sudden rise in the current is due to the liberation of an electron from each neutral atom producing an ion, M^+ .

If the applied voltage is increased further, there may again be a stage when the current shows a sudden rise. This is due to *the elimination of another electron from* each positively charged ion $(M⁺)$ produced earlier. The energy corresponding to this stage is known as the **second ionization energy (***IE***)2.** At this stage, doubly charged ions, M^{2+} , are produced. If the potential is increased even beyond this point, there may again be sudden and sharp rises in the current at certain points. These points correspond to the *loss of three or more electrons* and give the **third (***IE***)3**or **higher ionization energies** of the element. These changes may be represented as follows:
 $M \xrightarrow{\frac{(E)_1}{(E)}} M^+ \xrightarrow{e^-} e^-$

Ionization energy is measured in electron-volts (eV) as well as in joules or kilojoules. It may be remembered that $1 \text{ eV} = 1.602 \times 10^{-19}$ joule or 1.602×10^{-22} kilo joule.

The values presented in electron-volts give ionization energy *per atom* while those expressed in kilojoules represent ionization energy *per mole* (*i.e.,* per Avogadro's number of atoms) of the element. Thus, ionization energy of hydrogen is 13.595 eV **per atom** of hydrogen and $13.595 \times 1.602 \times 10^{-22} \times 6.022 \times 10^{23} = 1312.0$ Kj**per mole** of hydrogen.

Let us consider the first and the second ionization energies for lithium and
 $\begin{array}{ccc}\n\text{given below.} \\
\downarrow \text{Li} & + & \text{e}^{\cdot}; \\
\downarrow \text{Li} & + & \text{e}^{\cdot};\n\end{array}$ $\begin{array}{ccc}\n\text{(IE)} & = 520.1 \text{ kJ mol}^{-1} \\
\downarrow \text{Ti} & = 7207.2 \text{ kJ mol}^{-1}\n\end{array}$ sodium given below. $(LE) = 520.1 \text{ kJ mol}^{-1}$

As can be seen, the second ionization energies are very much higher than the first ionization energies. This is due to the fact that after the removal of an electron, the number of electrons decreases while the nuclear charge remains the same. Consequently, the remaining electrons are held more tightly by the nucleus and it

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becomes difficult to remove the second electron. Therefore, the second ionization energy is greater than the first ionization energy and, similarly, the third ionization energy is greater than the second ionization energy and so on. Thus, $(E)_{3}$ (*IE*)₂> $(IE)_1$.

Factors affecting ionization energy: The ionization energy of an element depends upon the following factors.

1. Atomic size:*The larger the atomic seize, the smaller is the ionization energy.* The reason for this is that as the size of the atom increases, the outer electrons lie farther away from the nucleus. Hence, according to Coulomb's law, the attractive pull of the nucleus on the outer electrons decreases and it becomes easier to knock out an electron from the outer shell of the atom.

2. Nuclear charge: The force of attraction between the nucleus and the outermost electron increases with increase in nuclear charge. Thus, the greater the nuclear charge, the greater is the energy needed to pull out an electron from the atom. Hence, *ionization energy increases with increase in nuclear charge.*

3.Screening effect or **shielding effect:***The large the number of inner shells, the smaller is the ionization energy.* The inner shells act as a screen or shield between the nucleus and the electrons in the outermost shell. This is known as **screening effect** or **shielding effect.** The larger the number of inner shells, the greater is the screening effect. Consequently, the electrons in the valence shell experience less attraction from the nucleus. Hence, the ionization energy would be low.

4. Orbital penetration effect or the effect of removal of *s, p, d* **and** *f* **electrons from the same energy shell:** The *s* electrons in their motion around the nucleus have greater probability of coming closer to the nucleus than the *p, d* or *f* electrons of the *same principal energy shell.* In other words, *s* electrons *penetrate more* towards the nucleus than *p* electrons and the penetrating power of the electrons in the given principal energy shell varies as *s*>*p*>*d*>*f*. Thus, the *s* electrons experience more attraction from the nucleus than the *p*, *d* or *f* electrons of the same principal energy shell. It follows, therefore, that *ionization energy for pulling out an s electron is maximum and it decreases in pulling out a p electron, a d electron or an f electron of the same principal energy shell.* We may thus say that ionization energy corresponding to the elimination of an electron from a given energy level decreases in the order *s*>*p*>*d*>*f* electron.

5. Electronic configurations: Certain electronic configurations are more stable than others. For example, *if an atom has fully filled or exactly half-filled sub-shells, its ionization energy is higher than expected normally from its position in the periodic table.* For example, beryllium and nitrogen in the second period and magnesium and phosphorus in the third period, have slightly higher ionization energies than would be expected. This is due to the *extra stability of the fully completed s sub-shell* in

beryllium and magnesium and that of the *exactly half-filled p sub-shell* in nitrogen and phosphorus.

Further, it is seen that He, Ne, Ar, Kr, Xe and Rn have highest ionization energies in their respective periods. This shows that an atom with s^2 , p^6 configuration (the so-called octet configuration) in its outer shell is highly stable. In this connection it may also be noted that Li^+ and Na^+ ions, which also have s^2p^6 configurations require very high energies, *viz.,* 7297.2 and 4563.5 kJ per mole to permit pulling out of an extra electron from them to give Li^{2+} and Na^{2+} ions, respectively.

Variation of ionization energy in the periodic table: The following periodic trends in ionization energy are observed.

a. Variation in a group:*In general, the ionization energy decreases in going from top to bottom in a group.* This is due to,

- i. Increase in size
- ii. Increase in shielding effect.

b. Variation along a period:*In general, the ionization energy increases as we move along a period from left to right.* It is due to,

- i. Decrease in size
- ii. Increase in nuclear charge
- iii. Shell is going towards completion

However, the variation in ionization energy along a period is not smooth. Some irregularities are distinctly observed. This is due to the fact that atomic size is not the only factor which determines the ionization energy.

Across the period third, the ionization energies of aluminium and sulphur are unexpectedly lower than the ionization energies of their preceding elements magnesium and phosphorous respectively. These anomalies are explained as follows:

Electronic configuration of aluminium $(3s^2p^1)$ is less stable than that of magnesium (3*s* 2) which has completely filled *s* sub-shell. Moreover, in aluminium the outermost electron is present in 3*p* orbital which is at a slightly higher energy level than the outermost electron in magnesium. The 3*p* electron of aluminium is thus less tightly held by the nucleus and hence the ionization energy of aluminium is less than that of magnesium.

Electronic configuration of phosphorous $(3s^2 p_x^1 p_y^1 p_z^1)$, in which all the *p* orbitals are *exactly half-filled,* is more stable than the electronic configuration of sulphur $(3s^2 p_x^2 p_y^1 p_z^1)$. Therefore, ionization energy of sulphur is less than that of phosphorous.

3. Electron affinity

Just as ionization energy measures the tendency of an atom to change into a cation $(M \rightarrow M^+ + e^-)$, the **electron affinity** (*EA*) gives a measure of the tendency of an atom to change into an anion $(X + e^- \rightarrow X^-)$. **Electron affinity** is defined as *the amount of energy released when an electron is added to the valence shell of a gaseous isolated atom.*

tom.
 $X_{(s)}$ + e⁻ \longrightarrow $X_{(s)}$ + Energy (*EA*) Atom Anion

The greater the energy released in the process of taking up the extra electron, the greater is the electron affinity. The electron affinity of an atom measures *the tightness with which it binds an additional electron to itself.* The electron affinities are expressed in eV per atom or kJ mol⁻¹.

Successive electron affinities: Like the second and higher ionization energies, the second and higher electron affinities are also possible. However, after the addition of one electron, the atom becomes negatively charged and the second electron is to be added to a negatively charged ion. **The addition of second** electron is opposed by the coulombic force of repulsion and *energy has to be supplied* for the addition of the second electron. If an atom has a spontaneous tendency, *i.e.,a positive tendency,* to gain an electron, then, conventionally, its electron affinity is said to be *positive* and if an atom is reluctant to gain an electron *i.e.,* it has a *negative tendency* to gain an electron and is forced to accept it, its electron affinity is said to be *negative.* Thus, in the case of oxygen, the first electron affinity (EA) ₁, is positive since 140.9 kJ is released when a mole of O atoms get converted to O⁻ ions. In other words, O atom has positive tendency to accept electron. However, the second electron affinity $(EA)_{2}$ is negative since 770 kJ of energy has to be supplied to convert 1 mole of $O⁻$ ions to O^{2-} ions.

Similarly in the case of sulphur, while the first electron affinity (EA) ₁ is positive since 200.7 kJ of energy is released when 1 mole of S atoms get converted to S^- ions, the second electron affinity $(EA)_2$ is negative since 333.2 kJ of energy has to be supplied to convert one mole of S^- ions to S^2 ions.

Thermodynamically, however, the energy released is given a *negative sign* and energy absorbed is given a *positive sign*. Accordingly, when a specie has a *positive* electron affinity, ΔH , accompanying the addition of an electron to the specie, is *negative* and if it has a *negative electron affinity,* Δ*H is positive.* Thus, for the reaction Cl + $e^- \rightarrow C$, while *EA* is positive, ΔH for the process is negative. In various calculations involving Δ*H* (as, for example, in Born-Haber cycle), the value for electron affinity of chlorine would be taken as $-348.5 \text{ kJ mol}^{-1}$ and not $+348.5 \text{ kJ}$ $mol⁻¹$.

Variation of electron affinity in the periodic table

In general, *electron affinity decreases in going from top to bottom in a* **group***and increases in going from left to right across a* **period.** This can be easily explained. On moving down a **group,** the atomic size increases and, therefore, the effective nuclear attraction for the electron decreases. Consequently, the atom will have less tendency to attract additional electron towards, itself, *i.e.,* its electron affinity would decrease. On moving across a **period,** on the other hand, the **atomic** size decreases and hence the force of attraction exerted by the nucleus on the electrons increases. Consequently, the atom has a greater tendency to attract the additional electron, *i.e.,* its electron affinity increases. Thus, as expected, electron affinities of metals are low while those of non-metals are high.

It is seen that halogens have high electron affinities. This is due to their strong tendency to gain an additional electron to change into the stable s^2p^6 configuration.

The electron affinity decreases from Cl \rightarrow Br \rightarrow 1, *i.e.*, on moving down the group, as discussed above. However, electron affinity of fluorine is *unexpectedly low.* It cannot be explained by any simple mechanism. It is probably due to small size of the atom. The addition of an extra electron produces high electron charge density in a relatively compact 2*p* sub-shell resulting in *strong electron-electron repulsion.* In case of chlorine the electrons are far away from one another in the third shell and an electron can easily be added to the third shell. Circumference of the third shell is large compared to the second so inter-electronic space is more and electron addition is easy to the third shell having seven electrons compared to the second shell having seven electrons.

Factors affecting electron affinity

1. Atomic size:Small sized atoms have high electron affinity than large size atoms.

2. Nuclear charge: Atoms with high nuclear charge has high electron affinity compared to atoms with small nuclear charge.

3. Electronic configuration: The electronic configurations *of the elements also*

influence their electron affinities considerably. Electron affinities of noble gases are zero. This is because their atoms have stable s^2p^6 configurations in their valency shells and there are no chances for the addition of an extra electron.Electron affinities of beryllium, magnesium, calcium and nitrogen are also practically zero. This is attributed to the extra stability of the fully completed *s* orbitals in Be $(2s^2)$, Mg $(3s^2)$ and Ca $(4s^2)$ and of the exactly half-filled 2p sub-shell in N $(2s^2 p_x^1 p_y^1 p_z^1)$. This, *if an atom has fully filled or exactly half-filled sub-shells, its electron affinity would be practically zero.*

The trends in electron affinities within a period are also irregular indicating once again that atomic size is not the only criterion for determining electron affinity. Thus, electron affinity of Be is less than that of Li although the atomic size of Be is less than that of Li. Similarly, electron affinity of N is less than that of O although the atomic size of O is less than that of N.

4. Electronegativity

The relative tendency of an atom to attract the shared pair of electrons towards itself is called electronegativity. The element with high attractive tendency for the shared pair of electron will have high electronegativity and vice versa. The term electronegativity has been defined differently by different investigators and each of them has suggested a method of his own to calculate electronegativities of different elements. The approaches of some of the investigators are discussed below.

Pauling's approach: Pauling defined electronegativity*as the power of an atom in a molecule to attract electrons to itself.*

Alfred and Rochow's approach: Alfred and Rochow defined **electronegativity***as the electrostatic force of attraction exerted by the nucleus of an atom on the valence electrons.*

Mulliken's approach:Mulliken suggested that *the average of the ionization energy* (*IE*) *and electron affinity* (*EA*) *of an atom should be a measure of the* **electronegativity***of the atom.*

Factors effecting electronegativity: Although the electronegativity of an element is conventionally assigned a definite value, yet it may differ from one molecule to another. The ability of an atom in a molecule to attract electrons towards itself depends upon its environment in the molecule. The electronegativity of an atom would thus depend upon the nature of the other atom with which it is attached in the molecule. The factors which largely determine the electronegativity of atoms are as follows.

1. Atomic size: Atoms of smaller size has high electronegativity compared to the large sized atoms.

2. Nuclear charge: Atoms of high nuclear charge has high electronegativity than atoms of small nuclear charge.

3. Nature of the shell: Atoms with nearly full filled shells has high electronegativity than those with less than half filled shells.

4. Charge on the atom: An atom which acquires a positive charge, either integral or partial, would tend to attract electrons more strongly than a neutral atom. Thus, a cation will be more electronegative than the parent atom which, in turn, would be more electronegative than its anion. Also, the higher the positive oxidation state of an atom in a species, the greater would be its electron-attracting power and hence the greater would be its electronegativity. For example, the oxidation state of central chlorine atom is +1 in HClO and +5 in HClO₃. Hence, the chlorine atom in HClO₃ will be more electronegative than in HClO. Accordingly, the release of hydrogen as H^+ ion in HClO₃ would be much easier than a similar change in HClO. In other words, HClO3*behaves as a stronger acid than* HClO.

5. Hybridization: We know that *s* electrons are more penetrating than the *p* electrons. Therefore, if an atom has hybrid orbitals with a greater *s* character, the electronic charge in such orbitals would remain closer to the nucleus of that atom. This means that *the electronegativity of the atom would increase with increase in scharacter of its hybrid orbitals.* For example, in methane, the carbon atom involves *sp* 3 hybridization of its orbitals so that the hybrid orbitals have 25% *s* character. In ethylene, the carbon atom involves sp^2 hybridization of its orbitals and consequently the *s* character of hybrid orbitals increases to 33%. In acetylene, the carbon atom involves *sp* hybridization of its orbitals and, therefore, the *s* character of hybrid orbitals increases of 50%. Accordingly, the electronegativity of carbon atom increases as we move from CH₄ through C₂H₄ to C₂H₂. Due to greater electronegativity of carbon atom in ethylene and acetylene, the electron pair of $C - H$ bond is pulled more towards carbon atom thereby facilitating the release of H atom as H^+ ion. Thus, while methane is neutral, ethylene is slightly acidic while acetylene is considerably acidic.

6. Effect of substituents: The electronegativity of an atom depends considerably upon the nature of the substituents attached to that atom. For example, the carbon atom in CF3I acquires a greater positive charge than in CH3I. Hence, the carbon atom in CF_3I is more electronegative than in CH_3I . The difference in the electronegativities of an atom caused by the substituents results in different chemical behaviour of that atom.

Variation of electronegativity in the periodic table

Electronegativity goes on increasing as we move along a **period.** This is due to increase in nuclear charge and decrease in atomic size. Electronegativity *decreases down the group* as atomic size increases.

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electronegativities

Applications of electronegativity

Electronegativities have very wide range of applications. Some of the important applications are given below.

- 1. Calculation of partial ionic character of a covalent bond.
- 2. Calculation of enthalpies of formation of compounds.
- 3. Calculation of bond length.
- 4. Explanation for bond angles.
- 5. Rationalization of reaction mechanism.
- 6. Explanation of diagonal relationship.
- 7. Deciding the nature of bonds.

5. Electrical conductivity

The ability of an element to pass electric current is called electrical conductivity. For electrical conduction free electrons are needed and free electrons are present in large size elements. Large size elements are at the left bottom of the periodic table which are metals. So electrical conductivity of metals is high while that of metalloids is low and non-metals are bad conductors. Electrical conductivity decreases from left to right in the periodic table and it increases down the group as the atomic size increases. The electrons becomes farther and farther from the nucleus as the atomic size increases so nuclear attraction on these electrons decreases, these becomes mobile and conductivity increases. In the period third; Na, Mg and Al are good conductors, Si is semiconductor and from P to Ar are non-conductors.

6. Shielding effect or screening effect

As we know that electrons in an atom are distributed in various shells and orbitals around the nucleus. The electrons of the outer shells are far away from the nucleus. The electrons of the outer shells are shielded from the nucleus by the electrons present in the inner shells. Thus the nuclear attraction on these outer shells electrons decreases due to the presence of inner shell electrons in between the nucleus and outer shells electrons. This effect is called shielding effect or screening effect.

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Shielding effect has a direct impact on periodic properties like atomic size, ionization energy and electron affinity etc.

Shielding effect across the period:In a period as we move from left to right across a period, the same shell is in the process of filling. The number of inner shells remains constant it means that no addition of new shells occurs as we move from left to right, so shielding effect remains constant.

Shielding effect down the group: In a group as we move from top to bottom, successive addition of shells occurs. It means that the outer shell is going farther and farther from the nucleus as the number of inner sells increases. The electrons in the inner shells shields the electrons of the outer shell from the nucleus so shielding effect increases progressively as we move down the group. This causes a decrease in the ionization energy and electron affinity values of elements down the group.

7. Melting point and boiling point

Melting and boiling point indicate the strength of binding forces among the particles of a substance. Stronger the binding forces among the particles more energy will be required for its breaking and hence high will be the melting and boiling point. Weaker the binding forces, less energy will be required for its breaking and low will be the melting and boiling point. Na, Mg and Al are metals and connected by metallic bonds. These exist in giant, polymeric crystalline forms so their melting and boiling points are high as the attractive forces are strong enough. The attractive forces in case of Silicon are weaker and hence its m.pt. and m.pt. is low. Phosphorous exists in tetra-atomic molecular form while Sulphur exist in octa-atomic molecular form. The attractive forces (Vander Waal's forces) in case of Sulphur are stronger as its molecular size is large compared to Phosphorous so the m.pt. and b.pt. of Sulphur are higher than Phosphorous. Argon exist in monoatomic molecular form and the atoms are connected by weak attractive forces so its m.pt. and b.pt. is low. Down the group in metals the size becomes larger and attractions become weaker so b.pt and m.pt decreases. In case of non-metals, down the group the polarization increases attractions becomes stronger and m.pt, b.pt increases.

Metallic character (electropositivity)

The electron losing tendency of an element is called its metallic character or electrropositivity. Greater the electron losing tendency of an element high will be its metallic character and vice versa. The element with large size and more shielding effect will have high electropositivity compared to small sized elements. The large size elements are at the left bottom of the periodic table so metallic character is high at the left bottom and it decreases as move from left to right in a period. Metallic character increases as we move down the group.

8. Oxidation state

The apparent charge on an atom in a molecule when the electrons are distributed is called oxidation state or oxidation number. The oxidation state of an element is related to the number of electrons that an atom losses, gains or shares with another atom in a compound. As from left to right in a period the valence shell electrons increases so oxidation state increases up to IVA and then decreases up to VIIIA. Oxidation state is variable, it may be positive, negative, zero or fractional. Down the group usually the oxidation state decreases due to inert pair effect phenomenon.

Chemical properties of the elements of period third

1. Reaction with water

Reaction of sodium with water: Sodium reacts with cold water and produce NaOH and H₂. The reaction is vigorous, spontaneous, fizziling, skating and exothermic.
 $2Na + 2H_2O \rightarrow 2NaOH + H_2$

$$
2Na + 2H_2O \rightarrow 2NaOH + H_2
$$

Reaction of magnesium with water: Magnesium reacts slowly with cold water forming magnesium hydroxide.

$$
Mg + 2H_2O \to Mg(OH)_2 + H_2
$$

Mg burns in steam with white flame and produce MgO.
 $Mg + H_2O \rightarrow MgO + H_2$

$$
Mg + H_2O \to MgO + H_2
$$

Reaction of aluminium with water: Aluminium powder reacts with steam and produce aluminium oxide and hydrogen gas. The reaction becomes slower with the passage of time.

$$
2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2
$$

Reaction of silicon with water: Silicon react with steam at red heat and form silicon dioxide and hydrogen gas.

$$
Si + 2H_2O \rightarrow SiO_2 + 2H_2
$$

Reaction of phosphorous with water: Phosphorous do not react with water.

Reaction of Sulphur with water: Sulphur does not react with water.

Reaction of chlorine with water: Chlorine dissolves in water forming a green solution. The reaction is reversible and a mixture of hydrochloric acid and

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$$

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hypochlorous acid is formed.

 $Cl_2 + H_2Of$ *HCl* + *HOCl*

In the presence of sunlight, hypochlorous acid decomposes and produces hydrochloric acid and oxygen gas.

 $2HOCl \rightarrow 2HCl + O_2$

Reaction of argon with water: Argon does not react with water.

2. Reaction with oxygen

Reaction of sodium with oxygen: Sodium burns in oxygen with a yellow flame and produces a white solid mixture of sodium oxide and sodium peroxide.
 $4Na + O_2 \rightarrow 2Na_2O$ (*Sodiumoxide*) mixture of so
 $+O_2 \rightarrow 2Na_2$

 $4Na + O₂ \rightarrow 2Na₂O$ (*Sodium oxide*)
 $2Na + O₂ \rightarrow Na₂O₂$ (*Sodium peroxide*)

Reaction of magnesium with oxygen: Magnesium burns in oxygen with an intense white flame to give a white solid magnesium oxide. \bullet

$$
2Mg + O_2 \rightarrow 2MgO
$$

Reaction of aluminium with oxygen: Aluminium powder burns in oxygen and form white aluminium oxide.

$$
4Al + 3O_2 \rightarrow 2Al_2O_3
$$

Reaction of silicon with oxygen: Silicon burn in oxygen if strongly heated and form silicon dioxide.

$$
Si + O_2 \rightarrow SiO_2
$$

Reaction of phosphorous with oxygen: White phosphorous (P₄) catches fire spontaneously in air producing white smokes and forming a mixture of phosphorous revolutions exponentially the smokes and forming a mixture of phosphorous revolutions or $P_4 + 3O_2 \rightarrow P_4O_0$ or $2P_2O_3$ *Phosphorous Penta* trioxide and pentaoxide.

Reaction of Sulphur with oxygen: Sulphur burns in air on gentle heating with a pale blue flame producing colorless sulphur dioxide gas.

 $S + O_2 \rightarrow SO_2$

Reaction of chlorine with oxygen: Chlorine reacts with air and form chlorine monoxide, dioxide, trioxide and pentaoxide.

 $Cl_2 + O_2 \rightarrow Cl_2O + Cl_2 + Cl_2O_3 + Cl_2O_5 + Cl_2O_7$

Reaction of argon with oxygen: Argon does not react with air.

3. Reaction with halogens

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$$

Reaction of sodium with chlorine: Sodium burns in chlorine with a bright orange flame producing white solid sodium chloride.
 $4Na + Cl_2 \rightarrow 2NaCl$

$$
4Na + Cl_2 \rightarrow 2NaCl
$$

Reaction of magnesium with chlorine: Magnesium burns in chlorine with an intense white flame to give a white solid magnesium chloride.

$$
Mg + Cl_2 \to MgCl_2
$$

Reaction of aluminium with chlorine: Aluminiumpowder react with chlorine on heating and form pale yellow aluminium chloride.

$$
2Al + 3Cl_2 \rightarrow 2AlCl_3
$$

Reaction of silicon with chlorine: Silicon reacts with chlorine if strongly heated and form a colorless liquid, silicon tetrachloride.

$$
Si + 2Cl_2 \rightarrow SiCl_4
$$

Reaction of phosphorous with chlorine: White phosphorous (P₄) burns in chlorine **action of phosphorous with chlorine:** White phosphorous (P₄) burns in chloride order value of phosphorous trichloride and pentachloride.
 $P_4 + 6Cl_2 \rightarrow 4PCl_3$ Phosphorous Trichloride (Colorless Fu min g Liquid)

producing a mixture of phosphorous trichloride and pentachloride.
 $P_4 + 6Cl_2 \rightarrow 4PCl_3$ Phosphorous Trichloride (Colorless 1) action of phosphorous with chiorine. While phosphorous (r_4) burns in

ducing a mixture of phosphorous trichloride and pentachloride.
 $P_4 + 6Cl_2 \rightarrow 4PCl_3$ Phosphorous Pentachloride (Straw Colored Solid)

Reaction of Sulphur with chlorine: Sulphur react with chlorine on gentle heating, producing orange, foul smelling liquid sulphurmonochloride. $2S + Cl_2 \rightarrow S_2Cl_2$

Reaction of chlorine with other halogens: Chlorine reacts with fluorine, bromine and iodine, forming fluoride, bromides and iodides, such compounds are called interhalogens.

Reaction of argon with chlorine: Argon does not react with chlorine. Xenon reacts with fluorine and form xenon diflouride, xenon tetraflouride and xenon hexafluoride.

Oxides of elements of period third

Oxides of period third are given in the table below.

Structure of oxides of period third: $Na₂O$, MgO and $Al₂O₃$ are ionic in nature and has giant, polymeric, three dimensional and networked structures. The ions in such structures are connected by strong electrostatic forces of attraction. The $SiO₂$ is polymeric in nature. Many $SiO₂$ combine and form a giant, polymeric, three dimensional and inter-locked structure like diamond. In silica each Si atom is

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attached to four oxygen atoms tetrahedrally and each oxygen atom is attached to two silicon atoms by single bonds. The trioxide (P_2O_3) and pentaoxide (P_2O_5) of phosphorous exist in dimeric forms P_4O_6 and P_4O_{10} . While the oxides of sulphur and chlorine exists in monomeric forms. There are London forces which connect the oxides of P, S and Cl with one another.

Melting and boiling points of the oxides of period third: Asthe oxides of sodium, magnesium and aluminium are ionic in nature. These ions are connected by ionic bonds with one another so their melting and boiling point are high. In case of silicon dioxide, many SiO_2 units combine with one another and form giant polymeric structure. All the bonds are covalent, so the m.pt and b.pt are lower than that of $Na₂O$, MgO and Al_2O_3 . In the oxides of P, S and Cl there exists London forces so their m.pt and b.pt are low. The m.pt and b.pt of elements of period third decreases from left to right.

Electrical conductivity of the oxides of period third: Electrical conductivity of a substance is due to free electrons or ions. The oxides of period third have no free electrons or ions in the solid form so these are bad conductors in the solid form. The ionic oxides of Na, Mg and Al are water soluble and give ions in the solution form so these oxides are good conductors in the molten or solution form. The oxides of Si, P, S and Cl are not ionizable in water so these are bad conductors.

Binary compounds: Compounds which consists of two type elements only. For example: CO, NO, HCl etc.

Ternary compounds: Compounds which consists of three type elements only. For example: $HNO₃$, $H₂SO₄$, $C₆H₁₂O₆$ etc.

Quarternary compounds: Compounds which consists of four type elements only. For example: Nitrobenzene, benzene sulphonic acid etc.

Hydrides:The binary compounds of hydrogen are called hydrides.

Halides:The binary compounds of halogens are called halides.

Nitrides:The binary compounds of nitrogen are called nitrides.

Carbides:The binary compounds of carbon are called carbides.

Borides:The binary compounds of boron are called borides.

Oxides:The binary compounds of oxygen are called oxides.

Classification of oxides:Oxides has been classified into the following types.

1. Basic oxides: The oxides which dissolve in water and form bases are called basic oxides. These oxides neutralize acids forming salt and water. Metallic oxides are basic in nature. These oxides increase the pH of water. Examples are; $Na₂O$, MgO and CaO etc.

2. Acidic oxides: The oxides which dissolve in water and form acids are called acidic oxides. These oxides neutralize bases forming salt and water. Non-metallic oxides are acidic in nature. These oxides decrease the pH of water. Examples are; CO_2 , SO_2 , $NO₂$ etc.

3.Neutral oxides: These oxides are neutral in nature. These do not affect the water

pH. Examples are; NO, CO, H_2O etc.

4. Amphoteric oxides: These oxides have dual nature. These behave as acidic as well as basic. These react with acids as well as bases. These neutralize acids and bases both. Examples are; Al_2O_3 , BeO, SnO, PbO etc.

Nature of oxides of period third:The oxides of Na and Mg are metallic so are basic in nature. The oxide of Al is amphoteric. The oxides of Si, P, S and Cl are nonmetallic so are acidic in nature.

Basic oxides: The oxides of Na and Mg are basic.

s of Na and Mg are basic.
 $Na₂O + H₂O \rightarrow 2Na⁺ + 2OH⁻$ $Na₂O + 2HCl \rightarrow 2NaCl + H₂O$ 2 $MgO + H_2O \rightarrow Mg^{2+} + 2OH^{-}$ $MgO + HCl \rightarrow MgCl₂ + H₂O$ **Amphoteric oxide:** The oxide of Al is amphoteric. oxide of Al is amphoteric.
 $Al_2O_3 + 6HCl \rightarrow AlCl_3 + 3H_2O$ $Al_2O_3 + 6HCl \rightarrow AlCl_3 + 3H_2O$
 $Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$ **Acidic oxides:** The oxides of Si, P, S and Cl are acidic. es of Si, P, S and Cl are acidic.
 $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$ $B_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ $B_3 + H_2O \rightarrow H_2SO_4$ $2O + H_2O \rightarrow 2$ $Cl_2O_7 + H_2O \rightarrow 2HClO_4$ $S O_3 + H_2 O \rightarrow H_2 SO$ $Cl_2O + H_2O \rightarrow H_2SO_4$
 $Cl_2O + H_2O \rightarrow 2HClO$ $_0 + 6H_2O \rightarrow H_2$
+ $H_2O \rightarrow H_2$ $H_2O \rightarrow H_2O$
+ $H_2O \rightarrow 2H$

Reactions of oxides of period third with water, acids and bases

The oxides of metals dissolve in water and form hydroxides.
 $Na_2O + H_2O \rightarrow 2NaOH$

$$
Na_2O + H_2O \rightarrow 2NaOH
$$

$$
MgO + H_2O \rightarrow Mg(OH)_2
$$

These oxides also react with acids and form salt and water.

react with acids and form sait a
 $Na₂O + 2HCl \rightarrow 2NaCl + H₂O$ with acids and form salt
+2HCl \rightarrow 2NaCl + H₂O

$$
MgO + HCl \rightarrow MgCl_2 + H_2O
$$

$$
MgO + HCl \rightarrow MgCl_2 + H_2O
$$

The oxides of non-metals dissolve in water and form acids.
 $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

$$
P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4
$$

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$$
SO_3 + H_2O \rightarrow H_2SO_4
$$

\n
$$
Cl_2O_7 + H_2O \rightarrow 2HClO_4
$$

These oxides also react with bases and form salt and water.

$$
SiO2 + 2NaOH \rightarrow Na2SiO3 + H2O
$$

$$
P4O10 + 3NaOH \rightarrow Na3PO4 + H2O
$$

Amphoteric oxides react with acids and bases both, forming salt and water.
 $Al_2O_3 + 6HCl \rightarrow AlCl_3 + 3H_2O$

$$
Al_2O_3 + 6HCl \rightarrow AlCl_3 + 3H_2O
$$

$$
Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O
$$

Chlorides of the period third elements

The chlorides of Na, Mg and Al are solids, having ionic bonding, while the chlorides of Si, P and S are liquids and has covalent bonds. The structures of NaCl and $MgCl₂$ are giant so their m.pt and b.pt are high. All the other chlorides have monomeric structures so their m.pt and b.pt are low. The chlorides of Na, Mg and Al are ionic so these are conductors in solution form. The chlorides of other elements of period third are covalent and bad conductors.

Hydroxides of period third elements

Compounds having hydroxide ion (OH^-) or hydroxyl group $(-OH)$ are called hydroxides.

Basic hydroxides: Compounds having *OH* ions are basic in nature. Metals hydroxides in which there are ionic bonds are basic (alkaline). For example NaOH and $Mg(OH)_2$ are basic. These are strong bases and neutralize acids.

Acidic hydroxides: The compounds having $-OH$ group are acidic in nature. The nonmetals hydroxides in which there are covalent bonds are acidic. $Si(OH)₄$, $H₃PO₄$, H₂SO₄ and HClO₄ are acidic. These are strong acids and neutralize bases.

Amphoteric hydroxides: The hydroxides which are acidic as well as basic are called amphoteric hydroxides. These behave as acids towards bases and behave as bases towards acids. Examples are $Al(OH)$ ₃ and Be(OH)₂.

In the period third the hydroxides of Na and Mg are basic, that of Al is amphoteric and the hydroxides of Si, P, S and Cl are acidic in nature.

Sodium hydroxide: It is also called caustic soda. It is a white solid with soapy and slippery touch. It is hygroscopic (water absorber) in nature. Its strong solution is corrosive to skin. It is soluble in water and evolve considerable amount of heat due to the formation of hydrates, NaOH.2H₂O.

Preparation:It is prepared by causticizing process and electrolytic process. Nelson cell is used for its preparation. Also Castner Kellner and Kellener Solvay cells are used. In Nelson cell brine is electrolyzed and H_2 , Cl_2 and NaOH are prepared. Brine is 30% solution of NaCl. 2 *NaCl* + $2H_2O \rightarrow 2$ *NaOH* + H_2 + Cl_2

$$
2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2
$$

Uses: It is used in soap industry. It is also used in petroleum refining and reclaiming

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$$

of rubber.

Magnesium hydroxide: It is also a white solid with soapy and slippery touch. It is hygroscopic (water absorber) in nature. Its strong solution is corrosive to skin. It is sparingly soluble in water.

Milk of magnesia: The suspension of magnesium hydroxide in water is called milk of magnesiawhich is used for the treatment of the acidity of stomach.

Preparation: It is obtained as a white precipitate when KOH (caustic potash) solution is added to a soluble magnesium chloride salt.

 $MgCl_2 + 2 KOH \rightarrow Mg(OH)_2 + 2 KCl$

The solubility of $Mg(OH)$ ₂ is enhanced by the addition of NH₄Cl to it. As the ammonium ions react with hydroxide ions and form ammonium hydroxide while the chloride ions react with magnesium ions and form magnesium chloride.
 $Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-$

$$
Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-
$$

\n
$$
2NH_4Cl \rightarrow 2NH_4^+ + 2Cl^-
$$

\n
$$
2NH_4^+ + 2OH^- \rightarrow 2NH_4OH
$$

\n
$$
Mg^{2+} + 2Cl^- \rightarrow MgCl_2
$$

More and more $Mg(OH)$ ₂ dissolves in order to supply hydroxide ions to the ammonium ions.

Aluminium hydroxide: It is an amphoteric hydroxide. It reacts with acids as well as with bases.

Preparation:Aluminium hydroxide can be prepared by the following two methods.

1. By the hydrolysis of AlCl₃
AlCl₃+3H₂O
$$
\rightarrow
$$
 Al(OH)₃+3HCl

Lakes:The precipitated hydroxide of aluminium has the capacity to absorb various dyes forming colouring matter called lakes.

2. By the reaction of ammonium hydroxide and aluminiumsulphate.

uring matter called lakes.

on of ammonium hydroxide and aluminiumsulphan
 $Al_2(SO_4)_3 + 6NH_4OH \rightarrow 2Al(OH)_3 + 3(NH_4)_2SO_4$

Aluminium hydroxide is amphoteric in nature. It react with acids and bases both forming salt and water. and water.
 $2Al(OH)_3 + 2NaOH \rightarrow 2NaAlO_2 + 4$ *d* water.
Al(*OH*)₃ + 2*NaOH* \rightarrow 2*NaAlO*₂ + 4*H*₂*O* + $2NaOH \rightarrow 2NaAlO_2 + 4H_2O$

$$
2Al(OH)_3 + 2NaOH \rightarrow 2NaAlO_2 + 4H_2O
$$

$$
2Al(OH)_3 + 2NaOH \rightarrow 2NaAlO_2 +Al(OH)_3 + 3HCl \rightarrow AlCl_3 + 3H_2O
$$

Silicon hydroxide: It is an unstable compound and is present in the polymeric form. It can be prepared by the reaction of silica with water at 800° C.

$$
SiO_2 + 2H_2O_{\frac{1}{4}}^{\frac{3}{4}} \sqrt[360^\circ]{\frac{6}{4}} \text{Si(OH)}_4
$$

The hydroxide of Si is acidic in nature as it has four –OH groups covalently bonded to Si.

Hydroxide of phosphorous: It is an acidic hydroxide as the three –OH groups are

covalently bonded to P. It can be prepared by the reaction of P2O5 with hot water.
\n
$$
P_2O_5 + 3H_2O \rightarrow 2H_3PO_4
$$
 (Ortho phosphoric acid)

Hydroxide of sulphur:It is an acidic hydroxide as the two –OH groups are covalently bonded to S. it can be prepared by contact and lead chamber process. When sulphur trioxide gas is dissolved in liquid water we get H_2SO_4 .

$$
SO_3 + H_2O \rightarrow H_2SO_4
$$

Hydroxide of chlorine:It is also an acidic hydroxide as the –OH group is covalently bonded to Cl. It can be prepared by the reaction of Cl_2O_7 with water.
 $Cl_2O_7 + H_2O \rightarrow 2HClO_4$ (Periodic acid)

$$
Cl_2O_7 + H_2O \rightarrow 2HClO_4
$$
 (Periodic acid)

$$
KClO_4 + H_2SO_4 \rightarrow KHSO_4 + HClO_4
$$

$$
KClO_4 + H_2SO_4 \rightarrow KHSO_4 + HClO_4
$$

The structures of ortho phosphoric acid, sulphuric acid and perchloric acid are given below.

The elements, **lithium, sodium, potassium, rubidium, cesium** and **francium,** constitute Group IA of the periodic table. These have single electron in the valence shell. They are highly reactive and readily decompose water even at room temperature yielding metal hydroxides which are strong alkalies. These elements are, therefore, known as **alkali metals**. Only lithium, sodium and potassium are safe to keep in the college laboratory the rest are violently reactive. The last element, francium, is radioactive. These are all good conductors of heat and electricity. These

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$$

are enough soft to be cut with knife. These are lighter metals, having low m.pt, b.pt and densities.

Atomic and physical properties

All the elements of Group I are silvery-white, soft and light metals. Some of their important physical constants are summed up in the Table.

Physical Properties of Alkali Metals

1. Atomic and Ionic Radii: Atomic radius *increases* on moving down the group from lithium to cesium, as shown in the Table. This is on account of the presence of an extra shell of electrons as we move down from one element to the other within the group.

An alkali metal changes into a positive ion by the loss of the solitary *s* electron of the outer shell. This leads to the elimination of the outer shell itself. At the same time, the charge on the nucleus becomes greater than the number of electrons and, therefore, the electrons are attracted more strongly towards the nucleus. As a result of

both these effects, *a positive ion is smaller than the corresponding atom.*

The electronic configurations of the alkali metal ions would evidently be similar to those of the noble gases, viz, s^2 (for Li⁺) or s^2p^6 (for Na⁺, K⁺, Rb⁺, Cs⁺). Since they have no unpaired electrons, these ions are *diamagnetic* and *colourless*.

2. Ionization Energies: The solitary *s* electron in the outer shell of these elements can be taken out relatively easily. Consequently, the ionization energies of these elements are relatively low. Further, as the atomic radius increases on moving down the group, the outer electron gets farther and farther away from the nucleus and, therefore, *ionization energy decreases on moving down from lithium towards cesium.*

3. Electronegativities: Since these metals are highly electropositive, their electronegativities, *i.e.,their tendencies to attract electrons,* are very low. Further, since electropositive character increases on moving down the group, *the electronegativity decreases in the same order.* When these elements react with other elements having high electronegativities (*e.g.,* the halogens), the compounds formed are ionic in character.

4. Melting Points: All the alkali metals are soft and having low melting points. This is due to the fact that they have only one valence electron per metal atom. Hence the energy binding the atoms in the crystal lattice of the metal is relatively low. The melting points invariably decrease in moving down from lithium towards cesium. Lithium, the first element, melts at $180\degree\text{°C}$ while cesium, the last element, melts at 28⋅5^oC. Thus, *the melting point decreases with increase in the size of the atom of the element.*

5. Boiling Points: The boiling points also *decrease* in the same order as the melting points. The boiling point of lithium is 1326° C while that of cesium is 690 $^{\circ}$ C.

6. Density: Density of a metallic element depends upon the type of packing of atoms in the metallic phase and also on their size. Group I elements have close packing of metal atoms in their lattices and because of the comparatively large size of these atoms, they have low densities. As can be seen from the table, density gradually *increases* in moving down from lithium towards cesium. Potassium, however, is lighter than sodium. Lithium, sodium and potassium are even lighter than water. The reason is that these metals have much larger molar volumes and hence much larger atomic radii than most other metals.

7. Molar Volumes: The ratio of molar mass $(g \text{ mol}^{-1})$ and density $(g \text{ cm}^{-3})$ is known as the molar volume (cm³mol⁻¹) of the element. Molar volume is seen to *increase* in moving down the group from Li to Cs. This is to be expected in view of increase in atomic radius.

8. Heat of Atomization: Heat of atomization measures the strength of metal−metal bond in the lattice of an element. Heat of atomization is maximum in the case of lithium and is much lower in the case of the next element which is sodium. The fall in

the case of the subsequent elements is relatively small. Thus, metal–metal bond strength is maximum in the case of lithium.

9. Electropositive Character: On account of their low ionization energies, these metals have great tendency to lose their valence electrons and thus change into positive ions:

$$
M \longrightarrow M^+ + e^-
$$

These elements are, therefore, said to have strong *electropositive* character. Since ionization energy decreases on moving down the group, *the electropositive character increases on moving down the group from lithium towards cesium.*

These elements are so highly electropositive that they emit electrons even when exposed to light **(photoelectric effect).** This property is responsible for their use in photoelectric cells. Cesium and potassium are used, in particular, for this purpose.

10. Formation of Univalent Positive Ions: As already mentioned, on account of relatively low ionization energies, these elements have a strong tendency to change into M⁺ ions. Hence, they form mostly ionic compounds. *The chemistry of these elements, therefore, is the chemistry of* M^+ jons $(L_i^+, Na^+,$ etc.). Since the ions have the stable noble gas configuration *viz.*, $n s^2$ or $n s^2 p^2$, in the valence shell, the *energy required to pull out another electron from the valence shell is very high.* Therefore, *the second ionization energies of alkali metals are very high.* Under ordinary circumstances, therefore, there is no possibility for the formation of M^{2+} ions in any of their compounds. *The alkali metals are thus* **univalent** *and form* **ionic compounds.**

However, in certain cases, they do form covalently bonded diatomic molecules like Li_2 (Li:Li), Na₂ (Na:Na) and Cs₂ (Cs:Cs). Li also forms covalently bonded organometallic compounds due to its high polarizing power.

11. Hydration of Ions: The alkali metal ions are *extensively hydrated. The smaller the size of the ion, the greater is the degree of hydration.* Thus, Li^+ ion, which is smallest in size and has the highest charge/size ratio (charge density) amongst the alkali metal ions, gets much more hydrated (*i.e.,* holds more water molecules in its hydration sphere) than Na⁺ ion and the latter gets more hydrated than K^+ ion and so on. The degree of hydration decreases on moving down the group form $Li⁺$ to $Cs⁺$.

12. Oxidation States: All the alkali metals exhibit an oxidation state of +1. This is because these metals *can lose their solitary outermost electron easily.* The second ionization energy is so high that the second electron is very rarely lost.

13. Reducing Properties, Oxidation Potentials: As is well known, oxidation *is a process in which electrons are lost* and **reduction***is a process in which electrons are*

gained. An *oxidizing agent,* therefore, is a substance which can *accept* electrons while a *reducing agent* is a substance which can *lose* electrons. Consider the formation of sodium chloride by burning of sodium in chlorine. Sodium, on account of low ionization energy, can *lose* an electron readily while chlorine, on account of its high electron affinity, can *accept* it readily.

$$
\begin{array}{ccc}\n\text{Na}_{(s)} & \xrightarrow{\text{heat}} \text{Na}_{(g)} \\
\text{Na}_{(s)} & \xrightarrow{\text{Na}^+}_{(s)} + \text{e}^- \\
1/2\text{Cl}_{2(s)} + \text{e}^- & \xrightarrow{\text{Cl}^-}_{(s)} \\
\text{Na}^+_{(s)} + \text{Cl}^-_{(s)} & \xrightarrow{\text{Na}^+Cl^-}_{(s)} \\
\text{Na}_{(s)} + 1/2\text{Cl}_{2(s)} & \xrightarrow{\text{Na}^+Cl^-}_{(s)}\n\end{array}
$$

Thus, sodium is a reducing agent while chlorine is an oxidizing agent. Evidently, an element which is a *reducing agent* must have *low ionization energy* while an element which is an *oxidizing agent* must have *high ionization energy* (or *high electron affinity*). Since ionization energy decreases on moving down from lithium to cesium, the reducing properties increase in the same order.

14. Characteristic Flame Colouration: All the alkali metals give *characteristic colours* in Bunsen flame. The reason is that when an alkali metal or any of its compounds is heated in a Bunsen flame, the electrons get excited to higher energy levels. When these electrons return to their original (ground) level, the *excitation energy* which had been absorbed by these, is *released* in the form of light in the visible region of the spectrum. Now for the same excitation energy, the energy level to which the electron in \mathbf{L} rises is lower than that to which the electron in Na rises and this, in turn, is lower than the level to which the electron in K rises and so on. These differences are on account of differences in the forces of attraction between the nucleus and the outermost electron. Consequently, when the electron returns to the ground state, energy released is lowest in Li and increases in the order: Li \rightarrow Cs. As a result of this, the frequency of the light emitted in the Bunsen flame will be minimum in the case of lithium. It increases in the order $Li \rightarrow Cs$. Thus, the colour of the flame is crimson red in the case of Li, golden yellow in the case of Na, violet in the case of K, red in the case of Rb and blue in case of Cs.

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Procedure of flame test: Take a clean loop of platinium wire and dipp it in HCl and then dip in the salt. Some salt will adhere to it and now put it on the flame and note the flame colour.

15. Lattice Energies: Salts of alkali metals consists of cations and anions only and are, therefore, called *ionic solids.* The **lattice energy** is defined as *the energy released when cations and anions in gaseous state are brought from infinity to their respective crystals sites to form one mole of the ionic crystal.* Thus, we have s and anions in gaseous state are brought from infinity to the
to form one mole of the ionic crystal. Thus, we have
 $Li^+_{(g)} + Cl^-_{(g)} \longrightarrow Li^+Cl^-_{(g)}$; $\Delta H = \text{Lattice energy of Li}^+Cl^$ o form one mole of the ionic crystal. Thus, we have
 \downarrow + Cl⁻ () \longrightarrow Li⁺Cl⁻ (); AH = Lattice energy of Li⁺Cl⁻ nd anions in gaseous state are brought from infinity to their resp
form one mole of the ionic crystal. Thus, we have
 $\begin{aligned} \n\begin{aligned}\n\text{(s)} + \text{CI}^{-} \\
\text{(s)} + \text{CI}^{-} \\
\text{(s)} + \text{CI}^{-} \\
\end{aligned}\n\end{aligned} \longrightarrow \text{Li}^{+}\text{CI}^{-} \\
\text{(s)} \longrightarrow \text{Cs}^{+}\text{CI}^{-$

 (g) \sim (g) \sim \sim (g) (g) (g) \sim (g) \sim \sim \sim (g) s to form one mole of the ionic crystal. Thus, we have
 $Li^+_{(g)} + Cl^-_{(g)} \longrightarrow Li^+Cl^-_{(g)}$; $\Delta H =$ Lattice energy of Li⁺Cl⁻
 $Cs^+_{(g)} + Cl^-_{(g)} \longrightarrow Cs^+Cl^-_{(g)}$; $\Delta H =$ Lattice energy of Cs⁺Cl $g(y)$ + Cl⁻(g) \longrightarrow Li⁺Cl⁻(g); ΔH
 $g(y)$ + Cl⁻(g) \longrightarrow Cs⁺Cl⁻(g); ΔH *H* m one mole of the ionic crystal. Thus, we
+ Cl⁻_(s) \longrightarrow Li⁺Cl⁻_(s); ΔH = Lattice e
+ Cl⁻_(s) \longrightarrow Cs⁺Cl⁻_(s); ΔH = Lattice e

Lattice energies of ionic solids are quite high. This is to be expected in view of *strong electrostatic attraction* between oppositely charged ions. When such ions come close together, the system acquires *minimum energy* and, therefore, a large amount of energy is released to the surroundings. As a general rule, **lattice energies***of salts of alkali metals having a given anion decrease with increase in atomic number of the alkali metal.*

16.Ionic Conductance: The alkali metal ions in aqueous solution have high electrical conductance. The electrical conductance of Li⁺ ion, which is the smallest of alkali metal ions, is expected to be the highest. Since ionic size increase on moving from Li to Cs, the ionic conductance is expected to decrease in the order:

 $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

However, we find by experiment that ionic conductance of $Cs⁺$ is the highest and that of \mathbf{L} ⁺ is the lowest. Thus, ionic conductance actually decreases in the order:

 $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$

This is evidently the *reverse* of what we expect. This anomaly arises from the fact that *alkali metal ions are hydrated to different extents*. The Li⁺¹ ion is hydrated to the maximum extent due to its high charge/ size ratio compared to other alkali metal ions. The extent of hydration *decrease* on moving from \overrightarrow{Li}^+ to \overrightarrow{Cs}^+ . Thus, \overrightarrow{Cs}^+ ion is the least hydrated. As a result of the variation in the extent of hydration, \overrightarrow{Li}^+ ion due to heavy hydration is the biggest while $Cs⁺$ ion due to much smaller hydration is the smallest. Thus, the *ionic size in aqueous solutions,* instead of increasing,

actually decrease on moving from $Li⁺$ to $Cs⁺$ as a result of which the ionic mobility *increases* as we move from Li⁺ to Cs⁺. Hence, *the ionic conductance*, instead of decreasing, *actually increases on moving from* Li⁺to Cs⁺.

Occurrence

Alkali metals are reactive so do not exist free in nature. These are present in the combined forms called minerals or ores like, oxides, hydroxides, carbonates, bicarbonates, sulphates, phosphates, silicates, nitrates, carbides, nitrates, nitrites, halides, cyanides, cyanates etc.

Mineral:The combined form of a metal is called its mineral. It is the source of a metal from which the metal can be extracted and isolated.

Ore:The rich mineral of a metal from which the metal can be extracted easily and economically is called ore.

Lithium is present the form of lipidolite, spodomene, amblygonite etc. Sodium in the form of natron, chile salt peter, halite, trona, borax etc. potassium is found in carnalite and sylvite form while cesium in the form of pollucite.

Chemical properties of IA

1. Reaction with water: All alkali metals except lithium react vigorously with water and form alkalies and hydrogen gas. Sodium reacts vigorously, fizzing and skating on the water surface. The reaction of potassium is more vigorous, it cracks and pops as hydrogen explodes. Down the group the reactivity increases.
 $2Na + 2H_2O \rightarrow 2NaOH + H_2$

$$
2Na + 2H_2O \rightarrow 2NaOH + H_2
$$

\n
$$
2K + 2H_2O \rightarrow 2KOH + H_2
$$

\n
$$
2Rb + 2H_2O \rightarrow 2RbOH + H_2
$$

2. Reaction with oxygen: All alkali metals react with oxygen and form three types of oxides i.e normal oxides, peroxides and super oxides.

Normal oxides: Oxides in which the oxidation state of oxygen is -2.

Peroxides: Oxides in which the oxidation state of oxygen is -1.

Super oxides:Oxides in which the oxidation state of oxygen is -1/2.

Lithium form normal oxide.

$$
4Li + O_2 \rightarrow 2Li_2O
$$

Sodium form normal and peroxides.

$$
4Na + O_2 \rightarrow 2Na_2O
$$

$$
2Na + O_2 \rightarrow Na_2O_2
$$

Potassium form peroxide and superoxide.

$$
2K + O_2 \rightarrow K_2O_2
$$

$$
K + O_2 \rightarrow KO_2
$$

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Rubidium and cesium catch fire in air and produce superoxides.

 $Rb + O_2 \rightarrow RbO_2$ $Cs + O_2 \rightarrow CsO_2$

Reactions of oxides with water

Normal oxides react with water and form hydroxides only.

 $Na_2O + H_2O \rightarrow 2NaOH$

Peroxides react with water and form hydroxide and hydrogen peroxide.

 $Na_2O_2 + H_2O \rightarrow 2NaOH + H_2O_2$

Superoxides react with water and form hydroxide, hydrogen peroxide and oxygen. $2 K O_2 + 2 H_2 O \rightarrow 2 KOH + H_2 O_2 + O_2$

Reactions of oxides with dilute acids

Normal oxides react with dilute acid and form salt and water only.
 $Na_2O + 2HCl \rightarrow 2NaCl + H_2O$

$$
Na_2O + 2HCl \rightarrow 2NaCl + H_2O
$$

Peroxides react with dilute acid and form salt and hydrogen peroxide.

 $Na_2O_2 + 2HCl \rightarrow 2NaCl + H_2O_2$

Superoxides react with dilute acid and form salt, hydrogen peroxide and oxygen.
 $2KO_2 + 2HCl \rightarrow 2KCl + H_2O_2 + O_2$

$$
2KO_2 + 2HCl \rightarrow 2KCl + H_2O_2 + O_2
$$

3. Reactions of alkali metals with chlorine: Alkali metals react with chlorine and form white, solid, crystalline, neutral, soluble chlorides.

$$
2Li + Cl2 \rightarrow 2LiCl
$$

\n
$$
2Na + Cl2 \rightarrow 2NaCl
$$

\n
$$
2K + Cl2 \rightarrow 2KCl
$$

\n
$$
2Rb + Cl2 \rightarrow 2RbCl
$$

\n
$$
2Cs + Cl2 \rightarrow 2CsCl
$$

4. Reaction of alkali metals with nitrogen: Only lithium reacts with nitrogen and form nitride, the other members of IA do not react with nitrogen.

$$
6Li + N_2 \rightarrow 2Li_3N
$$

\n
$$
6Na + N_2 \rightarrow \times
$$

\n
$$
6K + N_2 \rightarrow \times
$$

5. Reaction of alkali metals with hydrogen: The alkali metals react with hydrogen forming hydrides which are ionic in character and in which hydrogen is present as an anion. The hydrides are, therefore, represented at $M^+ H^-$, where M is an alkali metal. **6. Solubility in Mercury:** The alkali metals dissolve readily in mercury forming

$$
\begin{array}{c} \circ \\ \circ \end{array} 35
$$

what are called **amalgams.** The process is highly *exothermic.*

7. Solubility in Liquid Ammonia: All the alkali metals dissolve in anhydrous liquid ammonia giving deep blue solutions. The colour deepens with increase in concentration of the solution. The concentrated solutions are bronze in colour and possess *metallic luster.* The solutions are *good conductors of electricity* and are *paramagnetic* in nature.

Peculiar behavior: Differences in properties of the top element of a group from the rest of the group elements is called its peculiar behaviour. Peculiar behavior of the top element of a group is due to its small size, high charge density, high ionization energy etc. lithium, beryllium, boron, carbon, nitrogen, oxygen and fluorine are the top elements of their groups so these show peculiar behavior.

Fajan's rule:Fajan's rule states that "small sized ions with high charge density tend to form covalent compounds". Large size ions with smaller charge density will form ionic compounds while small size ions will tend to form covalent compounds. Like $Li⁺$ will tend to form covalent compounds while Na⁺ will form ionic compounds.

Diagonal Relationship

As already mentioned, lithium differs from the rest of its family members in many respects. However, it shows resemblance with magnesium, the second element of Group II. This is a case of **diagonal relationship***in which the first element of a group shows similarities with the second element in the next higher group in the next period,* as indicated below.

This diagonal relationship is due to *similar polarizing powers* of $Li⁺$ and Mg²⁺ ions despite the occurrence of different charges on these ions.

Effect of heat on the nitrates of IA

Nitrates of IA elements are colorless, soluble, neutral, crystalline, ionic solids which are formed when alkali metal hydroxides react with nitric acid.

Lithium nitrate decompose on heating and form lithium oxide, nitrogen dioxide and oxygen.

$$
4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2
$$

Nitrates of other metals of IA decompose and form nitrites and oxygen. 2 *NaNO*₃ \rightarrow 2 *NaNO*₃ $+$ *O*₃

Effect of heat on carbonates of IA

Carbonates of IA elements are white, alkaline, ionic, solids. These are formed when carbon dioxide gas is passed through the solution of alkali metals hydroxides.

Lithium carbonate decomposes on heating and gives lithium oxide and carbon dioxide.

$$
Li_2CO_3 \rightarrow Li_2O + CO_2
$$

Carbonates of other elements of IA are thermally stable and do not decompose even at high temperature.

Effect of heat on hydrogen carbonates of IA

The bicarbonates of alkali metals can be isolated as white solids when carbon dioxide gas is passed from the aqueous solution of alkali metal hydroxide.

Bicarbonates decompose on heating and form carbonates, carbon dioxide and water.

2 *NaHCO*₃ \rightarrow *Na*₂*CO*₃ \rightarrow *H₂O*

Thermal stability of bicarbonates of IA increases down the group due increasing size and decreasing charge density of the metal ion. Polarizing power of small sized ion with high charge density is high while large size ion with smaller charge density has low polarizing power. Cations of greater polarizing power distort the bicarbonate ion more and facilitate its decomposition compared to a cation of large size and low polarizing power.

Elements of IIA

The elements of IIA are called alkaline earth metals. These are quite reactive and tarnish in air. These are metals, alkaline in nature and exist in the earth crust in combined forms (minerals). These are white in colour except beryllium which is grey. **Beryllium, Magnesium, Calcium, Strontium, Barium and Radium** are members of IIA. These have two electrons in their valence shell.Radium corresponds to the alkaline earth metals in its chemical properties but, being a radioactive element, it is studied separately along with the other radioactive elements. The electronic configurations of these elements are given in the Table below.

General Characteristics

Physical Properties

Some of the important physical properties and other constants of alkaline earth metals are given in the table below.

1. Metallic Properties: Elements of Group II have typical metallic properties. They show good metallic luster and high electrical as well as thermal conductivity.

2. Metallic Bonding: While in alkali metals, there is a single valence electron per atom, in alkaline earth metals, there are two valence electrons per atom. Hence metallic bonding in Group II elements is stronger than that in Group I elements. As a result, the elements of Group II are *harder* and *denser* and have *higher melting* and *boiling points* than the elements of Group 1. The filled valence *s* energy band in these elements overlaps with the empty valence *p* energy band so that valence electrons can easily jump from filled energy levels of valence *s* energy band to empty energy levels of valence *p* energy band. These elements are, therefore, good conductors of heat and electricity.

3. Hardness: The alkaline earth elements are moderately hard. Although they are harder than alkali metals yet they can be cut with a sharp knife.

38 Some Physical Properties of Alkaline Earth Metals Property Be Mg Ca Sr Ba Ra

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4. Molar Volume: Molar volume is seen to increase regularly in moving from beryllium to radium. This is to be expected in view of increase in atomic radius (due to increase in the number of shells) on moving down the group in the same order.

5. Density: Density is seen to decrease slightly on moving down the group up to calcium but it increases considerably thereafter up to radium. These metals are seen to be considerably denser than the corresponding alkali metals of Group I.

6. Melting Points and Boiling Points: Melting points and boiling points do not show regular trends. However, these are higher than those of alkali metals.

7. Atomic and Ionic Radii: The atoms of these elements are smaller than those of the corresponding elements of Group I. This is due to higher nuclear charge of these atoms which tends to draw the orbital electrons inward *i.e.,* towards the nucleus. The ionic radii are seen to be smaller than the atomic radii. This is to be expected in view of the removal of two orbital electrons in the formation of the bivalent cation (*e.g.,* Mg^{2+} , Ca^{2+} , Ba^{2+}).

Atomic as well as ionic radius is seen to increase on moving down the group from Be to Ra on account of the presence of an extra shell of electrons at each step.

8. Heat of Atomization: Heat of atomization is seen to fall considerably on moving from Be to Mg. The subsequent change is rather small. This shows that metal-metal bond strength is maximum in the case of beryllium.

9. Ionization Energies: The first as well as the second ionization energy is seen to *decrease* on going down the group from beryllium to barium. This is to be expected on account of *increase in the atomic radius* and, therefore, greater distance between the nucleus and the outer electrons as we move down the group.

The ionization energy of radium, however, is slightly higher than that of barium. It has not been possible to offer any satisfactory explanation for this.

10. Hydration of Ions: The extent of hydration of the ions decreases with increase in atomic number and molar mass.

11. Electropositive Character: These elements, although fairly strongly electropositive, are not as strongly electropositive as the metals of Group 1. For example, unlike the alkali metals, these elements do not emit electrons on exposure to light. Since ionization energy decreases on moving down the group, the electropositive character increases on moving down the group.

12. Reducing Properties: (Oxidation Potentials). All the alkaline earth metals have a tendency to release electrons and change into bivalent cations.Hence, *they are strong reducing agents.*

 $M \hat{f}^{\lambda *}\dot{A}^{2+} + 2e^-$

The oxidation potential which is a measure of the tendency of an element to lose electrons (*i.e.,* a measure of electropositive character and strength as a reducing agent) increases on moving down the group.

13. Electronegativities: Since these elements have strong electropositive character, as mentioned above, they have low electronegativities which decrease on moving down the group. The value for calcium, however, is an exception.

14. Flame Colouration: When energy is supplied to these elements in a flame, their electrons are excited to higher energy states, as is the case with alkali metals under similar conditions. As the electrons drop back to the original energy levels, the extra energy is emitted in the form of visible light with characteristic colours as given below:

Ca :*brick red* Sr : *crimson* Ba : *grassy green* Ra : *crimson*

Beryllium and magnesium atoms are smaller. The electrons in these atoms are, therefore, more strongly bound. Hence these are not excited by the energy of the flame to higher energy states. These elements, therefore, do not give any colour in Bunsen flame.

Occurrence

Alkaline earth metals do not exist free in nature. These exist in combined

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forms. Ma and Ca are abundantly present in the rocks of earth crust.

Beryllium is present in the form of beryl. Magnesium is present in sea water, underground brines, magnesite $(MgCO₃)$, dolomite $(MgCO₃$.CaCO₃), asbestos $(CaSiO₃.3MgSiO₃)$, epsum salt $(MgSO₄.7H₂O)$ and soap stone. Calcium is present in the form of sea shells, calcite $(CaCO₃)$, gypsum $(CaSO₄.2H₂O)$, phosphorite, dolomite and asbestos. Strontium is present in the form of strontionite while barium is available in the form of barite, witherite and heavy spar.

Chemical properties

1. Reaction with water

These elements react with water forming hydroxides and liberating hydrogen gas. The reaction becomes vigorous down the group. Beryllium does not react with water and steam. Mg burns in steam and produce MgO and hydrogen gas.

 $Mg + H_2O_{(g)} \rightarrow MgO + H_2$

2. Reaction with oxygen

Elements of IIA react with oxygen and form oxides. Beryllium is reluctant to burn until in the powder form. Beryllium, magnesium and calcium form normal oxides while barium and strontium form peroxides.

$$
2Be + O_2 \rightarrow 2BeO
$$

\n
$$
2Mg + O_2 \rightarrow 2MgO
$$

\n
$$
2Ca + O_2 \rightarrow 2CaO
$$

\n
$$
Ba + O_2 \rightarrow BaO_2
$$

\n
$$
Sr + O_2 \rightarrow SrO_2
$$

3. Reaction with nitrogen

Alkaline earth metals react with nitrogen on heating and form nitrides. Nitride of Be is covalent while other elements form ionic nitrides.

$$
3Be + N_2 \xrightarrow{\Delta} Be_3N_2
$$

\n
$$
3Mg + N_2 \xrightarrow{\Delta} Mg_3N_2
$$

\n
$$
3Ca + N_2 \xrightarrow{\Delta} Ca_3N_2
$$

4. Reaction with halogens

All the alkaline earth metals combine with the halogens at elevated temperatures forming halides, $MX₂$. Beryllium halides are covalent while the rest are electrovalent and readily soluble in water. The solubility of the halides (except fluorides) decreases on moving down the group.

$$
\left(\begin{array}{cc} 41 \end{array}\right)
$$

$$
Mg + Cl_2 \xrightarrow{\Delta} \text{MgCl}_2
$$

5. Reaction with hydrogen:

All the elements, except beryllium, combine with hydrogen to form hydrides, MH2. Beryllium hydride cannot be prepared by direct combination of beryllium and hydrogen. It can, however, be produced by reacting beryllium chloride with lithium aluminium hydride.

$$
Mg + H_2 \xrightarrow{\Delta} MgH_2
$$

6. Formation of Amalgams and Alloys:

They form amalgams with Mercury and alloys with other metals.

7. Reaction with Acids:

These metals, on account of their oxidation potentials, readily liberate hydrogen from dilute acids. Beryllium reacts very slowly as its oxidation potential is the lowest.

8. Reaction with C:

All the elements, from magnesium to barium, give *ionic carbides*, MC₂, when the metals or their oxides are heated with carbon. Beryllium, gives $Be₂C$ and not BeC₂ when heated with carbon. Beryllium carbide, Be₂C, evolves *methane* on treatment with water while the other carbides evolve acetylene.

9. Complex formation:

Elements of IIA form certain complexes especially Be, Mg and Ca.

Peculiar Behaviour of Beryllium

Beryllium, the first element of Group II, differs considerably from the rest of the elements of this group. This is partly due to its *small size* and partly due to its *relatively high electronegativity.* The main points of difference are as follows.

1. Tendency to form ionic compounds: Ionization energy of beryllium (899 kJ mol⁻¹) is the highest of all the elements of the group. Consequently, it has *the lowest tendency to form the ion,* Be^{2+} . Accordingly it does not form ionic compounds readily.

2. Tendency to form covalent compounds: Electronegativity of beryllium (1∙5) is more than that of any other element of the family. Hence, its compounds with oxygen, chlorine, nitrogen, sulphur, etc., are more **covalent** in character than the

corresponding compounds of magnesium, calcium, strontium and barium.

3. Reaction with water: Beryllium does *not* react with water even at elevated temperatures. Its reaction with steam forming beryllium oxide, BeO, and liberating hydrogen is doubtful.

4. Oxidation potential: Beryllium has the *lowest oxidation potential,* which indicates that it has the *lowest electropositive character*. Consequently, BeO and Be(OH)₂, *are not at all basic in character.* They are, in fact, *amphoteric* and dissolve in acids to form salts and in alkalies to form beryllates.

5. Reaction with acids: Beryllium, on account of its relatively lower oxidation potential, *does not liberate hydrogen* from acids so readily as the rest of the metals of Group II do.

6. Reaction with hydrogen: Beryllium does not combine directly with hydrogen to give the hydride. All other elements of the group react directly. Beryllium hydride is a *covalent* compound. Magnesium hydride is also a covalent compound. The hydrides of the remaining elements are, however, *electrovalent* in character.

7. Reaction with halogens: All the metals of this group form halides by direct combination with the halogens at appropriate temperatures. Beryllium halides are, however, *covalent* while the other halides are *electrovalent* compounds.

8. Reaction with nitrogen: All the elements of this group burn in nitrogen to give nitrides, M3N2, as already stated. However, beryllium nitride is *volatile* while the other nitrides are not.

9. Formation of carbides: All the elements, from magnesium to barium, give *ionic carbides,* MC₂, when the metals or their oxides are heated with carbon. Beryllium, on the other hand, gives Be_2C and not BeC_2 when heated with carbon.

10. Formation of complexes: The alkaline earth metal ions do not form many complexes. However, beryllium ion, on account of its small size, gives a number of stable complexes. The tendency to form complexes decreases on moving down the group. Thus, barium forms very few complexes.

11. Flame coloration: Be do not imparts any color to the flame.

12. The oxides and hydroxides of Be are amphoteric in nature.

13. Be is hard having high m.pt. and b.pt. values.

Trends in solubility of hydroxides of IIA: Thehydroxides of IIA are ionic, crystalline, basic and soluble solids. These are hygroscopic in nature. The solubility of hydroxides of IIA in water increases down the group.

Trends in solubility of sulphates of IIA: Sulphates are neutral, ionic, crystalline solids. Sulphates can be prepared by the reaction of hydroxides and sulphuric acid. The solubility of sulphates of IIA decreases down the group. This is due to the increase in size as large sized ions are hydrated upto lesser extent. Calcium sulphate

is slightly soluble in water while strontium and barium sulphates are almost insoluble in water. When gypsum is heated to 120° C, it loses 75% water and plaster of Paris (calcium sulphate hemihydrates) is formed.
 $CaSO_4.2H_2O \longrightarrow CaSO_4. (1/2H_2O) + H_2O$

hemihydrates) is formed.
\n
$$
CaSO_4.2H_2O \xrightarrow{120^\circ C} CaSO_4.(1/2H_2O) + H_2O
$$

\nGypsum Plaster of Paris

Solubility of carbonates of IIA: Carbonates are white, ionic, crystalline, basic solids. All carbonates of IIA elements are insoluble in water while all dissolves in acids liberating carbon dioxide and hydrogen gas.
 $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$

$$
CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O
$$

Trends in thermal stability of nitrates of IIA: The nitrates of IIA become more and more thermally stable as we go down the group.
 $2Ca(NO_3)_2 \xrightarrow{\Delta} 2CaO + 4NO_2 + O_2$

$$
2Ca(NO3)2 \xrightarrow{\Delta} 2CaO + 4NO2 + O2
$$

Trends in thermal stability of carbonates of IIA:All carbonates of IIA decompose at red heat. Down the group the stability increases and thermal decomposition becomes difficult.

$$
CaCO_3 \xrightarrow{\Delta} CaO + CO_2
$$

Thermal stability of the carbonates of IIA is less than the IA

Cations of the IIA elements has smaller sizes and greater charge densities than the cations of alkali metals. The cations of greater charge density and smaller size has greater distortion ability of the carbonate ion and hence facilitate its decomposition hence the carbonates of IIA are less stable compared to IA.

The covalent nature of beryllium chloride: According to Fajan's rule "small sized ions with high charge density tends to form covalent compounds". The size of Be^{+2} is small and it has high polarizing power so it attract the electron cloud from chloride ion up to such an extent that the electrons seems to be paired between beryllium and chloride ions. This gives covalent nature to beryllium chloride. On the other hand the sizes of Mg, Ca etc. are large and have less polarizing power so their halides are ionic.

The amphoteric nature of beryllium oxide and hydroxide: The oxide and hydroxide of beryllium are amphoteric in nature. These act as acids as well as bases. These neutralize both acids and bases.

allize both acids and bases.

\n
$$
BeO + 2HCl \longrightarrow BeCl_2 + H_2O
$$
\n
$$
BeO + 2NaOH \longrightarrow Na_2BeO_2 + H_2O
$$
\n
$$
Be(OH)_2 + 2HCl \longrightarrow BeCl_2 + 2H_2O
$$
\n
$$
Be(OH)_2 + 2NaOH \longrightarrow Na_2[Be(OH)_4] \quad Or \quad Na_2BeO_2 + 2H_2O
$$

The elements of group IVA

Group IV Contains five elements, namely, **carbon, silicon, germanium, tin** and **lead.** Carbon is an essential constituent of all organic matter. Silicon is an important constituent of inorganic matter. Carbon and silicon are typical non-metals. Germanium has intermediate character while tin and lead are distinctly metals. These elements are present in the middle of the periodic table forming a link between more electropositive elements of IA, IIA and IIA and more electronegative elements of VA, VIA and VIIA. Carbon occurs hardly up to 0∙1 per cent in the earth's crust. However, combined with oxygen and hydrogen it occurs in all living tissues belonging to plant or animal kingdom and in petroleum and coal. It occurs as carbon dioxide in the atmosphere and as carbonates in rocks and minerals such as limestone, dolomite, etc. In free state, it occurs as coke, diamond and graphite.

Silicon occurs most abundantly, next only to oxygen, up to about 26 per cent in the earth's crust, as silica and silicates. It is also the most abundant element, after oxygen, in human body, being present to the extent of about 18 per cent, in combined state.

Germanium occurs rather sparsely. Tin occurs chiefly as $SnO₂$ in its ore known as *tin stone* while lead occurs as PbS in its ore known as *galena*.

Life is carbon based, semiconductors industries are Si and Ge based while the paints industries are lead based.

Electronic Configurations: The electronic configurations of elements of Group IV are shown in the Table.

| Element | At. No. | Electronic Configurations |
|----------------|---------|--|
| Carbon, C | | [He] $2s^2p^2$ [Ne] $3s^2p^2$ [Ar] $3d^{10}4s^2p^2$ [Kr] $4d^{10}5s^2p^2$ [Xe] $4f^{44}5d^{10}6s^2p^2$ |
| Silicon, Si | | |
| Germanium, Gel | 32 | |
| Tin, Sn | 50 | |
| Lead, | 82 | |

Electronic Configurations of Elements of Group IV

Thus, the general outer electronic configuration of the elements of this group may be ns^2 , np².

Carbon and silicon have 8 electrons in the penultimate shell (noble gas kernel) while the rest of the elements have 18 electrons in the penultimate shell. Carbon and silicon contain only *s* and *p* electrons while the rest of the elements also contain fully paired *d* electrons in the penultimate shells.

General Characteristics

Important physical properties and other physical constants of the elements of Group IV are shown in the Table.

| Property | Carbon | Silicon | Germanium | Tin | Lead |
|---|--------|---------|------------------|-----------|----------|
| Atomic number | 6 | 14 | 32 | 50 | 82 |
| Molar mass $(g \text{ mol}^{-1})$ | 12.000 | 28.086 | 72.59 | 118.89 | 207.19 |
| Density $(g \text{ cm}^{-3})$ | 3.52 | 2.49 | 5.35 | 7.30 | 11.34 |
| Atomic radius (\AA) | 0.77 | 1.11 | 1.22 | 1.41 | 1.44 |
| Molar volume $\text{cm}^3 \text{ mol}^{-1}$) | 3.4 | $11-4$ | 13.6 | $16-3$ | 18.27 |
| Melting point $({}^{\circ}C)$ | 3727 | 1410 | 937.5 | $231 - 8$ | 327.4 |
| Boiling point $(^{\circ}C)$ | 4833 | 2680 | 2830 | 2270 | 1725 |
| Electronegativity | 2.5 | 1.8 | 1.8 | $\cdot 8$ | 1.8 |
| Ionization energy ($kJ \text{ mol}^{-1}$) | 1086 | 786 | 761 | 708 | 716 |
| Oxidation states (stable) | $+4$ | $+4$ | $+2, 44$ | $+2, +4$ | $+2, +4$ |

Physical Properties of Elements of Group IV

1. Molar volume and atomic radius:Molar volumes and atomic radii, as expected, increase with increase in atomic number.

2. Melting points and boiling points: The melting point as well as the boiling point of carbon, the first element, is exceedingly high. The values decrease as we move from carbon to lead. The melting points of tin and led are relatively low.

3. Ionization energy: Ionization energy of carbon, the first element, is quite high, being 1086 kJ mol⁻¹. This is understandable in view of the small size of the carbon atom. There is a sharp decrease in the ionization energy as we move from carbon to the next element silicon. This is due to an appreciable increase in the size of the Si atom. There is, however, a very small decrease in ionization energy as we move from Si to Sn. This is because the *d* electrons which are now present in the inner configuration of Ge and Sn, shield the nuclear charge less effectively than is done by the s and *p* electrons. The outer electrons are, therefore, held strongly by the nucleus and hence, in spite of a sizeable increase in atomic radius, there is only a small decrease in ionization energy as we move from Si to Sn. In the last element, Pb, there are *f* electrons in the inner configuration which shield the nuclear charge less effectively even than the *d* electrons. Because of these two factors, the ionization energy of Pb, instead of decreasing, shows a marginal increase.

4. Oxidation states: All the elements have, in common, the oxidation state of +4. The $+4$ state is of much greater importance in carbon and silicon and $+2$ state becomes increasingly important for germinium, tin and lead.

5. Metallic and non-metallic character: The change from non-metallic to metallic character with increase in atomic number in the same group, is best illustrated in this

group, as already mentioned. The first two elements, carbon and silicon, are distinctly non-metals even though electrical properties of silicon are like those of a semi-metal. The third element, germanium, is partly non-metal and partly metal (*i.e.,* it is a semimetal) while the last two elements, tin and lead, are distinctly metals in their physical and chemical properties.

6. Electronegativity: Carbon is the most electronegative element of this group. The electronegativity decreases on moving down the group but not after silicon. This appears to be due to filling of the *d* orbitals in the case of germanium and tin and also the *f* orbitals in the case of lead.

7. Nature of bonds in their compounds: The elements of Group IV, on account of their high ionization energies, do not form stable M^{4+} ions. Their electronegativities are also sufficiently low to permit the formation of stable anions. All the same, carbon does have a tendency to form C_2^2 ions, as in certain carbides. Thus, calcium carbide is an ionic compound which may be represented as $Ca^{2+}C_2^2$. All the elements, and carbon and silicon in particular, show a covalency of 4.

The last three elements (Ge, Sn and Pb) have a tendency to form M^{2+} ions as well as M^{4+} ions. However, they prefer to form M^{2+} ions. Thus, Sn^{2+} and Pb^{2+} exist as stable ions and are much more common than Sn^{4+} and Pb^{4+} ions.

Sn (IV) and Pb (IV) compounds are more covalent than electrovalent in nature. This is to be expected from Fajan's rule according to which the smaller the ion, the greater is its tendency towards covalency. Sn^{4+} and Pb^{4+} ions have much smaller radii than Sn^{2+} and Pb^{2+} ions.

8. Formation of complexes: The tendency of an element to form complexes is favoured by (*a*) small size of its atom or ion (*b*) high charge (*c*) availability of vacant orbitals of appropriate energy.

Except for the first element carbon, the succeeding elements in this family have vacant *d* orbitals which permit formation of coordinate bonds with other atoms or ions having lone pairs of electrons. For example, silicon tetrafluoride which is a tetracovalent compound, can form complexes like $[SiF_6]^{2-}$.

Since Si orbitals in $\left[SiF_6\right]^2$ undergo sp^3d^2 hybridisation, the complex ion has an **octahedral structure.** The covalency of silicon thus rises to 6 in this complex ion.

Similarly, other elements of the group can also have a covalency of six due to availability of *d* orbitals, as in $\left[SnCl_6\right]^2$ ⁻ and $\left[PbCl_6\right]^2$ ⁻.

9. Tendency to form chains, Catenation: Carbon exhibits the remarkable property of **catenation,***i.e., to form chains of identical atoms.* Silicon has much smaller capacity to form chains. Germanium has still smaller tendency while tin and lead have hardly any tendency to do so. Thus, in Group IV elements, tendency to catenate decreases in the order $C > Si > Ge > Sn > Pb$.

As a result of catenation, carbon atoms can link together to form linear chains, branched chains and even rings of different sizes. The tendency of an element to form chains depends upon the strength of the element-element bond (bond energy) which is maximum in the case of carbon.

10. Allotropy: Most of the elements of Group IV show allotropy. Thus, carbon exists in three well-defined crystalline forms known as *diamond*, *graphite and buckyballs.* Besides these, there are microcrystalline forms which were previously regarded as amorphous. These are *coal, coke, charcoal, carbon black,* etc. All these have finely divided graphite structures. Silicon is known to exist in *crystalline* and *amorphous forms.* Germanium also exists in *two crystalline forms*. Likewise, tin exists in three solid forms: *grey tin, white tin* and *rhombic tin*.

Inert pair effect

The non-involvement of ns^2 electrons in the bond formation is called inert pair effect. It is the tendency of the ns^2 electron pair to remain inert and not to be used in bond formation.

Elements of IVA have four valence electrons, two in the ns and two in the np subshells. When all these electrons are involved in the bond formation then oxidation state will be $+4$. But at the bottom of the group there is tendency for the s^2 pair not to be used in bond formation. This is called inert pair effect which dominates in lead. So the oxidation state of lead is $+4$ and $+2$ both. In the $+2$ oxidation state both the ns² electrons are not involved in bond formation. The inert pair effect phenomenon is seen in Thallium of IIIA, Lead of IVA and Bismuth of VA groups. Inert pair effect increases down the group. As down the group the number of shells increases and also d and f orbitals are present along with s and p orbitals in the higher shells. The s and p orbitals have more shielding effect compared to d and f orbitals. Due to the less (poor) shielding effect of d and f orbitals the ns^2 electrons are tightly held by the nucleus and do not take part in bond formation and remain as inert pair.

Effects of inert pair effect on reactivity and properties of the molecules

Inert pair effect phenomenon affects the bonding, size, stability, reactivity and electronegativity of the compounds. The type of bonding is greatly affected by the inert pair effect. If there is inert pair effect then the bond will be ionic in nature. If the inert pair effect is absent in the bond will be covalent in nature. In the light of the above explanation we can say that $SnCl₂$ is ionic while $SnCl₄$ is covalent. Also PbCl₂ is ionic while PbCl₄ is covalent in nature. TlCl is ionic while $TICl₃$ is covalent. BiCl₃ is ionic and $BiCl₅$ is covalent. The ionic and covalent nature of compounds can also be predicted by Fajan's rule.

Chlorides of carbon, silicon and lead

$$
\begin{bmatrix} 48 \end{bmatrix}
$$

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Elements of IVA form tetrachlorides (MCl4) which are tetrahedral in shape due to $sp³$ hybridization. The stability of chlorides decreases down the group. Lead tetrachloride at the bottom is less stable and decompose to form $PbCl₂$ and $Cl₂$ gas. C, Si and Ge form tetrachlorides, their dichlorides are not known. Sn and Pb form dichlorides along with tetrachlorides. The dichlorides formation is due to the inert pair effect. Tetrachlorides are stable at the top of IVA while dichlorides are stable at the bottom.

Reaction with water

Carbon tetrachloride does not react with water it is due to its non polar and organic nature. Also the bulky chlorides on the small C atom do not allow the water molecules to reach the C atom. Si and Pbtetrachlorides react violently with water producing their respective oxides and fumes of HCl.
 $SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$

$$
SiCl4 + 2H2O \rightarrow SiO2 + 4HCl
$$

$$
PbCl4 + 2H2O \rightarrow PbO2 + 4HCl
$$

PbCl₂ is ionic and sparingly soluble in cold water but more soluble in hot water. The ionic lattice breaks and hydration of the Pb⁺² and Cl⁻ occurs.
 $PbCl_2 \xrightarrow{H_2O} Pb^{+2} + 2Cl$

$$
PbCl_2 \xrightarrow{H_2O} Pb^{+2} + 2
$$

Oxides of IVA

The elements of IVA form two types of oxides, monoxides and dioxides. In the monoxides these elements exist in $+2$ oxidation states while in the dioxides these exist in the +4 oxidation states. C, Sn and Pb form monoxides and dioxides both. Si and Ge form dioxides only.

Monoxides of IVA are CO, SnO and PbO.

Dioxides of IVA are CO_2 , SiO_2 , GeO_2 , SnO_2 and PbO_2 .

Acidic oxides of IVA are the oxides of C and Si which are non-metallic and covalent in nature.

Basic oxides of IVA are the oxides of Sn and Pb which are metallic and ionic in nature.

Structure of carbon dioxide

Carbon dioxide is a gaseous molecule. It is a green house gas and a global warming gas. It is triatomic linear molecule. It is non-polar molecule. Each O atom is connected by double bond to the C. Carbon atom in carbon dioxide is sp hybridized. The two sp hybridized orbitals of C are arranged at 180° . Each sp hybridized orbital form a sigma bond with both O atoms. The unhybridizedpy orbital of oxygen form a pi bond with the py orbital of one O atom. The unhybridizedpz orbital of C atom form

a pi bond with other O atom. Each bond in $CO₂$ is polar but the molecule is non-polar as the dipole moments of both the bonds cancel each other's effect. Carbon dioxide in the solid form is called dry ice.

Silicon dioxide is commonly known as silica. Silica has giant, covalent, three dimensional, networked, polymeric, interlocked structure just like diamond. Each Si is attached to four oxygen atoms tetrahedrally and each O is attached to two Si atoms. Each bond angle is 109.5° .

Silicon is also present in the silicates, opal, quartz and silicones or siloxanes forms.

Chemical garden or silica garden:Prepare a solution of sodium silicate in water of specific gravity 1.1. Place the solution in a beaker. Sprinkle crystals of some colored salts like nickel sulphide, ferrous sulphate etc. on the surface of the solution. Color shoots rises up and grows on like a plant on a long standing. This is called chemical garden or silica garden.

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Nature of oxides of IVA elements

The oxides of C and Si are acidic while those of Ge, Sn and Pb are amphoteric in nature.

The Element of VIIA (Halogens)

Group VII comprises of five elements, namely, **fluorine, chlorine, bromine, iodine** and **astatine.** They do not occur free but in the combined state they occur fairly abundantly in nature. Fluorine, chlorine, bromine and iodine constitute, respectively, 0∙6 to 0∙09, 0∙031, 0∙00016 and 0∙00003 per cent of earth's crust. Astatine is radioactive and occurs very sparsely.

Fluorine, chlorine, bromine and iodine have closely related properties and are known collectively as the **halogens** (Greek, *halos* = sea salts, *genes* = born) since the salts of the first three occur in sea water. On account of their close resemblance and gradual transition of physical and chemical properties, the halogens constitute a wellmarked group.

Electronic Configurations: The electronic configurations of the halogens are given in the Table.

Electronic Configurations of the Halogens

As is evident the halogens have the general outer electronic configurations $n s^2 p^5$.

General Characteristics of Group VII Elements

Some important physical **properties** of the halogens are given in the Table below.

1. Atomic volume, atomic radius and **density** increase regularly with increase in atomic number, as expected.

2. Ionisation energy:Ionisation energies of the halogens are very high indicating that they have very small tendency to lose electrons. The values, however, decrease on moving down the group, as expected. In the case of iodine, the value is comparatively low. This enables the iodine atom to lose an electron and form I^+ ion.

3. Electronegativity: The halogens have very high electronegativities. Fluorine is the most electronegative with electronegativity $= 4$. The values decrease as we move down the group from fluorine to iodine indicating a gradual decline in the nonmetallic character so much that the last element iodine, with an electronegativity of 2∙5, shows some metallic character also. For instance, it forms in a few cases a positive ion and has a metallic luster.

Physical Properties of the Halogens

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4. Non-metallic character: On account of high electronegativities, all the halogens are non-metallic in character. The non-metallic character, however, decreases as we move down the group. The last element, iodine, has comparatively very small electronegativity and exhibits metalloidal character. It has a metallic luster and has a tendency to lose an electron to form a +ive ion.

5. Colour: All the halogens are coloured. This is because of the absorption of visible light by their molecules resulting in the excitation of electrons. The excitation energy, evidently, depends upon the size of the halogen atom. The smaller the atom, the greater is the force of attraction between the nucleus and the outer electrons and hence greater is the amount of the energy required to raise the electrons to higher levels. Consequently, the excitation energy is very large in the case of fluorine and comparatively very small in the case of iodine. Hence, fluorine absorbs violet portion of the light which is associated with higher energy and thus appears *yellow.* Iodine, on the other extreme, absorbs yellow and green radiations which are associated with lower energy and thus appears *violet.* Similarly, we can account for the *greenish yellow*colour of chlorine and *orange red*colour of bromine.

6. Electron affinity: All the elements have high electron affinities. Therefore, they have a strong tendency to gain an electron to acquire noble gas configuration, $viz, s²p⁶$. Chlorine has the highest electron affinity which decreases gradually as we move down the group From Cl to I. The electron affinity of fluorine is lower than that of chlorine. The unexpectedly lower value is due to the small size of the atom. The addition of an extra electron in fluorine atom produces a high electron density in a relatively compact 2*p* subshell and, therefore, there is strong electron repulsion. Consequently, fluorine has lesser tendency to accept extra electron, that is, its electron affinity is low.

7. Oxidation states: It is evident from the Table that all the halogens have the configuration s^2p^5 in the outer shell in the ground state. These elements, therefore, tend to gain or share one electron to acquire noble gas configuration. Hence they show an oxidation state of −1 or +1, depending upon whether the element with which they combine is less electronegative or more electronegative than the halogen.

Since fluorine is the most electronegative element, it *always exhibits an oxidation state of* −1. It does not exhibit any positive oxidation state. Also, fluorine has no *d* orbitals in its valency shell and hence it cannot have any excited states. Consequently, it does not exhibit any higher oxidation state.

The other halogens exhibit higher positive oxidation states of $+3$, $+4$, $+5$, $+6$ and +7 as well because they have vacant *d* orbitals in their valence shells which allow for easy excitation of *p* as well as *p* and *s* electrons, as illustrated in the Fig.

In the first excited state, one pair of *p* electrons gets unpaired providing three unpaired electrons. This accounts for an oxidation state of $+3$. Thus, in the interhalogen compounds, CIF_3 , BrF_3 , and IF_3 , chlorine, bromine and iodine are in +3 oxidation state.

In the second excited state, both the pairs of *p* electrons get unpaired providing five unpaired electrons which account for an oxidation state of $+5$. Thus, in HClO₃, $HBrO₃$, and $HIO₃$, the halogens are in +5 oxidation state.

Similarly, in BrF₅ and IF₅, bromine and iodine are in $+5$ oxidation states. Iodine is also in $+5$ oxidation state in I_2O_5 .

In the third excited state, the pairs of *p* as well as *s* electrons get unpaired, providing seven unpaired electrons which account for an oxidation state of +7. Thus, in HClO₄ and Cl₂O₇, chlorine is in an oxidation state of $+7$ and in HIO₄, iodine is also in an oxidation state of +7. *Bromine does not exhibit +7 oxidation state.* Thus, compounds such as $HBrO₄, Br₂O₇$ are not known.

Chlorine and bromine exhibit oxidation states of $+4$ and $+6$ as well in their oxygen compounds, *e.g.*, CIO_2 , BrO_2 , and Cl_2O_6 and Br_2O_6 , respectively. Iodine exhibits an oxidation state of $+4$ in I_2O_4 .

8. Oxidizing power: Since the halogens, on account of high electron affinities, have a strong tendency to pick up electrons, they act as strong oxidizing agents. The oxidizing character, however, decreases on moving down the group. Fluorine is the strongest oxidizing agent and iodine is the weakest oxidizing agent. The stronger oxidizing character of F_2 in comparison to Cl_2 is mainly due to its relatively lower

bond dissociation energy and higher heat of hydration. It is the *oxidizing potential* and not the electron affinity alone *which controls the strength of an oxidizing agent in aqueous medium.*

It is not difficult for the student to realize now why fluorine is capable of forming compounds in which the metals are sometimes present in the usually high oxidation states.

9. Combination with metals and non-metals: All the halogens react with metals and also with many non-metals to form halides. Fluorine is the most reactive. The reactivity decreases as we move down the group. For instance, with sulphur, fluorine forms the hexafluoride (SF_6) , chlorine forms the tetrachloride (SCI_4) , bromine forms the dibromide $(SBr₂)$ whereas iodine does not react at all.

10. Reaction with water: The interaction of halogens with water provides another illustration of gradation in properties with increase in atomic number. For example, fluorine decomposes water very energetically; chlorine and bromine do so much less readily according to the equationwhile iodine scarcely reacts with water.
 $X_2 + H_2O \longrightarrow HOX + HX$

$$
X_2 + H_2O \longrightarrow HOX + HX
$$

11. Melting and boiling points: The melting and boiling points of halogens increases on moving down the group. Down the group size increases and momentary dipole formation becomes easier so strong London forces exists in large size momentary and induced dipoles that's why melting and boiling points increases down the group.

12. Bond enthalpies in halogens:Bond enthalpy is the amount of heat required to break one mole of covalent bonds in the gaseous substances. Bond energy gives us the information about the strength of a bond. If bond enthalpy is high the bond would be strong and vice versa.

Factors affecting bond enthalpy:Bond enthalpy depends upon the atomic size, polarity of the bond, multiplicity of the bond and bond length. Polar bond is stronger than non-polar. Triple bond is stronger than double and single. Bond of shorter bond length is stronger than the longer bond length bond. Small sized atoms form strong bonds and hence their bond enthalpies are higher compared to large size atoms. If the bond length is long, bond will be weak and bond enthalpy will be low. Multiplicity and polarity of the bond has direct relationship with the bond strength and bond enthalpy. The bond enthalpy of fluorine molecule is smaller than chlorine. It is due to the fact that F atoms are smaller in size and come so closer to one another during bond formation that there is repulsion between their electron pairs. From chlorine downward the bond enthalpy decreases as atomic size and bond length increases.

Bond enthalpies in hydrogen halides:As bond enthalpy depends upon the size of the atom and down the group in halogens size increases so bond enthalpy of halogen

hydrides or hydrogen halides decreases down. Down the group size increases, the shared electron pair becomes farther and farther from the nucleus hence bond length increases and bond strength decreases so bond enthalpy decreases. HF has high bond enthalpy than HCl which is stable than HBr and HBr is stable than HI. Bond enthalpy for HF is 568, for HCl is 432, for HBr is 366 and for HI is 298K.J.per mol.

Halogens as oxidizing agents

Reduction: The gain of electron is called reduction.

Oxidation: The loss of electron is called oxidation.

Oxidizing agents: The species which oxidize others and itself get reduces.

Reducing agents: The species which reduce others and itself get oxidize.

Reducing agents has the capability of gaining electrons from others. So these must have high electron affinity and high electronegativity. As halogens are highly electronegative and has high electron affinity values so these are good oxidizing agents. These can gain electrons from others and oxidize others and reduce itself as these gain the electrons. Like for example.

$$
2Na + Cl_2 \rightarrow 2Na^+Cl^-
$$

The order of decreasing oxidizing power of halogen molecules is given below.

 $F_2 > Cl_2 > Br_2 > I_2$

The order of decreasing oxidizing power of halogen atoms is given below. This is due to the higher electron affinity of chlorine.

$$
Cl > F > \beta r > I
$$

Chlorine and fluorine are such powerful oxidizing agents that these can oxidize colored dyes to colorless substances and cause bleaching. So these are used in bleaching agents.

When chlorine water is added to solution of KI, the solution becomes brown. This is due to the fact that chlorine oxidizes iodide ion into iodine molecule which has brown color and is insoluble in water.

 $2I^{-}$ + Cl_{2} \rightarrow I_{2} + $2Cl^{-}$

Chlorine also oxidizes bromide to bromine.

 $2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$

Halide ions as reducing agents

When halogens gain electrons these changes into halide ions. Now the halide ions when losses back the electrons these will get oxidize and will reduce other species, so the halide ions act as reducing agents. Which halide ion will loss the electron easily can give us the order of their strength as reducing agents. As iodide ion is large in size and it hold the electron weakly so it will loss the electron easily and will act as strong reducing agent. The electrons are tightly held in case of fluoride

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and chloride ions due to their small sizes so these will not loss the electron easily and will act as weak reducing agents. The decreasing order of halide ions as reducing agents is given as follows.

 $I^{-} > Br^{-} > Cl^{-} > F^{-}$ Bromide and iodide can reduce H₂SO₄ easily and itself get oxidizes.
 $H_2SO_4 + 2HBr \rightarrow Br_2 + SO_2 + 2H_2O$ le can reduce H_2SO_4 easily and itself
 $H_2SO_4 + 2HBr \rightarrow Br_2 + SO_2 + 2H_2O$ $H_2SO_4 + 2HBr \rightarrow Br_2 + SO_2 + 2H_2O_2$
 $H_2SO_4 + 8HI \rightarrow 4I_2 + H_2S + 4H_2O$

Halogen acids

Halogen hydrides or hydrogen halides are acidic in nature as these give H^+ in water. That's why these are known as halogen acids. Hydrogen halides are formed by the direct combination of halogens with hydrogen.

$$
HI + H_2O \rightarrow H_3O^+ + I^-
$$

Factors affecting the strength of halogen acids: Two factors decide the strength of halogen acids.

1. Bond polarity: The H-F bond is more polar than H-Cl, H-Br and H-I so HF must be more ionizable in water and must be more acidic compared to HCl, HBr and HI. According to the bond polarity the decreasing order of halogen acids would be.

 $HF > HCl > HBr > HI$

2. Bond energy: The bond energy of H-F is high than H-Cl, H-Br and H-I so HF will ionize hardly while HCl, HBr and HI will ionize easily in water. So HF must be less acidic and HI must be more acidic. The decreasing order of acidity of halogen acids on the basis of bond energy would be.

HI >HBr>HCl> HF

Final conclusion: Experimentally it is the bond energy and not the bond polarity which explain the acidity of halogen acids, so the order on the basis of bond energy is the correct order acidity of halogen acids. HI is the strongest acid while HF is the weakest.

Oxoacids of halogens: The oxoacids of halogens consist of O, H and X. HXO type oxoacids are called hypohalous acids. $HXO₂$ are halous acids, $HXO₃$ are halic acids and HXO_4 are known as perhalic acids.Acidity of oxoacids is the order of.
 $HClO_4 > HClO_3 > HClO_2 > HClO$

The salts of hypohalous acids are called hyphalites, those of halous acids are called halites and of halic acids are called halates while the salts of perhalic acids are called perhalates.

Chemical Properties of halogens

Chemically, fluorine is the most reactive of all the elements. It combines directly with almost all other elements (except nitrogen and oxygen) with extreme vigour forming fluorides. It also attacks many other compounds, particularly organic compounds.

1. Combination with hydrogen: Fluorine directly combines with hydrogen with explosive violence even in the dark, forming hydrogen fluoride.

2. Combination with metals: Fluorine attacks *all metals* forming fluorides, the intensity of attack depending upon the nature of the metals.

 $2Na + F_2 \longrightarrow 2NaF$

3. Combination with non-metals: Non-metals such as *carbon, sulphur, phosphorus, bromine, iodine, boron, silicon* burn in fluorine forming the highest fluorides (*e.g.,* PF5, SiF4, SF6, etc.). Metalloids such as *arsenic* and *antimony* burn in the gas forming lower fluorides.

4. Action of water: Fluorine reacts vigorously with water giving oxygen and ozone.
 $2F_2 + 2H_2O \longrightarrow 4HF + O_2$

$$
2F_2 + 2H_2O \longrightarrow 4HF + O_2
$$

3F_2 + 3H_2O \longrightarrow 6HF + O_3

5. Oxidizing action: Since fluorine readily attacks water giving oxygen and ozone, it acts as a powerful agent. In fact, fluorine is the strongest chemical oxidizing agent. It oxidizes chlorates to perchlorates, chromic salts to dichromates and a warm solution of potassium bisulphate to potassium persulphate.

6. Action of halogen compounds: Fluorine displaces other halogens (Cl_2, Br_2, I_2) from their corresponding halides. Thus,

$$
2KCl + F_2 \longrightarrow 2KF + Cl_2
$$

$$
2KBr + F_2 \longrightarrow 2KF + Br_2
$$

7. Action of glass and quartz: Fluorine readily attacks glass and quartz forming silicon fluoride, SiF4. But the reaction is extremely slow when the reactants are thoroughly freed from adsorbed water. Hence, *dry fluorine* can be easily manipulated in *dry* glass apparatus.

$$
\left[\begin{array}{cc} & 58 \end{array}\right]
$$

8. Action on hydrocarbons: As already mentioned, most of the organic compounds burn or explode when brought in contact with fluorine. The reaction of fluorine with hydrocarbons is also explosive. The initial reaction in the case of methane.
 $CH_4 + 2F_2 \longrightarrow C + 4HF$

$$
CH_4 + 2F_2 \longrightarrow C + 4HF
$$

9. Action on other compounds: Fluorine also reacts with ammonia giving nitrogen and a small amount of NF_3 along with some other products. Sulphur dioxide and hydrogen sulphide are also decomposed by fluorine. It does not react with oxygen or nitrogen even at a very high temperature.

10. Combination with halogen: Fluorine reacts with halogen forming a number of compounds known as *inter-halogen compounds.*

Interhalogen Compounds or Interhalogens: Each halogen combines with every other halogen to form compounds amongst themselves. These are known as interhalogens or interhalogen compounds, examples are ClF, BrF, IF, BrCl, ICI, IBr, CIF_3 , BrF_3 , ICI_3 , BrF_5 , IF_6 , ICI , ClF_3 , IF_5 , IF_7 etc.

Pseudohalides: There are several uni-negative groups which show certain characteristics of halide ions. These are called pseudohalides or pseudohalide ions. For example CN⁻, OCN⁻, SCN⁻, N₃</sub> SCSN₃_, SeCN⁻, etc.

Pseudohalogens: As each halide ion has a corresponding halogen, (chloride ion, for example, has chlorine as the corresponding halogen) attempts have been made to isolate pseudohalogens corresponding to pseudohalides. So far, only four pseudohalogens which are covalent dimmers of the pseudohalideions, have been isolated. Examples are $(CN)_2$, $(SCN)_2$, $(SCN)_2$, $(SCSN_3)_2$ etc.

Q.1. *Choose the correct answer from the given choices in each case.*

- (ii) The word Alkali means
	- (a) Base (b) Basic salt
	- (c) Ashes (d) Spirit

(iii) The elements which are most abundant in earth crust.

- (a) \check{S} i & Al (b) Ca & Mg
- (c) $B & A r$ (d) All

As a whole Si and Al are abundantly present in the earth crust while

Ans: Given in the theory.

(ii) Why the NaCl does not conduct electricity in solid state?

Ans: For conduction free mobile ions are needed either in solution form or in molten form. There are no mobile and free ions in the solid crystal lattice of NaCl, because

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ions are fixed at their positions so it is bad conductor. When NaCl is melted, the ions become free and mobile, then it will conduct electricity.

(iii) Rubidium is below potassium in Group I-A. Predict how it will react with. (a) Water (b) Chlorine and describe the products.

Ans: As we go down the group the reactivity of elements increases due to increase in their metallic character. So Rubidium will react vigorously with water and chlorine compared to Li, Na and K.

$$
2\text{Rb} + 2\text{H}_2\text{O} \longrightarrow 2\text{RbOH} + \text{H}_2
$$

 $2Rb + Cl_2 \longrightarrow 2RbCl$

(iv) Why halogens are so reactive?

Ans: Each element has a wish to have complete octet or duplet. For this purpose the elements either loss or gain or share their valence electrons with other elements. Metals are reactive as these are good electron losers while non metals are reactive as these are good electron acceptors. As halogens have seven electrons in the valence shell and need only one electron for octet completion so halogens try their best to gain single electron. That is the reason for high reactivity of halogens that their valence shell is almost complete. The high reactivity of halogens is due to their high electronegativity, high electron affinity and nearly full filled valence shell.

(v) What is flame test?

Ans: Given in the theory.

(vi) Write down any four characteristics of group II-A elements.

Ans: Given in the theory.

(vii) Explain the thermal stability of nitrates and carbonates of group II-A elements.

Ans: Given in the theory.

(viii) Why carbonates of group I-A elements are more thermally stable than those of group II-A?

Ans: Carbonates of group IA are thermally more stable than the carbonates of group IIA. It is because the IA elements are larger in size, having lesser charge density and

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have lesser polarizing power as compared to group II A element which are smaller in size, with high charge density and high polarizing power. The IIA elements can easily polarize the carbonate anion and release $CO₂$ easily. While on the other hand group IA elements do not have enough polarizing power to distort the carbonate anion and release $CO₂$, thus their carbonates are much more thermally stable than carbonates of group IIA elements. Also IA elements are good metals, good electron losers and tight ionic bond formers than IIA, so the compounds of IA are thermally more stable than those of IIA.

(ix) Why Beryllium differs from the members of its group?

Ans: Beryllium being the top member of the IIA and top member of every group has different properties from the rest of the group elements. This difference in properties of every top elements of a group from the rest of the group elements is called peculiar/unique/anomalous/unexpected behavior. The peculiarity is due to small size and high charge density of the top elements of each group. Beryllium having small size, high charge density, high electronegativity, high electron affinity, high ionization energy and low electropositivity so it show different behavior from the rest of the group elements.

(x) Explain the structure and stability of chlorides of group IV-A elements.

Ans: All elements of the IVA for tetrahalides which are tetrahedral in shape. In these halides the central atom is sp^3 hybridized and hence the bond angle is 109.5°. C, Si and Ge form tetrahalides while Sn and Pb form tetrahalides as well as dihalides. The halides of C and Si are non-polar and covalent hence insoluble in water while the halides of Ge, Sn and Pbare ionic/polar and water soluble. The dihalides of Sn and Pb are ionic in nature while their tetrahalides are covalent according to Fajan's rule. The tetrahalides of all the elements except lead are stable. Lead tetrahalide is unstable and changes into dihalide. The dihalide of lead is ionic and ionizable in water.

(xi) Why Fluorine is stronger oxidizing agent than chlorine?

Ans: Fluorine is a stronger oxidizing agent than other halogens due to its low bond bond dissociation energy, small size, high hydration of its ion and high electron affinity. The reduction potential of F is much higher than other halogens.

(xii) Why BeCl² is covalent and not ionic?

Ans: BeCl₂ is a covalent compound due to the fact that Be^{+2} is small in size with high charge density. The Be^{+2} tends to attract the electron pair from chlorine towards itself

and making the bond covalent in nature. According to Fajan's Rule small size and high charge density of cation results in formation of covalent bonding. As the size of Be^{2} is small and has high charge density compared to other members of the group so BeCl₂ is covalent in nature.

(xiii) Explain the amphoteric nature of Be (OH)2.

Ans: Be(OH)₂ is amphoteric in nature as it react both with acids and bases. It is basic in nature as Be is a metal and metal hydroxides are basic. It is acidic as according to Fajan's rule small sized ions with greater charge density tends to form covalent compounds. When the nature becomes covalent then acidic character arises in the compound. $Be(OH)_2 + HCl \longrightarrow BeCl_2 + H_2O$

Basic nature: Acidic nature: $Be(OH)_2 + HCl \longrightarrow BeCl_2 + H_2O$
 $Be(OH)_2 + 2NaOH \longrightarrow Na_2 \left[Be(OH)_4\right]$

(xiv) Why the atomic radius of Argon is larger than all the member of third period?

Ans: Argon is a noble gas and exists in monoatomic molecular form. Argon molecules are non-polar and joins/combines with one another by London forces (Vander Waal's forces). Half of the distance between the nuclei of two bonded Argons is taken as Vander Waal's radius. As Vander Waal's forces are weaker so Argon molecules will be far away from one another so the radius will be larger compared to covalent, ionic and metallic radius. This is the reason that atomic radius of Argon is larger than the rest of the elements of the period third.

(xv) Why fall in ionization energy occurs at Aluminum and Sulphur in same period?

Ans: Both Al and S show unexpected decrease in their ionization energies from the corresponding preceeding elements Mg and P respectively.

In case of Aluminum the last electron is present in the 3px orbital, which is of higher energy than the 3s orbital in case of Mg. The px orbital is farther from nucleus compared to s orbital. So electron removal from px is easy than from s orbital. Also when the single electron from the 3px orbital of Al is removed the 3s orbital will left full filled (stable). While in case of Mg the valence sub-shell is 3s which is already stable and closer to the nucleus and electron removal from it is difficult compared to the electron removal from the faraway and unstable px orbital. Therefore the ionization energy of Al is less than Mg.

In case of S the 3p sub-shell has four electrons and p sub-shell is stable in half filled form means when it has three electrons. Therefore the $4th$ electron from the px

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sub-shell will tend to loss easily so that it may remain with 3 electrons in the stable state. In case of P the p sub-shell is half filled and is stable so electron removal from it is difficult, while in case of S the p sub-shell will tend to gain stability by losing an electron to become half filled. Therefore the ionization energy of S is lower than P.

(xvi) Why the compounds of Sn^{4+} are covalent in nature while those of Sn^{2+} are **ionic?**

Ans: In case of Sn^{+4} the two electrons of s and two electrons of p sub-shell are involved in the bond formation, as the p electrons are faraway but s electrons are closer to the Sn nucleus and are tightly held so these two electrons are not lost by any means that's why Sn^{+4} compounds are always covalent. In case of Sn^{+2} the two electrons of p sub-shell are involved in the bond formation while the s electrons remain inert. As the p electrons are far away from the nucleus so can easily be lost and the compound formed will be ionic in nature. Also Sn^{+4} has small size and high charge density than Sn^{+2} which has large size and low charge density. So according to Fajan's rule the compound of Sn^{+4} (small size, high charge density) will be covalent and these of Sn^{+2} (small charge, larger size) will be ionic in nature.

LONG QUESTIONS

Q.3. Long Questions

(i) Explain halide ions as reducing agents and discuss their trends in reducing strength.

Ans: Given in the theory.

(ii) Discuss the atomic and physical properties of halogens.

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Ans: Given in the theory.

(iii) What is meant by bond enthalpy? Explain the bond enthalpies in halogens and hydrogen halides.

Ans: Given in the theory.

(iv) Discuss physical properties of Group-IVA elements.

Ans: Given in the theory.

(v) Discuss oxides of carbon family and explain inert pair effect in formation of ionic and covalent bond.

Ans: Given in the theory.

(vi) Discuss in detail acid base behavior of Group IV-A oxides.

Ans: Given in the theory.

(vii) What are the trends in thermal stability of nitrates and carbonates of Group II-A elements?

Ans: Given in the theory.

(viii) Write down atomic and physical properties of group I-A and group II-A elements.

Ans: Given in the theory.

(ix) How peroxides, simple oxides and nitrates of Group II-A elements are formed?

Ans: When IIA elements are burned with lesser amount of oxygen their normal oxides are formed. Beryllium is reluctant to burn in oxygen unless in the powder or dust form. When oxygen is used in larger amount then these elements form peroxides. When these elements are heated in the presence of nitrogen these form nitrides. The nitride of Be is covalent while others are ionic in nature. Nitrates of these elements are prepared when their hydroxides are neutralized by nitric acid.

(x) Explain the reaction of Group II-A elements with oxygen.

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Ans: Given in the theory.

(xi) Explain trends in reactivity of Group I-A elements with water.

Ans: Given in the theory.

(xii) Explain the properties of Hydroxides of third period elements.

Ans: Given in the theory.

(xiii) Explain the acid base behavior of oxides of third period elements.

Ans: Given in the theory.

(xiv) What is meant by inert pair effect? Explain inert pair effect in formation of ionic and covalent bond.

Ans: Given in the theory.