
NET JRF PGT
ASST PROFESSOR
Get your KIT
7690022111
PROFESSORS ADDA
PROFESSORS
ADDA


PROFESSORS ADDA


PROFESSORS ADDA
STOP SOLUTION FOR UGC

UNIT – 1

Inorganic Chemistry-I

Unit-1 Inorganic Chemistry-I

CHEMICAL PERIODICITY

Periodicity and its Cause

When the element are arranged in order of their increasing atomic numbers, elements with similar properties are repeated after certain regular intervals. This repetition of properties after certain regular intervals is called periodicity of properties. The cause of periodicity in properties is the repetition of similar electronic configuration after certain regular intervals.

Atomic and ionic radii : Four operational concepts of atomic radius are taken, e.g.,

1) **Van der Waals radius :** It is one half of the distance between two bonded atoms of two adjacent molecules in the solid state. It is related to effective packing size of the atom in the solid state.
2) **Covalent radius :** It is one- half of the distance between the nuclei of two covalently bonded atoms of the same element in molecule.

   For a homonuclear diatomic molecule –
   r covalent = 1/2 [Internuclear distance between two bonded atoms]

   or r covalent = 1 /2 [bond length]

   For a heteronuclear diatomic molecule (AB) in which the atoms A and B are linked by a singlecovalent bond, the bond length (d_{A-B}) is given by the relations-

   (i) When the atoms A and B have nearly the same electronegatives,$d_{A-B} = r_A + r_B$

   (ii) where, r_A and r_B are the covalent radii of the atoms A and B respectively.

   (iii) When the atoms A and B have different electronegatives.

   $$d_{A-B} = r_A + r_B - 0.09\ (x_A - x_B)$$

   where, x_A and x_B are the electronegativities of the atoms A and B respectively.
   This relation was given by **Shoemaker and Stevenson**

3) **Ionic radius (Pauling method) :** Size of the ion is inversely proportional to the effective nuclear charge (Z_{eff})

   $Z_{eff} = Z - S$,
   where Z = At. No.and
   S = Shielding constant

   Radius of ion (r ion)
   Radius of ion (r ion) = 1 / Z_{ef}

   (i) The size of a cation is always smaller than that of the corresponding atom due to decreases in number of shells and increase in effective nuclear charge.

(ii) The size of an anion is always layer than the parent atom because of decrease in effective nuclear charge.

4) **Crystal (or metallic radius) :** One- half of the distance between the nuclei of two adjacent metal atoms in the metallic close packed crystal lattice. The metallic radii are smaller than the Van der Waals radii.

(i) **Atomic and ionic radii** are determined from X-ray studies

(ii) **Van der Waals** radius of an element is always larger than its covalent radius.

(iii) In a group atomic and ionic radii increase from top to bottom due to increase in the number of shells and the corresponding increases in the screening effect of the inner electrons.

(iv) The atomic/ionic radii of representative elements decrease significantly from left to right in a period due to progressive increase in the effective nuclear charge. However, in case of transition elements, the size does not change much since the addition of electrons takes place in the penultimate d- orbital, i.e., (n–1) d-orbital, as a result of which the increase in nuclear charge is almost compensated by the screening effect.

(v) The atomic radii of inert gases are, in fact, Van der Waals radii since they do not form covalent bonds. Consequently, their atomic size is larger than the preceding halogens.

(vi) Isoelectronic species are neutral or ionic species which have the same number of electron, but different nuclear charges. The ionic radii of isoelectronic ions decrease with the increase in the magnitude of the nuclear charge e.g.,

$$Al^{3+} < Mg^{2+} < Na^{+} < Ne < F^{-} < O^{2-} < N^{3-}$$

(vii) The size of the cation decreases with the increase in oxidation state (for same element)r $Fe^{2+} > Fe^{3+}$.

Ex. Among the following species arrange the isoelectronic species in decreasing order of their size-

(i) O^{2-} (ii) Na (iii) F (iv) Mg^{2+}

(v) Cl (vi) Al^{3+} (vii) Ne

Sol. The isoelectronic species are O^{2-}, Mg^{2+}, Al^{3+} and Ne. The decreasing order of their size is $O^{2-} > Ne > Mg^{2+} > Al^{3+}$

The size of the species decreases as the nuclear charge increases.

Trend of atomic and ionic radii in the elements of first transition series of periodic table

In case of transition elements, the atomic and ionic radii first decreases till d sub-shell is exactly half filled and thereafter these nearly remain the same since the increase in size due to increasing shielding effect of inner d-electrons almost cancels the contractive effect of the increased nuclear charge.

Ex. Arrange the Li^{2+}, He^{+}, Be^{3+} in order of decreasing radii.

Sol. $He^{+} > Li^{2+} > Be^{3+}$,

Ex. Arrange Cl, H, O, N in decreasing order of Van der Waal's radii.
Sol. Cl > N > O > H

Q. Why the pair of elements Zr-Hf ; Nb-Ta ; Mo-W have almost similar size?
Ans. The elements in the third row of d-block (e.g., Hf, Ta, W) are preceded by the elements of thefirst row of the f-block, the lanthanides, in which 4f orbitals are being occupied. There orbitals have poor shielding properties and so the valence electron experience more attraction from the nuclear change, resulting in reduction of size (lanthanide contraction). This results in the sizes of second and third row transition elements being almost the same.

Ionization Potential or Energy :

The amount of energy required to remove an electron froman isolated gaseous atoms of an element to produce cation is known as ionization potential or energy.

Factors governing the ionization energy- Ionization energy depends upon the followingfactors-

1) **Nuclear Charge :** The ionization energy increases with increase in nuclear charge. Thisis due to the fact that with increase in nuclear charge, the electrons of the outer shell are more firmly held by the nucleus and thus greater energy is required to pull out an electrons from the atom. For example, the ionization energy increases as we move along a period from left to right due to increased nuclear charge.
2) **Atomic size or radius :** Ionization energy decreases as the atomic size increases. As the distance of the outer electrons from the nucleus increases with increase in atomic radius, the attractive force on the outer electrons are held less firmly and hence lesser amount of energy is required to knock them out.
   For example, ionization energy is found to decrease on moving down a group.
3) **Penetration effect of the electrons :** Ionization energy increases as the penetration effect of the electrons increases. Within the same shell, the penetration effect decreases in the order-
   s > p > d > f
   Obviously, if the penetration effect of the electron is more, it will be closer to the nucleus and hence will be held more firmly by the nucleus. Consequently, the ionization energy will be high.
4) **Shielding or screening effect of the inner shell electron :** As the shielding or the screening effect of the inner electrons increases, the ionization energy decreases.
5) **Electronic configuration i.e., Effect of exactly half- filled or completely filled or completely filled orbitals :** If an atom contains exactly half-filled or completely filled orbitals, then such as arrangement has extra stability. Therefore, the removal of an electron from such an atom requires more energy than expected.
   IE of a completely filled orbitals > half filled orbitals > partly filled orbitals.

The general trend and anomalies in the Values of Ionization Energies in periodic table

The IE decreases from top to bottom in a group due to increases in atomic size and screening effect in periodic table.

In general, the IE increases from left to right in a period due to a corresponding increase in the nuclear charge. However certain anomalies are observed in the values of IE. These are attributed either to the stability of the electronic configuration or penetration effect of the electrons. For example.

In second period IE_1 of Be is higher than that of B even though the nuclear charge of B is higher than that of Be and IE_1 of N is higher than that of O even though the nuclear charge of O is higher than that of N.

Thus, the trend of IE_1 in second period is Li < Be < B < C < N > O < F < Ne

It can be explained as -
Li < Be IE increase due to increased nuclear charge, Be > B although nuclear charge increases, but lesser energy is required to remove $2p^1$ electron of B due to less penetrations effect of p-orbital as compared to s-orbital to Be. B < C < N due to progressive increase in nuclear charge. N > O is dueto stable half-filled configuration of N. O < F < Ne is due to progressive increase in nuclear charge.

Similar variation, in the first ionisation enthalpies of the elements of third period have been observed. The trend is
Na < Mg > Al < Si < P < S < Cl < Ar

Within a period alkali metal has the lowest while the noble gas has the highest ionization energy.

Ex. The first ionization enthalpy values (kJ mol^{-1}) of group 13 are-

B	Al	Ga	In	Tl
801	577	579	558	589

Explain the deviation from general trend.

Sol. From B → Al decrease due to increase in size. From Al →Ga, the the extra d-electron do not shield the outer shell electrons from the nucleus, so Ga has higher value than Al. From Ga →In the increased shielding effect due to 4d-electron outweighs the effect of increased nuclear charge and hence I.E. of In is lower than that of Ga. From In →Tl the effect of increased nuclear charge outweighs the shielding effect due to 4f and 5d-electron and hence I.E. of Tl is higher than that of In.

The trend of successive Ionization energies
The trend of successive ionization energies are- $IE_3 > IE_2 > IE_1$

This is due to the reason that after the removal of first electron further electrons are to be removed against the increased change of the ion.

The number of valence electrons in an atom can be determined by examining its successive ionization energies one by one till a large jump in its value is found in going from one to the next higher successive ionization energy. For example, the number of valence electrons in Na is one because the value of its IE_2 >>> IE_1. Similarly the number of valence electrons in Mg is two because the value of its IE_3 >>> IE_2.

For second period elements, the order of IE_1 and IE_2 is –

IE_1 : Li < B < Be < C < O < N < F < Ne

IE_2 : Be < C < B < N < F < O < Ne < Li

The IE_2 of O is higher than that of F even though the nuclear charge of F is higher than thatof O. This is also due to the reason that in case of O the second electron has to be removed from the most stable half-filled configuration of O^+.

For third period, the order of IE_1 and IE_2 is

IE_1 : Na < Al < Mg < Si < S < P < Cl < ArI

E_2 : Mg < Si < Al < P < S < Cl < Ar < Na

Q. How the relative stabilities of various oxidation states of an element can be predicted on the basis of successive ionisation energies?

Ans. If the difference in ionization energies of two successive states is approx., equal to 10-15 eV, per atom (or 965-1450 kJ mol^{-1}) or less, the lower oxidation state is not stable. Conversely, if the difference is more than 15 eV, the lower oxidation state is more stable. For example, in case of Al, IE_1 = 6.0 eV, IE_2 = 18.6 eV, IE_3 = 28:4 eV and IE_4 = 120:0 eV,
Difference is successive ionization energies.

$IE_2 - IE_1$ = 18:6 – 6:0 = 12:6 eV
$IE_3 - IE_2$ = 28:4 – 18:6 = 9:6 eV
$IE_4 - IE_3$ = 120 – 28:4 = 91:6 eV

Since, the difference in successive ionization energies between $IE_2 - IE_1$ and $IE_3 - IE_2$ is less than 15 eV and that of $IE_4 - IE_3$ is much more than 15 eV, therefore +3 oxidation state of Al is most stable.

Mercury is the only metal which is liquid due to its very high ionisation energy and weakmetallic bonds.

Electron affinity and its trend in periodic table

Electron Affinity : The amount of energy released when a neutral gaseous atom accept an electron to form gaseous anion.

$$X_{(g)} + e^- \rightarrow X^-_{(g)} + EA_1$$

Similarly, second and third electron can be added and energy changes are called successive electron affinities. Since an atom has a natural tendency to accept an electron, therefore, the first electron affinity (EA_1) is always taken as positive (energy evolved. ΔH is negative). However, the addition of second electron to the negatively charged ion is opposed by electrostatic repulsion and hence the energy has to be supplied for the addition of second electron. Thus, the second electron affinity of an element is negative (energy absorbed, ΔH is positive).

$$O_{(g)} + e^- \rightarrow O^-_{(g)} \ : EA_1 = +141 \text{ kJ mol}^{-1}$$

$$O^-_{(g)} + e^- \rightarrow O_2^-{}_{(g)} : EA_2 = -780 \text{ kJ mol}^{-1}$$

In general the electron affinity decreases as we move down the group. In a periodelectron affinity increase from left to right.

1) Electron affinities of elements of group 15 increases as we move down the group fromP to Bi.
2) The electron affinities of the halogens (Group 17) elements are the highest. The electron affinity of Fluorine is however, unexpectedly lower than that of Cl. This is due to large electron repulsion in relatively small (compact) 2p sub shell. The actual order being Cl >F > Br > I.
3) Electron affinity of chlorine is maximum.
4) The electron affinities of elements having half-filled and completely filled orbitals are zero. For example, alkaline earth metals (Group 2), nitrogen noble gases etc. have practically zero electron affinities.
5) Electron affinities are indirectly measured with the help of Boron- Haber cycle.
6) The element having high values of electron affinity are capable of accepting electron easily. They form anion and electrovalent compounds. These elements are electronegativein nature.
7) The elements having high values of electrons affinity act as strong oxidising agents, for example, halogens.

Q. Why the electron gain enthalpies of N, O and F of second period are lower than the correspondingelements P, S and Cl of next period?

Ans. This is due to the reason that the elements of second period have the smallest atomic size amongst the elements in their respective groups. As a result, there are considerable electron electron repulsion within the atom itself and hence the additional electron is not accepted with same ease as the case with the remaining elements of the same group.

Q. The increasing order of reactivity among group 1 elements is Li < Na < K < Rb < Cs whereas that of group 17 is F > Cl > Br > I. Explain.

Ans. Group 1 elements have only one electron in their respective valence shell. The tendency to lose electron depends on ionisation enthalpy. Since, the I.E. decreases down the group, therefore, thereactivity of group 1 elements in the same order : Li < Na < K < Rb < Cs. Group 17 element have

7 electron in their valence shell and thus have a strong tendency to accept are more electron. The tendency to accept electrons depends upon their electrode potential. The electrode potential decreases in the order F > Cl > Br > I, therefore their reactivities also decrease in the same order.

Q. Account for the larger decrease in electron affinity between Li and Be despite the increase in nuclear charge.

Ans. The electronic configuration of Li and Be are [He] $2s^1$ and [He] $2s^2$, respectively. The additional electron enters the 2s orbital of Li, but the 2p orbital of Be and hence is much less tightly bound. In fact the nuclear charge is so well shielded in Be that electron gain is endothermic.

Electronegativity

Electronegativity of an element is the tendency of an atom of that element to attract the shared pair of electrons present between bonded atoms in a molecule. The electronegativity values for the representative elements increase along a period from left to right and decrease down a group. This is because as we move along the period from left to right, nuclear charge increases and atomic size decreases whereas when we move down the group, the atomic radius as well as the screening effect increases.

Fluorine is the most electronegative element and is given a value of 4.0 (Pauling's scale) whereas **cesium is the least electronegative element** (E.N. = 0:7) because of its largest size and maximum screening effect. In other words, **cesium is the most electropositive element and hence is the most metallic element in the periodic table.**

Where , $\Delta = E_{A-B} - \sqrt{E_{A-A} \times E_{B-B}}$

Here, E_{A-B}, E_{A-A} and E_{B-B} represent bond dissociation energies of the bonds, A–B, A–A and B–B respectively.

By giving a reference value of 2:1 to H, the electronegativities of almost all the elements have been calculated. On this scale fluorine has a maximum value of 4:0.

The Pauling and the Mulliken scales are related by the following expression –

$$\chi = \chi^{\text{Mulliken Pauling}} /2:8$$

Allred and Rochow's Method : According to this method, the electronegativity of an element A is given by the relation.

$$\chi = 0:744/ r^{2} + 0:359Z_{\text{eff}}$$

Where, Z_{eff} is the effective nuclear charge which is calculated with the help of **Slater's rules** and 'r' is the covalent radius of the atom in Angstroms (Å).

1) **Effect of electronegativity of the central atom on the bond angle of similar molecule:** In similar

molecules as the electronegativity of the central atoms decreases and the size increases, the bond angle decreases, e.g.

H_2O	$>H_2S$	$>H_2Se$	$> H_2Te$
104:5T	92:5	91:0T	90:5T
NH_3	$>PH_3$	$>AsH_3$	$>BiH_3$
107:5T	93:4T	91:5T	91:2T

2) **Effect of electronegativity of the surrounding atom on the bond angle of similar molecules :** In similar molecules as the electronegativity of surrounding atom decreases, the bond angle increases e.g.,

PF_3 <	PCl_3 <	PBr_3 <	PI_3
97T	100T	101:5T	102T

Exceptionally bond angle of PF_3 is greater than that of PH_3.

Q. Carbon of which compound among C_2H_6, C_2H_4 and C_2H_2 has highest electronegativity explain?

Sol. The carbon atoms in C_2H_6, C_2H_4 and C_2H_2 are in sp^3, sp^2 and sp hybridised state respectively.The electronegativity of C in the three hybridised state varies as $sp > sp^2 > sp^3$. As the s character of hybrid orbitals decreases, the electronegativity also decreases. Thus, C in C_2H_2 has highest electronegativity.

Screening Effect and Effective Nuclear Charge : In multielectron atoms, the inner electrons shield or screen the outer electrons from the attractive force of nucleus. As a result, the outer electrons experience less nuclear charge than the actual total nuclear charge. In other words, the effective nuclearcharge experienced by the outer electrons is less than the total nuclear charge.

$$Z_{eff} = Z - S$$

Where, Z = Nuclear charge, S = Screening constant.

From the knowledge of radical probability distribution graphs we know that 2s-electrons are more penetrating than 2p. In general, for a given energy level the penetration of electrons in various subshells is in the order.

s > p > d > f ..... order of penetration

Due to greater penetration s-electrons have maximum screening effect. For a given energy level, the screening effect of electrons in various subshells varies in the order.

s > p > d > f .... order of screening effects.

Calculation of Screening Constant (Slater Rules) : - The value of screening constant, S can be estimated by applying a set of empirical rules proposed by Slater. These rules are -

1) The electronic configuration of the element is first written and the subshells are arranged in the following order and grouping -

(1s) ; (2s, 2p) ; (3s, 3p) ; (3d) ; (4s, 4p) ; (4d) ; (4f) ....

2) For an electron is a group of s, p electrons, the value of the screening constant, S, is the sum of the following contributions :
   - (i) No contribution for electron in groups beyond the one considered.
   - (ii) An amount of 0:35 for each electron in the group considered (except in 1s group where, 0.30 is used instead of 0:35).
   - (iii) An amount of 0:85 for each electron in the next inner shell (n –1), i.e., from all electrons with quantum number n – 1.
   - (iv) An amount of 1:00 for each of all other inner shell electrons, i.e., from all electrons present in the (n – 2) th and the next inner shell.

3) For an electron considered in d or f group, rules 2 (i) and 2 (ii) above apply as such , however rules (iii) and (iv) are replaced with the rule that all other electrons lying to theleft of d or f groups contribute 1:00 each.

Let us understand these rules by calculating Z_{eff} for 3d-electron and for 4s-electron in titanium(Z = 22)

Ti(Z = 22) : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^2, 4s^2$

Grouping : $(1s^2)\ (2s^2, 2p^6)\ (3s^2, 3p^6)\ (3d^2)\ (4s^2)$

In case of 3d-electron, the electrons in 4s make no contribution and the electrons in the innershells make contribution 1:0 each. The second electron in 3d makes a contribution of 0:35.

∴ For 3d electron,
S = 18 V 1:0 + 1 V 0:35 = 18:35
Z_{eff} = 22 – 18:35 = 3:65

and
second energy levels make a contribution of 1:0 each.

∴ For 4s electron,
S = 10 V 1:0 + 10 V 0:85 + 1 V 0:35 = 18:85
Z_{eff} = 22 – 18:85 = 3:15

A 4s- orbital is filled earlier than a 3d-orbital : Consider a potassium atom (Z = 19), in which19th electron may enter a 4s or 3d orbital, after the configuration.

$1s^2, 2s^2\ 2p^6\ 3s^2\ 3p^6$

Z_{eff} for 19th electron when it enters the 4s-orbital Z_{eff} = 19 – 0 V 0: 35 + 8 V 0:85 + 10 V 1:0
= 19 – 16:80 = 2:20

In case of 4s-electron the second electron in 4s-subshell makes contribution of 0:35 to S.
All the Z_{eff} for 19th electron when it enters the 3d- orbital
Z_{eff} = 19 – 0 V 0:35 – 18 V 1:0
= 19 – 18 = 1:00

Thus, a 4s electron would be subjected to greater electrostatic attraction due to higher Z_{eff} than a 3d electron. Hence configuration $3s^2$ $3p^6$ $4s^1$ would be association with lower energy and would be more stable than $3s^2$ $3p^6$ $3d^1$

1) **The transition metal atoms lose ns electrons first during ionisation :** This is due to the fact that Z_{eff} felt by ns electron in less than the Z_{eff} felt by (n–1)d electron as calculated by Slater's rules.
2) **Trend in successive ionisation energies is $IE_1 < IE_2 < IE_3$:** This is because the Z_{eff} goes an increasing with each removal of electron from an atom.
3) **An anion is always bigger and cation is smaller in size than the parent atom.**
4) **Atomic size in a period goes on decreasing with increase in atomic number.**

Hannay and Smith relationship : Hannay and Smith relationship is a method of calculating percentage ionic character on the basis of electronegativity difference between two atoms. It is givenas –

% ionic character = $16(\chi - \chi) + 3:5 (\chi - \chi)^2$

χ_A and χ_B electronegativity difference between two atoms.

Q. How the radius ratio is related with the co-ordination number and structure of ionic crystal?

Ans. The permitted coordination number and structural arrangement of anions around cations fordifferent $r+/r_1$ ratio are given in Table -

Limiting radiusratio, $r^+/r^{\tilde{n}}$	Permitted co-ordinationnumber	Structural Arrangement	Example
0:155 – 0:255	3	Plane Trigonal	B2O3
0:255 – 0:414	4	Tetrahedral	ZnS
0:414 – 0.732	6	Octahedral	NaCl
0:732 – 1:00	8	Cubic	CsCl

1) Osmium (Os) has the highest oxidation state (+8) or valency (8).
2) Among solids osmium has the highest density of 22:6 while among liquids, mercury has the highest density of 13:6.
3) Among metals, tungsten (W) has the highest melting point (3683 K) while among non- metals carbon has the highest melting point (4000 K). Of all the element, helium, however, has the lowest boiling point (4:2 K)
4) Chemical species (elements, neutral molecules and their cations and anions) which contain one or more unpaired electrons are attracted by the magnetic field and hence are said to be **paramagnetic.** For example, alkali metals, O_2, NO, NO_2 etc. Further more the number of unpaired electrons, greater is the extent of paramagnetism.

5) In contrast, chemical species in which all the electrons are paired are repelled by the magnetic field and hence are said to be **diamagnetic.** For example, alkaline earth metals and their M^{2+} ions, Zn^{2+}, Cd^{2+}, Hg_2^{2+}, CO, NO^+, NO $^+$ etc.

Atomic Volume

Atomic volume is defined as the volume in cc occupied by one gram atom of the element in the solid state and hence is commonly called gram atomic volume. It is obtained by dividing the atomic weight of the element by its density; i.e,

Atomic volume = Atomic weight / Density

In other words atomic volume is the volume in cc occupied by 6.023 V 10^{23} atoms of an element (Avogadro's number). Thus the atomic volumes of the element should be the volumes occupied by the same number of the atoms. The volume occupied by a single atom may be obtained by dividing gram atomic volume with Avogadro's number of atoms. However, this conclusion is not very accurate due to certain variable factors which in turn, depend on the mannerin which the atoms are packed in various elements. It is a common practice to use the term gram atomic volume for volume per atom for assignment of sizes of atoms.

Figure : Atomic volume versus atomic number curve

Group	s-block elements		p-block elements					
Period	IA	IIA	IIIA	IVA	VA	VIA	VIIA	Zero
1	(1) H 14.1							(2) He 31.8
2	(3) Li 13.1	(4) Be5.0	(5)B 4.6	(6)C 5.3	(7) N 17.3	(8) O 14.0	(9) F 17.1	(10) Ne 16.8
3	(11) Na 23.7	(12) Mg 14.0	(13) Al 10.0	(14) Si 12.1	(15)P 17.0	(16)S 15.5	(17) Cl 18.7	(18) Ar 24.4
4	(19)K 45.3	(20) Ca 29.9	(31) Ga11.8	(32) Ge 13.6	(33) As 13.1	(34) Se 16.5	(35) Br 23.5	(36) Kr 32.2
5	(37) Rb 55.9	(38) Sr 33.7	(49) In 15.7	(50) Sn 16.3	(51) Sb 18.4	(52) Te 20.5	(53)I 25.7	(54) Xe 42.9
6	(55) Cs 70.0	(56) Ba 39.0	(81) Tl 17.2	(82) Pb 18.3	(83) Bi 21.3	(84) Po –	(85) At –	(86) Rn –

Table : Atomic Volume (in cc) of s- and p-block Elements. The Numbers Given in Parentheses Indicate the Atomic Numbers

Lother Meyer plotted the atomic volumes (in cc) of different elements against their atomic numbers and obtained a graph shown in figure. An inspection of this graph shows that the curve has five complete well- defined loops and a fraction of the sixth. It may be seen that the maxima of the curve are occupied by the alkali metals (most electropositive elements) while the minima are occupied by C (Atomic number, Z = 6), Al (Z = 13), Ni(Z = 28), Rh (Z = 45) and Os(Z = 76). It may also be seen that when we proceed further from alkali metals, the atomic volumes on each occasion first decrease and then increase again till a sharp maximum is reached at the next alkali metal. Not only alkali metal butall the element belonging to the same group lie at corresponding position on the curve.

The position of lanthanides [Ce(Z = 58) to Lu(Z= 78)] is to be noted. The expected increase in their atomic volumes is not observed in the curve because as the atomic number increases the additional electrons enter into the inner(p – 2)th shell. This causes a contraction in the atomic volumes of lanthanides.The decrease in atomic volumes on proceeding from Ce to Lu is called lanthanide contraction.

Variation of Atomic Volume in a Period and a Group :

1) **In a group :** Atomic volume increases more or less regularly in going down a group (see table). The increase in atomic volume in going down a group is due to the increase inthe number of shells. The larger the number of shells, the bigger is the volume of atom.
2) **In a period :** In going from left to right in a period, it varies cyclically, i.e., it decreasesat first for some elements, becomes minimum in the middle and then increases (see table). The variation of atomic volume in going from left to right in a period is influenced by the following two factors:
   (i) **Nuclear charge :** We known that the nuclear charge(i.e. atomic number) increasesby one, as we move from left to right in a period. The increased nuclear charge attracts each electron more strongly towards the nucleus, resulting in a decrease in the volume of the atom.
   (ii) **Number of valence electrons :** Towards the close of a period, due to an increase in the number of valence - electrons (i.e., electrons in the valence shell) the volume of the atom increases, so that it may accomodate all the electrons.
3) These two factors, one causing an increase and the other causing a decrease, combine to result that in a period atomic volume decreases at first for some elements, becomes minimum in the middle and then increases.

Polarizing Power and Polarizability

In our discussion on the electrostatic model of bonding in ionic substances, we only considered the coulombic attraction between two oppositely charged ions. Such a model was useful in explaining the behaviour of completely ionic solids such as NaCl or CsCl etc. However, in other compounds such as LiCl or AgCl, the ions not only exert coulombic attraction, but are also polarized due to mutual polarization and their behaviour is modified. For example, LiCl is soluble in non- polar organic solvents whereas NaCl or CsCl is insoluble in these solvents. The polarizing effect introduces a varying degree of non-polar character (i.e., covalence) in these ionic substances. The degree of non- polar character (or covalence) in compounds helps us in predicting certain properties such as melting point, boiling point, etc, (because covalent substances have low melting and boiling points).

Anions are larger in size than cations and therefore their electron cloulds are less tightly held.A small highly charged cation shall, therefore, distort the electron cloud of the large anions in a manner that it increases the electron density between the nuclei. For example, the large iodide ion by itself is perfectly symmetrical. However, when a small positively charged lithium ion comes close to the iodide ion, the anion is pulled towards the positive lithium ion. The iodide ion is said to polarized. The polarizationeffect intorudces covalence in LiI molecule.

The power of an ion to distort the other ion is known as its polarizing power and the tendency of the ion to distortion is known as its polarizability. The polarizing power of a cation is proportional to its charge/ radius ratio. In a compound consisting of large negative ions and small positive ions, the polarization may be so marked that the bond becomes covalent, Examples of such ionic covalent compounds include $AlCl_3$, $FeCl_3$, SnI_4 etc.

No polarization + Anion polarization – + Polarization $^{-}$ Effect Covalent bond

Fajan discussed the variation in non- polar character of ionic compounds in terms of polarization effects. He considered that covalent bonding was an extreme example of polarization between two atoms where maximum electron density is between the two nuclei.

Fajan's Rules : Covalent Character in Ionic Compound

Fajan proposed the following rules for the prediction of non-polar character between two ions.

1) High charge of the cation or anion.
2) Small size of positive ion
3) Large size of negative ion

1) **High charge of cation or anion :** The highly charged cation will exert more polarization on the electron density of the anion and will introduce more covalence in its compounds. On the other hand, the highly charged anion will get more readily polarized. Therefore, the polarizing power of a cation and polarizability of an anion will increase with increase in the charge of the ions.
2) **Small size of cation :** The small sized cation will have charge density and therefore it will be able to distort (polarize) the electron cloud of the anion effectively.
3) **Large size of anion :** The polarizability (to be able to get distorted) of an anion increase with increase in its size because its electron charge cloud is not firmly held by its own nuclear charge and can be thus readily polarized by incoming cations.

Periodic Trends:

Among the main group elements the size of the cations increases in moving down a group, therefore tendency of covalent bond formation decreases. For example Li^+ is more polarizing than other members (Na^+, K^+ etc) of group1. Therefore, compounds of lithium are covalent in nature while similar compounds of sodium and potassium are ionic.Thus, LiCl is covalent in nature while NaCl or KCl are ionic and that's why LiCl is soluble in organic solvents while NaCl or KCl are insoluble in these solvents.

In moving along a period, the size of the cations decreases and therefore degree of covalence increase in their compounds. For example in moving from lithium to carbon, through beryllium and boron in the second period, the size of the cation decreases and tendency for covalent bond formation increases.

However, as we descend a group, the size of the anions increases their polarizability increases and their compounds become more covalent. For example, in the series F^-, Cl^-, Br^- and I^-, bromidesand iodides are more covalent than the corresponding chlorides and fluorides.

Ex. Which of the following ions has large tendency for polarization?

(i) Li+, Na+ (ii) Mg^{2+}, Al^{3+}
(iii) K^+, Ag^+ (iv) Cl^-, I^-

Sol. (i) Li^+ (ii) Al^{3+}
(iii) Ag^+ (iv) I^-

Metallic Character

A useful generalization in chemistry is the division of elements into metals and non-metals. This classification of elements is based on certain physical and chemical properties. A substance is termed metallic if it has a silvery lustre and is a good conductor of heat and electricity. Metals are electropositivein character and have a high tendency to lose electrons:

$$M \rightarrow M^+ + e^-$$

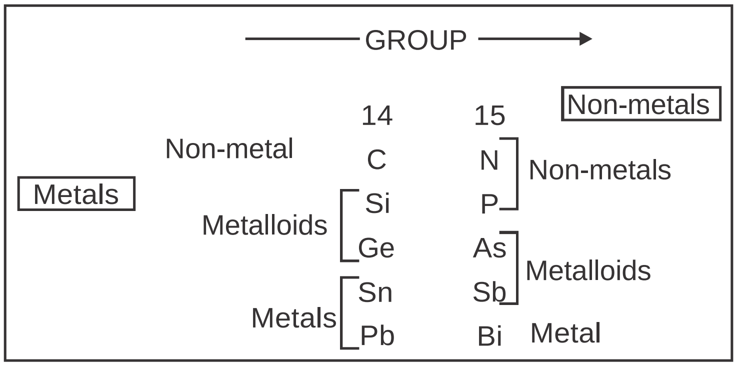
Since this reaction is closely to the ionization energy of an element, therefore, we may say that the two properties are closely interlinked. The lower the ionization energy of an element, greater is its tendency to undergo this reaction and so more electropositive and metallic that element would be.

Periodic Trends in Metallic Behaviour

1) **Variation in a period :-** Metallic character decreases while non- metallic character increaseas we move along a period (from left of right). As we move in a period the size decreases,IE increase and thus, metallic character decreases.

   Element ⌉of |Na Mg A l Si P S Cl 3rd Period||⌋Metals Semi−metals Non−metals

2) **Variation in a group :** Metallic character increases in a group as we move from top to bottom. On moving down a group, size of the atom increases, ionization energy decreasesand therefore, metallic character increases. For example, in group 14, carbon is a non- metal, silicon and germanium are metalloids (show both metallic and non- metallic behaviour) while tin and lead are distinctly metallic. Similarly, in group 15, nitrogen and phosphorus are non-metals, arsenic and antimony show many metallic properties and bismuth is a typical metal.



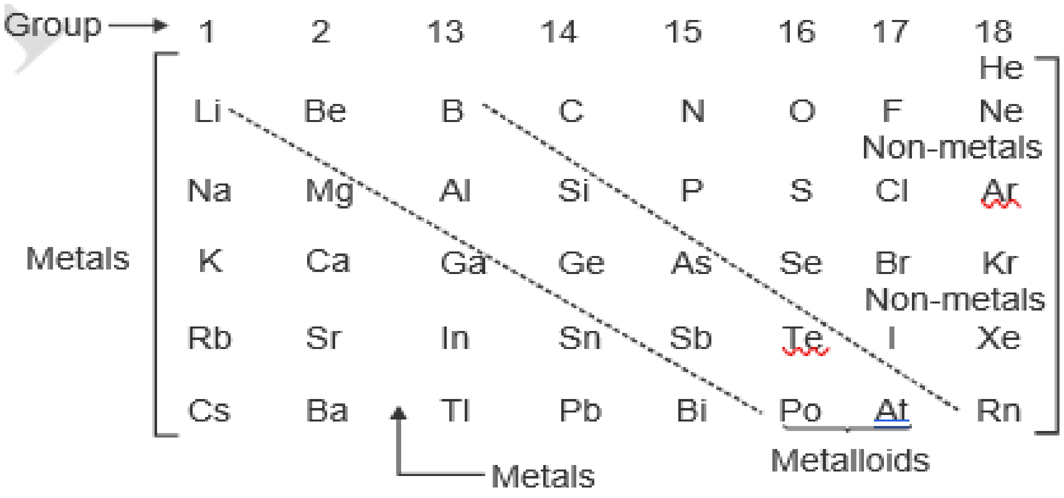
Elements in group 1 are strongly electropositive elements (metallic) while elements of group 17 are strongly electronegative (non- metal). It means that along a period (as the size of the atoms decreases and their ionization energy increases) there is a change from metallic to non-metallic character. Somewhere between these two extremes, we come across elements which show characteristic propertiesof both metals and non-metals. These elements are called metalloids. A classification of main group elements in these categories is shown on next page.

Cause of Metallic and the Non-Metallic Character

The element on the left hand side of the Periodic Table contain very few electrons than are required to attain the stable octet and they achieve this configuration by losing their extra valence electrons. These elements crystallize out in one of the close packed arrangements with the valence electron grouped together to make up a sea of negative charges which binds the entire lattice of M^+ ions.

On moving along a period this tendency to acquire closed shell configuration by losing valence electron diminishes whereas tendency to share its electrons with neighbours increases. The arrangementof atoms in space is determined by the number of covalent bonds and this is turn will determine the shape of the crystal. The elements form giant molecules, e.g., the tetrahedral structure of diamond orthe network type structure of silicates. Further on, we observe that the number of electrons required to form a stable octet are few and these elements do so by sharing electrons and forming diatomic molecules such as N_2, F_2, Cl_2, I_2, etc.

Since there are no unpaired electrons left over to form covalent bonds with other similar atoms or molecules, the forces which hold these solids together are the weak van der Waals' forces. These elements, therefore, form molecular crystals. Because of their complete shell, the noble gases do not form molecules. However, on cooling they form molecular crystalline solidsbecause even the weak van der Waals' forces of attraction which exist between the atom are strong enough to bind them into crystal lattice.



Although it is common amongst chemists to talk in terms of electronegativity of an element, yet it is useful to retain the concept of electropositivity (which is exactly the converse of electronegativity) while describing metals. Some useful generalization are :

(i) Oxides of electropositive metals are basic in character and from ionic compounds.
(ii) Electropositive elements from salts which are generally hydrated.
(iii) Salts of electropositive metals do not form oxy salts.

Ex. (i) Given are the following atoms:
Na, Al, O, S, Te, Rb, H, Cs
Arrange these atoms in the order of (a) increasing atomic radius (b) atom with maximum ionization energy ; (c) atom with maximum electron affinity; (d) atom with most metallic character.
(ii) Which is the least electronegative elements?

Sol. (i) (a) H < O < S < Al < Te < Na < Rb < Cs
(b) H
(c) S
(d) Cs
(ii) Cs

Density

H 0.071						
Li 0.53	Be 1.89	B 2.34	C 2.26	N 0.81	O 1.14	F 1.11
Na 0.97	Mg 1.74	Al 2.70	Si 235	P 0.82	S 2.07	Cl 1.56
K 0.86	Ca 1.55	Ga 5.91	Ge 5.36	As 5.70	Se 4.70	Br 3.12
Rb 1.53	Sr 2.60	In 7.30	Sn 6.00	Sb 6.00	Te 6.10	I 4.93
Ca 1.90	Ba 3.50	Tl 11.85	Pb 11.34	Bi 9.80	Po –	At –

Melting and Boiling Points

Melting and boiling points of main group elements are given Table. These values are dependent upon the nature of the binding forces operating in the crystalline elements. The magnitude of binding forces varies with the number of valency electrons which take part in bonding. On moving along a period, the number of valency electrons increases progressively from one per atom for first group element to a maximum of four for the fourteenth group elements, and consequently the melting points show a corresponding increase.

Sudden decrease in the melting point in moving from carbon to nitrogenis due to a change in their crystal structures, i.e., from the giant structure of carbon to the soft molecularcrystals of nitrogen. Molecular crystals have low melting points because of the weak van der Waals' forces operating between the molecules. Generally speaking, the melting point of a molecular crystal depends on its molecular weight. Substances with high molecular weights exhibit high melting points.

Table : Melting and Boiling Point (^{O}C) of some Main- Group Elements*

−259.2 H −252.8						
186 Li 1336	1280 Be 2477	2180 B −3650	⌧ 4100 C 4830	−210.1 N −195.8	−218.8 O −183.0	−219.6 F −187.8
98 Na 880	650 Mg 1120	660 Al 2467	1420 Si 3280	44.2 P 280	114.5 S 444.6	−101 Cl −34
62.3 K 759	8.50 Ca 1492	29.78 Ga 2403	945 Ge 2850	817 (36mm) As 613	217.6 Se 684.8	−72 Br 59.5
38.5 Rb 700	770 Sr 1370	156.6 In 2080	231.9 Sn 2623	630.5 Sb 1587	452 Te 990	113.6 I 184.5
28.5 Cs 670	710 Ba 1638	303.6 Tl 1457	327.4 Pb 1751	271.3 Bi 1564	254 Po 962	(−) Ar (380)

The variation of melting points in a group does not show any regular behaviour. The interval between the melting and boiling point of elements which form molecular crystals is quite small. This is because the force operating in molecular crystals are the weak van der Waals forces. Only a small amount of energy is required to separate the particles (evaporation) after these have undergone melting. Elements which form gaint molecules (element in the middle of the Periodic Table) have their atoms heldby strong covalent forces and are operative in the molecule even after the substance has undergone fusion. Therefore, they have high boiling points and the difference between their boiling points and melting points is very large.

Oxidising and Reducing Nature

In general, oxidation is the lose of electron or electrons from an atom, ion or molecule and reduction is the gain of electron or electrons, by an atom, ion or molecule. The two processes occur simultaneously. We may note that in a reaction the more electronegative atoms pulls electrons from the less electronegative atom, a process which is very close to oxidation-reduction reaction. Oxidising and reducing power is measured in terms of ET, the standard electrode potential (M^+e^- □□[□ M.ET).

different electrode reactions are arranged in the order of their standard electrode potentials, we obtain what is known as electro- chemical series or in other words oxidation- reduction series. Metals at the top of the series have a ready tendency to lose electrons, have large negative ET values and are powerful reducing agents. On the other hand, element with positive ET values are strong oxidising agents. A partial list of standard electrode potentials of main group elements is given in Table.

Table : Standard Electrode Potentials (E^o, in volts) at 25°C

H^+/H0.00						
Li^+/Li −3.045	Be^{2+}/Be −1.84	B^{3+}/B −0.87				F/F^- 2 +2.80
Na^+/Na −2.714	Mg^{2+}/Mg −2.37	Al^{3+}/Al −1.66			S/S^{2-} +0.51	$Cl2/Cl^-$ 2 +1.36
K^+/K −2.92	Ca^{2+}/Ca −2.87	Ga^{3+}/Ga −0.52		As^{3+}/As +0.25		$Br2/Br^-$ 2 +1.08
Rb^+/Rb −2.99	Sr^{2+}/Sr −2.89	In^{3+}/In −0.34	Sn^{2+}/Sn −0.14	Sb^{2+}/Sb +0.21		$I2/I^-$ 2 +0.54
Cs^+/Cs −3.02	Ba^{2+}/Ba −2.90	Ti^{3+}/Ti −0.34	Pb^{2+}/Pb −0.18	Bi^{3+}/Bi +0.23		

oxidation states varying from – 3 to 1. In the fourteenth group, the tendency is to form covalent compounds instead of gaining or losing electrons. In short, we may say that as one moves along a period, e.g., the third period, the positive oxidation state increases and reaches a maximum value at aluminimum. The negative oxidation state decreases from – 3 to –1 as we move from phosphorus to chlorine.

1) Inert Pair Effect

In a group, the maximum oxidation state shown by a p-block element is equal to the total numberof its valency electrons, i.e., the sum of its s- and p-electrons which is the same as the old group numbers. In addition to the usual oxidation state, some p-block elements also show another oxidation state, which differs from the group oxidation state by a step of two. A list of elements which show this behaviour is given below.

13	14	15	16
Ga	Ge	–	–
In	Sn	Sb	Te
Tl	Pb	Bi	–

These elements occur in the form of following cations:
In^+, Tl^+, Sn^{2+} and Te^{2+}. The greater stability of lower oxidation states (than the group oxidation state) of the heavier p-block elements is explained in terms of inert pair effect. The formation of these ions involves the removal of only p-electrons. The two s-electrons remain a part of the inner core of the electrons and are termed as inert pair.

Causes of Inert Pair Effect

1) **Penetration of ns $e^{\tilde{n}}$ in the 18-electron shell-**One of the explanations offered for the inert pair effect refers to the penetration of the outer electrons in the 18 electron shell which is immediately preceding them. They are, therefore, nearer the nucleus and are more strongly held by the atom. Consequently, the energy required to ionize these s-electrons is very high and it cannot be compensated by the energy which may be released when two additional bonds are formed. Therefore, this pair of s-electrons in heavier p-block elements does not take part in bond formation and acts as a part of the inner core.

2) **Decreasing Covalent Character:** Another explanation which has been offered for this effect refers to the decrease in the covalent bond forming ability of heavy elements due to a decrease in the strength of their covalent bonds. Thus, as the size of the atom increases, its valence electron get farther away from the nucleus and so their effective overlap and hence the strength of their bonds decreases,

3) **Relativistic Effects-**For heavier elements, there is an additional influence on atomic size, namely relativistic contraction. The speed of an electron in heavier atoms (when Z is large) must increase, in order for it to stay in the orbit, otherwise it may fall in the nucleus due to increased attraction. This increase in the speed of an electron in heavier atoms leads to its increase

   in mass [theory of relativity, $\frac{m =}{m_0} \left(1-\left(\frac{v}{c}\right)^2\right)$] and consequent decrease in its radius

   (i.e., electrons in heavier atoms come closer to their nuclei). This raises their binding energies. This increased stability of the 6s electrons in heavier post-transition elements (Tl, Pb, Bi...) reduces their availability for bonding and is responsible for these elements to exhibit valencies two less than the group valence as in Tl(I), Pb(II) and Bi(III).

Ex. Which compound is more stable toward oxidation: $SnCl_2$ or $PbCl_2$?

Sol. $PbCl_2$. Because the effect of the inert pair in the 6th period is more than that in the 5th period.

Nature of Different Compounds

1) **Oxides:** These compounds may be classified into three types :

(i) Basic Oxides
(ii) Acidic Oxides
(iii) Amphoteric oxides, depending on their behaviour towards water, acids and alkalies.

(i) **Basic Oxides :** They are formed by the combination of oxygen with highly electropositive metals. For example, alkali and alkaline earth metals form basis oxides. They are soluble in water and react vigorously to give alkaline solutions. They react with acids to formsalts. They are ionic in nature with high melting and boiling points. A few of their examplesinclude Li_2O and MgO.

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$

(ii) **Acidic Oxides :** They are formed by the combination of oxygen with non-metals. They react with alkalies to form salts. They dissolve in water to give acidic solutions. These compounds are covalent in nature and are usually gaseous or volatile liquids or solids. Some examples include B_2O_3, CO_2, SiO_2, SO_2, SO_3, N_2O_5 and P_2O_5,

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

Basic and acidic oxides often combine to give salts.

$$\underset{(Acid)}{CO_2} + \underset{(Base)}{2KOH} \longrightarrow \underset{(Salt)}{K_2CO_3} + H_2O$$

$$\underset{(Acid)}{SiO_2} + \underset{(Base)}{Na_2O} \xrightarrow{\text{Fusion}} Na_2SiO_3$$

(iii) **Amphoteric Oxides :** They are formed by weakly electropositive elements such as Be, Al, Ga, Sn etc. They show basic as well as acidic behaviour depending on reaction conditions, i.e., they react with bases as acidic oxides and with acids as basic oxides. Amphoteric oxides are mainly ionic in nature and have high melting and boiling points.

For example, Acidic Behaviour

$$\underset{(Acid)}{Al_2O_3} + \underset{(Base)}{2NaOH} \longrightarrow \underset{(Sod.metaaluminate)}{2NaAlO_2} + H_2O$$

Basic Behaviour

$$\underset{(Base)}{Al_2O_3} + \underset{(Acid)}{6HCl} \longrightarrow 2AlCl_3 + 3H_2O$$

Table : Parameters of the Oxides of Third Period

Element	Na	Mg	Al	Si	P	S	Cl
Electronegativity	1.0	1.2	1.3	1.7	2.1	2.4	2.8
Electronegativity difference between element and O (Electronegativity of oxygen is 3.5)	2.5	2.3	2.2	1.8	1.4	1.1	0.7
Oxide Behaviour	Na_2O Strongly basic	MgO Basic	Al_2O_3 Amphoteric	SiO_2 Weakly Acidic	P_2O_5 Weakly Acidic	SO_2 Strongly Acidic	Cl_2O_7 Very strongly Acidic

The change from basic to acidic character takes place because of the increasing electronegativity of the element as we move along a period. The electronegativity difference between an element on the left side of the Periodic Table and oxygen is very large and therefore these oxides are ionic. The electronegativity difference between oxygen and element on the righ side of the Periodic Table is small and therefore their oxides are covalent . For example oxides of elements of the third period are givenin Table to illustrate their behaviour.

It has been observed that acidic, amphoteric or basic character of the oxides is also governedby the size of the cation.

Size of the cation	Behaviour
Less than 50 pm Between 50 to 90 pmGreater than 90 pm	Acidic AmphotericBasic

Other oxides :
There are some other oxides, when are inert, and do not dissolve in acid or bases. For example, N_2O or CO.

Ex. Which is the most acidic oxide : Al_2O_3,Tl_2O_3, Tl_2O?
Sol. Al_2O_3. Acidity decreases as we move down the group and with lowering in oxidation state. $Tl_2O$is most basic.

HYDRIDES :
Hydrogen may accept an electron to form hydride ion.

$$H(g) + e^- \longrightarrow H^-(g)$$

This tendency of the hydrogen to form the negative ion is much lower than halogens. For example,

$$\frac{1}{2}H (g) \longrightarrow H(g); \qquad \Delta H = 218 \text{ kJ mol}^{-1}$$

$$H(g) + e^- \longrightarrow H^- (g); \qquad \Delta H = -67 \text{ kJ mol}^{-1}$$

The overall reaction is

$$\frac{1}{2}H_2(g) + e^- \longrightarrow H^- (g) ; \Delta H = +151 \text{ kJ mol}^{-1}$$

$$\frac{1}{2}Br_2(g) + e^- \longrightarrow Br^-(g) ; \Delta H = -232 \text{ kJ mol}^{-1}$$

Therefore, owing to the endothermic character of the H^- ion, only the most electropositive metals form ionic hydrides. Other elements of the main group generally from covalent hydrides. Classificationof main group hydrides is given in Table.

IONIC HYDRIDES

These hydrides are formed by the most electropositive (Group I and II) elements with the exception of Be and Mg. They are also known as **saline** or **salt- like hydrides.** The ionic nature of these compounds is shown by their high conductance at their melting points and also by the observation that on electrolysis of their melts, hydrogen is liberated at the anode.

Ionic hydrides are prepared by direct reaction between metal and H_2 at 300T to 700TC. The rates are in the order Li > Cs > K > Na

Ionic hydrides are crystalline solids, while when pure they react spontaneously with water and acids according to the reaction.

$$MH + H^+ \longrightarrow M^+ + H_2$$

The standard potential for H_2/H^- couple is about –2.25 V, showing that H^- is a powerful reducing agent.

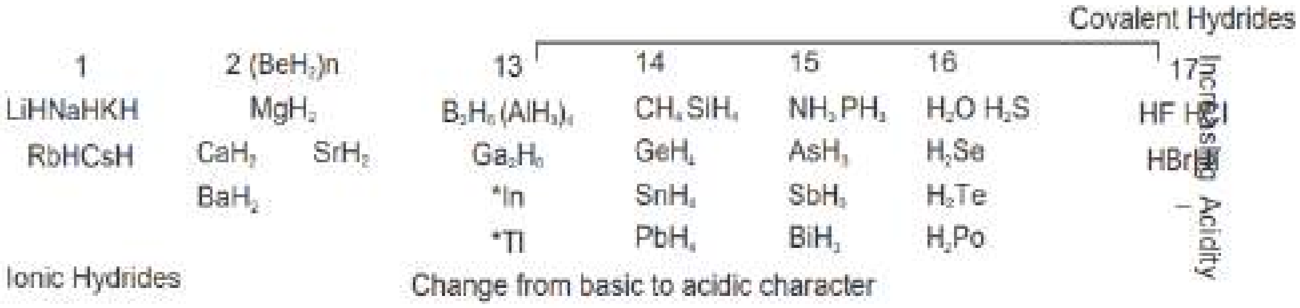
LiH
NaH
KH
RbH
CsH
NaCl type Structure

MgH_2 Rutile structure

CaH_2
SrH_2
BaH_2 Slight distortedhcp

BeH_2 and MgH_2 can be prepared by the thermal decomposition of $Be(CMe_3)_2$ and $MgEt_2$, respectively. BeH_2 has a polymeric structure with bridging hydrogen atoms (as in boranes).

Table : Some Hydrides of Main Group Elements



Covalent Hydrides

1	2 $(BeH_2)n$		13	14	15	16	17
LiHNaHKH	MgH_2		B_2H_6 $(AlH_3)_x$	CH_4 SiH_4	NH_3 PH_3	H_2O H_2S	HF HCl
RbHCsH	CaH_2	SrH_2	Ga_2H_6	GeH_4	AsH_3	H_2Se	HBr HI
	BaH_2		*In	SnH_4	SbH_3	H_2Te	
			*Tl	PbH_4	BiH_3	H_2Po	

Increasing Acidity

Ionic Hydrides

Change from basic to acidic character

Ionic hydrides are strongly basic in nature and along a given period the hydrides becomes increasingly acidic as the atomic number increases. The acid strength of the hydrides increases from left to right and from top to bottom. Two factors may be important in determining the acid strength of non-metal hydrides :

1) The electronegativity of the non-metal, i.e., the polarity of the X-H bond, (where, X = non- metal)

2) Strength of the X-H bond (say its bond energy).

In the series CH_4, NH_3, H_2O, HF, the X-H bond becomes more polar because of the increasing electronegativity of X in moving from C to F. This means that the hydrogen atom acquires an increasing partial positive charge and therefore it becomes easier to ionise as a proton (H^+). We can similarly explain the increase in acidity in moving from SiH_4 to HCl (via PH_3 and H_2S) due to increasing electronegativity of X. Both CH_4 and SiH_4 do not behave as acids in water because the C–H and Si–H bonds have very little polarity.

In going down a group, the acidity of the hydrides increases. This can be explained in terms of the decreasing bond energies of the X-H bonds. As the size of X increases, the bond electron densityis at a greater distance from the nuclei that it is holding and so the bond becomes weaker. Thus, it becomes easier to break the X-H bond and the acid strength increases.

Thus, HI is the strongest acid among the HF, HCl and HBr compounds. The base strengths of the hydrides vary in just the opposite manner. Their basicity decreases from left to right. Basicity depends on the availability of an unshared electron pair to which a proton can be added. Both CH_4 and SiH_4 do not have an unshared electron pair so they do not behave as bases.

From NH_3 to HF, the electronegativity of X increases which causes the unshared electron pair to be held more strongly and thus makes them less available for sharing with a proton. Therefore, the base strength decreases ; NH_3 is a base water is a much weaker base and HF does not behave as a base. With increased size of the atom X, the unshared pair becomes larger and less localized. It, therefore, attracts a proton less strongly than a smaller and more concentrated unshared pair. Thus, PH_3 is a muchweaker base than NH_3. Similarly, water is a much weaker base and H_2S has no basic properties in water.

Ex. Oxygen atom is H_2O has two lone pairs whereas nitrogen in NH_3 has only one unshared electron pair but still NH_3 is a stronger base than H_2O Explain.

Sol. Base strength does not depend on the number of unshared pair but depends on the availability of the unshared pair for sharing with a proton. Although H_2O contains two unshared pairs of electrons, it accepts only one proton to give the H_3O^+ ion. The positive charge thus created attracts the remaining unshared pair and makes it much less available for sharing with another proton. Thus, the H_4O^{2+} ion has never been observed.

HALIDES

Most of the elements (except He, Ne and Ar) react with halogens to form halides. The order of reactivity of the halogens decreases as we descend from fluorine to iodine. The nature of bonding in halides depends on :

1) Nature of the halogen atom, and
2) Nature of the second element

1) **Nature of the Halogen :** Many metals exhibit their highest oxidation state in the fluorides. They are generally ionic compounds. The corresponding chlorides are covalent in nature. The degree of covalence increases further in compounds of bromine and iodine (the same conclusions can be predicited by Fajan's rules).

2) **Nature of the second element :** The choice of the second element plays an important role in determining the nature of bonding in halides.

   (i) Ionic lattices containing X^- ions are formed by electropositive metals such as s-block elements. In case of ionic halides, the solubility decreases in the order.

   iodide > bromide > chloride > fluoride

   (ii) Solubility is governed by lattice energy which also increases in the same order (as the ionic radii of X^- decreases).

   (iii) Covalent lattices or complex ions are readily formed by electropositive metals of p-block elements. Amongst the covalent halides, the order of solubility varies as :

   chloride > bromide > iodide

   (iv) This may be explained in terms of increasing covalent character due to increased polarization as size of the X^- ion increases.

   (v) Molecular halides are formed by non-metallic elements including hydrogen. They are usually volatile. They do not volatilize if present in polymeric form. For example, Teflon $(-CF_2-)_n$ is non-volatile. Similarly, $AlCl_3$ and SnF_4 which are molecular in the gas phase but due to the tendency of the metal atom to have a higher coordination number (4 and 6, respectively for Al and Sn in these examples), the solids acquire extended structures.

   (vi) Because of the high electronegativity of fluorine, most molecular fluorides are polar in nature. Because of the low dissociation energy of F_2 and the relatively high energy of bond with fluorine (C–F 486 kJ mol^{-1}), molecular fluorides are formed exothermally. The high electronegativity of fluorine has strong influence on the properties of molecules containing fluorine. For example.

$CH_3COOH \longrightarrow$ Weak acid

$(CH_3)_3N \longrightarrow$ Basic and pyramidal

$CF_3COOH \longrightarrow$ Strong acid

$(CF_3)_3N \longrightarrow$ Non- basic and planar

NH_3NF_3 Basic

Non- basic

Reactivity

Properties of a molecular halide depend on the elements involved. However, one general propertyis their easy hydrolysis. For example,

$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl$ $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$ $SiCl_4 +$
$4H_2O \longrightarrow Si(OH)_4 + 4HCl$

When the central atom has its maximum stable coordination number, as in CCl_4 or SF_6, the compound is unreactive and is not hydrolysed by water. The oxidation state of metal ion also influences the bonding in metal halides. For example, higher the oxidation state of the metal ion, smaller will be its radius and this in turn will favour covalent bonding. By similar analogy, lower oxidation state shall favour ionic bonding.

Thus $PbCl_4$ is covalent while $PbCl_2$ is ionic.

From this discussion it may be concluded that along a period ionic character of the halides decreases while covalent character increases. However, as we move down a group the degree of ionic character in halides increases.

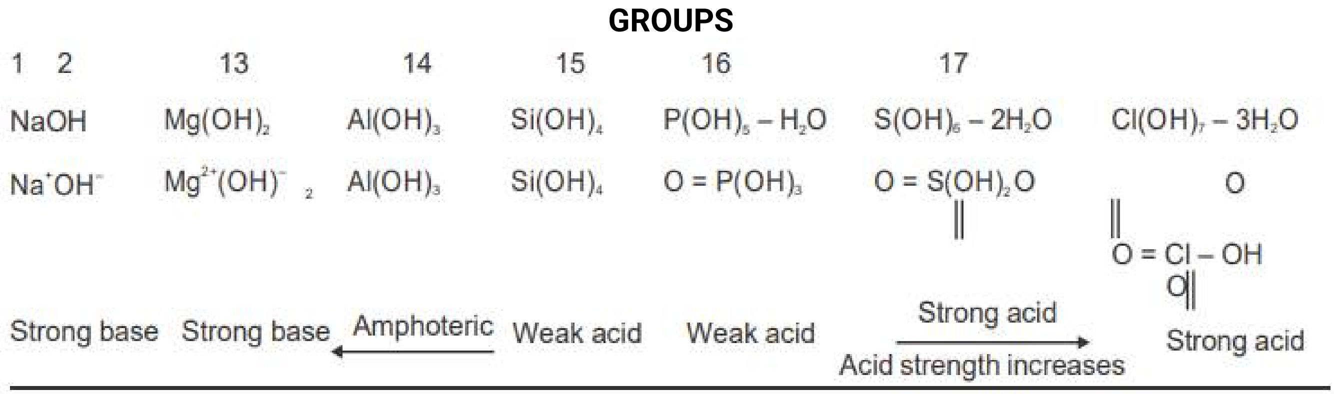
Ex. Which is more reducing : $SnCl_2$, $PbCl_2$?

Sol. $SnCl_2$, because $PbCl_2$ is more stable and is thus a weaker reducing agent.

OXO- ACIDS

Phosphorous acid, phosphoric acid, sulphuric acid, perchloric acid are members of an important class of compounds called oxo-acids. Oxo-acids contain one or more OH groups attached to an electronegative atom, X. They have the general formula $XO_m\ (OH)_n$, where m = 0,1,2 .... and n = 1,2,3...

For example, H_2SO_4 may be written as $SO_2(OH)_2$, m = 2 and n = 2 and phosphoric acid, H_3PO_4 can be written as $PO(OH)_3$, where m = 1 and n = 3 nitric acid, HNO_3 or $NO_2\ (OH)$, where m = 2 andn = 1,



Compounds of elements of groups 1 and 2 containing OH groups are ionic hydroxides, Na^+OH^- , Mg^{2+} (OH_2^-) and are therefore strong bases.

How do we know then that a compound containing OH groups is going to behave as anacid or a base?

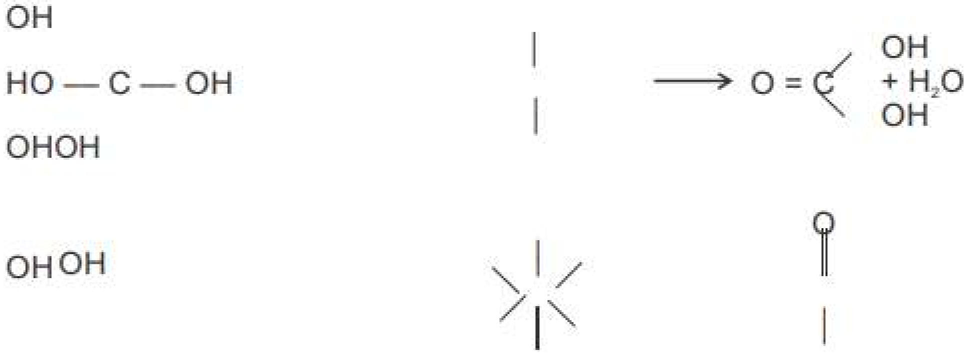
If the atom X in XOH has a low electronegativity, the X–O bond is polar with the oxygen atom having a negative charge and X a positive charge :

$$\overset{\delta+}{X}-\overset{\delta-}{O}-H$$

When this is the case as in NaOH or $Mg(OH)_2$ X –– O ó H ionizes to give X+ and OH^-. When X has a high electronegativity, X –– O bond is less polar and so XOH has a decreased tendency to ionize as X+ and OH–. This O – H bond becomes polar.

$$X-\overset{\delta-}{O}-\overset{\delta+}{H}$$

There is an increased tendency for the hydrogen to be donated as a proton to give XO^- and H+. Therefore, acid strength increases with increasing electronegativity of X (and base strength decreases). The oxo-acids often do not carry the same number of hydroxyl groups that would be expected from their valencies. Instead pairs of OH groups are replaced by doubly bonded oxygen (= O). For example,



Some Special Characteristics of p-Block (Main-Group) Elements

Among the p-block elements the first element in each group differs from the other members in two major respect :

1) Small size and
2) Lack of d-orbitals

SIZE OF ATOMS

Distinctive properties of second row elements are their small atomic size and high electronegativity values. Both these properties can be attributed to the small number of inner shell electrons, only two ($1s^2$), so that the second row valence electrons are strongly bound. Their small size favours covalent character in their compounds, more so as we move towards the right with increase in Z. From carbon onwards the small atomic size favours strong single and multiple bonding because of good orbital overlap at close approach between the bonding atoms.

Later in the row, beginning with nitrogen and onwards, although multiple bonding is still favoured (because of good p□ overlap), single bonds are greatly weakened when lone pairs are present because of the strong repulsion at close approach (e.g. weakly bonded nature of H_2O_2 and F_2 in contrast to the strongly bonded nature of element boron and diamond).

A unique property of the second-row elements (say C, N, O, F) is their strong tendency to form double and triple bonds. This may be attributed to:

1) High electronegativities of these elements; and
2) Strong repulsion between the electron pairs in their valence shells.

These element can hold two or more electron pairs in the bonding region. A double bond occupies less space than two single bonds. Therefore, these elements can minimize electron pair reulsions in their valency shells by forming multiple bonds.

For example, carbonic acid is $(OH)_2$ C = O but silicic acid is $Si(OH)_4$; carbon dioxide(O = C = O) is a volatile monomeric gas while silica (SiO_2) is a polymeric solid containing single bonds between silicon and oxygen. We may further note that oxygen (O = O) and nitrogen (N Ξ N) gases exist as diatomic molecules whereas heavier members in their groups, form S_8 and P_4 molecules. In the third row, pπ-bonding is less favourable, because of poorer pπ overlap for the larger atoms. Single bond formation is favoured relative to multiple bonding as in comparison of N_2 or NO with P_4 or P_4O_{10}.

Absence or Presence of d-Orbital

First row elements of the p-block lack d-orbital in their valence shell while heavier elements in each group have d-orbitals. The presence of these orbitals affects the chemistry of the heavier elements in a number of ways:

1) **Coordination Number :** The valence shell configuration of the first row elements of p- block elements is $2s^2\ 2p^n$ and the next available orbital is 3s which is separated from 2p energy level by a very large energy gap and is therefore not available for bonding. This means that the maximum number of electron pairs is four. The first row elements canthus have a maximum coordination number of four (by using one 2s and three 2p orbitals). By contrast the elements of the next period (configuration $3s^2\ 3p^n$) can make 3d orbitals available which are only slightly higher in energy than the 3p orbitals*. These elements can use empty d-orbitals to increase

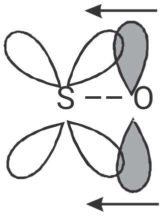
their coordination number. The expenditure of energy in promoting one of the valence electrons to the easily available d-orbitals is so modest that the energy released on the formation of two additional bonds will more than that compensate for it. For example, boron forms BF_6 while aluminum can form AlF^{3-} ion.

2) **Reactivity Differences :** Due to the availability of d-orbitals, elements of the third period are more reactive than those of the second period. For example, CCl_4 does not interact with water while $SiCl_4$ is highly susceptible to attack by water.
3) **Strength of the Homonuclear Single Bonds :** The bond energies of diatomic molecules of first row elements are distinctly low as compared to diatomic molecules of second row elements.

For example, bond dissociation energy of F_2 is 155 kJ mol^{-1} and that of Cl_2 is 243 kJ mol^{-1}. The low values of F–F, O–O and N–N may be due to the greater repulsion among the non-bonding electron of these small molecules. The repulsion term for molecules of second and subsequent rows is not very significant due to their large size. These elements make use of available d-orbitals in bonding and reduce any repulsiondue to non-bonding electrons.

dπ-pπ Bonding

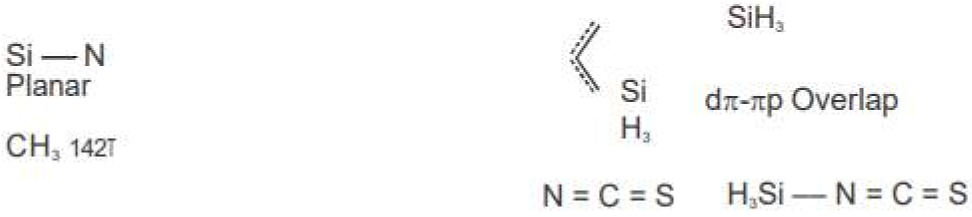
The heavier members among the p-block elements exhibit multiple bonding by involving d-orbitals. For example, 3d orbitals are involved in dπ-pπ multiple bonding between sulphur and oxygen in SO_2 and SO_3.



dπ-pπ

Similarly we can explain the formation of double bond in $Cl_2S = O$ and $Cl_2Se = O$ in terms of d□-p□ bonding. Participation of d-orbitals in bonding among compounds of the second period elements leads to the delocalization of the lone pair of N or O in their compounds.

For example, delocalization of lone pair into a back-bonding p orbital of the silicon atom makes trisilylamine planar and silyl isothoicyanate linear. This also leads to lowered basicity among silyl compounds.



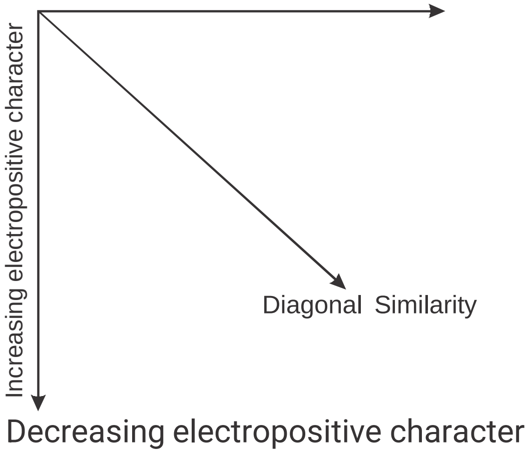
Diagonal Relationship

One of the important features of the elements of the second period of the Periodic Table is that they resemble with the element to their lower right in the third period (i.e., diagonally opposite element) more than their own congeners. The diagonal relationship is best illustrated by the following pairs of elements of the Periodic Table.

Li	Be	B	C
Na	Mg	Al	Si

The reasons for similarity between the diagonally opposite members are:

1) The electropositive nature of the elements increases on descending a group but decreasesas we move from left to right. Consequently, the electropositive nature of two diagonally opposite elements will be very similar.
2) On moving from left to right, charge on the ions increases but their size decreases which causes an increase in the polarizing power of the ions. On moving down a group, size increases and polarizing power decreases. However, on moving diagonally these two effects partly cancel each other and there are a few similarities in the behaviour of the elements.



It is interesting to note that inspite of different valencies of the elements, the type and strength of the bond formed and the properties of their compounds are often very similar. Among p-block element stiking diagonal similarity is only observed between boron and silicon. Other elements of the p-block show very feeble diagonal similarity and therefore are excluded from our discussion.

CHEMICAL BONDING AND STRUCTURE OF MOLECULES

Chemical Bond :

Every system in this universe has a tendency to acquire a state of minimum energy. Since, isolated atoms generally have higher energy as compared to combined atoms, therefore, isolated atoms have a natural tendency to form aggregates (element or compound) which have lower energy than individual atoms.

In the formation of aggregates, the extent of lowering of energy varies from system to system but generally if the lowering exceeds 40 kJ/mol of atoms, we can say that chemical bonds are formed to provide species (molecules) which can exist indepedently and have distinct physical and chemical properties.

A chemical bond may be defined as "the force which holds atoms or ions together".

"The phenomenon of union of two or more atoms involving redistribution of electrons, so that each atom involved in bonding acquires stable configuration in order to gain stability is known as chemical bonding".

Ionic Bond

Bond formed by the complete transference of an electron (or electrons) from one atom to another atom is known as electrovalent or ionic bond.

For example. When sodium reacts with chlorine ions with opposite electric charges are formed during the chemical reaction.

$$2Na(s) + Cl\,(g) \rightarrow 2Na^{+}Cl^{-}\,(s) \quad _{2}$$

The oppositely charged ions are held together by Coulombic forces. The system will be at a lower potential energy when the two oppositely charged ions are close to each other than when they are far apart.

GENERAL CHARACTERISTIC OF IONIC COMPOUNDS

1) **Melting Point:** Ionic compounds have high melting points. The electrostatic force of attraction (ionic bond) between cations and anions is strong. It takes a lot of energy to overcome this attraction in order to allow move more freely and form a liquid.

   Factors affecting the melting point of compound are :

   (i) **The charge on the ions** In general, the greater the charge, the greater the electrostatic attraction (cation-anion interaction), the stronger the ionic bond, the higher the melting point. For example:

Ionic compound	Melting point (°C)	Cation charge	Anion charge
NaCl	801	+1	−1
MgO	2800	+2	−2

   (ii) **The size of the ions** Smaller ions can pack closer together than larger ions so the electrostatic attraction is greater, the ionic bond is stronger, the melting point is higher. For example:

Ionic compound	Melting point (°C)	Cation charge (pm)
NaF	1270	Na^+ = 99
KF	857	K^+ = 136
RbF	775	Rb^+ = 148
CsF	683	Cs^+ = 169

   As the radius of the cations increases down group I from Na^+ to Cs^+, the melting pointsof the fluorides decrease. Similarly.

Ionic compound	Melting point (°C)	Cation charge (pm)
NaF	1270	F^- = 99
NaI	925	I^- = 206

2) **Hardness:** Ionic compounds are hard and brittle. The strong ionic bonds between the cations and the anions hold the ions in a very rigid lattice so smaller ions can pack closer together than larger ions and hence are hard. Hardness depends upon.

(i) **Charge of ions** Hardness increases with increase in charge on the ion for crystals of similar interionic distances for ionic compounds having similar structure. For example :

Ionic compound	Interionic distance (Å)	Charge	Hardness (Mohs)
LiClSrO	2.57 2.57	Li = + 1, Cl = –1 Li = + 2, Cl = – 2	Less hard (3.0) More hard (3.5)

LiCl and SrO both have similar structure of NaCl type.

(ii) **Ionic Radii** For a given charge hardness increases with decrease in interionic distance for crystals with similar structure.

Ionic compound	Interionic distance (Å)	Charge	Hardness (Mohs)
CaO	2.40	Ca = + 2, O = – 2	Max hardness (4.5)
SrO	2.57	Sr = +2, O = – 2	More hard than BaO(3.5)
BaO	2.77	Ba = + 2, O = – 2	Least hard (3.3)

On Mohs scale hardness of diamond is 10.

Noble gas type cation configuration (ns^2, np^6) are harder than cations with pseudo noble gas typeor non-noble gas type or other configuration. For example :

Ionic compound	Electronic configuration of cation	Hardness (Mohs)
CaF_2CdF_2	Ca^{2+} = $3s^2$, $3p^6$ Cd^{2+} = $4s^2$, $4p^6$, $4d^{10}$	Max hardness (6.0) More hard than BaO(4.0)

3) **Brittleness:** Ionic solids are brittle. When a stress is applied to the ionic lattice, the layers shift slightly. The layers are arranged so that each cation is surrounded by anions in the lattice. If the layers shift then ions of the same charge will be brought closer together. Ions of the same

charge will repel each other, so the lattice structure breaks down into smaller pieces.

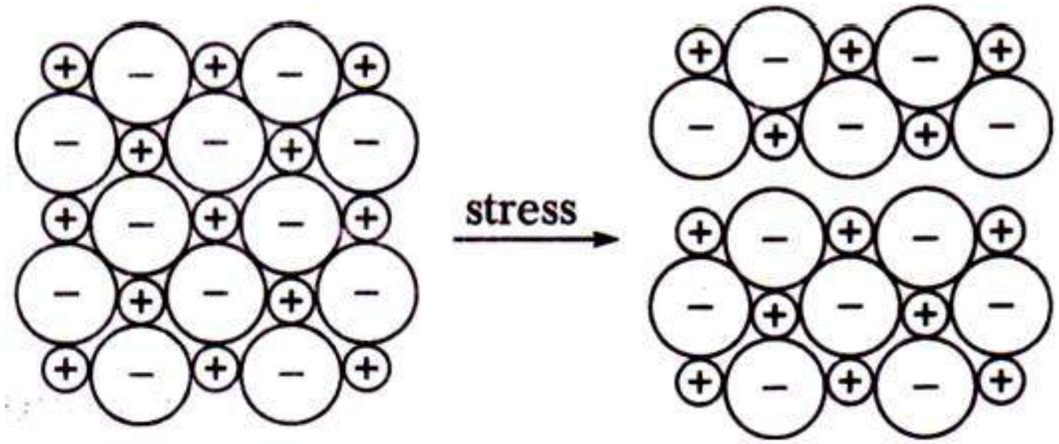


Figure : Crystal lattice and effect of stress

4) **Solubility:** As "Like dissolves like", ionic compounds dissolve in polar solvents, especially those that ionize, such as water and ionic liquids. They are usually appreciably soluble in other polar solvents such as alcohols, acetone and dimethyl sulphoxide as well. Ionic compounds tend not to dissolve in non-polar solvents such as diethyl ether or petrol.

   When the oppositely charged ions in the solid ionic lattice are surrounded by the opposite pole of polar molecule, the solid ions are pulled out of the lattice and into the liquid. When this force is more than the electrostatic attraction of the lattice, the ions become dissolved in the liquid.

5) **Conductivity:** In order for a substance to conduct electricity it must contain mobile particles capable of carrying charge.

	Ionic Solid	**Ionic liquid**	**Aqueous Solution**
Mobility of ions	very poor	good	good
Electrical conductivity	very poor	good	good

Solid ionic compounds do not conduct electricity because the ions (charged particles) are locked into a rigid lattice or array. The ions cannot move out of the lattice, so the solid cannot conduct electricity.When molten, the ions are free to move out of the lattice structure.
Cations (positive ions) move towards the negative ielectrode (cathode) $M^+ + e^- \rightarrow M$.
Anions (negative ions) move towards the positive electrode (anode) $X^- \rightarrow X + e^-$

When an ionic solid is dissolved in water to form an aqueous solution, the ions are released from the lattice structure and are free to move so the solution conducts electricity just like the molten (liquid) ionic compound.

COVALENT BOND

A type of chemical bond in which there is mutual sharing of electrons between two atoms is called covalent bond. It is further classified into single, double, and triple covalent bond with respect to mutual sharing of one, two and three bonds respective. Their symbols are single (–), double (=) and triple (Ξ) lines between two atoms according to their type of covalent bond like one for single, two for double and soon (e.g., Cl –– Cl).

Valence Bond Theory

According to this theory, a covalent bond is formed by the overlapping of two atomic orbitals of proper energy and proper symmetry. This theory was given by Hietler and London and extended by Pauling and Slater.

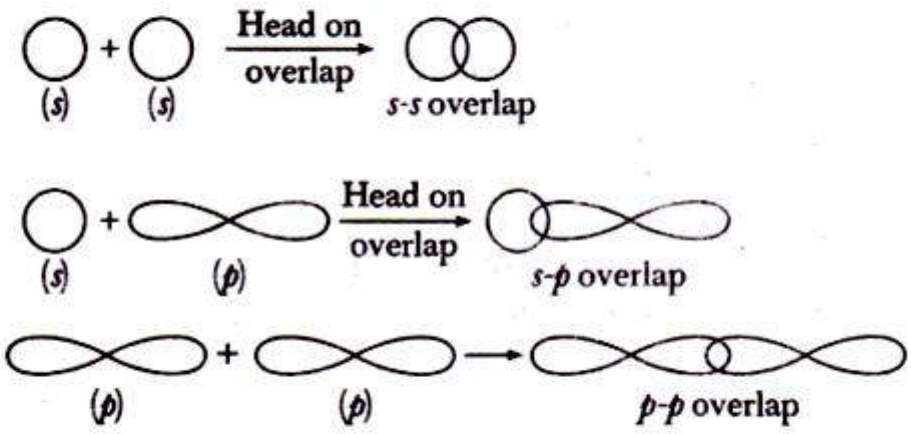
Hietler and London Concept

1) For a covalent bond to form, two atoms must come closer to each other so that orbital of one atom overlaps with the other.
2) Overlapping orbitals must have :
   (i) half-filled nature, i.e., must have unpaired electron.
   (ii) antispin electrons.
3) As a result of overlapping, **a new localized bond orbital** is formed, in which probability of finding electron pair is maximum.
4) Covalent bond energy arises due to:
   (i) electrostatic attraction between nuclei and the accumulated electron cloud.
   (ii) cancellation or attraction between spins of antispin electrons.
5) Greater is the overlapping, lesser will be the bond length, more will be the attraction and more will be bond energy and the stability of bond.

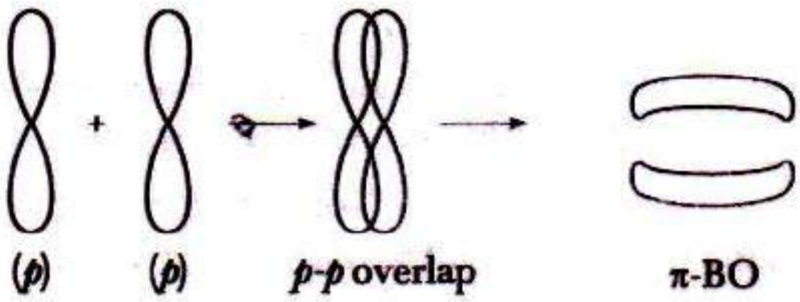
Pauling and Slater Extension

1) The extent of overlapping depends upon
   (i) nature of orbitals involved in overlapping.
   (ii) nature of overlapping.
2) More closer the valence shells are to the nucleus, more will be the overlapping and the bond energy will also be high. Bond energy of $1 - 1 > 1 - 2 > 2 - 2 > 2 - 3$ shells.
3) Between two subshells of same energy level, the subshells more directionally concentrated shows more overlapping. Bond energy : 2s-2s < 2s-2p < 2p-2p.
4) s-orbitals are spherically symmetrical and thus show only head on overlapping. On the other hand, p-orbitals are directionally concentrated and thus, show either head on overlapping or lateral overlapping.

Formation of σ-bond (σ-Bond is formed by the axial overlapping of atomic orbitals)



Formation of π-bond (π-bond is formed by the sideways overlapping of atomic orbitals).



Head on overlapping is stronger than lateral or sideways overlapping.

$$\therefore \quad \text{B.E.} \qquad \underbrace{p-p}_{\text{Lateral overlapping}} < \underbrace{s-s < s-p < p-p}_{\text{Head on overlapping}}$$

Valence Bond Theory treatment of π-bonding : The bonding in CINO

The overlap of the sp^2 hybrid orbitals of N with the 3 p-orbital of Cl and the 2p-orbital of O give the two -bond and it is overlap of the "left over" p orbital on N with the appropriate orbital on O that forms the (2p-2p) -bond between the two atoms.

Wave Mechanical Treatment to VBT

VBT utilises the following wave mechanical principles:

1. If ψ_A and ψ_B are the wave functions for any two completely independent (non-interacting) systems A and B, then the total wave function ψ for these independent systems, taken together, would be given by :

2. If the wave function for a many-electrons system has characteristics of several wave functions ψ_1 ψ_2, ψ_3, ...ψ_n, then according to the Ritz principle of linear combination, the wave function ψ closest to the true wave function of the system is given by

$$\psi = c_1\psi_1 + c_2\psi_2 + c_2\psi_3 + ... + c_n\psi_n \text{ ......} \qquad .... \qquad (2)$$

where c_1, c_2 .... c_n are the various coefficients. These coefficients are so adjusted as to give a state of lowest energy, i.e., a state of maximum stability. The function ψ should be normalised so that

$$c_1^2 + c_2^2 + c_3^2 + ... = 1 \qquad ... \qquad (3)$$

UNIT – 2

Inorganic Chemistry-II

UNIT-2 Inorganic Chemistry-II

S-BLOCK ELEMENT

Occurrence

Since, all these elements are extremely reactive so they do not occur in free state. Being most electropositive elements, they are found in nature as cations combined with the most electronegative anions such as chloride ions. Thus, the main source of sodium is sodium chloride present in sea water and as large deposits on earth while that of potassium is carnallite, $KCl.MgCl_2.6H_2O$. Lithium, rubidium and cesium are present in minute quantities in some alumino silicates. Francium is radioactive with very short half-life, therefore, it does not occur in nature. Sodium (2.6%) and potassium (2.4%) are high inabundance in the earth's crust (lithosphere).

Extraction of Alkali Metals

The extraction of group 1 metals cannot be carried out by usual procedures due to the following difficulties :

1) These metals cannot be prepared by the reduction of their oxides as elements of these groups are themselves the strongest reducing agents.
2) These elements react with water, therefore, the method of displacing them from their solutions by using elements in the electrochemical series is not possible.
3) These elements can be prepared by the electrolysis of their aqueous solutions using mercury cathode only wherein they form amalgams but the recovery of the metal from the amalgam is quite difficult. Moreover, during electrolysis of aqueous solutions the liberated metal at the cathode starts reacting with water to form metal hydroxide.

Keeping in view the above difficulties, alkali are usually isolated by the electrolysis of their fused metal halides containing another metal halide (in order to lower the melting point).

Electronic Configuration

The atom of alkali metals in the ground state consists of electron in s-orbital outside a noble gas core. This similarity in the electronic configuration of all these element is reflected in the similarities of their physical and chemical properties as discussed below.

Physical Properties

Important physical properties of alkali metals are set out in Table. We shall confine our discussion to only first five members of the family of alkali metals as very little is known about the last member, namely, francium which is a radioactive element. A correlation between atomic structure and physical properties is discussed below. Attempt has been made to explain the physical properties of alkali metals on the basis of two facts, namely,

1) loose binding of s-electrons; and
2) size of the alkali metal atoms and ions.

Loose Binding of S-Electrons :

In alkali metals the noble gas core shields the s-electrons from the direct attraction of the charge of the atomic nucleus. Therefore, the s-electron is very loosely held. The consequences of loose binding of s-electrons are :

1) **Ionisation Energy :** The first ionization energy of all these elements is low. This is the main factor which enables these metals to form positive ions readily and thus behave as electropositive elements.

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

Table : Physical Properties of Alkali Metals

Property	**LithiumLi**	**SodiumNa**	**PotassiumK**	**RubidiumRb**	**CesiumCs**
Atomic Number Electronic Configuration Atomic Radius, pm Ionic radius, M^{+}, pm Ionisation energies kJ/g atom □ Eº, M+/M(V) Electronegativity Heat of atomisation (at 25ºC,1 atm), kcal mol^{-1} Atomic volume Atomic weight Density g/cc Melting point, ºC Boiling point, ºC Colour of the ?ame Ionic conductances of M ion $□^{-1}$	3 [He] $2s^{1}$ 123 68 527 7303 −3.04 1.0 38 12.97 6.94 0.53 180 1336 Carmine red 33.5	11 [Ne] $3s^{1}$ 157 97 502 4570 −2.71 0.9 26 23.68 22.99 0.97 98 883 Yellow43.5	19 [Ar] $4s^{1}$ 203 133 427 3076 −2.92 0.8 21 45.39 39.10 0.86 63.5 759 Violet64.6	37 [Kr] $5s^{1}$ 216 148 410 2662 −2.99 0.8 19.5 55.80 85.47 1.53 39 700 Reddish violet67.5	55 [Xe] $6s^{1}$ 235 169 381 2427 −3.02 0.7 18.7 69.95 132.91 1.90 28.5 670 Blue68.0

The second ionisation energy is fairly high which implies that the loss of the second electron is quite difficult. This is due to the fact that the second electron has to be pulled out from the noble gas core. Hence, it can be concluded that the chemistry of these elements is essentially of unipositive ions. Trend in the group On moving down the group, the ionization energy decreases because the s-electrons are getting away from the nucleus due to the addition of new shells. Therefore, their attraction for the nucleus decreases and the electrons can be removed by expending less energy. Hence, their electropositive character (i.e., the ability to lose an electron) increases.

2) **Reducing Property :** The tendency of alkali metals to act as strong reducing agents is obvious from the fact that these metals liberate H_2 from water and acids.

$$2M + H_2O \rightarrow 2MOH + H_2 \ \boxtimes$$
$$2M + 2HCl \rightarrow 2MCl + H_2 \ \boxtimes$$

This property may be attributed to their strong tendency to lose their outermost (ns^1) electron. Reducing power is measured in terms of the standard electrode reduction potentials ($M^+ + e^-$ ⊠⊠⊠ M,E°).

These elements show very high negative E° values (See Table), which suggests that they are extremelypowerful reducing agents and since, lithium metal has the highest value (E° = –3.04 V) therefore, it isthe strongest reducing agent among the alkali metals.

However, we have earlier observed that lithium atom loses its ns^1 electron with difficulty (it has the highest IE value) relative to other alkali metals (Cs atom has the lowest IE value). Consequently lithium should have mininum reducing power because of its maximum IE value. As a matter of fact lithium has the maximum reducing power.

Then how to explain this discrepancy?

This can be explained as follows:

The IE values obviously do not reveal the complete picture. The reducing action of an alkali metal in aqueous solution is represented as :

$M(s)$ ⊠ $M^+(aq) + e^-\ (aq)$ ...(i)

The process of reduction may be visualized to take place through the following three steps:

Step 1 : In this step the metal in the solid state, M(s) is evaporated to the gaseous state, M(g). Energy is required for this step and is called the sublimation energy.

M(s) + Sublimation energy ⊠ M(g) ...(ii)

For alkali metals sublimation energies are almost the same with only a little variation.

Step 2 : In this step, the outermost (ns^1) electron is removed to form $M^+(g)$ cation.

$M(g) + IE \rightarrow M^+(g) + e^-$ ...(iii)

In this process also energy is required. As already discussed the IE value for Li atom is the maximum among the alkali metal atoms.

Step 3 : In this step the gaseous cation, $M^+(g)$ obtained in the Step II gets hydrated to form $M^+(aq)$ ion. In this step energy is liberated in the form of hydration energy.

$M^+(g) + H_2O \rightarrow M^+(aq)$ + Hydration energy ...(iv)

$Li^+(g)$ ion, being the smallest atom in size, gets hydrated to the maximum, i.e., it can attach the maximum number of water molecules around it (because of its very high charge density). Hence, Li^+ has the maximum value of hydratoin energy. This value decreases rapidly from Li → Na and then there is a gradual decrease to Cs. The standard reduction potential, E°, is the summation of three terms (2) + (3) + (4)

$$E^o = (2) + (3) + (4)$$

Thus, when we compare with each other the values of sublimation energy, ionization energy and hydration energy, we observe that the E° value has the maximum negative value for lithium. Although IE of Li is maximum in the 2nd step, this high value is more than compensated by the large value of hydration energy (of Li^+ (ag)) released in the 3rd step. Trend in the group Except lithium, the negative value of E° for the elements down the group increases indicating greater reducing character.

3) **Photoelectric Effect :** The low energy photons (i.e., light) can eject the loosely held s- electron from the surface of these metals. Therefore, these metals especially cesium are used in photoelectric cells which are sensitive to blue light.

1) **Electronegativity :** The values of electronegativity for the alkali metals are very low. Thisis because these elements have a tendency to lose rather than gain an electron. Trend in the group The value of electronegativity decreases from lithium to cesium indicating decreasing tendency of the elements to hold their s-electron.

2) **Colouration To The Flame :** The elements give characteristic colouration to the flame. Their salts, particularly chlorides, when heated in a Bunsen burner flame on platinum wire, dissociate into atom (and not ions). The outermost electron is excited to higher energy states. An electron which is ina higher energy state must lose its excess energy to the surrounding and revert back to original energy level. This excess energy is emitted as light. This emitted light will correspond to a definite energy jump in the atom and is characteristic of the atom in question. The emitted light for each alkali metal will correspond to definite energy jumps corresponding to some definite frequency of the visible part of the spectrum. For this reason, alkali metal compounds impart characteristic colour to the flames, see Table.

1) **Electrical Conductivity :** It has been established that in metals, it is the valence electrons that hold the individual atoms together in the crystal. In fact, metals are often described as "islands" of

shielded nuclei in a ìsea” of valence electrons. Among the alkali metals, this ìsea” is very diffuse andthe binding in the solid is relatively weak. Therefore, the valence electrons move freely from one metal ion to another without much difficulty with the result that these metals have high electrical conductivity.

2) **Ionic Compound Formation :** Since, these elements are highly electropositive, they react readily with highly electronegative elements by the transfer of their s-electron. Therefore, the atoms in their compounds so formed have large electronegativity differences resulting in the formation of ionic bonds. However, these elements also show covalent bonding in certain cases. For example, the vapoursof alkali metals contain some diatomic molecules such a Na_2, Cs_2 which are covalently bonded. The strength of the covalent bond in diatomic molecules decreases down the group. Another proof of their ability to form covalent compounds is furnished by the formation of organo-metallic compounds such as CH_3Li, C_2H_5Li, $C_6H_5CH_2Na$.

Sizes of Atoms and Ions

The atoms of the alkali metals have the largest size which is evident from the values of atomic volume and atomic radii listed in Table. Even after the loss of s-electron, the ions of the alkali metals have comparatively large values. The large size along with only one valence electron per metal atom results in the loosely packed metal lattices of alkali metals. As a consequence of this :

1) They are soft metals and are malleable and ductile.
2) They have high lustre.
3) They have low melting and boiling points.
4) They have low heats of atomisation which are indicative of weak interatomic bonds inalkali metals.
5) They have low density because of their large atomic volume.

All of these properties can be accounted for in terms of their structure. The alkali metals crystallize with a body centred cubic lattice in which the lattice points are occupied by M^+ ions. The valence electrons (one from each atom) make up a sea of electron charge cloud which is spread allover the lattice. Since, these electrons are not fixed in positions, they can move freely throughout the metal and thus are responsible for the high electrical conductivity.

The silvery lustre of these metals can also be attributed to the presence of highly mobileelectrons of the metallic lattice. The softness, malleability and ductility which are exhibited by alkali metals can also be explained in terms of the binding forces operating in these metals. The force of attraction holding the metal lattices together is principally electrostatic attraction betweem metal ions (M^+) and the valence electron cloud. Since, these forces are uniform in all directions (non-directional), there are no preferred positions or orientations of metal ions. Therefore, metal ions can be easily moved from one lattice position (or layer) to another.

Trend in the group As we move down the group, atomic volume, atomic radii and ionic radii increases. Down the group, the large atoms exert weaker attraction on one another because electrostaticforces decrease with increasing internuclear distance. Therefore, as we go down the group, the metals become soft, their melting and boiling point as well as heats of atomisation decrease.

Ex. Which of the following alkali metals has the lowest m.p. (°C) ?

Li, K, Cs

Sol. Cs

Ex. Which of the following has the maximum E° (M^+/M) value ?

Li, K, Cs

Sol. Li

Ex. Which of the following is a better reducing agent ?

Na or Cs

Sol. Cs

Ex. Which of the following alkali metals is the most electropositive ?

Li, Na, K,Rb and Cs

Sol. Cs

Ex. Both Na and K are present in equal abundance in the earth's crust, but Na is about 30 times as abundant as K in the oceans. Why?

Sol. Because K is bigger in size than Na, therefore, potassium salts with larger anions are lesssoluble and are thus retained behind while more soluble Na salts carried to the sea. Also K is more tightly bound with the complex silicates and alumino silicates in the soil and are thus retained.Potassium ions are preferentially absorbed by plants Na ions proceed to the sea.

Chemical Properties

The first ionisation energies and electronegativities of alkali metals are the lowest of all the elements. Moreover, the heats of atomisation of these elements are relatively low. These properties contribute to the high chemical reactivity of these elements especially towards electronegative elements such as chlorine and oxygen. Their important chemical properties are discussed below :

1) Oxides, Peroxides and Superoxides

When alkali metals are burnt in a free supply of air, the main product depends on the metal :

Li forms mainly the oxide, Li_2O, Na forms the peroxide, Na_2O_2 and the heavier elements K, Rb, Cs form the superoxide, MO_2. However, under the appropriate conditions pure compounds M_2O,M_2O_2 and MO_2 can be prepared for all the alkali metals.

i) **Oxides**

a) Pure Li_2O is prepared by thermal decomposition of Li_2O_2

$$Li\ O \xrightarrow{450°C} Li\ O + {}^{1}O$$
2 2 2 2 2

(ii) Sodium oxide (Na_2O) can be prepared by any one of the following reactionsNa O + 2Na

$\xrightarrow[2\ \ 2]{}$ 2Na O

NaOH + Na $\longrightarrow$ Na O + $\overset{2}{1}$ H

2 2 2

NaNO

+ 3Na $\longrightarrow$ 2Na O + ^{1}N

2 2 2 2

b) The normal oxides of other alkali metals (K, Rb and Cs) can be prepared by similar reactions. Li_2O and Na_2O are white, K_2O yellowish white, Rb_2O bright yellow and Cs_2O orange in colour. The compounds are stable towards heat and decompose only slightly below 500ºC. The oxides M_2O (Li, Na, K, Rb) have the antinuorite structure. The structure is related to CaF_2 (fluorite) structure but with the sites occupied by cations and anions are interchanged.

ii) **Peroxides**

The peroxides contain

O^{2-} (isoelectronic to F) 2 2

a) Li_2O_2 is prepared by the reaction of LiOH▥H_2O with H_2O_2 and dehydration of the subsequent hyperperoxide by gentle heating under reduced pressure.

$$LiOH▥H_2O + H_2O_2 \longrightarrow LiOOH▥H_2O + H_2O$$

2LiOOH▥H_2O

$$\xrightarrow{\Delta} Li_2O_2 + H_2O_2 + H_2O + H_2O$$

(White solid)

b) Na_2O_2 is prepared by oxidizing Na to Na_2O in a limited supply of air and then allowingit to react with more O_2 to give a pale-yellow powder of Na_2O_2.

$$2Na + \frac{1}{2}O_2 \longrightarrow Na_2O \xrightarrow{\frac{1}{2}O_2} Na_2O_2$$

(Pale – yellow)

c) The heavier alkali metal peroxides cannot be prepared by the above method because of their further oxidation to superoxides, MO_2. They are best prepared by the quantitative oxidation of the metals in liquid NH_3.

$$O \xrightarrow{e} \quad e$$

(e_{am} = electron in ammonia)

Sodium peroxide (Na_2O_2) finds use in industry as a bleaching agent for fabrics, paper, pulp, wood, etc. It is also used as a powerful oxidizing agent. Its reactions with CO and CO_2 gives Na_2CO_3.

$$Na_2O_2 + CO \longrightarrow Na_2CO_3$$

$$Na_2O_2 + CO_2 \longrightarrow Na_2CO_3 + \frac{1}{2}O_2$$

Ex. Why sodium metal forms peroxide in preference to its oxide?

Sol. The positive charge density around Na (relative to small Li) is small and so it is unable to provide stability to a high electron density oxide ion (O^{2-}). However, it can easily hold on to relatively large peroxide ion $(O - O)^{2-}$. The positive charge density of Na^+ is strong enough to prevent further oxidation of peroxide to superoxide (O_2^{-}) iom

iii) **Superoxides**

The superoxides contain the paramagnetic O_2^{-} ion.

a) LiO_2 is prepared by matrix isolation experiments at 15 K.

b) NaO_2 is prepared by reacting Na with O_2 at 450°C and 150 atm pressure.

c) Heavier alkali metals form KO_2 (orange), RbO_2 (brown) and CsO_2 (orange) as normal products when these elements are burnt in air. The heavier peroxides show the tetragonal CaC_2 structure.

Ex. Account for the increasing stability of peroxide and superoxides as the size of the alkali metalions increases.

Sol. It may be explained in terms of the Stabilization of the larger anions. This may be attributed to increasing lattice energy effects.

Distinctive Reactions between The Various Oxides

The various oxides are readily hydrolysed by water.

$$M_2O + H_2O \longrightarrow 2M^+ + 2OH^-$$

$[O^{2-} > O^-]$ by larger cations.

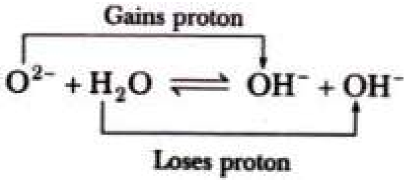
$$M_2O_2 + 2H_2O \longrightarrow 2M^+ + 2OH^- + H_2O_2$$

$$2MO_2 + 2H_2O \longrightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$

The different types of oxides can be identified by these reactions.

ii) Hydroxides

The normal oxides contain the oxide ion, O^{2-} which is an extremely strong base. Hence, they react with water to form hydroxide be proton exchange as :



The alkali metal hydroxides are the strongest bases known. The strength of a base depends on the separation of hydroxide ion from the cation. Two factors are mainly responsible for the separation of hydroxide ion from cation as :

i) **Polarity of Bond :** The greater the polarity of the bond, the greater is the ease of ionisation. The alkali metal hydroxides do not greatly differ in polarity and this factor is not of much significance here.

ii) **The Internuclear Distance between The Oxygen of The Hydroxide and The Metal Atom**

Since, the cation size increases from lithium to cesium, hence, inter-nuclear distance increases with increasing atomic number of the metal. This results in greater separation of hydroxide ion from the metal ion. Consequently, the separation between the metal ion and OH^- ion becomes easier, Therefore, the strength of the bases increase from LiOH to CsOH.

2) Halides

Alkali metals react vigorously with halogens to form metal halides of the general formula MX where M is an alkali metal ion and X is the halide ion. Alkali metal halides are "ideal" ionic compounds, i.e., their physical and chemical properties can be interpreted with reasonable accuracy on the assumptionthat ions are present in solid state.

The heats of formation (ΔH_f) decrease in magnitude through the series MF, MCl, MBr and MI (M = alkali metal ion). This may be attributed to the increase in repulsion of anions and the coulombic force of attraction decreases due to increase in interionic distance.

Ex. The reaction $2MX + X'_2 \rightarrow 2MX' + X_2$ proceeds only if X'_2 is lighter than X_2.Why ?
Sol. This is true because only in this situation ΔH will be negative.

Ex. The reaction $MBr(s) + M'(s) \rightarrow M'Br(s) + M(s)$ proceeds only if M' is heavier than M. Why?
Sol. This is true because ΔH will be negative when a heavier metal atom replaces M. Heat of formation is more negative for a heavier metal bromide.

The structure and stability of alkali metal halides are determined in part by the lattice energies and radius ratio effects as discussed below :

i) **Lattice Energy Effect :** It is observed that lithium fluoride is insoluble in water whereas fluorides of other alkali metals are soluble. This is because the small lithium cation is in combinationwith small fluoride anion. This results in a high value for the lattice energy of LiF and thus it does not dissolve in water. LiCl has exceptionally low melting point. LiCl lattice is very unstable because of the very small size of the Li^+ ion. The $Li^+/\ Cl^-$ radius ratio is 0.33, which is much below the minimum (0.414) requiredfor adopting NaCl type structure.

ii) **Radius-Ratio Effects :** Alkali metal halides furnish a beautiful example of how coordination number increases with an increase in the size of the cation. The radius ratio in CsCl (Cs^+/Cl^- = 0.93) allows a coordination number 8 while radius ratio for NaCl ($Na^+/\ Cl^-$ = 0.52) allows a coordination number of 6. Lithium, potassium and rubidium also exhibit coordination number 6 in their chlorides, though theoretically lithium should show coordination number 4 only. This anomalous behaviour of lithium is thought to be due to more favourable lattice energy acquired by achieving a higher coordinationnumber.

3) Carbonates

All alkali metals form carbonates of the formula, M_2CO_3. The stability of alkali metal carbonates increases as we move down the group. Lithium carbonate, Li_2CO_3 is unstable and decomposes on heating.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

The instability of lithium carbonate is due to small size of Li^+ ion which cannot stabilize large sizedcarbonate ion. On the other hand, Li^+ ion forms stable compound with small O^{2-} ion.

4) Hydration of Alkali Metal Ions

M^+ (aq)	Li^+(aq)	Na^+(aq)	K^+(aq)	Rb^+(aq)	Cs^+(aq)
Hydration energy ; kcal mol	– 121	–95	– 76	– 69	– 62

Alkali metal ions in general show low heats of hydration (as compared to other metal ions) because they possess low charge density, i.e., low charge to radius ratio. The ability to conduct electric current depends upon the size of the hydrated ions. Since, lithium is the most heavily hydrated, it moves slowly under the effect of electric current and thus exhibits the lowest conductivity of all alkali metal ions. On the other hand, Cs atom though the largest atom, is the least hydrated and conducts current most efficiently. Their conductivity power varies in the order : Cs^+(aq) > Rb^+(aq) > K^+ (aq) > Na^+ (aq) > Li^+ (aq)

Ex. Among alkali metal halides the lattice energy (U_0) is greatest for LiF and smallest for CsI. Explain.

Sol. In the expiession for lattice energy, r_0 (the internuclear distance) plays a predominant role. Since, r_0 has the smallest value for LiF and the largest value for CsI and so this accounts for the variation in the values.

Ex. ΔH^o_f values are much smaller for the hydrides of alkali metals than for the corresponding alkali metal halides. Explain.

Sol. The lower ΔH^o_f values for MH may be attributed to the much higher heat of dissociation of H_2 compared to X_2.

5) Solution of Alkali Metals in Liquid Ammonia

If a small piece of an alkali metal is dissolved in liquefied ammonia, the latter becomes blue in colour. If more alkali metal is added in the ammonia, a point is reached when a bronze coloured phase separates out and floats on the blue solution. Further addition of metal results in the disappearance of blue solution and its complete conversion to bronze solution. Evaporation of ammonia from the bronze solution allows one to recover unchanged alkali metal. This unusual behaviour has fascinated chemists since its in 1864. The interpretation is as follows.

Properties of Blue Solution

The blue solution exhibits the following characteristics :

(i) Its colour, which is independent of the metal.

(ii) Its density, which is very similar to that of pure ammonia.

(iii) Its conductivity, which is in the same range as those of other electrolytes in ammonia.
(iv) Its paramagnetism, indicating unpaired electrons.
(v) Its reversible nature.
(vi) Its strongly reducing nature.

This has been interpreted in terms of ionisation of alkali metal to form alkali metal cations and electrons which are solvated by ammonia.

$$M \xrightarrow[NH_3]{\text{Dissolve in}} M^+(\text{amm.}) + \left[e(NH_3)_x\right]^-$$

The dissociation into cation and electron accounts for the electrical conductivity. The presence of a large of number of unpaired electrons is responsible for the paramagnetism. The blue colour results due to an absorption band that has a maximum at 5000 Å. The absorption results due to the absorption of photons by the electrons as they are excited to a higher energy level. The dilute solutions thus consist of **free electrons** (thus showing reducing behaviour); such solutions are metastable and when catalysedgive hydrogen and amide

$$\left[e(NH_3)_x\right]^- \xrightarrow[\text{(catalyst)}]{Fe_2O_3} NH_2^- + H_2 + (x-1)NH_3$$

Amide

Properties of Bronze Solution

The bronze solution show the following characteristics :
(i) bronze colour with a metallic lustre;
(ii) very low densities;
(iii) conductivities in the range of metals;
(iv) magnetic susceptibilities similar to those of pure metals.

All these properties are consistent with a model describing the solution consisting of aggregates of metal atoms (M_2, M_3, etc.) which are moved apart by interspersed molecules of ammonia. The electrons behave essentially in a manner as they would in metals.

Reducing Properties of Solution of Alkali Metals in Liquid Ammonia

These metal solutions are extremely strong reducing agents, much stronger than could exist in water because the oxidizing power of water is greater than that of ammonia. Some important examples of their reducing action are :
(a) Reduce metal halides to free metal.

(b) Reduce sodium nitrite to sodium hydronitrite.

(c) Remove halogen atom from organic molecule.

$$C_2H_5Cl + 2e^- \longrightarrow C_2H_5^- + Cl^-$$

(d) Remove hydrogen atom from acetylenic hydrocarbons.

$$CH_3C \equiv CH + e^- \longrightarrow CH_3C \equiv C^- + H$$

(e) Solutions of alkali metals in liquid NH_3 form alkali metal superoxides and peroxide,

$$O_2 \xrightarrow[\text{am}]{e^-} O_2^- \xrightarrow[\text{am}]{e^-} O_2^{2-}$$

(f) Transition metals are reduced to unusually low oxidation states, i.e.,

$$K_2[Ni(CN)_4] + 2K \xrightarrow[240K]{NH_3} K_4[Ni(CN)_4]$$

$$[Pt(NH_3)_4Br_2] + 2K \xrightarrow[240K]{NH_3} [Pt(NH_3)_4] + 2KBr$$

Ni^{II} and Pt^{II} are reduced to Ni(0) and Pt(0), respectively.

(g) Salts of several main - group elements are reduced to form polyanions such as $Na_4[Sn_4]$, $Na_3[Sb_9]$, $Na_3(Sb_7)$, etc.

(h) Species containing hydrogen react with liberation of hydrogen gas

$$GeH_4 + e^- \xrightarrow{\text{am}} GeH_3^- + \frac{1}{2}H_2$$

$$AsH_3 + e^- \xrightarrow{\text{am}} AsH_2^- + \frac{1}{2}H_2$$

$$EtOH + e^- \xrightarrow{\text{am}} EtO^- + \frac{1}{2}H_2$$

These reactions have great synthetic utility. These solutions have been developed as versatile reducing agents for organic compounds that are otherwise difficult or impossible to reduce.

6) Solutions of Alkali Metals in other Solvents

The alkali metals are also soluble in aliphatic amines and hexa-methylphosphoramide, $P(NMe_2)_3$ and give coloured solutions which are also strong reducing agents. However, these solutions are less stable easily decompose into amide and H_2. Larger alkali metals K, Rb and Cs give solutions in THF, ethylene glycol, dimethyl ether and act as reducing agents.

Lithium in Relation to Its Congeners

It is observed from the above discussion of the properties of alkali metals that lithium differs from its congeners far more than the congeners differ amongst themselves. The main reasons for the different properties of lithium as compared to other alkali metals are:

i) The extremely small size of lithium atom and its ion.

ii) The polarizing power of lithium ion is the greatest of all the alkali metal ions which results in its tendency towards solvation and covalent bond formaton. The increased covalent character of its compound makes them more soluble in organic (non-polar) solvents. However, other alkali metal salts are insoluble in organic solvents.

iii) Lithium has the highest ionisation energy and electronegativity when compared to other alkali metals.

Difference between Lithium and Its Congeners

Main points of difference between lithium and its congeners are given below :

(i) Lithium is harder and lighter than other alkali metals.

(ii) Its melting and boiling points are high and it can be melted in dry air without losing its brilliance.

(iii) Due to its high ionization energy it does not react with oxygen below 373 K.It reacts slowly with water or with liquid bromine.

(iv) Due to its small size, it readily combines with small anions such as hydrides, carbides and nitrides to form stable compounds. The combination of two elements both with small ions confers a high lattice energy on the crystal. These reactions of lithium are highly exothermic.Lithium hydride is far more stable to heat than other alkali metal hydrides.

(v) Due to its small size lithium combines with oxygen to form lithium oxide while other alkali metals form peroxides and superoxides.

(vi) Lithium oxide dissolves in water quietly while others do it more energetically.

(vii) Lithium hydroxide is sparingly soluble in water and is a weak base.

(viii)Lithium hydroxide decomposes at red heat forming Li_2O whereas other alkali metalhydroxides sublime unchanged as $(MOH)_2$.

(ix) Lithium chloride is deliquescent and is soluble in alcohol as well as pyridine.

(x) Lithium decomposes on heating to form Li_2O and CO_2. The size of Li^+ makes Li_2O lattice more stable as compared to Li_2CO_3 lattice. However the bigger size of the other alkali metal ions make the M_2O lattices less stable as compared to the M_2CO_3 lattice and hence they do not decompose.

(xi) Lithium nitrate on heating forms Li_2O, NO_2 and O_2 while other alkali metal nitrates form nitrites and oxygen.

$$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$
$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

The explanation for the decomposition of lithium nitrate into lithium oxide and not lithium nitrite is the same as given for the decomposition of lithium carbonate.

(xii) When acetylene gas is passed over heated lithium metal, it does not form lithium acetylidewhile other alkali metals form metal acetylides on reaction with acetylene.

(xiii)Lithium hydrosulphide, LiSH is thermally unstable while the hydrosulphides of other alkali metals are stable can without extensive decomposition.

(xiv) Some of the lithium salts such as Li_2CO_3 , Li_3PO_4 and LiF are insoluble in water while the corresponding compounds of other alkali metals are soluble.

(xv) Lithium us the only alkali metal which combines with silicon when the two are heated together to form lithium silicide. Li_6Si_2-dark violet, hygroscopic crystals.

(xvi) Lithium when heated in ammonia forms imide, Li_2NH while other alkali metals form amides, MNH_2.

(xvii) $LiClO_4$ is remarkably soluble in alcohol, acetone, and ethyl acetate due to the strong solvation of Li^+ ion whereas perchlorates of other alkali metals are almost insoluble in alcohol, acetone and ethyl acetate.

(xviii) Li_2SO_4 is the only alkali metal sulphate which does not form double salts such as alums.

(xix) Lithium ion shows a tendency to form complexes with ammonia, water (to form hydrates) and forms a large number of organo lithium compounds.

Diagonal Relationship of Lithium with Magnesium

One of the important features of elements of second period of Periodic Table is that they resemble with the element at their lower right in the third period (i.e., diagonally opposite element) more than their own congeners. The diagonal relationship is best illustrated by the following pairs of elements of the Periodic Table.

Li Be B C

Na Mg Al Si

The reasons for similarities between the diagonally opposite members are :

(a) The elements become more electropositive down a group but less electropositive from left to right. This results in the similarity in the electropositive character of the diagonally opposite elements.

Decreasing electropositive character

Increasing polarizing power

(b) Similarly, on moving from left to right, charge on the ions increases but their size decreases which causes an increase in the polarizing power of the ions. However, on moving downa group the size increases and polarizing power decreases. On moving diagonally these two effects partly cancel each other so that the behaviour of these elements is quite similar. It is interesting to note that in spite of their different valencies, the type and strength of the bonds formed and the properties of their compounds are often very similar

Lithium resembles more with its diagonally opposite element magnesium than with the other members of the metals as is evident from the following points :

(i) The radii of Li^+ (60 pm) and Mg^{2+} (65 pm) are almost equal.

(ii) The atomic radii of Li (122 pm) and Mg (136 pm) are comparable.

(iii) The atomic volumes of solid Li (12.97 cc) and Mg (14.00 cc) are quite similar.

(iv) Electronegativity of Li (1.00) and Mg (1.20) are quite comparable.

(v) Polarizing power

$$\frac{\text{Ionic charge}}{(\text{Ionic radius})^2} \rightarrow \text{of both the element is similar.}$$

(vi) ⍰H,(enthalpies of vaporization) of both these elements are comparable.

(vii) Lithium has a high boiling point (1609 K) which is comparable with that of magnesium (1373 K).

(viii)Lithium is the hardest of all the alkali metals but is comparable to that of magnesium.

(ix) Lithium is the only alkali metal which on burning in an atmosphere of oxygen forms a normal oxide, Li_2O and not a peroxide or superoxide. Magnesium ribbon when burnt in oxygen also forms magnesium oxide, MgO.

(x) Out of all the alkali metal carbonates and nitrates, only Li_2CO_3 and $LiNO_3$ are unstable and decompose on eating forming its oxide. Similarly, $MgCO_3$ and $Mg(NO_3)_2$ on heating form MgO.

(xi) Among the alkali metals only lithium when heated in an atmosphere of nitrogen forms an ionic nitride, Li_3N. Magnesium when heated in nitrogen also forms an ionic nitride, Mg_3N_2.

(xii) Of all the alkali metal hydroxides, only lithium hydroxide is less soluble in water, less basicand decomposes on heating to form Li_2O. Magnesium hydroxide is also sparingly soluble,less basic and decomposes on heating to form MgO.

(xiii)The lithium ion and its compounds are more heavily hydrated than those of the other alkali metal ions. Most of the magnesium compounds are also hydrated, e.g $MgCl_2$⍰$6H_2O$; $MgSO_4$⍰ $7H_2O$.

(xiv) Li_2CO_3, LiF, Li_3PO_4 are the only alkali metal salts which are insoluble in water. The corresponding magnesium compounds are also insoluble in water.

(xv) Both the elements directly combine with carbon to form carbides.

(xvi) Of all alkali metal chlorides, only LiCl is soluble in organic solvents such as pyridine and alcohol. Magnesium chloride is also soluble in alcohol.

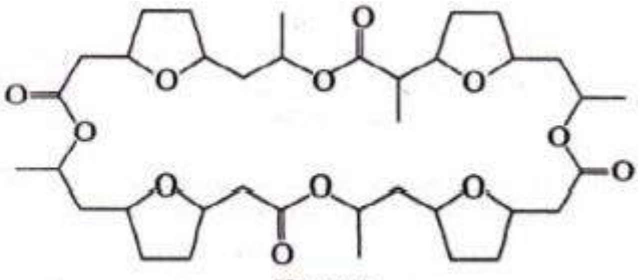
(xvii) Lithium perchlorate and magnesium perchlorate are extremely soluble in alcohol.

(xviii) Due to their covalent nature, the complex hydrides of lithium and magnesium are soluble in organic solvents, e.g., $LiAlH_4$, RMgX are soluble in ether.

Coordination Chemistry of Alkali Metal Ions

Coordination chemistry as known for transition metals with conventional ligands (say NH_3) is lacking for both alkali metals (M^+) and alkaline earth metals (M^{2+}) due to their very weak coordinating (or complexing) ability. These metals ions were thought to be inadequate for complexation due to their small charge to size ratio. The lack of physico-chemical properties such as UV visible and magnetic properties which help to detect even weak metal-ligand interactions, was a significant reason for this delayed exploration of complexation ability of groups I and II metal cations.

Application of X-ray crystallography to the study of biologically important molecules, such as antibiotics showed that some of these molecules are involved in the complexation of M^+ (Na^+, K^+) or M^{2+} (Ca^{2+}, Mg^{2+}) ions. For example, the antibiotic nonactin functions by transporting potassium ions out of cells. This molecule prefers to bind K^+ ions over Na^+ ions, i.e., it is not only capable of binding a weakly coordinating K^+ but is also highly selective.

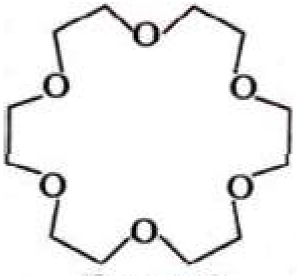


Nonactin

These studies revealed insight into the underlying parameters of **complexation and selectivity.** The stability of these natural complexes is attributed to a large number of donor sites present in a single molecule which can act (donate) simultaneously, i.e., wrap around the cation. The selectivity or preference of a ligand for a particular cation is determined by the size of the '**cavity'** generated by each ligand when it wraps around the metal cation. Several such studies on natural systems gave chemists an insight into the design of synthetic donor molecules which may be able to form complexes with M^+ and M^{2+} ions, i.e., which may be able to mimic the natural systems.

Synthetic Molecules (Macrocycles) that can Bind Alkali/Alkaline Metal Cations

Recent developments led to the synthesis of large-ring crown ethers. These compounds are cyclic polymers of the simple molecule ethylene glycol, $(OCH_2CH_2)_n$ and are given the name x-crown-y, where x is the total number of atoms in the ring and y is the number of oxygens. For example, the cyclic hexamer of ethylene glycol is 18-crown-6.

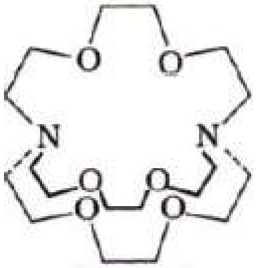


18-crown-6

The crown ethers have the ability to bind cations strongly and selectively. The crown ether, 18-crown-6 can solvate potassium cation. The interior of the crown ether is made up of donor oxygen atoms, but the exterior (boundary wall) is made of $-CH_2 - CH_2 -$ units, i.e., it has hydrocarbon properties. As a result, the complexed ion is soluble in non-polar organic solvents. For example, $KMnO_4$ which is normally insoluble in benzene, dissolves readily in this solvent in the presence of 18-crown-6.

In the last 20 years or so, a large number of synthetic crown ethers have been synthesized. A relationship between the structure of crown ether and its ability to solvate a particular cation has been observed. For example,18-crown-6 shows high affinity for K^+, 15-crown-5 for Na^+,and 12-crown-4 forLi^+. Measurement of molecular models of these molecules shows that the 'cavity size' for each molecule matches the ionic size of the cation which is strongly bonded by the molecule.

The molecules are said to "recognize" its most and this phenomenon is called **"molecular recognition".** More recent researches have yielded better preorganized ligands, like the diamino tetraether commonly called **cryptands** (macrobicyclic polyethers), which are even more selective than crown ether. Since, then hundreds of modifications of crown ethers (such as changing the ring size, kind of substituents, and the types of donor atom) and macropolycyclic (cage) compounds with unusual shapes have and their complexation properties have been investigated.



Cryptand

The reaction,

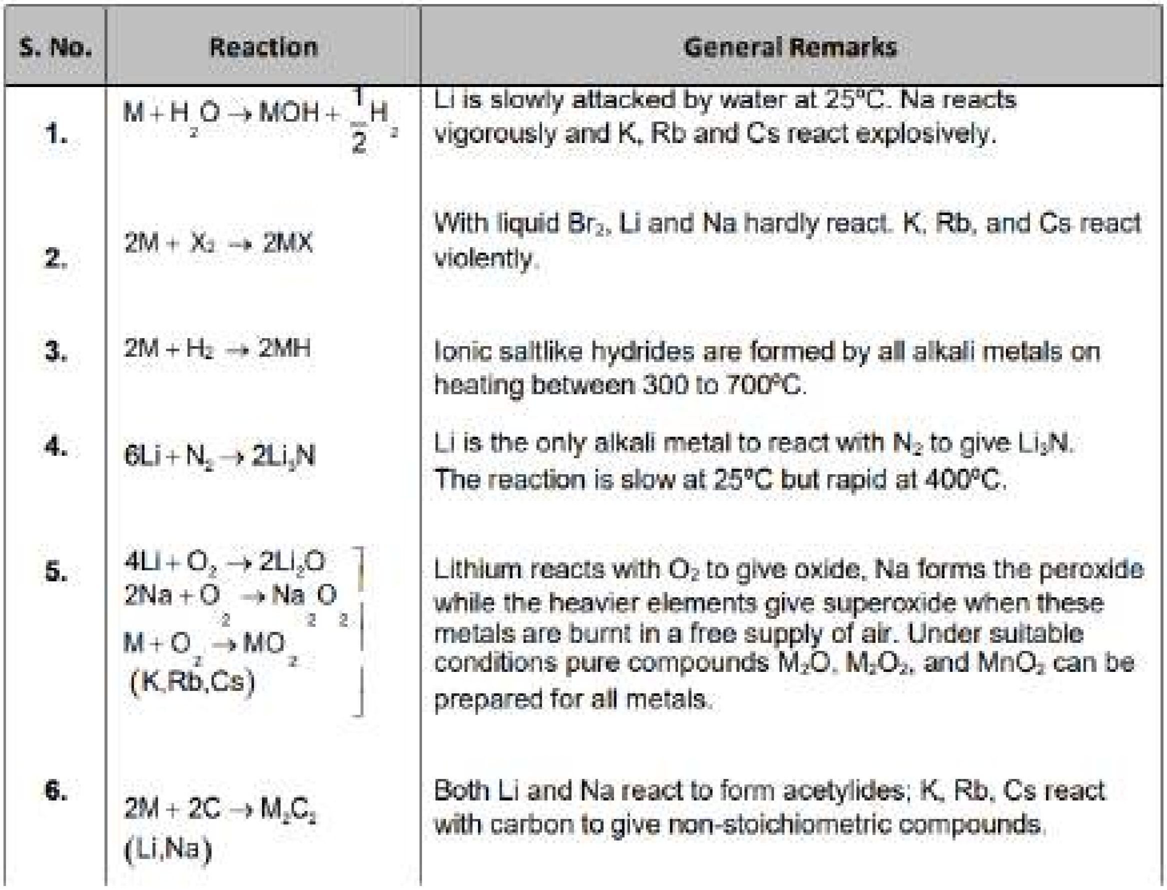
$2Na\ (g) \rightarrow Na^+\ (g) + Na^-\ (g)$ ...(5)

is endothermic ($\Delta H = + 4.38\ kJ\ mol^{-1}$). However, in the presence of a crypt ligand, in ethylenediamine (en) solution, the compound.

$[Na(2,2,2 - crypt)]^{+} Na^{-}$

is obtained which is stable at 263 K. The lattice energy and complexation of the Na+ by the crypt ligand compensates for the loss in energy in reaction (5) above Naturally occurring cyclic polypeptides can also complex alkali and alkaline earth metal ions and thus help in their transport in the living system.

The ability to complex and stabilize alkali metal cations has been helpful in the isolation of several new compounds which otherwise could not be synthesized. For example, the isolation of the compound $Cs^{+} Au^{-}$.This compound is unique as it is formed between two metals and not between a metal and a non-metal. Normally, we would expect that on mixing two metals, an alloy may be formed. The experimental technique involves stabilizing and isolating the alkali metal cation with macrocyclic polyether before reacting it with gold to give $[Ma (macrocycle)]^{+} Au^{-}$, etc.



S. No.	Reaction	General Remarks
1.	$M + H_2O \rightarrow MOH + \frac{1}{2}H_2$	Li is slowly attacked by water at 25°C. Na reacts vigorously and K, Rb and Cs react explosively.
2.	$2M + X_2 \rightarrow 2MX$	With liquid Br_2, Li and Na hardly react. K, Rb, and Cs react violently.
3.	$2M + H_2 \rightarrow 2MH$	Ionic saltlike hydrides are formed by all alkali metals on heating between 300 to 700°C.
4.	$6Li + N_2 \rightarrow 2Li_3N$	Li is the only alkali metal to react with N_2 to give Li_3N. The reaction is slow at 25°C but rapid at 400°C.
5.	$4Li + O_2 \rightarrow 2Li_2O$ $2Na + O_2 \rightarrow Na_2O_2$ $M + O_2 \rightarrow MO_2$ (K,Rb,Cs)	Lithium reacts with O_2 to give oxide, Na forms the peroxide while the heavier elements give superoxide when these metals are burnt in a free supply of air. Under suitable conditions pure compounds M_2O, M_2O_2, and MnO_2 can be prepared for all metals.
6.	$2M + 2C \rightarrow M_2C_2$ (Li,Na)	Both Li and Na react to form acetylides; K, Rb, Cs react with carbon to give non-stoichiometric compounds.

Chemistry of Alkaline Earth Metals

The elements of this group are also known as **alkaline earth metals** because of the following two reasons

(i) Their oxides are similar to those of alkali metal oxides, i.e., their oxides with water will give hydroxides which are alkalies.

(ii) The name "earth" was given by chemists to substances like alumina which remained unchanged even on heating. Calcium and barium oxides could stand very high temperatures, they were also called "earths". Thus, the metals calcium, barium and strontium came to be known as alkaline earth metals. The name is now applied to all the elements of group 2.

Occurrence

These elements do not occur in free state because of their highly reactive nature. Beryllium does not occur in abundance and is difficult to extract, therefore, it is an unfamiliar element. Magnesium and calcium occur in considerable aounts in the earth's crust. Strontium and barium do not occur as concentrated ores but are easy to extract and are familiar elements. Radium is extremely scarce and was first isolated by Madame Curie in 1910. Because of its radioactive nature, little is known about the chemistry of radium.

Extraction of Elements

Alkaline earth metals are quite reactive like the alkali metals. Therefore, the same difficulties arise during their isolation as were mentioned under 'extraction of alkali metals'. These metals are usually isolated by the electrolysis of their fused metal halides containing sodium chloride (which lowers the melting point and increases the electrical conductivity of alkaline earth metal halides).

Extraction of Beryllium Fichter method

Beryllium chloride is mixed with sodium chloride in the molar ratio 2 : 1. The mixture is fusedin a nickel crucible which serves as a cathode and a carbon anode is dipped into it. On electrolysis, the metal is collected at the cathode. Since, at high temperatures beryllium forms an alloy with nickel, therefore, nickel crucible is kept cooled by water.

The metal (when required for use in nuclear reactors) is purified by distillation in vacuum andis cast into rods under argon.

Physical Properties of Group 2 Elements

The atoms of the alkaline earth metals in the ground state contain two electrons in s-orbital outside a noble gas core. This similarity in the electronic structure of all these elements are reflectedand they are having similar physical and chemical properties.

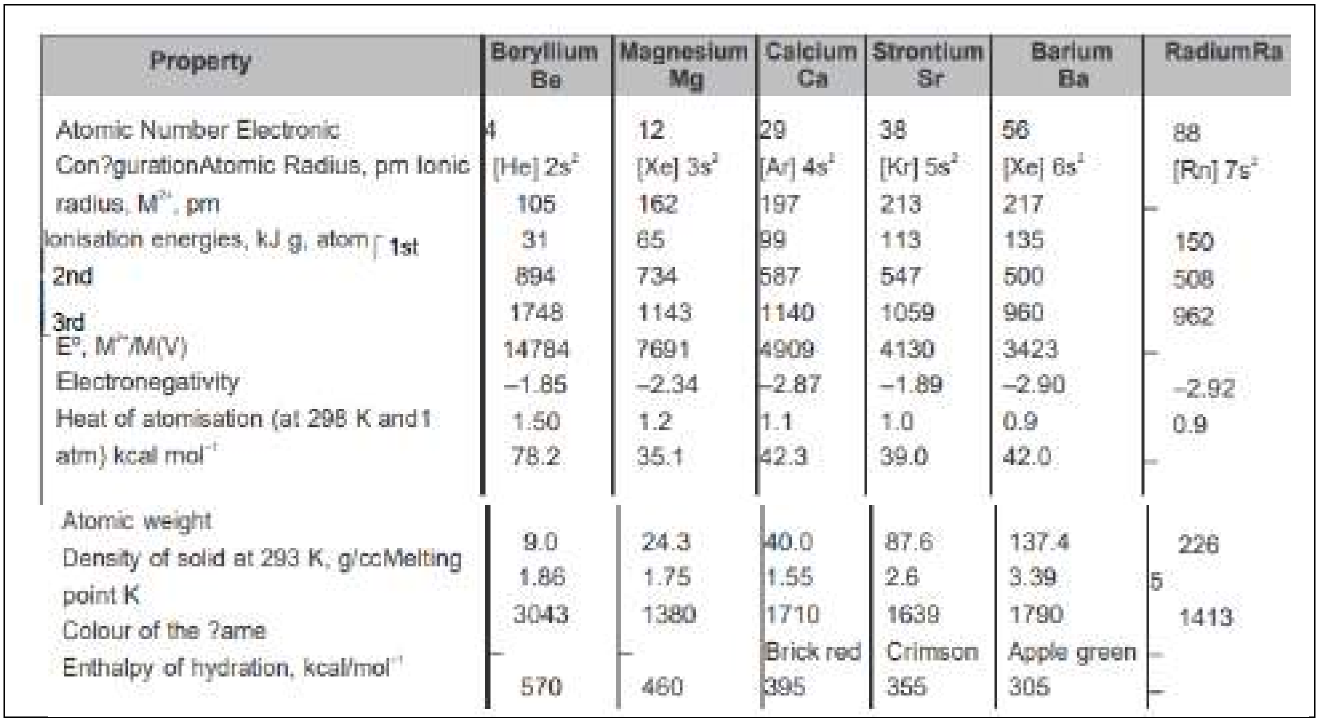
Important physical properties of alkaline earth metals are depicted in Table. A correlation between atomicstructure and physical properties of these elements are discussed below :

1) **Loose Binding of s-Electrons**

Just as in alkali metals, the noble gas core shields the s-electrons from direct attraction of the nuclear charge of alkaline earth metals. Therefore, the s-electrons are very loosely held. The consequencesof loose binding of s-electrons are :

(i) **Formation of Dipositive (M^{2+}) Ions :** The formation of predominantly M^{2+} ions of the alkaline earth metals can be explained in terms of their :

Table : Physical Properties of Alkaline Earth Metals



Property	Beryllium Be	Magnesium Mg	Calcium Ca	Strontium Sr	Barium Ba	RadiumRa
Atomic Number Electronic	4	12	29	38	56	88
Con?gurationAtomic Radius, pm Ionic	$[He]\ 2s^2$	$[Xe]\ 3s^2$	$[Ar]\ 4s^2$	$[Kr]\ 5s^2$	$[Xe]\ 6s^2$	$[Rn]\ 7s^2$
radius, M^{2+}, pm	105	162	197	213	217	–
Ionisation energies, kJ g. atom 1st	31	65	99	113	135	150
2nd	894	734	587	547	500	508
3rd	1748	1143	1140	1059	960	962
E°, M^{2+}/M(V)	14784	7691	4909	4130	3423	–
Electronegativity	–1.85	–2.34	–2.87	–1.89	–2.90	–2.92
Heat of atomisation (at 298 K and 1	1.50	1.2	1.1	1.0	0.9	0.9
atm) kcal mol^{-1}	78.2	35.1	42.3	39.0	42.0	–
Atomic weight	9.0	24.3	40.0	87.6	137.4	226
Density of solid at 293 K, g/ccMelting	1.86	1.75	1.55	2.6	3.39	5
point K	3043	1380	1710	1639	1790	1413
Colour of the ?ame	–	–	Brick red	Crimson	Apple green	–
Enthalpy of hydration, kcal/mol^{-1}	570	460	395	355	305	–

(i) electronic configuration;

(ii) ionisation energies; and

(iii) size

Fruther ionisation to give M^{3+} ions is ruled out because values for the third stage ionization energies are extremely high (See Table) and cannot be recovered by the formation of an additional bondin hypothetical MX_3 molecules.

Why group 2 metals do not form 'MX' type compounds?

The non-existence of MgCl (s) or MX may be attributed in the much higher standard enthalpyof formation of $MgCl_2$(s) or MX_2,

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$
$$\Delta H^o_f = -642 \text{ kJ mol}^{-1}$$

This suggest that $MgCl_2(s)$ is far more stable than the hypothetical MgCl(s) and it undergoes complete and rapid disproportionation.

$2MgCl(s) \rightarrow Mg(s) + MgCl_2(s)$

ΔH^o

disprop

$= -\,^{392} = -196\ kJmol^{-1}2$

These values also suggests that if some clever experiment can be thought which would hinder disproportionation of MgCl(s), then MgCl(s) may be isolated.

Trend in The Group

The first and second ionisation energies decrease from beryllium to barium because of increasing size of the atoms down the group. The higher values of the ionisation energies of radium indicate that in is slightly less reactive than barium. The reduced of radium is due to the fact that it comes after series of elements in the Periodic Table exhibit **lanthanide contraction.** Therefore, size of the radium atom also decreases resulting in an increase of the ionisation energy.

1)Reducing Agents : The high negative values of standard electrode potentials (E°) listed in Table indicate that in aqueous solution these elements are good reducing agent quite comparable to alkali metals and this is due to their large hydration energies. The high negative E° values of these elements mean that they all react vigorously with dilute acid, $H^+(aq)$. Those with very high negative values react vigorously with water also.

Trend in the group There is a gradual increase in the E° values of these elements indicating stronger tendency to act as reducing agents as we move down the group.

2) Colouration to The Flame : Except beryllium and magnesium, the chlorides of these elements produce characteristic colour in flame due to easy excitation of electrons to higher energy levels. In case of Be and Mg, the excitation energy is very high (because of their high ionization energies) and therefore their salts do not impart any colour to the flame.

Sizes of Atoms and Ions

The atoms and ions of alkaline earth metals are smaller than those of the preceding alkali metals because of the increased nuclear charge. This contraction in size results in higher ionization energiesof these metals as compared to alkali metals. In moving down, the group the sizes of atoms and ions increases as new shells are added.

Electronegativity

From beryllium to radium, electronegativity values decrease indicating greater tendency for ionic compound formation down the group. However, the electronegativity values of alkaline earth metals are very close to those of alkali metals. The high electronegativity of beryllium is suggestive of its tendencyto form covalent compounds.

The enthalpies of hydration for alkaline earth metal ions have two notable features

(i) The enthalpy of hydration decreases as the size of the ion increases.

(ii) More heat is evolved upon hydration (i.e., high enthalpy of hydration) of alkaline earth etal ions than the preceding alkali metal ions. This difference can be attributed to the increased chargeon the alkaline earth metal ions. Even though Na$^+$ and Ca^{2+} have nearly the same radii, the enthalpy of hydration of Ca^{2+} is nearly four times that of Na$^+$. This suggests that, in general, the hydration enthalpy is proportional to the square of the charge on the ion and this relation is obeyed in fact to a fair approximation.

It is the increase in hydration enthalpy with ionic charge that is responsible for the existence of the alkaline earth metal ions in the +2 oxidation state in aqueous solutions.

Ex. Although the energies required to (i) vaporize and (ii) ionize alkaline earth metal atom to the ions are much greater than those required to produce the M^{2+} ions of the group 2 elements, yet they form divalent salts.

Sol. The exceptionally high lattice energies in the solid salts (due to small dipositive ions) and thehigh hydration energies of the M$^+$(aq) ions compensate for the increased energies in steps (i)and (ii) above.

Chemical Properties

The combined effect of decreased size and increased charge make the alkaline earth metal ions far better polarizers or 'distorters' than the alkali metal ions. Their oxides are thus more covalent and their hydroxides are less basic than those of the alkali metals. The oxides of beryllium and magnesium are so tightly held together in the solid state that they are insoluble in water. Due to its extremely small size, beryllium has a unique chemical behaviour. It tends to be covalent in its compounds while magnesium tends to be partly ionic and in some compounds it is covalent. However,calcium, strontium, barium and radium form a closely allied series with the following systematic group trends in physical and chemical properties.

(i) Rates of reaction of the metals with hydrogen increases.

(ii) The tendency of the crystalline salts to form hydrates increases.

(iii) Solubilities of halides (except fluorides), sulphates and nitrates decreases.

(iv) Solubilities of halides in ethanol decreases.

(v) Thermal stability of peroxides, carbonates and nitrates increases. Compounds of alkaline earth metals are, in most instances, less soluble in water than the corresponding alkali metal compounds. This is mainly due to the following two reasons.

(vi) The alkaline earth metal ions are doubly charged.

(vii) The sizes of alkaline earth metal ions are smaller than the alkali metal ions. As a result of the above factors the lattice energies of the alkaline earth metal compounds are larger than those of the corresponding alkali metal compounds which lead to the decreased solubility of the compounds of alkaline earth metals in water.

(Lattice energy may be defined as the energy required to convert one mole of the ionic lattice into the gaseous ions. Lattices with smaller ions have higher lattice energies. Ionic compounds with higher lattices energies have low solubility because for dissolution, at first, energy equivalent to that of lattice energy has to be supplied to break the lattice into separate ions which then get solvated.)

Some important compounds of alkaline earth ìmetals are discussed below :

Oxides

Lattice energies of alkaline earth metal oxides are sensitive to the size of the M^{2+} ion because the sizes of O^{2-} ion and M^{2+} ions are quite comparable. Therefore, oxides of smaller alkaline earth metal cations are more stable than those of larger M^{2+} ions. It may thus be concluded that with decreasing size of the cation, the alkaline earth metal oxides are stabilized which favours the decomposition of their carbonates into oxides.

Preparation

(i) The oxides of alkaline earth metals are produced when these elements are burnt in air.

$2M(s) + O_2(g) \rightarrow 2MO(s)$

(ii) However, when magnesium is burnt in air, oxide formation is accompanied by the formation of the nitride :

$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

Both these reaction are highly exothermic and energy is released as both heat and light. When barium is heated in air or oxygen at 600°C, the peroxide, BaO_2 is obtained.

(iii) The oxides are also prepared by decomposing the carbonates by heat :

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)CaCO_3\ (s) \rightarrow CaO(s) + CO_2(g)$$

(Limestone) (Lime or Quickline)

Properties

(i) All the oxides are white crystalline solids. BeO shows excellent refractory properties.

(ii) The oxides of Mg, Ca, Sr and Ba, all have the sodium chloride structure (6 : 6) except BeO which has a Wurtzite (4 : 4) structure.

(iii) They are extremely stable. MgO has a very high melting point and it is insoluble in water. This may be attributed to the very strength of the interionic forces. The electrostatic force of attraction between an M^{2+} ion and an X^{2-} ion is **four** times the force between an M^{2+} ion and an X^{-} ion at the same distance apart. Their melting points and lattice energies decrease with increasing size of the cation, as we go down in the group.

(iv) The alkaline earth metal oxides are basic. They react with acids to give salts. For example,

$MgO + 2HCl \rightarrow MgCl_2 + H_2O$

(v) BeO and MgO are very tightly held in the solid state. BeO is very hard and has a very high melting point. It is amphoteric in nature. It reacts with strong acids to give $[Be(OH_2)_4]^{2+}$ ions. It reacts with strong bases to give $[Be(OH)_4]^{2-}$ ions. This behaviour may be attributed to the small size and doubly positive charge on the beryllium ion. BeO is insoluble in water. MgO reacts very slowly with water to give insoluble hydroxide :

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

Hydroxides

Calcium oxide reacts exothermally with water to give calcium hydroxide, $Ca(OH)_2$ or slaked lime. It has a low solubility in water.

$CaO(s) + H_2O(\ell) \rightarrow Ca(OH)_2(s)$; $\Delta H^o = -65$ kJ mol^{-1}

A saturated solution of $Ca(OH)_2$ is called limewater and it is often used as a test for CO_2. When CO_2 is bubbled through limewater, the solution turns cloudy, because of the formation of insoluble $CaCO_3$.

$Ca(OH)_2(aq) + CO_2(aq) \rightarrow CaCO_3(s) + H_2O(\ell)$

If the passage of CO_2 is continued further, the precipitate dissolves due to the formation of soluble $Ca(HCO_3)_2$.

$CaCO_3(s) + CO_2(g) + H_2O(\ell) \rightarrow Ca(HCO_3)_2(aq)$

Calcium hydroxide is a strong base. It is completely dissociated into its ions:

$Ca(OH)_2(s) \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$

Lime (CaO) and slaked lime ($Ca(OH_2$) are very important commercial bases because they are cheap and are easily available. Lime is used in making glass and cement. It is also used in removing SiO_2 and other acidic oxides in various metallurgical processes. For example, in the smelting of iron,it forms a slag such as $CaSiO_3$. Magnesium hydroxide, is only slightly soluble in water. A suspension of magnesium hydroxide in water is called **milk of magnesia.** It is used as an **antacid,** as a medicineto cure excess acidity in the stomach.

The solubility of hydroxides of alkaline earth metals in water increases as we go down the group. This may be attributed to a decrease in lattice energy.

The basicity of the oxides and hydroxides of the alkaline earth metals increases as we go down the group from Be to Ba. This may be attributed to the increasing electropositive character of the metal atom.The hydroxides of alkaline earth metals are less basic than alkali metal hydroxides. This may be attributed to the former having higher ionisation energies, smaller ionic sizes and bipositive on the ions.

$Be(OH)_2$	Amphoteric
$Mg(OH)_2$	Mildly basic
$Ca(OH)_2$	Moderate to strong bases
$Sr(OH)_2$	
$Ba(OH)_2$	Strong base; as strong as alkali metal hydroxides

Hydrides

All the elements of this group form hydrides of the type MH_2.

Preparation

1) BeH_2 cannot be prepared by the direct combination of Be and H_2. It is prepared by reducing $BeCl_2$ by LiH or $LiAlH_4$

$BeCl_2 + 2\ LiH \xrightarrow{Ether} BeH_2 + 2LiCl$

or $2BeCl_2 + LiAlH_4 \xrightarrow{Ether} 2BeH_2 + LiCl + AlCl_3$

2) BeH_2 and MgH_2 are also obtained by thermal decomposition of $Be(CMe_3)_2$ and $MgEt_2$, respectively.

3) The saline hydrides (CaH_2 SrH_2 and BaH_2) are prepared by direct reactions between the metals and H_2 between 150–250°C.

4) The hydrides of Ca, Sr or Ba can also be prepared by reduction of their oxides or halides with hydrogen.

Properties

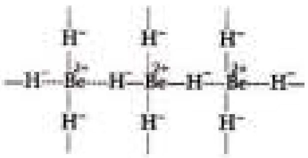
(i) BeH_2 is difficult to obtain pure. It is a covalent is polymeric compound, $(BeH_2)_n$. MgH_2 is partly ionic while the other hydrides are ionic solids.

(ii) They react with water, releasing H_2. They are used as reducing agents. $MH_2 + 2H_2O \rightarrow M(OH)_2 + H_2$

Calcium hydride is a strong reducing agent but not as powerful as the hydrides of alkali metals. It reacts with water, but the reaction is not vigorous. For its moderate reactivity towards water, CaH_2 is often used in the laboratories as a drying agent (particularly ethers) and is a portable source of hydrogen gas.

Structure

Beryllium hydride is a three-dimensional polymeric solid. It is quite ionic in nature and may be



thought of as formally made up of ionic Be^{2+} and H^- ions.

Alternatively, it may be considered to be an electron-deficient molecule, polymerized by meansof BeHBe 3-centre bonds (as in diborane) and its structure is probably similar to that of $BeCl_2$ or $BeMe_2$.

Halides Preparation

Alkaline earth metals combine directly with halogens at appropriate temperatures to form metal halides of the general formula MX_2. Beryllium chloride is prepared by the action of Cl_2 or HCl on the metal.Anhydrous $BeCl_2$ is obtained by the action of Cl_2 at high temperatures on a mixture of BeO and carbon.

$BeO + C + Cl_2 \xrightarrow{800^\circ C} BeCl_2 + CO$

Properties

Alkaline earth metal halides show a variety of structures depending upon the relative sizes of the ions. For example, beryllium ion having the **smallest size** (along with a high positive charge) exhibits covalent character in its halides. Beryllium chloride has lower melting and boiling points as well as much lower conductivity in the fused state than the other alkaline earth metal chlorides.

Beryllium chloride dissolves in water in an exothermic reaction to form $[Be(H_2O)_4]Cl_2$. Anhydrous $BeCl_2$ is insoluble in chloroform, carbon tetrachloride, CS_2 and benzene but readily soluble in diethylether, acetone, nitromethane, ammonia and amines. This is because the oxygen and nitrogen donor solvents form complexes with $BeCl_2$ of composition $BeC1_2 \cdot L_2$ (L = donor molecule).

Structure

Beryllium chloride, $BeCl_2$ has an unusual chain structure in the solid state. The chain arises because of free electron pairs on chlorine atoms which form intermolecular coordinative covalent bonds as shown in fig.

In this, Be is considered to be sp^3 hybridized with ClBeCl bond angle considerably lower than the tetrahedral angle (of 109.5°C) due to lesser repulsive interactions between Be atoms. Coordination number of Be is 4. In vapour phase, beryllium chloride exists as a dimer with sp^2 hybridisation (Fig.). **Beryllium atom is 3-coordinated.**

The dissociation of dimer into monomer is complete at higher than 750°C. At 560°C, the vapours contain 20% dimeric molecules and 80% monomer. In monomeric form $BeCl_2$ vapour is linear with sp hybridization (Fig.). Beryllium has C.N.= 2

Fig. : Structure of $BeCl_2$ vapour Beryllium chloride chain structure is broken by (i) Weak ligands

(L) like Et_2O, $(CH_3)_2\,C = O$, CH_3NO_2, etc., to form 4 coordinated molecular complexes $BeCl_2 \cdot L_2$ and by (ii) strong ligands (L) like H_2O, NH_3, py etc., to form ionic complexes $[BeL\ ]^{2+}$, $[Cl\ ]^{-}$. In both cases, beryllium is sp3 hybridization with tetrahedral arrangement of ligands. The fluorides of alkaline earth metals (except BeF_2) are because of the large values of their lattice.The chlorides, bromides and iodides of earth metals (except beryllium) are fairly ionic ionic character increases as the atomic number of the cation increases in the group. Most of the anhydrous alkaline earth metal halides in the fluorite type structure.

CarbidesPreparation

Alkaline earth metals from calcium to barium (or their oxides) when heated in an electric arc furnance with carbon form carbides of the general formula MC_2.

$$CaO + 3C \rightarrow CaC_2 + CO$$

Properties

1) These carbides are ionic acetylides
2) They have sodium chloride type structure with M^{2+} replacing Na^{+} replacing $[C = C]^{2}$ Cl^{-}
3) On reaction with water, they liberate C_2H_2 gas.

Carbonates

Calcium and magnesium carbonates are minerals and are the most important preparative sources of these metal.

1) **Thermal Stability :** Unlike the alkali metal carbonates (except Li_2CO_3), they decomposewhen heated

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

The stability of the carbonates of these metals increases on moving down the group. This is indicated by the values of the decomposition temperatures of these carbonates as given below :

$BeCO_3$ = 25°C, $MgCO_3$ = 540°C, $CaCO_3$ = 900°C,$SrCO_3$ = 1290°C, $BaCO_3$ = 1360°C

The instability of $BeCO_3$ may be attributed to strong polarizing effect of small Be^{2+} cation on the large polarizable CO_3^{2-} ion.

2) **Solubility :** Solubility of carbonates decreases as the size of the metal ion increases (thistrend is opposite to that observed for fluorides and hydroxides). This may be attributedto decrease in hydration energy of the M^{2+} ions as size increases. Since, the size of the carbonate ion is quite large (say 300 pm) variation in the size of the cation has little effect on lattice energy. Thus, for

carbonates the term hydration energy is crucial than lattice energy in determining their solubility in water.

Sulphates

Magnesium sulphate is soluble in water and crystallizes out as $MgSO_4 \cdot 7H_2O$ **(Epsom salt).** In medicine, it is used as a purgative. Calcium sulphate occurs in nature as the mineral gypsum, $CaSO_4 \cdot 2H_2O$. When gypsum is heated to a little above 100°C, it loses three quarters of its water of crystallization, giving a white powder,

$CaSO_4 \cdot \frac{1}{2}H_2O$, which is called **plaster of Paris.**

$$CaSO_4 \cdot 2H_2O \xrightarrow{Heat} CaSO_4 \cdot \frac{1}{2}H_2O + \frac{3}{2}H_2O$$

A paste of plaster of Paris and a little water quickly sets to a hard mass. The formation of the dihydrate is accompanied by an increase in volume which is very valuable in making plaster casts. **Solubility of Alkaline Earth Metal Sulphates** It decreases regularly from $BeSO_4$, and $MgSO_4$ which are very soluble in water to $CaSO_4$, which is only slightly soluble, to $SrSO_4$ and $BaSO_4$, which are insoluble.

Uses

Like all heavy elements barium absorbs X-rays strongly. If a suspension of $BaSO_4$ is swallowed, it coats the alimentary canal. The X-ray photographs of the alimentary canal can be recorded, which is otherwise transparent to X-rays. Barium is poisonous, but the solubility of $BaSO_4$ is extremely small that it passes through the body without causing any ill effects.

Limestone Caves, Stalactites, and Stalagmites

Natural water is slightly acidic as it contains dissolved CO_2.

$$2H_2O + CO_2 \rightleftharpoons H_3O^+ + HCO_3^-$$

This acidity is enough to dissolve insoluble $CaCO_3$ rocks into soluble $Ca(HCO_3)_2$.

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

In an underground stream, the soluble $CaHCO_3$ is continually washed away. The above equilibrium is never achieved and so $CaCO_3$ continues to dissolve, and thus over a very long time underground caves are formed. The most impressive and beautiful features of these caves is the formation of stalactites, and stalagmites. They are formed by the reverse reactions by which the caves are first formed. Water passing through limestone cave is saturated with $Ca(HCO_3)_2$. It seeps through to the roof of a Cave and forms a drop hanging from the roof. The water slowly evaporates, some CO_2 is lost, the equilibrium shifts to the left (as per Le-Chatelier's principle) and Ca^{2+} ions are redeposited as $CaCO_3$.

This slow process over a long period results in the formation of conical shaped stalactites. The same drop of watermay fall from the roof to the floor, where it evaporates slowly again depositing a small amount of $CaCO_3$. If drops keep falling at the same spot, over a period of time, a stalagmite is built up. Sometimes, it may grow sufficiently to Join a stalactite to form a column.

Table : Some Typical Reactions of Group 2 Elements

Reaction	General Remarks
$M + 2H_2O \rightarrow M(OH)_2 + H_2$	Be reacts with steam; Mg with hot water and Ca, Sr and Ba react rapidly with cold water.
$M + 2HX \rightarrow MX_2 + H_2$	All the metals react with acids, liberating hydrogen.
$Be + 2NaOH \xrightarrow{2H_2O} Na_2[Be(OH)_4] + H_2$	Be is amphoteric.
$2M + O_2 \rightarrow 2MO$	Normal oxide is formed by all group members with excess oxygen.
$Ba + O_2 \rightarrow BaO_2$	Ba also forms the peroxide.
$M + H_2 \rightarrow MH_2$	Ionic 'salt-like' hydrides are formed at high temperatures by Ca, Sr, and Ba.
$3M + N_2 \rightarrow M_3N_2$	All the metals form nitrides at high temperatures.
$3M + 2P \rightarrow M_3P_2$	All the metals form phosphides at high temperatures.
$M + S \rightarrow MS$	All the metals form sulphides.
$M + F_2 \rightarrow MF_2$	All the metals form fluorides.
$M + Cl_2 \rightarrow MCl_2$	All the metals form chlorides.
$M + Br_2 \rightarrow MBr_2$	All the metals form bromides.
$M + I_2 \rightarrow MI_2$	All the metals form iodides.
$M + 2NH_3 \rightarrow M(NH_2)_2 + H_2$	All the metals form amides at high temperatures.

Ex. When Mg is burnt in air it forms a white product which when dissolved in water smells ofammonia. Explain.

Sol.

$$3Mg + N_2 \rightarrow Mg_3N_2$$

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$$

Uses of Alkaline Earth Metals

1) **Beryllium** It is used in X-ray windows as scavenger in alloys, as moderator in fission reactions.

2) **Magnesium** It is used in the manufacture of alloys; as reducing agent, e.g., extraction of uranium; in Grignard's reagent and in containers for nuclear fuels.

3) **Calcium** It is used as scavenger, e.g., removal of water from ethanol; air from radio valves.

4) **Strontium and Barium** They are used as scavengers.

Diagonal Relationship of Beryllium with Aluminium

It has already been mentioned that one of the distinguishing features of the elements of the second period of the Periodic Table is that they resemble more with their diagonally opposite members than their own congeners. The anomalous behaviour of beryllium is mainly due to its tiny size (size of beryllium ion is 1/8th that of magnesium ion and 1/64th that of barium ion). Therefore, it does not resemble with its congeners but there is a great similarity in the physical and chemical properties of beryllium and aluminium. In fact, the resemblance between beryllium and aluminium is so that they are considered to be ideal diagonal partners in the Periodic Table. Some of the important points of similaritiesare discussed below :

i) Though the ionic radius of beryllium (31 pm) is considerably lesser than that of aluminium(50 pm) the charge/radius ratio for the two ions are quite close.

	Be	**Al**
Charge on the ion	+2	+3
Ionic radius (pm)	31	50
Charge/radius ratio	6.4	6.0

Since, charge/radius ratio is a measure of the deforming power of the ions, therefore, itcan be conclude that both Be^{2+} and Al^{3+} have similar deforming powers.

ii) Electronegativities of both the elements are 1.5.

iii) Enthalpy of vaporization for both is 293 kJ.

iv) The standard electrode reduction tentials of both are of the same order [Be^{2+}/Be, –1.70; Al^{3+}/Al, –1.67 V].

v) In nature, both occur together in beryl $3BeO \cdot Al_2O_3 \cdot 6SiO_2$.

vi) The chemistry of berylliuna is expected to be dominated by its tendency to form covalent compounds because of its tiny size and high charge. Thus, compounds of beryllium have lower melting points, are soluble in organic solvents and get hydrolysed by water. In this respect, they resemble closely with compounds of aluminium. Magnesium does show some tendency to form covalent compounds but other alkaline earth metals do not form covalent compounds.

vii) Out of the alkaline earth metals, only beryllium is resistant to the attack of conc. HNO_3 owing to the formation of an inert and imprevious oxide film on its surface. Aluminium is also resistant to the attack of conc. HNO_3 due to a similar oxide film formation on its surface.

viii) Among the alkaline earth metals, only beryllium forms beryllate on reaction with caustic alkalies with the evolution of hydrogen. Similarly, aluminium forms aluminate ions.

ix) Out of the oxides of alkaline earth metals, only beryllium oxide is extremely hard, non- volatile, has very high melting point and is amphoteric. Aluminium oxide shares all these properties.

x) Like anhydrous aluminium chloride, anhydrous beryllium chloride is soluble in organic solvents; catalyses Friedel-Crafts reaction and behaves as a Lewis acid.

xi) Out of the alkaline earth metal carbides, only beryllium carbide yields methane on hydrolysis. Similarly, aluminium carbide gives methane on hydrolysis.

$$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4 Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$$

xii) Among the alkaline earth metals, only beryllium forms many chelate type complexes specially with oxygen donors. Aluminium also forms metal chelates with oxygen donors.

Structure of Metallic Crystals

Before we discuss the structures of metallic crystals, it would be useful to discuss the close - packing of identical spheres in space. We shall soon appreciate that metals adopt structures which closely resemble the arrangement acquired by hard spheres in three-dimensional space. It is assumed that atoms in metals behave like hard spheres.

The Close-Packing of Spheres

In most of the structures encountered in inorganic chemistry, it is observed that the structures assumed are simply a consequence of the most efficient packing of the units involved. Since, these unitsmay be either atoms, ions or molecules of **approximately spherical shape,** it may be of interest to study the most efficient ways of packing of hard spheres of equal size in three dimensions.

If a large number of spheres of equal size are put in a container and shaken, they will arrange themselves in a manner so as to occupy minimum volume. The arrangement of such spheres in one plane is shown in Fig. The arrangements shown in Fig. (a) is more economical than that shown in Fig. (b). The packing is closest when the spheres arrange themselves so that their centres are at the corners of an equilateral triangle (Fig.). Each sphere in the closest packed arrangement is in contact with six other spheres as shown in Fig. The centres of each of these six spheres are arranged hexagonally. The number of spheres which are actually in contact with a particular sphere is called the coordination number of that sphere. The coordination number is six when spheres are arranged in a close packed arrangement in one plane.

Three-Dimensional Close Packing

Now, if we start building successive layers on top of the first layer, spheres marked A (Fig.), we soon realize that spheres of second layer may be placed either on the hollows which are marked B or the other set of hollows which are marked as C. It may be noted that while building the second layer,we cannot place spheres both on hollows B and C.

As shown in Fig. we may build the second layeron hollows marked B.

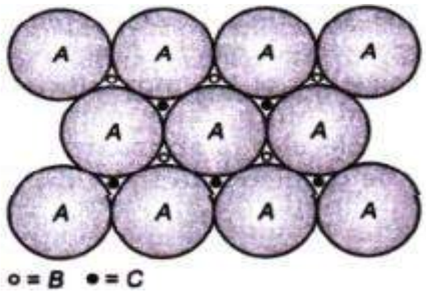


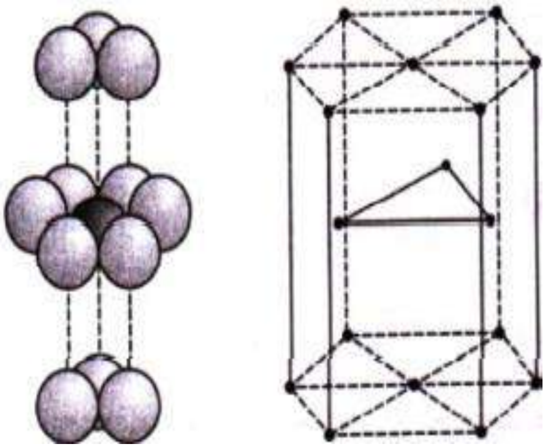
Fig. (a) : Site created by layer 1 and available to accept atoms inlayer 2 either on hollows called B' or 'C' ways:

Fig. (b) : Covering of all 'B' sites by atoms in the second layer makingthe 'C' sites unavailable for occupancy by close-packed atoms.

However, for building the third layer we again have a choice of arranging spheres in two different

(i) The third layer of spheres may be placed the hollows of the second layer, so that sphereof the third layer lies strictly above sphere of the first layer. In such an arrangement thefirst and the third layers are identical. This arrangement of close packing spheres is referred to as ABA arrangement packing of spheres.

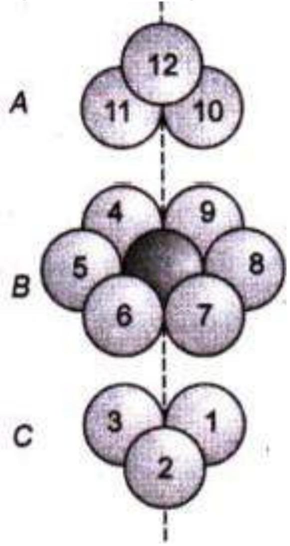
(ii) Alternatively, the third layer of spheres may placed on the second set of hollows which marked C in the first layer. These hollows left uncovered while arranging the second layer of spheres. This arrangement of packing denoted as ABC type packing.



When the ABABABA.... arrangement of packing continued indefinitely, the system possesses symmetry. This would imply that the structure a six-fold axis of symmetry which is perpendicular the planes of the close-packed spheres. Such an arrangement of three dimensional packing of spheres shown in Fig. Because of its hexagonal symmetry, this arrangement is referred to as hexagonal close packing of spheres abbreviated as hcp.

When the ABCABC... arrangement of packing is continued (i.e., every fourth layer is situated directly above the first layer) the system then possesses cubic symmetry. The arrangement is shown in Fig. The structure now has three 4-fold axes of symmetry. The arrangement is called cubic close packing spheres and is often abbreviated as ccp. It is clear from this diagram that in this arrangement have a sphere at the centre of each face of the unit cube. This arrangement of spheres is also knownas face centred cubic (fcc).

Fig. (b) : Face centred cubic arrangement (as seen along a 3-fold axis) In both these arrangements, i.e., hcp and ccp, it is obvious that each sphere is surrounded by twelve equidistant spheres. There are six spheres which are in contact in the same plane and three eachin adjacent layers, one just above, and the other just below. The coordination number of each sphere in both these close packed arrangement is twelve. This is shown in figure. For illustration the spheresof top and bottom layers are shown apart.



In both these type of close packed arrangements, maximum volume of space, i.e., 74% is actually occupied by the spheres. It may also be understood here that any irregular arrangement like ABABC- ABABC, etc., possesses neither cubic nor hexagonal symmetry.

Structure Adopted By Metals

The structure of most of the metals (from s- and d-blocks of the periodic chart) belong either to one or more of the three simple types of structures.

i) Cubic close packed (face- centred cubic)

ii) Hexagonal close packed

NET JRF PGT
ASST PROFESSOR
Get your KIT
7690022111
PROFESSORS ADDA

PROFESSORS ADDA


PROFESSORS ADDA
NAGAR, RAJA PARK, JAIPUR (RAJ.)


PROFESSORS ADDA

CSIR NET Chemical Sciences: Interdisciplinary Topics

Part:- 1CSIR NET Chemical Science Interdisciplinary Topics

- Medicinal chemistry ,
- Supramolecular Chemistry
- Environmental chemistry
- Chemistry in nanoscience and technology
- Catalysis and green chemistry(100 MCQs)

Q1. Which of the following is a common approach in medicinal chemistry to improve the pharmacokinetic properties of a drug molecule?

A) Increasing its molecular weight indefinitely.

B) Introducing highly polar functional groups to reduce absorption.

C) Prodrug strategy, where an inactive compound is metabolized into an active drug.

D) Decreasing its metabolic stability.

Answer: C) Prodrug strategy, where an inactive compound is metabolized into an active drug.

Q2. Which of the following is a key non-covalent interaction involved in molecular recognition in supramolecular chemistry?

A) Covalent bond

B) Ionic bond

C) Hydrogen bonding

D) Metallic bond

Answer: C) Hydrogen bonding

Q3. The phenomenon where the properties of materials change significantly when their dimensions are reduced to the nanoscale (1-100 nm) is primarily due to:

A) Bulk properties becoming dominant.

B) Quantum confinement and increased surface area to volume ratio.

C) Increased gravitational forces.
D) Decreased chemical reactivity.
Answer: B) Quantum confinement and increased surface area to volume ratio.

Q4. Assertion (A): Green chemistry aims to minimize the generation of hazardous waste.
Reason (R): One of the twelve principles of green chemistry is "Prevention," which advocates for preventing waste formation rather than treating or cleaning it up after it has been created.
A) Both A and R are true and R is the correct explanation of A.
B) Both A and R are true but R is NOT the correct explanation of A.
C) A is true but R is false.
D) A is false but R is true.
Answer: A) Both A and R are true and R is the correct explanation of A.

Q5. Which type of catalysis involves the catalyst and reactants being in the same phase?
A) Heterogeneous catalysis
B) Homogeneous catalysis
C) Biocatalysis
D) Photocatalysis
Answer: B) Homogeneous catalysis

Q6. The primary method for synthesizing carbon nanotubes (CNTs) involves:
A) Grinding bulk graphite.
B) Chemical Vapor Deposition (CVD).
C) Sol-gel synthesis.
D) Electrochemical deposition.
Answer: B) Chemical Vapor Deposition (CVD).

Q7. Statement I: Persistent Organic Pollutants (POPs) are chemicals that persist in the environment, bioaccumulate through the food web, and pose a risk to human health and the environment.

Statement II: DDT and PCBs are examples of POPs.

A) Both Statement I and Statement II are true.

B) Both Statement I and Statement II are false.

C) Statement I is true, but Statement II is false.

D) Statement I is false, but Statement II is true.

Answer: A) Both Statement I and Statement II are true.

Q8. "Prodrugs" are designed in medicinal chemistry to:

A) Increase drug toxicity.

B) Bypass metabolic barriers or improve drug delivery to target sites.

C) Reduce drug stability.

D) Make drugs more reactive towards non-specific targets.

Answer: B) Bypass metabolic barriers or improve drug delivery to target sites.

Q9. Match List I with List II regarding types of supramolecular hosts:

List I

a. Crown Ethers

b. Cryptands

c. Cyclodextrins

d. Calixarenes

List II

1. Bicyclic or polycyclic polyethers that encapsulate guest ions.
2. Cyclic oligosaccharides with a hydrophobic cavity for guest binding.
3. Cyclic polyethers with a planar arrangement that bind alkali metal ions.
4. Bowl-shaped macrocycles derived from phenols, with tunable cavities.

Which of the following is the correct match?

A) a-3, b-1, c-2, d-4

B) a-1, b-2, c-3, d-4

C) a-2, b-3, c-4, d-1

D) a-4, b-1, c-2, d-3

Answer: A) a-3, b-1, c-2, d-4

Q10. The primary goal of "phytoremediation" in environmental chemistry is to:

A) Use microorganisms to clean up contaminated soil.

B) Use plants to extract, degrade, or contain environmental pollutants.

C) Use chemical reagents to precipitate heavy metals.

D) Use physical methods to remove pollutants from water.

Answer: B) Use plants to extract, degrade, or contain environmental pollutants.

Q11. Assertion (A): Nanoparticles are often used in catalysis.

Reason (R): Their extremely high surface area to volume ratio provides a large number of surface atoms acting as active sites, enhancing catalytic activity.

A) Both A and R are true and R is the correct explanation of A.

B) Both A and R are true but R is NOT the correct explanation of A.

C) A is true but R is false.

D) A is false but R is true.

Answer: A) Both A and R are true and R is the correct explanation of A.

Q12. In catalysis, the "turnover freQuency (TOF)" measures:

A) The total amount of product formed per mole of catalyst.

B) The number of catalytic cycles completed per active site per unit time.

C) The activation energy of the catalyzed reaction.

D) The stability of the catalyst.

Answer: B) The number of catalytic cycles completed per active site per unit time.

Q13. Statement I: Targeted drug delivery aims to deliver therapeutic agents specifically to diseased cells or tissues, minimizing off-target effects.
Statement II: Nanoparticles are extensively explored as drug delivery vehicles due to their size and modifiable surfaces.
A) Both Statement I and Statement II are true.
B) Both Statement I and Statement II are false.
C) Statement I is true, but Statement II is false.
D) Statement I is false, but Statement II is true.
Answer: A) Both Statement I and Statement II are true.

Q14. The "lock-and-key" model is commonly used to describe molecular recognition in:
A) Polymer synthesis.
B) Enzyme-substrate interactions.
C) Oxidation-reduction reactions.
D) Acid-base chemistry.
Answer: B) Enzyme-substrate interactions.

Q15. Which of the following is a "bottom-up" approach for synthesizing nanomaterials?
A) Ball milling
B) Lithography
C) Self-assembly
D) Laser ablation
Answer: C) Self-assembly

Q16. Assertion (A): Photodegradation is a common process in environmental chemistry.

Reason (R): Many organic pollutants can be broken down by UV radiation from sunlight, either directly or via photocatalysis.

A) Both A and R are true and R is the correct explanation of A.
B) Both A and R are true but R is NOT the correct explanation of A.
C) A is true but R is false.
D) A is false but R is true.

Answer: A) Both A and R are true and R is the correct explanation of A.

Q17. Match List I with List II regarding common drug targets:

List I

a. Enzymes
b. Receptors
c. Ion channels
d. Nucleic acids

List II

1. Molecules that bind specific signaling molecules and transmit signals.
2. Biological macromolecules that catalyze biochemical reactions.
3. DNA or RNA molecules that can be targeted by drugs to inhibit replication or transcription.
4. Proteins that regulate the flow of ions across cell membranes.

Which of the following is the correct match?

A) a-2, b-1, c-4, d-3
B) a-1, b-2, c-3, d-4
C) a-3, b-4, c-1, d-2
D) a-4, b-1, c-2, d-3

Answer: A) a-2, b-1, c-4, d-3

Q18. Which of the following is a "top-down" approach for fabricating nanostructures?

A) Chemical precipitation
B) Molecular beam epitaxy

C) Electron beam lithography
D) Sol-gel method
Answer: C) Electron beam lithography

Q19. "Biomagnification" in environmental chemistry refers to:
A) The increase in population size of organisms.
B) The increase in concentration of a pollutant as it moves up the food chain.
C) The breakdown of pollutants by biological processes.
D) The absorption of pollutants by individual organisms from the environment.
Answer: B) The increase in concentration of a pollutant as it moves up the food chain.

Q20. The primary goal of "drug discovery" is to:
A) Market existing drugs more effectively.
B) Develop new chemical entities (NCEs) that can treat diseases.
C) Analyze drug interactions.
D) Optimize manufacturing processes for drugs.
Answer: B) Develop new chemical entities (NCEs) that can treat diseases.

Q21. Which type of catalysis is characterized by the catalyst being in a different phase from the reactants, often involving adsorption onto the catalyst surface?
A) Homogeneous catalysis
B) Heterogeneous catalysis
C) Biocatalysis
D) Photocatalysis
Answer: B) Heterogeneous catalysis

Q22. Assertion (A): The "click chemistry" concept is highly valued in drug discovery and materials science.

Reason (R): It involves highly efficient, robust, and selective reactions that are easy to perform and generate minimal byproducts, enabling rapid synthesis of complex molecules.

A) Both A and R are true and R is the correct explanation of A.
B) Both A and R are true but R is NOT the correct explanation of A.
C) A is true but R is false.
D) A is false but R is true.

Answer: A) Both A and R are true and R is the correct explanation of A.

Q23. Statement I: "Atom economy" is a principle of green chemistry that aims to maximize the incorporation of all atoms from reactants into the final product.

Statement II: A reaction with 100% atom economy produces no waste byproducts.

A) Both Statement I and Statement II are true.
B) Both Statement I and Statement II are false.
C) Statement I is true, but Statement II is false.
D) Statement I is false, but Statement II is true.

Answer: A) Both Statement I and Statement II are true.

Q24. Which of the following is a common method for stabilizing nanoparticles in solution to prevent aggregation?

A) Increasing temperature.
B) Using capping agents or surface ligands.
C) Reducing surface charge.
D) Increasing particle size.

Answer: B) Using capping agents or surface ligands.

Q25. "Electrochemistry" plays a significant role in:

A) Catalytic converters.
B) Fuel cells and batteries.
C) Industrial fermentation.
D) Photovoltaic cells (solar cells).
Answer: B) Fuel cells and batteries.

Q26. Assertion (A): Zeolites are shape-selective catalysts.
Reason (R): Their porous structure and precisely defined pore sizes allow only reactant molecules of specific shapes and sizes to enter and react within their channels.
A) Both A and R are true and R is the correct explanation of A.
B) Both A and R are true but R is NOT the correct explanation of A.
C) A is true but R is false.
D) A is false but R is true.
Answer: A) Both A and R are true and R is the correct explanation of A.

Q27. Match List I with List II regarding methods of nanomaterial characterization:
List I
a. TEM (Transmission Electron Microscopy)
b. SEM (Scanning Electron Microscopy)
c. AFM (Atomic Force Microscopy)
d. XRD (X-ray Diffraction)
List II

1. Provides internal structure, crystallinity, and defects at high resolution.
2. Provides surface morphology and elemental composition.
3. Provides surface topography and physical properties at nanoscale.
4. Provides crystal structure, phase identification, and average particle size.

Which of the following is the correct match?
A) a-1, b-2, c-3, d-4

B) a-2, b-1, c-4, d-3
C) a-3, b-4, c-1, d-2
D) a-4, b-1, c-2, d-3
Answer: A) a-1, b-2, c-3, d-4

Q28. The process of converting atmospheric nitrogen (N2) into ammonia (NH3) using a catalyst at high temperature and pressure is the:
A) Ostwald process
B) Haber-Bosch process
C) Contact process
D) Solvay process
Answer: B) Haber-Bosch process

Q29. "Combinatorial chemistry" is a strategy in drug discovery that aims to:
A) Synthesize only one compound at a time.
B) Synthesize a large library of compounds rapidly and efficiently for screening.
C) Focus on natural product isolation only.
D) Predict drug activity using computational methods.
Answer: B) Synthesize a large library of compounds rapidly and efficiently for screening.

Q30. The major concern with heavy metal pollution in environmental chemistry is that:
A) They are readily biodegradable.
B) They are highly volatile.
C) They are non-biodegradable and tend to bioaccumulate and biomagnify.
D) They are always found in very low concentrations.
Answer: C) They are non-biodegradable and tend to bioaccumulate and biomagnify.

Q31. Statement I: Nanomaterials can have different properties (e.g., optical, electrical) compared to their bulk counterparts.

Statement II: This is due to Quantum confinement effects and increased surface area to volume ratio.

A) Both Statement I and Statement II are true.
B) Both Statement I and Statement II are false.
C) Statement I is true, but Statement II is false.
D) Statement I is false, but Statement II is true.

Answer: A) Both Statement I and Statement II are true.

Q32. Assertion (A): "Atom Economy" is a crucial principle in green chemistry.

Reason (R): It measures the efficiency of a chemical reaction by calculating the percentage of reactant atoms incorporated into the desired product, minimizing waste.

A) Both A and R are true and R is the correct explanation of A.
B) Both A and R are true but R is NOT the correct explanation of A.
C) A is true but R is false.
D) A is false but R is true.

Answer: A) Both A and R are true and R is the correct explanation of A.

Q33. Which type of pollution is primarily responsible for the formation of acid rain?

A) Heavy metal contamination
B) Particulate matter
C) Sulfur dioxide (SO_2) and nitrogen oxides (NO_x)
D) Plastic waste

Answer: C) Sulfur dioxide (SO_2) and nitrogen oxides (NO_x)

Q34. The "Meissner effect" is a characteristic property of:

A) Semiconductors

B) Ferromagnetic materials
C) Superconductors
D) Piezoelectric materials
Answer: C) Superconductors

Q35. Match List I with List II regarding types of catalysts:
List I
a. Homogeneous catalyst
b. Heterogeneous catalyst
c. Enzyme catalyst
d. Photocatalyst
List II

1. Usually a solid, operates in a different phase from reactants.
2. Operates in the same phase as reactants, often organometallic complexes.
3. Biological macromolecule, highly selective.
4. Uses light energy to drive chemical reactions.

Which of the following is the correct match?
A) a-2, b-1, c-3, d-4
B) a-1, b-2, c-4, d-3
C) a-3, b-4, c-1, d-2
D) a-4, b-1, c-2, d-3
Answer: A) a-2, b-1, c-3, d-4

Q36. Which of the following is a common approach for "phytoremediation"?
A) Bioaugmentation (adding microbes)
B) Using plants to accumulate or degrade pollutants in soil or water.
C) Incineration of contaminated soil.
D) Landfilling contaminated waste.

Answer: B) Using plants to accumulate or degrade pollutants in soil or water.

Q37. Assertion (A): Drug receptors exhibit specificity.
Reason (R): Drugs bind to specific receptors based on their complementary shape, charge, and chemical properties, leading to a specific biological response.
A) Both A and R are true and R is the correct explanation of A.
B) Both A and R are true but R is NOT the correct explanation of A.
C) A is true but R is false.
D) A is false but R is true.
Answer: A) Both A and R are true and R is the correct explanation of A.

Q38. Statement I: Nanoparticles can be used as catalysts for various chemical reactions.
Statement II: Their high surface area to volume ratio provides a large number of active sites, enhancing catalytic activity.
A) Both Statement I and Statement II are true.
B) Both Statement I and Statement II are false.
C) Statement I is true, but Statement II is false.
D) Statement I is false, but Statement II is true.
Answer: A) Both Statement I and Statement II are true.

Q39. "Bioremediation" is a process that:
A) Uses chemicals to neutralize pollutants.
B) Uses living organisms (e.g., microorganisms) to remove or detoxify pollutants.
C) Involves physical separation of pollutants.
D) Converts pollutants into solid waste.
Answer: B) Uses living organisms (e.g., microorganisms) to remove or detoxify pollutants.

Q40. Which of the following is a common green chemistry metric?
A) Reaction yield
B) Atom economy
C) Product purity
D) Cost of reagents
Answer: B) Atom economy

Q41. The "binding energy" of a host-guest complex in supramolecular chemistry is primarily a measure of:
A) The strength of covalent bonds formed.
B) The strength of non-covalent interactions between host and guest.
C) The activation energy of the reaction.
D) The stability of the host molecule itself.
Answer: B) The strength of non-covalent interactions between host and guest.

Q42. Assertion (A): Nanoparticles are extensively used in sunscreens.
Reason (R): Nano-TiO_2 and nano-ZnO absorb UV radiation efficiently, providing broad-spectrum UV protection without leaving a white residue on the skin.
A) Both A and R are true and R is the correct explanation of A.
B) Both A and R are true but R is NOT the correct explanation of A.
C) A is true but R is false.
D) A is false but R is true.
Answer: A) Both A and R are true and R is the correct explanation of A.

Q43. Match List I with List II regarding common nanomaterials and their properties/applications:
List I
a. Gold Nanoparticles (AuNPs)

b. Quantum Dots (QDs)
c. Carbon Nanotubes (CNTs)
d. Graphene
List II

1. Size-dependent fluorescence, used in imaging and displays.
2. Exceptional strength, electrical conductivity, used in composites and electronics.
3. High electrical conductivity, transparent, used in touchscreens and sensors.
4. Surface Plasmon Resonance, used in biosensors, catalysis, drug delivery.

Which of the following is the correct match?
A) a-4, b-1, c-2, d-3
B) a-1, b-2, c-3, d-4
C) a-2, b-3, c-4, d-1
D) a-3, b-4, c-1, d-2
Answer: A) a-4, b-1, c-2, d-3

Q44. The process of "green synthesis" of nanomaterials emphasizes:
A) High temperature and pressure methods.
B) The use of hazardous chemicals and solvents.
C) Environmentally friendly and sustainable methods, minimizing toxic reagents.
D) Large-scale industrial production only.
Answer: C) Environmentally friendly and sustainable methods, minimizing toxic reagents.

Q45. Statement I: Acid rain has a pH typically lower than 5.6.
Statement II: Acid rain can cause damage to forests, aQuatic ecosystems, and infrastructure.
A) Both Statement I and Statement II are true.

B) Both Statement I and Statement II are false.

C) Statement I is true, but Statement II is false.

D) Statement I is false, but Statement II is true.

Answer: A) Both Statement I and Statement II are true.

Q46. Which of the following is a key strategy in medicinal chemistry to avoid rapid metabolism and increase drug half-life?

A) Introduce easily hydrolyzable ester bonds.

B) Increase lipophilicity to promote rapid excretion.

C) Introduce metabolically stable groups (e.g., fluorine atoms, bulky substituents).

D) Use prodrugs that are rapidly activated.

Answer: C) Introduce metabolically stable groups (e.g., fluorine atoms, bulky substituents).

Q47. Assertion (A): Supramolecular chemistry is often described as "chemistry beyond the molecule."

Reason (R): It focuses on the non-covalent interactions between molecules that lead to the formation of larger, more complex assemblies.

A) Both A and R are true and R is the correct explanation of A.

B) Both A and R are true but R is NOT the correct explanation of A.

C) A is true but R is false.

D) A is false but R is true.

Answer: A) Both A and R are true and R is the correct explanation of A.

Q48. Statement I: Catalytic converters in automobiles use heterogeneous catalysts.

Statement II: They convert harmful pollutants (e.g., CO, NOx, unburnt hydrocarbons) into less harmful substances (e.g., CO2, N2, H2O).

A) Both Statement I and Statement II are true.

B) Both Statement I and Statement II are false.

C) Statement I is true, but Statement II is false.

D) Statement I is false, but Statement II is true.

Answer: A) Both Statement I and Statement II are true.

Q49. Which of the following is a common method for synthesizing Quantum Dots (QDs)?

A) Arc discharge

B) Hot-injection method

C) Lithography

D) Ball milling

Answer: B) Hot-injection method

Q50. Match List I with List II regarding common air pollutants and their sources:

List I

a. Sulfur dioxide (SO2)

b. Nitrogen oxides (NOx)

c. Carbon monoxide (CO)

d. Particulate matter (PM)

List II

1. Incomplete combustion of fossil fuels (e.g., vehicle exhaust).
2. Industrial processes, power plants burning fossil fuels.
3. Combustion processes at high temperatures (e.g., vehicle engines, power plants).
4. Combustion of fossil fuels, industrial processes, dust, wildfires.

Which of the following is the correct match?

A) a-2, b-3, c-1, d-4

B) a-1, b-2, c-3, d-4

C) a-3, b-4, c-1, d-2

D) a-4, b-1, c-2, d-3

Answer: A) a-2, b-3, c-1, d-4


NET JRF PGT
ASST PROFESSOR
Get your KIT
7690022111
PROFESSORS ADDA


PROFESSORS ADDA


PROFESSORS ADDA
Arti


PROFESSORS
ADDA

CSIR NET Chemical Sciences Unit 1: Interdisciplinary

- Medicinal chemistry
- Supramolecular Chemistry
- Environmental chemistry
- Chemistry in nanoscience and technology
- Catalysis and green chemistry

Q. 1. What is the study of the properties and interactions of molecules that form stable non-covalent complexes?
Answer: Supramolecular chemistry

Q. 2. Who coined the term "supramolecular chemistry" in 1978?
Answer: Jean-Marie Lehn

Q. 3. What type of interaction is the primary driving force for host-guest complexation?
Answer: Non-covalent interactions

Q. 4. Give an example of a synthetic receptor commonly used in supramolecular chemistry.
Answer: Crown ether

Q. 5. What are molecular assemblies held together by weak, reversible bonds called?
Answer: Self-assemblies

Q. 6. What type of molecular architecture features two or more interlocked rings without covalent bonds?
Answer: Catenane

Q. 7. What type of molecular architecture features a ring threaded onto a dumbbell-shaped molecule?
Answer: Rotaxane

Q. 8. What is the binding of a molecule (guest) within the cavity of another molecule (host)?
Answer: Host-guest chemistry

Q. 9. What term describes the selective binding of a host to a particular guest?
Answer: Molecular recognition

Q. 10. Which non-covalent interaction involves the overlap of electron clouds between aromatic rings?
Answer: Pi-pi stacking

Q. 11. What forces become significant over short distances, arising from temporary dipole moments?
Answer: Van der Waals forces

Q. 12. What are the cyclic oligosaccharides commonly used as hosts for drug delivery?
Answer: Cyclodextrins

Q. 13. What class of supramolecular systems can switch between different states upon external stimuli?
Answer: Molecular switches

Q. 14. What are synthetic systems that mimic biological functions like transport or catalysis?
Answer: Artificial enzymes

Q. 15. What is the process where molecules spontaneously arrange into ordered structures?
Answer: Self-assembly

Q. 16. What is the term for a system where components are held together by metal-ligand coordination bonds?
Answer: Metal-organic framework (MOF)

Q. 17. What type of supramolecular gel forms through non-covalent interactions between small molecules?
Answer: Low-molecular-weight gel

Q. 18. What is the use of supramolecular principles in the design of new materials?
Answer: Supramolecular materials

Q. 19. What supramolecular system is important for ion transport across membranes?
Answer: Ion channels

Q. 20. What is the term for a molecular entity capable of performing mechanical-like movements?
Answer: Molecular machine

Q. 21. What is the branch of chemistry that involves the design and synthesis of pharmaceutical drugs?
Answer: Medicinal chemistry

Q. 22. What is the relationship between the chemical structure of a drug and its biological activity?
Answer: Structure-Activity Relationship (SAR)

Q. 23. What are the four main stages of drug disposition in the body (pharmacokinetics)?
Answer: ADME

Q. 24. What does ADME stand for in pharmacokinetics?
Answer: Absorption, Distribution, Metabolism, Excretion

Q. 25. What is a compound that is inactive but is converted into an active drug in the body?
Answer: Prodrug

Q. 26. What term describes a drug that binds to a receptor and produces a biological response?
Answer: Agonist

Q. 27. What term describes a drug that binds to a receptor but blocks its biological response?
Answer: Antagonist

Q. 28. What is the primary molecular component that a drug interacts with to exert its effect?
Answer: Drug target

Q. 29. What type of drug targets are enzymes that carry out specific biochemical reactions?
Answer: Enzyme inhibitors

Q. 30. What type of drug targets are often cell surface proteins that bind signaling molecules?
Answer: Receptors

Q. 31. What is the measure of a drug's effectiveness in producing a desired effect?
Answer: Efficacy

Q. 32. What is the measure of the concentration or dose required to produce a given effect?
Answer: Potency

Q. 33. What phase of clinical trials assesses drug safety in a small group of healthy volunteers?
Answer: Phase 1

Q. 34. What phase of clinical trials evaluates drug efficacy and dose range in a larger group of patients?
Answer: Phase 2

Q. 35. What phase of clinical trials confirms efficacy and monitors side effects in large patient populations?
Answer: Phase 3

Q. 36. What is the process of chemically modifying a drug to improve its properties?
Answer: Drug optimization

Q. 37. What is the ratio between the toxic dose and the effective dose of a drug?
Answer: Therapeutic index

Q. 38. What type of forces drive the binding of drugs to their targets, often non-covalent?
Answer: Intermolecular forces

Q. 39. What is a specific example of a functional group commonly used in drug design?
Answer: Carboxylic acid

Q. 40. What class of drugs is used to treat bacterial infections?
Answer: Antibiotics

Q. 41. What is the study of the chemical composition and processes of the natural environment?
Answer: Environmental chemistry

Q. 42. What is the atmospheric layer containing ozone that protects Earth from UV radiation?
Answer: Stratosphere

Q. 43. What class of compounds was primarily responsible for ozone depletion?
Answer: CFCs

Q. 44. What phenomenon describes the warming of Earth's atmosphere due to trapped greenhouse gases?
Answer: Greenhouse effect

Q. 45. What are the major greenhouse gases?
Answer: CO2, CH4, N2O, H2O

Q. 46. What atmospheric phenomenon results from the emission of sulfur and nitrogen oxides?
Answer: Acid rain

Q. 47. What is the pH of normal rainwater?
Answer: 5.6

Q. 48. What term describes the excessive growth of algae due to nutrient enrichment in water bodies?
Answer: Eutrophication

Q. 49. What are substances that cause harm to living organisms upon exposure?
Answer: Pollutants

Q. 50. What is the accumulation of toxic substances in living organisms through the food chain?
Answer: Biomagnification

Q. 51. What heavy metal is a neurotoxin commonly found in polluted water and fish?
Answer: Mercury

Q. 52. What is the maximum concentration of a pollutant that can be tolerated by an organism?
Answer: Tolerance limit

Q. 53. What is the process of cleaning up contaminated environmental sites?
Answer: Remediation

Q. 54. What type of remediation uses microorganisms to degrade pollutants?
Answer: Bioremediation

Q. 55. What type of remediation uses plants to absorb or degrade pollutants?
Answer: Phytoremediation

Q. 56. What is the study of the effects of toxic substances on living organisms?
Answer: Toxicology

Q. 57. What are particulate matter and gases released into the atmosphere by human activities?
Answer: Air pollutants

Q. 58. What is the major source of atmospheric carbon monoxide?
Answer: Incomplete combustion

Q. 59. What is the colorless, odorless gas produced by the decay of organic matter, a potent greenhouse gas?
Answer: Methane (CH4)

Q. 60. What term describes pollutants that persist in the environment and bioaccumulate?
Answer: Persistent organic pollutants (POPs)

Q. 61. What is the branch of chemistry dealing with materials structured at the nanoscale (1-100 nm)?
Answer: Nanoscience

Q. 62. What effect causes properties of materials to change dramatically at the nanoscale?
Answer: Quantum size effect

Q. 63. What term describes the ratio of surface atoms to bulk atoms, increasing significantly at nanoscale?
Answer: Surface-to-volume ratio

Q. 64. What are semiconductor nanocrystals that emit specific colors of light when excited?
Answer: Quantum dots

Q. 65. What is a single layer of carbon atoms arranged in a hexagonal lattice?
Answer: Graphene

Q. 66. What are cylindrical nanomaterials composed of rolled-up graphene sheets?
Answer: Carbon nanotubes (CNTs)

Q. 67. What are spherical carbon molecules with a cage-like structure, e.g., C60?
Answer: Fullerenes

Q. 68. What metal nanoparticles exhibit unique optical properties due to Surface Plasmon Resonance?
Answer: Gold nanoparticles

Q. 69. What synthesis approach involves building nanostructures atom by atom or molecule by molecule?
Answer: Bottom-up approach

Q. 70. What synthesis approach involves reducing larger materials into nanoscale dimensions?
Answer: Top-down approach

Q. 71. What is the use of nanoscale materials for drug delivery within the body?
Answer: Nanomedicine

Q. 72. What are nanoscale devices that can detect specific molecules or environmental conditions?
Answer: Nanosensors

Q. 73. What is the use of nanomaterials to improve catalytic efficiency?
Answer: Nanocatalysis

Q. 74. What is the self-assembly of nanoparticles into larger ordered structures?
Answer: Nanoparticle assembly

Q. 75. What property of gold nanoparticles allows them to generate heat upon light absorption?
Answer: Photothermal effect

Q. 76. What are the long, slender nanomaterials with diameters in the nanoscale range?
Answer: Nanowires

Q. 77. What type of microscopy is crucial for visualizing individual nanoparticles and their structures?
Answer: Electron microscopy

Q. 78. What technique is used to deposit thin layers of material onto a substrate, common in nano-fabrication?
Answer: Thin film deposition

Q. 79. What are materials with a nanoscale structure that provides new or enhanced properties?
Answer: Nanomaterials

Q. 80. What is the term for the interaction of engineered nanomaterials with biological systems?
Answer: Nano-bio interface

Q. 81. What is a substance that increases the rate of a chemical reaction without being consumed?
Answer: Catalyst

Q. 82. How do catalysts increase reaction rates?
Answer: Lower activation energy

Q. 83. What type of catalysis involves the catalyst and reactants in the same phase?
Answer: Homogeneous catalysis

Q. 84. What type of catalysis involves the catalyst and reactants in different phases?
Answer: Heterogeneous catalysis

Q. 85. What are biological catalysts, typically proteins?
Answer: Enzymes

Q. 86. What is the specific site on an enzyme where the substrate binds?
Answer: Active site

Q. 87. What industrial process produces ammonia using an iron-based catalyst?
Answer: Haber-Bosch process

Q. 88. What industrial process converts syngas into liquid hydrocarbons using metal catalysts?
Answer: Fischer-Tropsch synthesis

Q. 89. What are porous aluminosilicate minerals widely used as heterogeneous catalysts?
Answer: Zeolites

Q. 90. What is the number of moles of product formed per mole of catalyst per unit time?
Answer: Turnover number (TON)

Q. 91. What concept describes how many times a catalytic cycle can be repeated before the catalyst deactivates?
Answer: Turnover frequency (TOF)

Q. 92. What branch of chemistry aims to design chemical products and processes that reduce or eliminate hazardous substances?
Answer: Green chemistry

Q. 93. How many principles of green chemistry were proposed by Paul Anastas and John Warner?
Answer: Twelve

Q. 94. What green chemistry principle aims to maximize the incorporation of all materials used in the final product?
Answer: Atom economy

Q. 95. What green chemistry principle focuses on preventing waste generation rather than treating it?
Answer: Prevention

Q. 96. What green chemistry principle encourages the design of safer chemical syntheses?
Answer: Safer synthesis

Q. 97. What is the use of water as a solvent in chemical reactions, promoted by green chemistry?
Answer: Aqueous solvents

Q. 98. What green chemistry principle promotes the use of renewable raw materials?
Answer: Renewable feedstocks

Q. 99. What technique involves heating reactants without a solvent, a green chemistry approach?
Answer: Solvent-free synthesis

Q. 100. What is the replacement of hazardous chemicals with less hazardous alternatives?
Answer: Substitution