

CHE 102 LECTURE MATERIAL (GROUP 1A, IIA & 1VA,ELEMENTS)

Alkaline Earth Metals and their Compounds(Group IIA or 2, ns^2)

POSITION OF ALKALINE EARTH METALS IN PERIODIC TABLE

The group IIA of the periodic table consists of six elements-beryllium, magnesium, calcium, strontium, bariums and radium. These elements are collectively called as alkaline earth metals because their earths (the old name for oxide) are basic (alkaline) and group IIA is known as alkaline earth group. The oxides of three principal members calcium strontium and barium were known much earlier than the metals themselves. These oxides were alkaline in nature and existed in the earth and were named alkaline earths. The metals when discovered were also called alkaline earths. This term is now applied to all the six elements of group IIA.

Element	Symbol	The most important minerals
Beryllium	Be	$\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$
Magnesium	Mg	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Calcium	Ca	$\text{MgCO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Strontium	Sr	SrCO_3
Barium	Ba	BaSO_4 , BaCO_3
Radium	Ra	It is found in uranium ores

The first member beryllium is less active than other members and shows some abnormal properties like lithium in 1A group. However, it shows resemblance with aluminium (a member of Iird group). *i.e.* diagonal relationship. The last member, radium is radioactive in nature. Each member of this group occupies a place just after the members of IA group in various periods of periodic table except first period.

IA	Li 3	Na 11	K 19	Rb 37	Cs 55	Fr 87
IIA	Be 4	Mg 12	Ca 20	Sr. 38	Ba 36	Ra 88

The members of this group show a marked resemblance in their properties and possess same electronic configuration. There is gradual gradation in the properties with the increase of atomic number. This justifies their inclusion in the same group of periodic table. The main properties are discussed below for this justification.

Electronic Configuration

The valence electron configuration of the atoms of the group IIA elements is ns^2 , where n is the period number. The arrangement or the distribution of electron on various subshells in the atoms of alkaline earth metals is given below

Element	At. No.	Electronic Configuration	Configuration of the valency shell
Beryllium	4	$1s^2 2s^2$	$[\text{He}]2s^2$

Magnesium	12	$1s^2 2s^2 2p^6 3s^2$	$[\text{Ne}]3s^2$
Calcium	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	$[\text{Ar}]4s^2$
Strontium	38	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$	$[\text{Kr}]5s^2$
Barium	56	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2$	$[\text{Xe}]6s^2$
Radium	88	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6 7s^2$	$[\text{Rn}]7s^2$

The outermost shell of these elements has two electrons and the penultimate shell contains 8 electrons except the first member which contains 2 electrons. Since, the last electron enters ns orbital, these are s-block elements. Beryllium shows somewhat abnormal properties as its electronic configuration is slightly different than the rest of the members. Because of their similarity in electronic configuration [noble gas] ns^2 , they are included in the same group, i.e., IIA of the periodic table and closely resemble each other in the physical and chemical properties.

2. Physical Properties

(a) Physical state: All the group IIA elements are metals and too reactive, so that cannot occur in the uncombined state in nature. They are all silvery white metals. They have greyish white lustre when freshly cut, but tarnish soon after their exposure in air due to surface oxidation.

They are soft in nature but harder than alkali metals because metallic bonding is stronger than 1A elements due to possession of 2 valency electrons. However, hardness decreases with increase in atomic number.

(b) Atomic and ionic radii: The size of the atom increases gradually from Be to Ra, on account of the presence of an extra energy shell at each step. The atoms are large but smaller than corresponding IA elements since the extra charge on the nucleus attracts the electron cloud inwards. Their ions are also large and size of the ion increases from Be^{2+} to Ra^{2+} .

Atomic volume also increases as the atomic number increases

(c) Density: These metals are denser than alkali metals in the same period because these can be packed more tightly due to their greater nuclear charge and smaller size. The density decreases slightly up to calcium and then increases considerably up to radium. Irregular trend is due to the difference in the crystal structure of these elements.

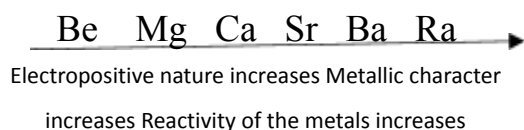
(d) Melting and boiling points: The melting and boiling points of these elements are higher than corresponding alkali metals. This is due to the presence of two electrons in the valency shell and thus, strongly bonded in the solid state. However, melting and boiling points do not show any regular trend because atoms adopt different crystal structures.

(e) Ionisation energies and electropositive character: The first and second ionisation energies of these metals decrease from Be to Ba. The second ionisation energy in each case is higher than the first, nearly double the first ionisation energy.

The ionisation energy of last member, radium, is slightly higher than that of barium and it is difficult to explain this anomalous behaviour.

Symbol	Abundance in earth's crust p.p.m	Atomic radius A ⁰	Ionic radius A ⁰	Density g/cc	Ionization potentials	
					1 st eV	2 nd eV
Be	6	0.89	0.31	1.8	9.3	18.2
Mg	20.9	1.36	0.65	1.7	7.6	15.0
Ca	36.3	1.74	0.99	1.6	6.1	11.9
Sr	300	1.91	1.13	2.6	5.7	11.0
Ba	250	1.98	1.35	3.5	5.2	10.0
Ra	1.3x10 ⁻⁴	-	1.50	5.0	5.3	10.1

Although, the ionisation energies of these elements are higher than those of alkali metals, yet these are sufficiently low to make these atoms to lose two electron of their valency shell to form M²⁺ ions and achieve the inert gas configuration. These metals are thus, strongly electropositive in nature but less than corresponding alkali metals. The electropositive character increases from Be to Ba. Metallic character and reactivity are directly linked with the tendency to lose electron or electrons, te with electropositive nature. Thus, these characters increase gradually from Be to Ba.



(f) Oxidation states: The alkaline earth metals form a basic oxide with general formula RO. All show a stable oxidation state +2 in their compounds. The second ionisation energy is nearly double the first ionisation energy for all these elements. This should cause these elements to exhibit a stable +1 oxidation state and form compounds like BaCl, SrBr, CaI etc., instead of BaCl₂, SrBr₂, CaI₂, etc. However, the lattice energy increases as the charge on the ion increases. The increase in the lattice energy on account of the second electron from ns² is much more than the energy required (second ionisation energy) to remove it. Hence, the stability of +2 oxidation state is due to high lattice energy. The second factor responsible for +2 oxidation state is the hydration energy which is high for M²⁺ ions. On account of the availability of energy, the process does not stop to M⁺ state but reach to M²⁺ state readily.

Since, the bivalent ions, M²⁺, have an inert gas configuration, it is very difficult to remove the third electron and hence oxidation state higher than +2 is not possible.

Amongst alkaline earth metals, beryllium has the highest ionisation energy, i.e., least electropositive in nature. Thus, beryllium has the minimum tendency to form Be²⁺ ion and hence a number of compounds of beryllium are covalent in nature.

(g) Hydration of ions and hydration energy: The M^{2+} ions of alkaline earth metals are extensively hydrated to form hydrated ions, $[M(H_2O)_x]^{2+}$ and during hydration a huge amount of energy, called hydration energy, is released.



The degree of hydration and the amount of hydration energy decreases as the size of the ion increases from Be^{2+} to Ba^{2+}

The hydration energies of alkaline earth metal ions are higher than those of alkali metal ions and thus the compounds of alkaline earth metals are more extensively hydrated than alkali metals. Magnesium chloride and calcium chloride exist as $MgCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$, respectively, while sodium chloride and potassium chloride exist as NaCl and KCl.

The ionic mobilities or ionic conductance of these ions increase from $[Be(H_2O)_x]^{2+}$ to $[Ba(H_2O)_x]^{2+}$ because $[Be(H_2O)_x]^{2+}$ becomes heavy due to high degree of hydration.

(h) Electronegativity : The tendency to attract electrons is low. The electronegativity values are thus small and decrease from Be to Ra.

Symbol	m.pt.(K)	b.pt.(K)	Oxid. Potential (Volt.)	Electronegativity
Be	1560	2745	1.97	1.5
Mg	924	1363	2.36	1.2
Ca	1124	1767	2.84	1.0
Sr	1062	1655	2.89	1.0
Ba	1002	2078	2.92	0.9
Ra	973	-	-	-

(i) Conductivity : On account of the presence of two loosely bond valency electrons per atom which can move freely throughout the crystal lattice, the alkaline earth metals are good conductors of heat and electricity.

(j) Flame colouration: In the case of Ca, Sr, Ba and Ra, the electrons can be excited by the supply of energy to higher energy levels. When the excited electrons return to the original level, the energy is released in the form of light. In beryllium and magnesium, the electrons are tightly held and hence excitation is rather difficult, thus do not show flame colouration. Ca, Sr, Ba and Ra impart a characteristic colour to the flame. Ca-brick red; Sr-crimson; Ba-green; Ra-crimson

(k) Reducing nature: The alkaline earth metals have the tendency to lose electrons and change into bivalent cation:

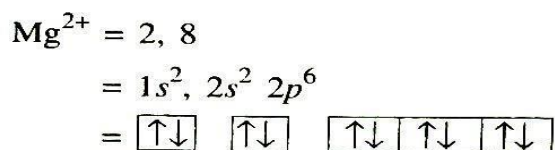


Hence, they act as strong reducing agents. The reducing nature increases as the atomic number increases.

Strength of a reducing agent is linked with the value oxidation potential. The values of the oxidation potential increases from Be to Ba, hence the strength as a reducing agent increases in the same order.

The oxidation potentials are lower than those of the alkali metals, hence, the alkaline earth metals are weaker reducing agents than alkali metals. The reason for the lower values of oxidation potentials is due to high heats of atomisation (sublimation) and ionisation energies.

(1) Colour and magnetic property: Since, the divalent ions have noble gas configuration with no unpaired electrons, their compounds are diamagnetic and colourless unless the anion is coloured. The metals are also diamagnetic in nature as all the orbitals are fully filled with spin paired electrons, e.g.,



Chemical Properties

(a) Occurrence: Alkaline earth metals are reactive elements and hence do not occur free in nature. Magnesium and calcium are found in abundance in nature. Beryllium is not very abundant. Strontium and barium are much less abundant. Radium is a rare element. Calcium and magnesium are the most common and commercially useful of the alkaline earth elements. We can see in the table given below, calcium is the fifth and magnesium is the eighth most abundant element in the earth's crust.

Ten most Abundant Elements in the Earths Crust

No.	Element	Mass percentage	No.	Element	Mass percentage
1	Oxygen	46.6	6	Sodium	2.8
2	Silicon	27.7	7	Potassium	2.6
3	Aluminum	8.3	8	Magnesium	2.1
4	Iron	5.1	9	Titanium	0.4
5	Calcium	3.6	10	Hydrogen	0.1

Like the alkali metals, the group IIA elements occur in nature as silicate rocks. They also occur as carbonates and sulphates, and many of these are commercial sources of alkaline earth metals and compounds.

These metals occur in nature largely as carbonates, sulphate and silicates.

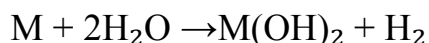
(b) Extraction: The metals of this group are not easy to produce on account of following reasons: (i) The metals cannot be produced by chemical reduction because they are themselves strong reducing agents and they react with carbon and form carbides.

(ii) They are strongly electropositive and react with water and so aqueous solutions cannot be used for displacing them with another metal.

(iii) The electrolysis of aqueous solutions of their salts produces hydrogen at cathode rather than the metal as the metal reacts with water. Electrolysis of an aqueous solution can be carried out by using mercury as cathode, but recovery of the metal from amalgam is difficult.

These metals are best isolated by electrolysis of their fused metal halides containing NaCl. NaCl lowers the fusion temperature and makes the fused mass as good conductor of electricity.

(c) Reactivity towards water: Calcium, strontium, barium and radium decompose cold water readily with evolution of hydrogen.



Magnesium decomposes boiling water but beryllium does not react with water, even when red hot, its protective oxide film survives even at high temperature as its oxidation potential is lower than the other members.

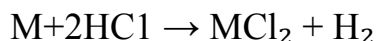
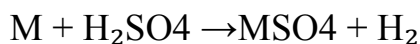
Reactivity of alkaline earth metals increases as we move down the group as the oxidation potential increases. However, the reaction of alkaline earth metals is less vigorous than alkali metals.

(d) Reactivity towards atmosphere: Except beryllium, these metals are easily tarnished in air as a layer of oxide is formed on their surface. The effect of atmosphere increases as the atomic number increases. Barium in powdered form bursts into flame on exposure to air.

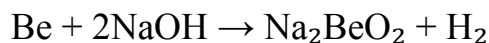


(Ca, Sr or Ba)

(e) Reactivity towards acids: Like alkali metals, the alkaline earth metals freely react with acids and displace hydrogen.

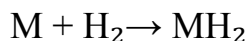


Beryllium behaves differently as it dissolves in caustic alkalies also with liberation of hydrogen. It is due to diagonal relationship with aluminium. Be is thus amphoteric in nature.

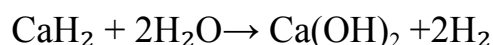


(f) Affinity for non-metals: Alkaline earth metals have great affinity for non-metals. They directly react with non-metals at the appropriate temperature.

(i) Reaction with hydrogen: Except beryllium, all combine with hydrogen directly to form hydrides of the type MH_2 when heated with hydrogen.



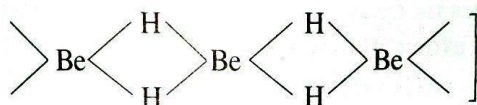
BeH_2 and MgH_2 are covalent in nature while other hydrides are ionic in nature. Calcium, strontium and barium hydrides liberate hydrogen at anode on electrolysis in the fused state. Ionic hydrides are violently decomposed by water evolving hydrogen, CaH_2 is technically called hydrolith and used on large scale for the production of hydrogen.



$[BeH_2]$ is not obtained by direct combination of beryllium and hydrogen. It is formed by reacting beryllium chloride with lithium aluminium hydride.

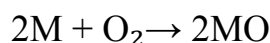


It is polymeric. $(BeH_2)_n$ possesses hydrogen bridges. Three centre bonds are present in which a banana shaped molecular orbital covers three atoms $Be \cdots H \cdots Be$ and contains two electrons. Hydrogen atoms lie in the plane perpendicular to the plane of molecule containing beryllium atoms.



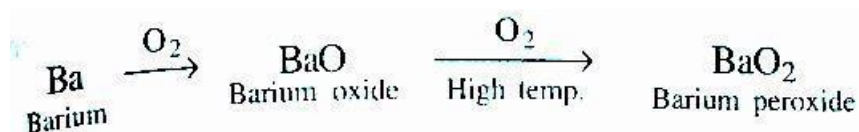
The stability of the hydrides decreases with increasing atomic number because the metallic nature of the elements increases.

(ii) Reaction with oxygen (Oxides and Hydroxides): Except Ba and Ra, these elements when burnt in oxygen form oxides of the type MO .



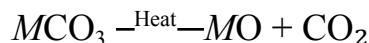
Beryllium metal is relatively unreactive and does not react below $600^\circ C$. but the powder form is much more reactive and burns brilliant. The element. Mg burns with dazzling brilliance evolving a lot of heat.

Barium and radium, being highly electropositive, form peroxides.



Thus, the affinity for oxygen increases on moving down the group.

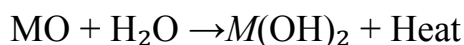
BeO is usually formed by ignition of the metal, but the other metal oxides (*MO* type) are usually obtained by thermal decomposition of the carbonates, MCO_3 .



The oxides are very stable compounds (BeO and MgO are used as refractory materials) and white crystalline solids. Except BeO (predominantly covalent), all the other oxides are ionic and possess NaCl structure (face centred cubic). The reason for high stability is due to high lattice energy values which, however, decrease as the size of the metal ion increases.

Oxide	MgO	CaO	SrO	BaO
Lattice energy (kJ mol ⁻¹)	3923	3517	3312	3120

Except BeO, which is amphoteric in nature, other *MO* oxides are basic in nature as they combine with water to form basic hydroxides. This reaction is highly exothermic.



(where, $M = Ca^{2+}$, Sr^{2+} or Ba^{2+})

Basic nature of the oxides increases gradually from BeO to BaO.

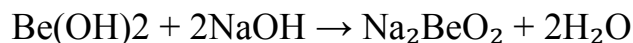
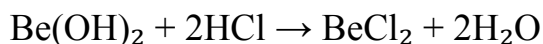
BeO*	MgO	CaO	SrO	BaO
Amphoteric	Weakly basic	Basic	Strongly basic	

(*The amphoteric nature is supported by its reaction with acids as well



[BeO and MgO are insoluble in water as these are tightly held together in the solid state.]

Be(OH)₂ is amphoteric, but the hydroxides of other alkaline earth metals are basic. The basic strength increases gradually.



Sod. beryllate

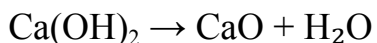
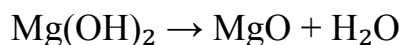


Beryllate ion

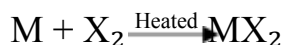
The solubility of the hydroxides increases with increase of atomic number of the alkaline earth metals. This is due to the fact that decrease in lattice energy is more than decrease in hydration energy on moving down the group. The increasing solubility can also be explained on the basis of values of their solubility products which increase from Be(OH)₂ to Ba(OH)₂. Be(OH)₂ and Mg(OH)₂ are almost insoluble in water.

Metal hydroxide	Be(OH) ₂	Mg(OH) ₂	Ca(OH) ₂	Sr(OH) ₂	Ba(OH) ₂
Solubility product	1.6x10 ⁻²⁶	8.9x10 ⁻¹²	1.3x10 ⁻⁴	3.2x10 ⁻⁴	5.4x10 ⁻³ (K _{sp})

The hydroxides decompose on heating. The thermal stability increases from Be(OH)₂ to Ba(OH)₂.



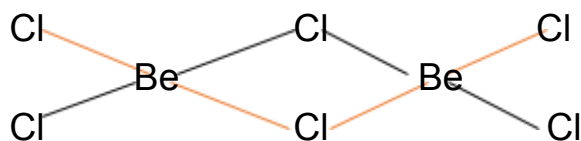
(iii) Reaction with halogens (Halides): The alkaline earth metals directly combine with halogens, when heated with them.



The alkaline earth metal halides can be obtained by the action of halogen acids on metals, their oxides, hydroxides and carbonates.



Beryllium halides are covalent in nature. This is due to small size and high charge of Be²⁺ ion, i.e., it has high polarising power. The glassy forms of halides are known to have chains of ----X₂Be X₂Be----.



The halides of the type MX₂ (fluorides, chlorides, bromides and iodides) of other metals are ionic solids. The solubility of these halides decreases with increasing atomic number of the metal as there is decrease in hydration energy with the increase in the size of the metal ion. Solubility of BeF₂ will therefore be greater than BaF₂.

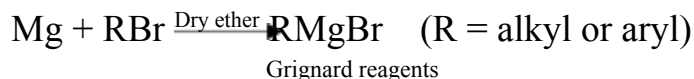
As the ionic character increases on moving down the group. the melting points and their conductivity increase from magnesium halides to barium halides. They are good conductors in molten state.

The halides are hygroscopic in nature and readily form hydrates, e.g., MgCl₂.6H₂O,

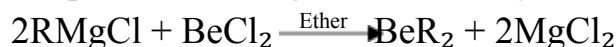
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, etc. Calcium chloride has a strong affinity for water and is used as a dehydrating agent. However, BeCl_2 fumes in moist air due to its hydrolysis.



(k) Organo-metallic compounds : Both Be and Mg form an appreciable number of compounds with M-C bonds but only a few are known for Ca, Sr and Ba. Grignard reagents are very important in organic chemistry which can be used to form a wide variety of organic compounds.



BeCl_2 reacts with Grignard compounds forming reactive dialkyls and diaryls.



Dialkyls and diaryls of Mg, Ca, Sr and Ba can also be obtained by similar reactions.

SOLUBILITY OF COMPOUNDS OF ALKALINE EARTH METALS

In the case of the compounds of Ca, Sr and Ba the following facts are observed:

- (i) The solubility of hydroxides, fluorides and oxalates increases from calcium to barium.
 - (ii) The solubility of carbonates, sulphates and chromates decreases from calcium to barium.
- The solubility of an ionic compound depends on two factors: (i) lattice energy and (ii) hydration energy. These two factors oppose each other. If lattice energy is high, the ions will be tightly packed in the crystal and, therefore, solubility will be low. If hydration energy is high, the ions will have greater tendency to be hydrated and, therefore, the solubility will be high.

In the case of hydroxides, fluorides and oxalates the lattice energies are different, i.e., lattice energy decreases as the size of the cation increases. This tends to increase the solubility as it overcomes the counter effect of decrease in hydration energy. Hence, the solubility of the hydroxides, fluorides and oxalates increases from Ca to Ba.

In the case of carbonates, sulphates and chromates the anions are large in size and small changes in cation size do not alter the lattice energies, i.e., lattice energies are about the same. However, the hydration energies decrease from Ca^{2+} to Ba^{2+} . Hence, the solubility of carbonates, sulphates and chromates decreases from calcium to barium.

COMPARING GROUP 1A AND GROUP 11A: ALKALINE & ALKALINE EARTH METALS

The groups IA and IIA are placed at the extreme left corner of the periodic table. The elements of these two groups belong to the S block as the differentiating electron enters the S orbital in all these elements. As the S-orbital can accommodate only two electrons, these two groups (IA & IIA) belong to the S-block of the Periodic table. The elements of these two groups have a strong metallic nature.

IA Group Elements or Alkali Metals

The Group IA of the long form of the periodic table consists of six elements, lithium, sodium, potassium, rubidium, cesium and francium. The general electronic configuration of all these elements is ns^1 . As all these elements are having one electron in the valence shell they are placed in the IA group.

All these elements are collectively called as alkali metals as the hydroxides of these metals are soluble in water and these solutions are highly alkaline in nature.

Among all the elements in this group, Lithium shows some abnormal properties. However, lithium resembles magnesium present in the IIA group. This resemblance is due to diagonal relationship. The only radioactive element in this group is francium. It is highly radioactive with a very small half-life period of 21 minutes.

Atomic and Ionic Radii:

In every period the alkali metal atoms have the largest size in the periodic table. The monovalent ion is smaller than the parent atom. On moving down the group as a new shell is added, the atomic radius increases.

Ionization Energy:

Because of their large size, the alkali metals' ionization energies are very much reduced and therefore the values slowly go lower in the group from Li to Cs. This is because the effect of increasing size decreases the nuclear pull over the outer most electron.

Melting Points and Boiling Points:

Alkali metals have low melting points and the values of melting points decrease gradually down the group. Due to their larger atomic size, the binding energies of their atoms within the crystal lattice are reduced being the cause therefore of a low melting point. Further on moving down the group, their atomic size increases, and the strength of metallic bond decreases which causes decrease in melting points.

IIA Group Elements Or Alkaline Earth Metals

The Group IIA of the long form of the periodic table consists of six elements, beryllium, magnesium, calcium, strontium, barium and radium. The general electronic configuration of all these elements is ns^2 . As all these elements are having two electrons in the valence shell they are placed in the IIA group.

The oxides and hydroxides of these elements are alkaline in nature and are available in the earth's crust. So, these elements are also known as 'Alkaline Earth Metals'. Among these elements, Radium is radio active.

Electronic configuration:

There are two electrons in the valence shell of these elements. Their general electronic configuration may be represented as ns^2 where 'n' is the number of the orbit. The compounds of these elements are ionic.

DIFFERENCE BETWEEN ALKALINE EARTH METALS AND ALKALI METALS

Both alkaline earth metals and alkali metals are s-block elements as the last differentiating electron enters the ns -orbital. They resemble with each other in many respects but still there are certain dissimilarities in their properties on account of different number of electrons in the valency shell, smaller atomic radii, high ionisation potential, higher electronegativity, etc. The main points of difference between alkaline earth metals and alkali metals are given below:

Properties	Alkaline earth metals	Alkali metals
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(i) Electronic configuration	Two electrons are present in the valency shell. The configurations is ns^2 .	One electron is present in the valency shell. The configuration is ns^1 .
(ii) Valency	Bivalent.	Monovalent.
(iii) Electropositive nature	Less electropositive.	More electropositive.
(iv) Hydroxides	Weak bases, less soluble and decompose on heating.	Strong bases, highly soluble and stable towards heat.
(v) Bicarbonates	These are not known in free state. Exist only in solution.	These are known in solid state.
(vi) Carbonates	Insoluble in water. Decompose on heating.	Soluble in water. Do not decompose on heating (Li_2CO_3 is an exception).
(vii) Action of nitrogen	Directly combine with nitrogen and form nitrides.	Do not directly combine with nitrogen.
(viii) Action of carbon	Directly combine with carbon and form carbides.	Do not directly combine with carbon.
(ix) Nitrates	Decompose on heating evolving a mixture of NO_2 and oxygen.	Decompose on heating evolving only oxygen.
(x) Solubility of salts	Sulphates, phosphates, fluorides, chromates, oxalates, etc., are insoluble in water.	Sulphates, phosphates, fluorides, chromates, oxalates, etc., are soluble in water.
(xi) Physical properties	Are less reactive and comparatively harder metals. High melting points. Diamagnetic.	Soft, low melting points. Paramagnetic.
(xii) Hydration of compounds	The compounds are extensively hydrated. $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$ are hydrated chlorides.	The compounds are less hydrated. $NaCl$, KCl and $RbCl$ form non-hydrated chlorides
(xiii) Reducing power	Weaker, as ionisation potential values are high and oxidation potential values are low.	Stronger, as ionisation potential values are low and oxidation potential values are high.

Elements of Group IVA or 14

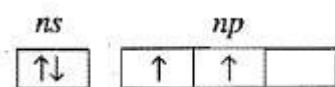
(Elements of Carbon Family, $ns^2 np^2$)

Group IVA or 14 of long form of periodic table consists of six elements-carbon (C), silicon (Si), germanium (Ge), tin (Sn), lead (Pb) and ununquadium. These six elements constitute a family known as carbon family. These are *p*-block elements as the last differentiating electron is accommodated in *np* shell. These elements have four electrons in their valency shell and thus placed in the IVth group. The elements of this group show similarities as well as gradation in properties with rise of atomic number and thus their inclusion in the same group is justified on the basis of electronic configuration and physical and chemical properties which are described below

1- Electronic configuration : The electronic configuration of the members of this group are:

Element	At.NO.	Electronic configuration	Inert gas core
Carbon - C	6	$1s^2 2s^2 2p^2$	[He] $2s^2 2p^2$
Silicon - Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$	[Ne] $3s^2 3p^2$
Germanium – Ge	32	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$	[Ar] $3d^{10} 4s^2 4p^2$
Tin – Sn	50	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^2$	[Kr] $4d^{10} 5s^2 5p^2$
Lead – Pb	82	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f_{14} 5s^2 5p^6 5d_{10} 6s^2 6p^2$	[Xe] $4f_{14} 5d_{10} 6s^2 6p^2$
Ununquadium – Uuq	114	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f_{14} 5s^2 5p^6 5f_{14} 5d_{10} 6s^2 6p^6 6d_{10} 7s^2 7p^2$	[Rn] $5f_{14} 6d_{10} 7s^2 7p^2$

The configurations show that these elements have same number of electrons in the valency shell, i.e., 4 electrons in the valency shell, two of which are in *s*-orbital while remaining two in *p*-orbitals. Thus, they have $ns^2 np^2$ configuration, i.e., *s*-orbital is paired while two *p*-orbitals are unpaired.



The penultimate shell of carbon contains 2 electrons (saturated), of silicon contains 8 electrons (saturated), of germanium contains 18 electrons (saturated) while Sn and Pb contain 18 electrons (unsaturated) each. This shows why carbon differs from silicon in some respects and these two differ from rest of the members of this group. The close resemblance between the elements is quite striking in the case of elements of the first and second groups, but this becomes less evident in the elements of third group and still less evident in the fourth group. **2. Occurrence of the elements :**

Carbon is extremely wide spread in nature. It is an essential constituent of all living matter as proteins, carbohydrates and fats. Carbon is the seventeenth and silicon the second most abundant element by mass in the earth's crust. Carbon is found both in native and combined states. Silicon occurs very widely as silica and a wide variety of silicate minerals and clays. Germanium is only found in traces in some silver and zinc ores, and in some types of coal.

No doubt that the abundance of tin and lead is comparatively low, but they occur as concentrated ores. Tin is mined as cassiterite, SnO_2 and lead is found as galena ore, PbS . In the fusion reactions occurring on stars and sun, carbon acts as catalyst. The energy released in the process is called stellar energy.

The last member, ununquadium (114) is recently discovered element. It is synthetic, radioactive and unstable element. Not much is known about its properties.

3.Non-metallic and metallic character :

The change from non-metallic to metallic character with the increase of atomic number is best illustrated by this group. Carbon, the first element, is a non-metal, silicon, the second element has most of the properties of a non-metal but its electrical properties and some of the physical properties are those of a semi-metal (metalloid). Germanium is a metalloid (properties are mixed, i.e., of a metal and a non-metal) while last two members Sn and Pb are distinctly metals.



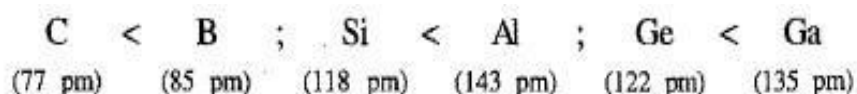
The change from non-metallic to metallic character is due to less effective nuclear charge and increased number of available orbitals with increase in the size of the atom.

4. Atomic radii atomic volume :

Atomic radii and atomic volume increase gradually on moving down the group. The size increases due to the effect of extra shell being added from member to member.

	C	Si	Ge	Sn	Pb
Atomic radius (pm)	77	118	122	140	146
At.volume(ml)	3.4	11.4	13.6	16.3	18.27

It is observed that there is large increase in atomic radius from carbon to silicon but from silicon onwards, the increase is comparatively small from member to member. This is due to the fact that shielding effect of $s^2 p^6$ electrons of the penultimate shell in silicon is large while the shielding effect of d^{10} electrons in Ge and Sn and $d^{10} f^4$ electrons in Pb is less. In the same period, the atomic radii of group 14 elements are smaller than the corresponding elements of group 13. This is due to fact that effective nuclear charge increases when we move from group 13 to group 14. This brings contraction in size.



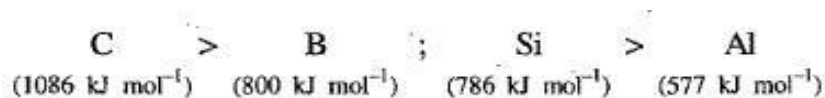
5. Ionisation potential :

The ionisation potentials decrease gradually from carbon to lead but not systematically as in groups I and II. The value of lead is slightly higher than expected due to lanthanide contraction.

		C	Si	Ge	Sn	Pb
Ionisation	$\Delta_i H_1$	1086	786	761	708	715
enthalpy	$\Delta_i H_2$	2352	1577	1537	1411	1450
(kJ mol ⁻¹)	$\Delta_i H_3$	4620	3228	3300	2942	3081
	$\Delta_i H_4$	6220	4354	4409	3929	4082

Large decrease in ionisation potential from C to Si is due to increase in size of the atom. Decrease in ionisation potential from silicon onwards is comparatively smaller due to less screening effect of d^{10} electrons in Ge and Sn and due to d^{10} or f^4 electrons in Pb. The slight increase in the ionisation energy from Sn to Pb is due to lanthanide contraction and increase of 32 units of nuclear charge in Pb over Sn, i.e. valency electrons are more tightly held in Pb.

The first ionisation energies of group 14 are higher than the corresponding elements of group 13 in the same period



The increase is due to decrease in size and increase in charge on nucleus of group 14 elements in the same period.

6. Melting and boiling points:

Carbon has an extremely high melting point (4100°C). Silicon melts appreciably lower than carbon but the values of silicon and germanium are still high. (Si = 1420°C; Ge = 945°C). They have the very stable diamond like structure in which smaller atoms are closely packed. Tin and lead are metallic and have much lower melting points (Sn = 232°C; Pb = 327°C) because the M-M bonds are weaker. They do not use all the four outer electrons for metallic bonding

The boiling point of carbon is exceedingly high. It decreases in silicon and then increases in germanium. However, the boiling point decreases from germanium to lead.

7. Electronegativity:

The electronegativity values do not decrease in a regular manner. Carbon is the most electronegative element while Si, Ge, Sn and Pb possess nearly the same values. This is due to filling of *d*-orbitals in Sn and Ge and also *f*-orbitals in lead.

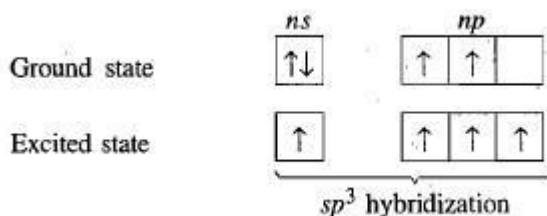
	C	Si	Ge	Sn	Pb
Electronegativity	2.5	1.8	1.8	1.8	1.9

8. Allotropy :

Except lead , all other elements of this group show allotropy. For example, carbon exists as diamond, graphite, coal, charcoal and lampblack; silicon exists in two forms, crystalline and amorphous; germanium exists in two crystalline forms and tin exists in three forms; grey tin, white tin and rhombic tin.

9. Valency :

All these elements show a covalency of 4. The tetravalency is explained on the basis of the shifting of one of the paired *ns* electrons to the vacant *np* orbital in the same shell.

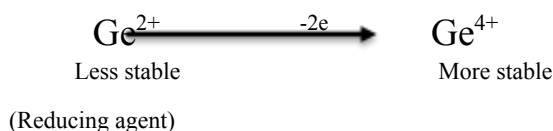


These four half filled orbitals mix together to give four sp^3 hybrid orbitals resulting in a tetrahedral structure and each having one unpaired electron.

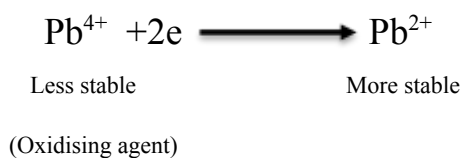
When ns^2 electrons of outermost shell do not participate in bonding it is called inert pair and the effect is called inert pair effect. The last three elements have a tendency to form M^{2+} ions as well as M^{4+} ions. Since, the inert pair effect increases from Ge to Pb, the stability of M^{4+} ions decreases and that of M^{2+} ions increases. Thus, the stability of these ions follows the following order:



The compounds of Ge^{2+} are unstable while compounds of Ge^{4+} are stable. Thus, the compounds of Ge^{2+} get oxidised into Ge^{4+} easily and act as reducing agents.



The compounds of Sn^{2+} are less stable than Sn^{4+} . Thus Sn^{2+} compounds also act as reducing agents. In the case of lead, Pb^{2+} compounds are more stable than Pb^{4+} compounds. the Pb^{2+} compounds, thus, act as oxidizing agents.



Since M^{4+} ions are smaller than M^{2+} ions, in general, M^{4+} compounds behave as covalent due to high polarisation (small size and high charge) and M^{2+} compounds are ionic.

10. Multiple bonding :

Carbon, the first member of group 14, possesses a pronounced ability to form stable p_{π} - p_{π} multiple bonds (double and triple bonds) with itself and with other first row elements such as nitrogen and oxygen. The compounds containing $>\text{C}=\text{C}<$, $-\text{C}\equiv\text{C}-$, $-\text{C}\equiv\text{N}$, $>\text{C}=\text{O}$, and $>\text{C}=\text{S}$ bonds are common. Graphite, an allotropic form of carbon, is also an example of p_{π} - p_{π} bonding. Silicon and other elements of this group show their reluctance in forming p_{π} - p_{π} multiple bonding due to their large atomic sizes. However, silicon and other elements of this group have vacant d -orbitals in their valence shell. These elements can form d_{π} - p_{π} double bonds with nitrogen and oxygen. This bond is formed by the donation of an electron pair from filled $2p$ -orbitals of N or O to the vacant $3d$ -orbitals of silicon or other elements of group 14. The existence of d_{π} - p_{π} bonding explains the structures of trimethylamine, $(\text{CH}_3)_3\text{N}$, and trisilylamine $\text{N}(\text{SiH}_3)_3$ and their basic nature.

In trimethylamine, the N atom undergoes sp^3 -hybridisation giving tetrahedral configuration. The geometry of the molecule is pyramidal as one of the tetrahedral positions is occupied by a lone pair. p_{π} - d_{π} bonding cannot occur in this molecule as carbon does not have d -orbitals. This

lone pair, $\text{:N(CH}_3)_3$, can be donated to Lewis acids and thus it shows a basic nature. In trisilylamine, sp^2 -hybridisation occurs giving trigonal planar geometry to the molecule. The lone pair of electrons is present in unhybridised p -orbital. This overlaps with empty d -orbital of any one of the silicon atoms forming $p\pi-d\pi$ back bonding. Due to non-availability of lone pair, this molecule does not show basic nature.

11. Catenation :

The linking of identical atoms with each other to form long chains is called catenation. All the elements of this group have the property of catenation. However, this property decreases from carbon to lead. Thus, carbon has the maximum property of catenation, silicon has much lesser tendency, germanium has still lesser tendency whereas tin and lead hardly show this property. The decrease of this property is associated with $M-M$ bond energy which decreases from carbon to lead.

C—C	83 kcal/mol
Si—Si	54 kcal/mol
Ge—Ge	40 kcal/mol
Sn—Sn	37 kcal/mol

The reason for greater tendency of carbon for catenation than other elements may further be explained by the fact that C-C bond energy is approximately of the same value as the energies of bonds between carbon and other elements. On the other hand Si-Si bond is weaker than the bonds between silicon and other elements.

C—C	83 kcal/mol	Si—Si	54 kcal/mol
C—O	86 kcal/mol	Si—O	88 kcal/mol
C—Cl	81 kcal/mol	Si—C	186 kcal/mol

Thus, carbon forms a number of compounds in which a large number of carbon atoms are linked together in the form of straight chains, branched chains or closed rings. The property of catenation is responsible for a very large number of compounds of carbon.

12. Maximum covalency :

Carbon has only two energy shells, K and L. L shell (outermost shell) has four orbitals $2s$, $2p_x$, $2p_y$, and $2p_z$. These four orbitals can accommodate a maximum of 8 electrons forming four covalent bonds. Thus, maximum covalency of carbon is four because it has no d -orbitals or vacant orbitals which can be used to accommodate more electrons. The remaining elements, however, have vacant d -orbitals. These permit the formation of coordinate bonds with other atoms or ions having lone pairs of electrons. For example, SiF_4 can combine with 2F^{1-} ions.



Thus, the maximum covalency of silicon can be 6. Similarly, other members can show maximum covalency of six involving sp^3d^2 hybridization.

Since all these elements except carbon satisfy the following three conditions for the formation of complexes, they have the tendency to form complexes using d -orbitals. (i) small size of the atom or ion

- (ii) high charge
- (iii) availability of vacant orbitals of appropriate energy.

13. Reactivity:

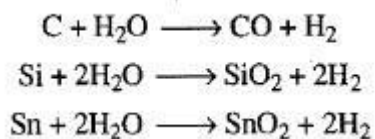
The elements of this group are relatively less reactive but reactivity increases down the group. Lead often appears more unreactive than expected. This is partly due to surface coating of the oxide and partly due to the high overpotential for the reduction of H^+ to H_2 at a lead surface.

- (i) Reactivity towards air : These elements react with the oxygen of the air on strong heating when their oxides are formed.



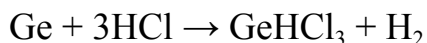
Mono-oxides CO , SiO , GeO are also known. SiO is unstable.

- (ii) Reactivity towards water : C , Si and Ge are unaffected by water. However, on red heating, these elements except lead decompose steam.



Lead is unaffected by water, probably, because of a protective oxide film.

- (iii) Reactivity towards acids : Non-oxidising acids do not attack carbon and silicon, Germanium is not attacked by dilute HCl . However, when metal is heated in a stream of HCl gas, germanium chloroform is formed.



Tin dissolves slowly in dilute HCl but readily in concentrated HCl



Lead also dissolves in dilute HCl

Lead also dissolves in dilute HCl

Lead dissolves in concentrated HCl forming chloroplumbous acid, but the reaction stops after sometime due to deposition of $PbCl_2$.