

Chapter-13

s - and p - Block Elements

Elements of group I-A (Alkali Metals) and Group II-A constitute s-block. They have their valence electrons in s-orbital. S-block has only metals however hydrogen and helium are exceptions, these two are non-metals.

Elements of group III-A, IV-A, V-A, VI-A, VII-A and VIII-A constitute p-block. They have their valence electrons in p-orbital. P-block consists of metals as well as non-metals.

3rd Period (Sodium to Argon)

Trend in Physical properties:

Electronic configuration:

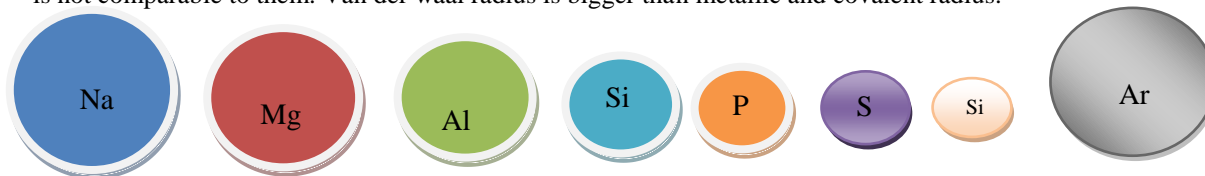
The 3rd shell starts from sodium and completes at argon.

$_{11}\text{Na}$	→	$1s^2, 2s^2, 2p^6, 3s^1$	= [Ne], $3s^1$
$_{12}\text{Mg}$	→	$1s^2, 2s^2, 2p^6, 3s^2$	= [Ne], $3s^2$
$_{13}\text{Al}$	→	$1s^2, 2s^2, 2p^6, 3s^2, 3p^1$	= [Ne], $3s^2, 3p^1$
$_{14}\text{Si}$	→	$1s^2, 2s^2, 2p^6, 3s^2, 3p^2$	= [Ne], $3s^2, 3p^2$
$_{15}\text{P}$	→	$1s^2, 2s^2, 2p^6, 3s^2, 3p^3$	= [Ne], $3s^2, 3p^3$
$_{16}\text{S}$	→	$1s^2, 2s^2, 2p^6, 3s^2, 3p^4$	= [Ne], $3s^2, 3p^4$
$_{17}\text{Cl}$	→	$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$	= [Ne], $3s^2, 3p^5$
$_{18}\text{Ar}$	→	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$	= [Ne], $3s^2, 3p^6$

Trend in atomic radii:

Generally atomic radii decrease in a period from left to right across the period due to increasing nuclear charge.

For Na, Mg and Al metallic radii are considered. For Si, P, S, and Cl covalent radii are considered while for Argon van der waal radius is taken into consideration. Metallic radii and covalent radii are comparable while van der waal is not comparable to them. Van der waal radius is bigger than metallic and covalent radius.



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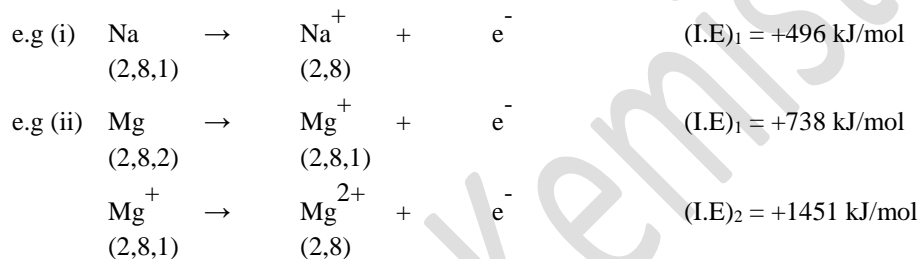
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Ionization energy:

“The energy required to remove the most loosely bound electron from an isolated atom (gaseous atom) or gaseous ion to make cation is called Ionization Potential or Ionization Energy.”

Ionization energy is an endothermic process in which energy is absorbed so sign for this energy is +ve. This energy is required to overcome the force of attraction of nucleus on the electron. After removal of first electron hold of nucleus on remaining electrons increases so Second I.P is greater than First I.P because more energy is required to remove the second electron and so on.



By I.E values we can determine number of valence electrons and valency of an atom. e.g.

	1 st I.E	2 nd I.E	3 rd I.E	4 th I.E
Li	520	7,298	11,815	-
Be	899	1,757	14,848	21,006

In case of Li there is a sudden jump in value of its 2nd I.E which means this is electron of its inner shell so its valence shell has only one electron and thus its valency is one.

In case of Be there is a sudden jump in value of its 3rd I.E which means this is electron of its inner shell so its valence shell has two electrons and thus its valency is two.

Factors affecting I.E or I.P:

- Nuclear Charge:** With increase in nuclear charge, hold of nucleus increases on electrons so more energy will be required to remove electrons. Thus more is the nuclear charge more will be the I.E and vice versa.
- Atomic Size:** Smaller is the size of atom, more will be the hold of nucleus on electrons so more energy will be required to remove electrons. Thus smaller is the atomic size more will be the I.E and vice versa.
$$\text{I.E} \propto 1/r^2$$
- Shielding Effect:** Greater the shielding effect of lower shells less will be the hold of nucleus on electrons of outer shell so low will be the I.E and vice versa.
- Penetration Effect:** Fraction of time which the electrons of outer orbitals spend near nucleus is called penetration effect. The order of this effect and thus I.E is
$$s > p > d > f$$
- Electronic Configuration:** Completely filled and half-filled orbitals are more stable and thus their electrons are difficult to remove so their I.E is high. Thus elements of Groups 1A, IIA and VIIIA have extra ordinary high I.E.

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Trend of 1st ionization energy in Periodic Table:

Generally I.E increases in a period from left to right due to decreasing atomic size and increasing nuclear charge. But anomalies are observed at group IIA and VA they have extra ordinary high I.E. This is due to the reason that they have completely filled or half-filled outer orbitals which are more stable and thus their electrons are difficult to remove so their I.E are high. Group II-A has outer completely filled s-orbital while group V-A has outer half-filled p-orbital so they have extraordinary high ionization energies.

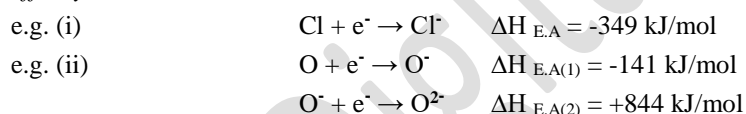
e.g. trend of Ionization Energy in 2nd and 3rd period is

Groups	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
Elements of period II	Li	Be	B	C	N	O	F	Ne
Ionization Energy (kJ)	520	900	801	1086	1402	1314	1681	2081
Elements of period III	Na	Mg	Al	Si	P	S	Cl	Ar
Ionization Energy (kJ)	496	738	578	786	1012	1000	1251	1521

On other hand in a group I.E decrease from top to bottom due to increasing atomic size.

Electron Affinity:

“The energy released or absorbed when an electron is added to a gaseous atom or gaseous ion is called electron affinity.”



Trend of Electron Affinity:

Elements of period III	Na	Mg	Al	Si	P	S	Cl	Ar
Electron affinity	-53	230	-50	-120	-74	-200	-349	35

Generally electron affinities increase across the period (from left to right). However group II-A elements due to their complete s-orbital have positive values for their first electron affinities. Similarly group VIII-A elements also have positive values for their first electron affinities due to complete p-orbital.

Second electron affinities are positive for all elements.

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Electronegativity:

“The tendency of an atom to attract shared pair of electrons is called electronegativity.”

Trend in electronegativity:

Electronegativity increases across the period (from left to right) due to increasing nuclear charge and decreasing atomic size.

Elements of period III	Na	Mg	Al	Si	P	S	Cl	Ar
Electronegativity	0.93	1.31	1.81	2.02	2.19	2.58	3.16	-

As Argon does not form covalent bonds hence it cannot be assigned electronegativity value.

Electrical Conductivity:

“The ability of a substance to conduct electricity is called electrical conductivity.”

Metals possess free electrons (valence shell electrons) so they conduct electricity but nonmetal cannot conduct electricity as they do not possess free electrons. However carbon (graphite) has free p-electrons so it also conduct electricity.

Trend in electrical conductivity:

Electrical conductivity increases from sodium to aluminum. Silicon is semiconductor. From Phosphorus to Argon are non-metals and non-conductors.

Elements of period III	Na	Mg	Al	Si	P	S	Cl	Ar
Electrical conductivity	0.26	0.42	1.00	0.10	0	0	0	0

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Melting and Boiling Points:

“The temperature at which solid and liquid exist in equilibrium is called melting point.”

“The temperature at which vapour pressure of liquid becomes equal to atmospheric or external pressure is called boiling point.”

Trend in Melting and Boiling Points:

The melting and boiling points increases across the period (from left to right) up to middle and then decreases.

Elements of period III	Na	Mg	Al	Si	P	S	Cl	Ar
Melting Point (K)	371	922	933	1683	317	392	172	84
Boiling Point (K)	1156	1380	2740	2628	553	718	238	87

Trend in Chemical Properties:

Reaction with Water:

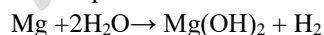
Reactivity of elements with water in period from left to right decreases up to middle and then become irregular.

Sodium reacts with cold water vigorously producing sodium hydroxide and hydrogen gas. Reaction is highly exothermic.

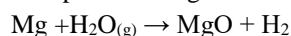


Magnesium do not show appreciable reaction with cold water, it react with hot (boiling) water.

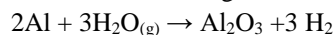
When a clean coil of magnesium is dropped in cold water it gets covered with bubbles of hydrogen which floats it to the surface of water. As a result of reaction magnesium hydroxide is also produced which get deposited on the surface of magnesium and thus stops further reaction.



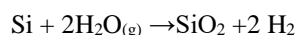
Magnesium burns in steam and produce magnesium oxide (white colour) and hydrogen gas.



Aluminum powder reacts with steam on heating. But reaction is very slow due to oxide layer on aluminum.



Silicon reacts with steam at red heat.

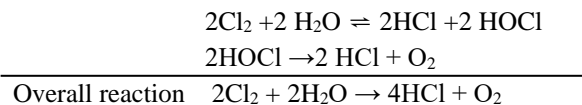


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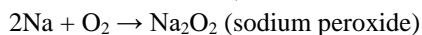
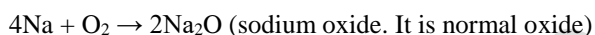
Chlorine reacts with water and produces hydrochloric acid and hypochlorous acid. The reaction is reversible. Hypochlorous acid in presence of sunlight slowly decomposes to hydrochloric acid and oxygen gas.



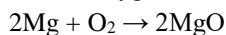
Argon does not react with water.

Reaction with Oxygen:

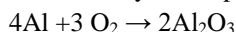
Sodium (Group I-A) burns in oxygen with yellow flame and produces a mixture of sodium oxide and sodium peroxide. Both are white solids.



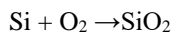
Magnesium (Group II-A) burns in oxygen with intense luminous flame and produce white solid magnesium oxide.



Aluminum (Group III-A) will burn only if it is powdered, otherwise oxide layer on it prevents reaction.



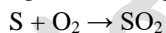
Silicon (Group IV-A) burns only on very strong heating.



White Phosphorus (Group V-A) readily catches fire in air and burns with white smoke producing phosphorus (III) oxide and phosphorus (V) oxide.



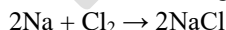
Sulphur burns in oxygen on gentle heating with a pale blue flame producing sulphur dioxide gas.



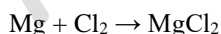
Argon does not react with oxygen.

Reaction with Chlorine:

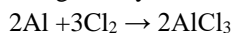
Sodium (Group I-A) burns in chlorine with bright orange flame and produces a white solid sodium chloride.



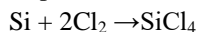
Magnesium (Group II-A) burns in chlorine with intense luminous flame and produce white solid magnesium chloride.



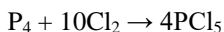
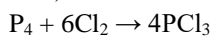
Aluminum (Group III-A) will react with chlorine when dry chlorine is passed over aluminum foil placed in a long tube. Reaction occurs on heating. Pale yellow aluminum chloride is produced.



Silicon (Group IV-A) reacts with chlorine when chlorine is passed over heated powder of silicon. A colourless liquid silicon tetra chloride is produced.



White Phosphorus (Group V-A) burns in chlorine producing phosphorus (III) chloride and phosphorus (V) chloride.

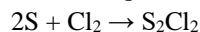


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Sulphur reacts with chlorine if chlorine is passed over heated sulphur and disulphur chloride (Sulphuryl chloride) is produced which is orange coloured liquid having foul smell.



Argon does not react with chlorine.

Compounds of Third Period:

Oxides of Third Period:

Binary compounds of oxygen are called oxides.

Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀	SO ₃	Cl ₂ O ₇
-	-	-	-	P ₄ O ₆	SO ₂	Cl ₂ O

Structure of oxides:

Oxides of sodium, magnesium and aluminum are giant ionic structures, oxide of silicon is giant molecular structure, oxide of phosphorus is dimer, while oxides of sulphur and chlorine are discrete molecules.

Melting and Boiling points of oxides:

Melting and boiling points of oxides of sodium, magnesium and aluminum are high due to their giant ionic structures. They have strong ionic bonds so high energy is required to break these bonds, thus their melting and boiling points are high.

Melting and boiling points of oxide of silicon are high due to its giant molecular structure. It has strong covalent bonds so high energy is required to break these bonds, thus its melting point and boiling point are high.

Melting and boiling points of oxides of phosphorus, sulphur and chlorine are low because they exist as discrete molecule. They have weak van der Waal forces so little energy is required to overcome these forces, thus their melting and boiling points are low. Strength of Van der Waal forces depends upon size, shape and polarity of molecules.

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀	P ₄ O ₆	SO ₃	SO ₂	Cl ₂ O ₇	Cl ₂ O
Melting Points (°C)	1280	2900	2040	1610	340	23.8	-17	-72	-92	-120.6
Boiling Points (°C)	1950	3600	2977	2230	360	173.1	45	-10	82	2

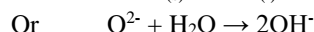
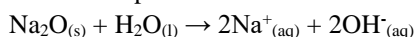
Electrical conductivity of oxides:

The covalent oxides do not conduct electricity as they do not possess free electrons also they do not have ions. However ionic oxides in molten state or aqueous state conduct electricity due to movement of their ions.

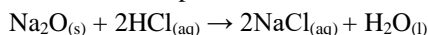
Acidic and basic behaviour of oxides:

Across the period basic strength of oxides decreases while acid strength increases. Thus oxides of Na and Mg are basic. Oxide of Al is amphoteric while oxides of Si, P, S, and Cl are acidic.

Sodium oxide reacts vigorously with water and produces alkaline solution.



Sodium oxide being base also reacts with acids and produces salt and water.

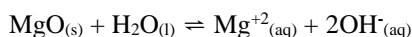


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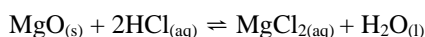
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Magnesium oxide is slightly soluble in water. It also produces alkaline solution.

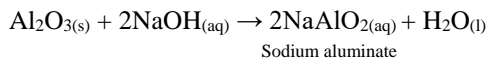
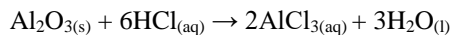


Magnesium oxide being base also reacts with acids and produces salt and water.

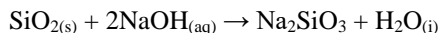


CaO also show same behaviour $\text{CaO}_{(s)} + 2\text{HCl}_{(aq)} \rightleftharpoons \text{MgCl}_{2(aq)} + \text{H}_2\text{O}_{(l)}$

Aluminum oxide being amphoteric oxide reacts both with dilute acids and dilute alkalis.

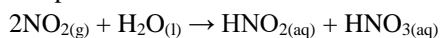


Silicon oxide does not react with water however it reacts with alkalis as it is weak acid.

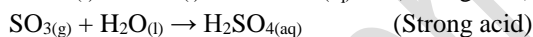
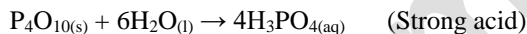


However CO_2 can react with water $\text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{CO}_{3(aq)}$ (Carbon belongs to 2nd period)

Oxide of nitrogen reacts with water and produces two acids.



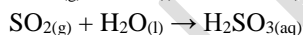
Oxides of P, S and Cl react with water and produce strongly acidic solution.



However Cl_2O produce comparatively weak acid.



SO_2 also react with water



The following table is showing summary of trend in physical properties of oxides:

Formula of Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10} P_4O_6	SO_3 SO_2	Cl_2O_7 Cl_2O
State of oxide	Solid	Solid	Solid	Solid	Solid Solid	Liquid Gas	Liquid Gas
Electrical Conductivity	Good	Good	Good	Very poor	Nil	Nil	Nil
Structure of Oxides	Giant ionic Structure	Giant ionic Structure	Giant ionic Structure	Giant molecular Structure	Discrete molecules	Discrete molecules	Discrete molecules
Nature of Oxide	Strongly alkaline	Weakly alkaline	Amphoteric	Acidic	Acidic	Acidic	Acidic

Chlorides of Third Period:

The following table is showing summary of trend in physical properties of chloride:

Formula of Oxide	NaCl	MgCl_2	Al_2Cl_6	SiCl_4	PCl_3	S_2Cl_2
State of Chlorides	Solid	Solid	Solid	Liquid	Liquid	Liquid
Melting points(°C)	801	708	192.4	- 69	- 93.6	- 80
Boiling points(°C)	1465	1418	423	57	74	136
Electrical Conductivity in liquid state	Good	Good	Very poor	Nil	Nil	Nil
Structure of Chlorides	Giant ionic Structure	Giant ionic Structure	Molecular Structure	Discrete molecules	Discrete molecules	Discrete molecules
Nature of Chlorides	Ionic	Partly ionic	Partly ionic	Polar Covalent	Polar Covalent	Polar Covalent

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Addition of chlorides to water	Dissolves readily	Dissolves readily	Dissolves readily	Reacts with water producing fumes of HCl	Reacts with water producing fumes of HCl	Reacts with water producing fumes of HCl
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Chlorides of Na and Mg are giant ionic, having ionic bonds which are strong so their melting and boiling points are high. While chlorides of Al, Si, P and S are discrete molecules having weak van der Waal forces so their melting and boiling points are low.

Hydroxide of Third Period:

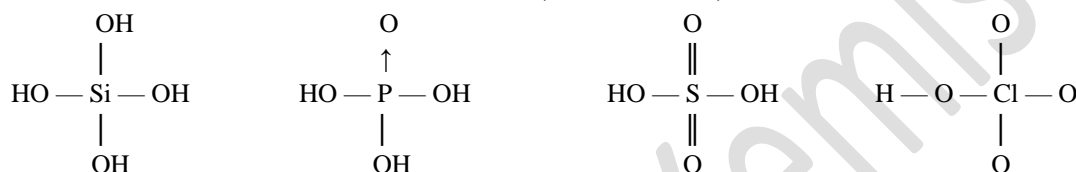
Hydroxides are the compounds in which OH⁻ (hydroxide) ion is attached to metals through ionic bonds or OH (neutral) group attached to non metals through covalent bonds.

The ionic hydroxides are basic in nature e.g. NaOH and Mg(OH)₂.

Aluminum hydroxide Al(OH)₃ is amphoteric.

The covalent hydroxides are acidic in nature e.g. Si(OH)₄ or H₄SiO₄, H₃PO₄, H₂SO₄ and HClO₄.

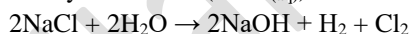
(Ortho Silicic acid)



Sodium Hydroxide (NaOH):

Preparation:

Sodium hydroxide is prepared by electrolysis of brine (NaCl_(aq)) in Nelson Cell.



Properties:

- (i) It is white solid.
- (ii) It is ionic in nature.
- (iii) It has soapy touch i.e. slippery touch.
- (iv) It has corrosive action for skin.
- (v) It has bitter taste.
- (vi) It is hygroscopic.
- (vii) It is highly soluble in water and the process is highly exothermic due to formation of hydrates.
- (viii) It is soluble in alcohol.

Uses:

- (i) It is used in soap industry.
- (ii) It is used for refining of petroleum.
- (iii) It is used for reclaiming rubber.
- (iv) It is used for making mercerized cotton.
- (v) Its aqueous solution is used to open blocked drainage pipes.
- (vi) It is used in acid base titration.

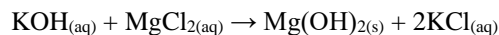
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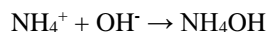
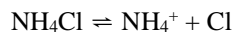
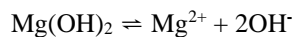
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Magnesium Hydroxide [Mg(OH)₂]:*Preparation:*

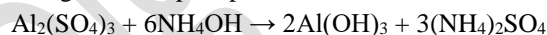
Magnesium hydroxide is obtained as white precipitate when caustic potash (KOH) solution is added to solution of soluble magnesium salt.

*Properties:*

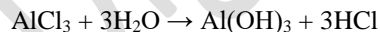
- (i) It is white solid.
- (ii) It is ionic in nature.
- (iii) It has soapy touch.
- (iv) It has corrosive action for skin.
- (v) It has bitter taste.
- (vi) It is hygroscopic.
- (vii) It is soluble in water.
- (viii) Its solubility in water tremendously increases by adding ammonium chloride to its solution. This is due to the fact that ammonium ions remove OH⁻ ions. So the equilibrium of Mg(OH)₂ gets disturbed and according to Le Chatelier's Principle equilibrium shifts to the right.

**Aluminum Hydroxide [Al(OH)₃]:***Preparation:*

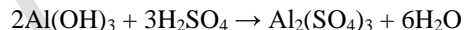
- (i) When some alkali solution is added to aqueous aluminum salt solution, aluminum hydroxide is obtained as white gelatinous precipitate.



- (ii) It can also be prepared by hydrolysis of AlCl₃.

*Properties:*

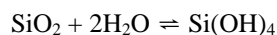
- (i) It is soluble in acids and alkalis.
- (ii) It is amphoteric.

*Use:*

It is used to absorb various dyes forming a colouring matter known as "lakes".

Silicon Hydroxide:

Silicon hydroxide is prepared by reaction of SiO₂ with water at 800°C.



Silicon hydroxide is unstable so it is polymerized.

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Group I-A Elements

Elements of Group I-A are called alkali metals due to alkaline nature of their oxides and hydroxides.

The electronic configuration of group I-A elements is:

Alkali Metals		
${}^3\text{Li}$	$1s^2, 2s^1$	$[\text{He}]2s^1$
${}^{11}\text{Na}$	$1s^2, 2s^2, 2p^6, 3s^1$	$[\text{Ne}]3s^1$
${}^{19}\text{K}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$	$[\text{Ar}]4s^1$
${}^{37}\text{Rb}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^1$	$[\text{Kr}]5s^1$
${}^{55}\text{Cs}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^1$	$[\text{Xe}]6s^1$
${}^{87}\text{Fr}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^1$	$[\text{Rn}]7s^1$

Occurrence:

Both alkali metals and alkaline earth metals are very reactive so they do not exist free in nature and exist in combined state.

Sodium: Its compounds constitute about 3% of the earth crust. The most important ore of sodium is Rock salt or Halite (NaCl). Its large deposits are found throughout world. In Pakistan its deposits are found in Khewra, Warcha and Bahadarkhel (Karak). It is also found in sea water. Other ores of sodium are Chile saltpeter (NaNO_3), Natron ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$), Trona ($\text{Na}_2\text{CO}_3 \cdot 2\text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) and Borax (Tincal) [$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$].

Potassium: Its important ores are Feldspar (KAlSi_3O_8), Sylvite (KCl) and Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). Deposits of these ores are found in Germany, New Mexico and Searles Lake in California.

General Physical Properties of Alkali metals (group IA):

- (i) **Softness:** They are soft and their softness increases down the group. Sodium is so soft that it can be cut even by a blunt knife.
- (ii) **Luster:** They have silvery luster when freshly cut.
- (iii) **Nature:** They are malleable.
- (iv) **Melting boiling points:** They have low melting and boiling points and which decrease down the group.

Element	Li	Na	K	Rb	Cs
Melting Point ($^{\circ}\text{C}$)	1085	97.8	63.7	38.9	28.7
Boiling Point ($^{\circ}\text{C}$)	1330	892	760	688	670
- (v) **Electrical conductance:** They are good conductors of heat and electricity.
- (vi) **Atomic radii:** Their atomic radii increase down the group due to addition of more and more shells.

Element	Li	Na	K	Rb	Cs
Atomic Radius (A°)	1.55	1.90	2.35	2.48	2.67
- (vii) **Electropositivity:** They are highly electropositive and electropositivity increases down the group.

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- (viii) **Electronegativity:** Their electronegativities are very low. Their electronegativities decrease down the group.

Element	Li	Na	K	Rb	Cs
Electronegativity (Pauling scale)	1.0	0.9	0.8	0.8	0.7

- (ix) **Ionization Energies:** Their ionization energies are very low. So they can easily lose their electrons. Ionization energy decreases down the group.

Element	Li	Na	K	Rb	Cs
1 st Ionization Energy(e.v)	5.4	5.1	4.3	4.2	3.9

- (x) **Density:** Their densities increase down the group, however fluctuation occurs at potassium.

Element	Li	Na	K	Rb	Cs
Density (g/cm ³)	0.534	0.972	0.86	1.53	1.903

- (xi) **Reducing ability:** They are good reducing agents.

- (xii) **Flame test:** They give characteristic colours to Bunsen burner flame. When they are heated in the flame their electrons jump to higher orbits. Then on dropping back they emit visible light of different colours.

Element	Li	Na	K	Rb	Cs
Colour of flame	Crimson red	Golden yellow	Lilac/violet	violet	violet

Procedure:

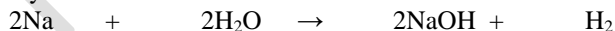
Paste of salt is made in conc HCl then a wire of platinum is dipped in the paste and is then brought to the blue flame of Bunsen burner. The colour of flame is observed and identification is made.

Chemical Properties:

Alkali metals are very reactive.

Reaction with water:

Alkali metals are very strong reducing agents so they react vigorously with water and reduce it to hydrogen gas and themselves oxidize to metal hydroxide.



Reaction is highly exothermic so the hydrogen produced catches fire. Vigorousness of reaction increases down the group.

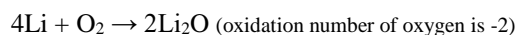
Lithium shows slow reaction. Sodium shows vigorous reaction, fizzing and skating about on the water.

Potassium shows more vigorous reaction. It cracks and pops as hydrogen burns. Rubidium and cesium explode violently on contact with water.

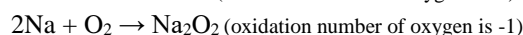
Reaction with oxygen:

Alkali metals are very reactive with air. Reactivity increases down the group. So Li, Na and K are stored in kerosene oil while Cs and Rb are stored in sealed glass tube to prevent air to contact.

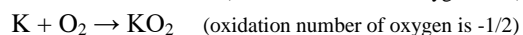
Usually Lithium produces normal oxide



Sodium often produces peroxide



Potassium, Rubidium and Cesium produce superoxide



Reaction with Nitrogen:

Only Lithium reacts with nitrogen of the air and produces lithium nitride. $6\text{Li} + \text{N}_2 \rightarrow 2\text{Li}_3\text{N}$

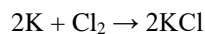
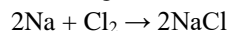
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Reaction with chlorine:

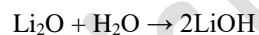
Sodium burns in chlorine with orange flame. Other alkali metals also burn in chlorine and produce white solid metal chloride.

**Compounds of Alkali Metals (Group I-A):****Oxides:**

Alkali metals on direct reaction with oxygen produce their oxides. Oxides of group I-A are basic in nature.

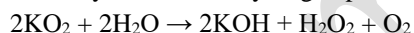
Reaction with water:

Normal oxides on reaction with water produce metal hydroxide.

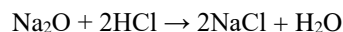
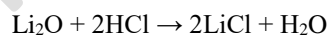


Peroxides on reaction with water produce metal hydroxide and hydrogen peroxide. $\text{Na}_2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2\text{O}_2$

Super oxides on reaction with water produce metal hydroxide and hydrogen peroxide and oxygen.

*Reaction with dilute acids:*

Normal oxides on reaction with dilute acid produce metal chloride and water.

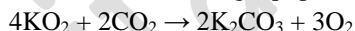


Peroxides on reaction with dilute acid produce metal chloride and hydrogen peroxide. $\text{Na}_2\text{O}_2 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O}_2$

Super oxides on reaction with dilute acid produce metal chloride and hydrogen peroxide and oxygen.

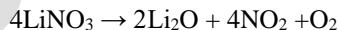


- Potassium super oxide (KO_2) is used in breathing equipments of mountaineers for getting oxygen from carbon dioxide.

**Nitrates:***Effect of Heat on Nitrates:*

Nitrates of alkali metals on heating decompose and produce metal nitrites and oxygen. $2\text{NaNO}_3 \rightarrow 2\text{NaNO}_2 + \text{O}_2$

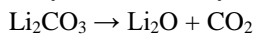
However nitrate of lithium on heating decompose to produce metal oxide, nitrogen dioxide (Brown colour gas) and oxygen.



(Brown)

Carbonates:*Effect of Heat on Carbonates:*

Carbonates of alkali metals are thermally stable and they do not decompose on heating. However Lithium Carbonate decomposes on heating.



- Carbonates of group I-A are more stable than that of group II-A. Cations of first group have less charge so less charge density. Therefore, their polarizing power will be low so less covalent character and hence their carbonates are more stable.

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Bicarbonates:*Effect of Heat on Hydrogen Carbonates:*

Hydrogen Carbonates or Bicarbonates of alkali metals are thermally unstable and so they decompose on heating.



Thermal stability of hydrogen carbonates (bicarbonates) group I-A and group II-A increases down the group. Thus LiHCO_3 decompose easily and CsHCO_3 decompose difficultly.

Explanation: A cation with high charge density causes significant polarization of anion. This creates some covalent character in the compound that decreases the stability and assists in its thermal decomposition. This is due to **Fajans' Rule**. Which states, "**Small size cations having high charge density tends to make covalent compounds?**"

As the size of cation increases down the group its charge density decreases accordingly. Therefore, its polarizing power also decreases in the same order. This means covalent character decreases down the group and consequently ionic character increases. And, therefore, thermal stability increases down the group.

- Hydrogen carbonates of group I-A are more stable than that of group II-A. Cations of first group have less charge so less charge density. Therefore, their polarizing power will be low so less covalent character and hence their hydrogen carbonates are more stable.
- Sodium bicarbonate (NaHCO_3) is baking soda. It is used as source of CO_2 in baking process.



It is also used in fire extinguishers.

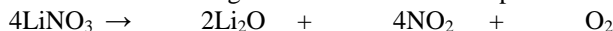
Peculiar Behaviour of Lithium:

Lithium being 1st member of the family shows some differences with rest of the members of its family.

- Melting and boiling point of Lithium are much higher than other members of its family.
- Lithium is hard metal while other elements of the group are soft metals.
- Lithium forms normal oxide while others form peroxide and superoxide.
- LiOH is less basic than that of others.
- Lithium reacts with nitrogen and forms nitride while others do not.
- Lithium reacts with carbon and forms carbide while others do not.
- Carbonate and phosphate of Lithium are insoluble in water while that of others are soluble.
- Li_2CO_3 is unstable and decomposes on heating while carbonates of other are stable even on heating.



- LiCl is somewhat covalent and is soluble in organic solvents, while chlorides of other are ionic and soluble in water.
- Lithium reacts with water very slowly while other reacts violently.
- Nitrate of Lithium produce oxide on heating while nitrates of others produce nitrite.



- LiOH is unstable and decomposes on heating while hydroxides of other are stable even on heating.



- Lithium ion (Li^+) is heavily hydrated than those of others.

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Group II-A Elements

Elements of Group I I-A are called alkaline earth metals. This is due to reason that they are earth making alkaline metals. Their oxides and hydroxides are alkaline in nature.

The electronic configuration of group II-A elements is:

Alkaline Earth Metals		
${}^4\text{Be}$	$1s^2, 2s^2$	$[\text{He}]2s^2$
${}^{12}\text{Mg}$	$1s^2, 2s^2, 2p^6, 3s^2$	$[\text{Ne}]3s^2$
${}^{20}\text{Ca}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$	$[\text{Ar}]4s^2$
${}^{38}\text{Sr}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2$	$[\text{Kr}]5s^2$
${}^{56}\text{Ba}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2$	$[\text{Xe}]6s^2$
${}^{88}\text{Ra}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^6, 7s^2$	$[\text{Rn}]7s^2$

Occurrence:

Magnesium: It is very abundant in rocks of earth's crust. It is found in sea water and springs water. Its mineral are Dolomite ($\text{MgCO}_3 \cdot \text{CaCO}_3$), Magnesite (MgCO_3), Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), Soap stone (Talc) [$\text{Mg}_2(\text{Si}_2\text{O}_5)_2 \cdot \text{Mg}(\text{OH})_2$], and Asbestos [$\text{CaMg}_3(\text{SiO}_3)_4$].

Calcium: It is very abundant in rocks of earth's crust. It is present in sea shells. Its important mineral are Calcite or Lime stone or Marble (CaCO_3), Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

General Physical Properties of Alkaline earth metals (group II-A):

- (i) **Atomic radii:** Their atomic radii increase down the group due to addition of more and more shells.
- | | | | | | | |
|------------------------------|------|------|------|------|------|------|
| Element | Be | Mg | Ca | Sr | Ba | Ra |
| Atomic Radius (Å) | 1.12 | 1.60 | 1.74 | 1.91 | 1.97 | 2.22 |
- (ii) **Ionization Energies:** Their ionization energies decrease down the group. However Ra shows slightly higher ionization energy than that of Ba.
- | | | | | | | |
|---|-----|-----|-----|-----|-----|-----|
| Element | Be | Mg | Ca | Sr | Ba | Ra |
| 1 st Ionization Energy (e.v) | 9.3 | 7.6 | 6.1 | 5.7 | 5.2 | 5.3 |
- (iii) **Electronegativity:** Their electronegativities are very low. Their electronegativities decreases down the group.
- | | | | | | | |
|-----------------------------------|-----|-----|-----|-----|-----|-----|
| Element | Be | Mg | Ca | Sr | Ba | Ra |
| Electronegativity (Pauling scale) | 1.5 | 1.2 | 1.0 | 1.0 | 0.9 | 0.9 |
- (iv) **Melting boiling points:** Their melting and boiling points have no regular trend.
- | | | | | | | |
|------------------------------------|------|------|------|------|------|------|
| Element | Be | Mg | Ca | Sr | Ba | Ra |
| Melting Point ($^\circ\text{C}$) | 1289 | 651 | 851 | 771 | 727 | 700 |
| Boiling Point ($^\circ\text{C}$) | 2500 | 1105 | 1494 | 1381 | 1850 | 1700 |
- (v) **Flame test:** They give characteristic colours to Bunsen burner flame. When they are heated in the flame their electrons jump to higher orbits. Then on dropping back they emit visible light of different colours.
- | | | | | |
|-----------------|--------------|-----------|-------------|-------|
| Element | Mg | Ca | Sr | Ba |
| Colour of flame | Bright white | Brick red | Crimson red | Green |

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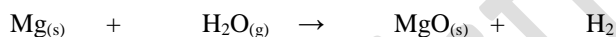
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Chemical Properties:

Alkaline earth metals are reactive but less reactive than that of alkali metals.

Reaction with Water:

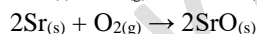
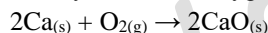
Alkaline earth metals react slowly with water. Their reactivity with water increases down the group. Be do not react with water, Mg reacts with boiling water or steam and produce magnesium oxide and liberates hydrogen gas.



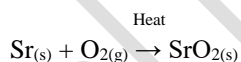
While others (Ca, Sr, Ba) can react with cold water and produce metal hydroxides along with hydrogen gas.

**Reaction with Oxygen:**

All they react with oxygen except Be and produce normal oxides. Be do not react due to having strong protective layer of BeO, however powdered Be may react with oxygen.



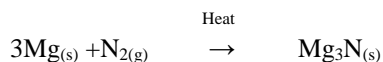
Sr and Ba on heating in air produce peroxides. But this ability is not shown by Be, Mg and Ca



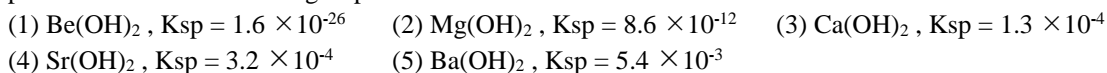
- Solubility of oxides increases down the group.
- Oxides of group II-A are basic in nature.
- CaO is called quick lime. Its reaction with water produces Ca(OH)₂ and the reaction is called slaking. Solid Ca(OH)₂ is called slaked lime while aqueous solution of Ca(OH)₂ is called lime water.

Reaction with Nitrogen:

All they react with nitrogen of the air on heating and produce their nitride. These nitrides are ionic and solid. However nitride of Be is covalent.

**Compounds of Alkaline Earth Metals (Group II-A):****(i) Hydroxides:***Solubility:*

Solubility of hydroxides of alkaline earth metals increases down the group. It means their solubility products increase down the group.

*Explanation:*

Solubility depends upon two factors Lattice energy and Heat of Hydration.

- Lattice energy: Higher is lattice energy lower will be the solubility.
- Heat of hydration: Higher is the heat of hydration higher will be solubility.

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Lattice energy decreases down the group so solubility should increase down the group. Heat of hydration also decreases down the group so solubility should decrease down the group. The two factors are acting oppositely. Lattice energy decreases gradually down the group. On other hand heat of hydration decreases little down the group due to smaller size of hydroxyl ion, therefore, dominating factor is lattice energy. Hence solubility of hydroxide increases down the group.

- $\text{Mg}(\text{OH})_2$ being less soluble in water produce suspension in water. The suspension of $\text{Mg}(\text{OH})_2$ is called milk of magnesia. It is used for the treatment of acidity of stomach.
- Solid $\text{Ca}(\text{OH})_2$ is called slaked lime while aqueous solution of $\text{Ca}(\text{OH})_2$ is called lime water. It is used for qualitative and quantitative analysis of CO_2 .

(ii) **Sulphates:**

Solubility:

Solubility of sulphates of alkaline earth metals decreases down the group. It means their solubility products decrease down the group. CaSO_4 is sufficiently soluble in water while BaSO_4 is almost insoluble in water.

Explanation:

Solubility depends upon two factors Lattice energy and Heat of Hydration.

- (c) Lattice energy: Higher is lattice energy lower will be the solubility.
 (d) Heat of hydration: Higher is the heat of hydration higher will be solubility.

Lattice energy decreases down the group so solubility should increase down the group. Heat of hydration also decreases down the group so solubility should decrease down the group. The two factors are acting oppositely. Lattice energy decreases gradually down the group, therefore, its effect is not significant. On other hand heat of hydration decreases rapidly down the group, therefore, it is dominant factor and thus solubility of sulphates decreases down the group.

(iii) **Carbonates:**

Solubility:

All the carbonates of alkaline earth metals are insoluble in water. However they are soluble in acids.

Thermal Stability:

Thermal stability of carbonates of alkaline earth metals increases down the group and it is evident from their temperature of decomposition.

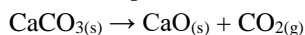


Explanation:

Two factors are responsible for the stability of the carbonates.

- (i) Smaller is the metal ion more is the lattice energy of the resulting metal oxide and hence higher is the stability of the oxide and the carbonate forming this oxide will be less stable. Thus going down the group stability of oxide decreases so stability of their carbonates increases.
- (ii) A cation with high charge density causes significant polarization of anion. This creates some covalent character in the compound that assists in its thermal decomposition. Thus, as size of cation increases down the group, its charge density decreases accordingly. Therefore its polarizing power also decreases in the same order. This means that the covalent character of carbonates decreases down the group. Hence there is a corresponding increase in thermal stability of carbonates going down the group.

Thermal decomposition of carbonates produces metal oxide and carbon dioxide.



(iv) **Nitrates**

Thermal Stability:

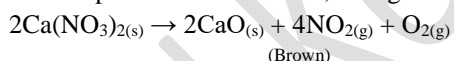
Thermal stability of nitrates of alkaline earth metals increases down the group.

Explanation:

Two factors are responsible for the stability of the nitrates.

- (i) Smaller is the metal ion more is the lattice energy of the resulting metal oxide and hence higher is the stability of the oxide and the nitrate forming this oxide will be less stable. Thus going down the group stability of oxide decreases so stability of their nitrate increases.
- (ii) A cation with high charge density causes significant polarization of anion. This creates some covalent character in the compound that assists in its thermal decomposition. Thus, as size of cation increases down the group, its charge density decreases accordingly. Therefore its polarizing power also decreases in the same order. This means that the covalent character of nitrates decreases down the group. Hence there is a corresponding increase in thermal stability of nitrates going down the group.

Thermal decomposition of nitrates produces metal oxide, nitrogen dioxide and oxygen.



Peculiar Behaviour of Beryllium:

Beryllium being 1st member of the family shows some differences with rest of the members of its family.

- (i) Beryllium atom is very small so according to Fajan's rule which states that small highly charged cations tend to form polar covalent compounds thus its compounds are somewhat covalent.
- (ii) It is as hard as iron while other members of the family are soft.
- (iii) Melting and boiling point of Beryllium are much higher than other members of its family.
- (iv) Halides of Beryllium are soluble in organic solvents while that of other are soluble in water.
- (v) Oxide and hydroxide of Beryllium is amphoteric while that of others are basic in nature.

$$\text{Be}(\text{OH})_2 + 2\text{HCl} \rightarrow \text{BeCl}_2 + 2\text{H}_2\text{O}$$

$$\text{Be}(\text{OH})_2 + 2\text{NaOH} \rightarrow \text{Na}_2[\text{Be}(\text{OH})_4]$$
- (vi) It is the only member of the family which on reaction with alkalis liberates hydrogen.

$$\text{Be} + 2\text{NaOH} \rightarrow \text{Na}_2\text{BeO}_2 + \text{H}_2$$
- (vii) Beryllium is resistant to complete oxidation due to its BeO coating.
- (viii) It does not react even with boiling water.
- (ix) Oxides, nitrides, sulphides, chlorides etc of group II-A are ionic but that of Be are covalent.

Explanation:

Polarizing power of both Be^{2+} as well as that of Cl^- ion is so high. So Be^{2+} sufficiently pulls electrons from Cl^- ion, such that electron pair is effectively shared. This is the reason that BeCl_2 is covalent. This is in accordance with Fajan's rule.

- (x) Alkaline earth metals impart colour to flame but Be does not impart any colour to the flame.
- (xi) Oxide of Be is insoluble in water.

Group IV-A Elements

This group of elements is placed in middle of periodic table.

The electronic configuration of group IV-A elements is:

Group IV-A		
${}_6\text{C}$	$1s^2, 2s^2, 2p^2$	$[\text{He}]2s^2, 2p^2$
${}_{14}\text{Si}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^2$	$[\text{Ne}]3s^2, 3p^2$
${}_{32}\text{Ge}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^2$	$[\text{Ar}]3d^{10}, 4s^2, 4p^2$
${}_{50}\text{Sn}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^2$	$[\text{Kr}]4d^{10}, 5s^2, 5p^2$
${}_{82}\text{Pb}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^2$	$[\text{Xe}]4f^{14}, 5d^{10}, 6s^2, 6p^2$

Melting and Boiling Points:

Element	Melting Point (°C)	Boiling Point (°C)
C	3600	4827
Si	1420	2355
Ge	937	2830
Sn	232	2560
Pb	328	1744

C, Si and Ge have giant atomic structure and they have strong covalent bonds so their melting points are high. Decrease in melting point from C to Ge is due to increasing atomic size because of which covalent bonds are weakened. Sn and lead are metals and their atoms are bigger so their metallic bonding is weak hence their melting points are low.

Metallic Character:

Metallic character decreases down the group. In group IV-A change from non-metal occurs. C and Si are non-metals, Ge is metalloid while Sn and Pb are metals.

Oxidation states:

C shows +4 (as in CCl_4), -4 (as in Be_2C), -1 (as in Na_2C_2) oxidation states.

Si shows +4 oxidation state.

Ge, S, and Pb show +2 and +4 oxidation states.

So the most common oxidation state of group elements is +4.

Inert Pair Effect:

“The tendency of an element not to involve its pair of electrons of s orbital in bond formation is called inert pair effect.”

If hybridization occurs then electrons of s-orbital will not be inert and if no hybridization occurs then electrons of s-orbital will be inert.

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- (i) Promotion of one of s-electron to p-orbital followed by sp^3 hybridization of orbitals needs energy to be provided for the process.
- (ii) Formation of four covalent bonds involving the hybrid orbitals releases energy.

If energy released in the formation of four covalent bonds is more than the energy absorbed in the promotion of electron from s-orbital to p-orbital, then hybridization will occur and element will not show inert pair effect.

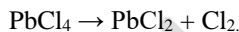
On other hand If energy released in the formation of four covalent bonds is less than the energy absorbed in the promotion of electron from s-orbital to p-orbital, then no hybridization will occur and element will show inert pair effect.

Inert pair effect increases down the group. As atomic radius increases down the group and bigger atoms make weak covalent bonds so energy released during bond formation is less than the energy absorbed during promotion of electron from s to p so no hybridization occurs and s-electrons remain inert.

Elements on the top shows no inert pair effect thus their oxidation state in the compounds will be +4 while lead being larger atom often shows inert pair effect and in its most compounds its oxidation state is +2. Higher oxidation state tends to covalent bond formation while lower oxidation state tends to ionic bond formation. So C forms covalent bonds while Pb forms ionic bonds.

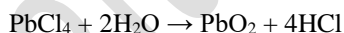
Chlorides:

Carbon, silicon and lead form tetra chlorides (CCl_4 , $SiCl_4$ and $PbCl_4$). As these elements are sp^3 hybridized so their tetra chlorides are tetrahedral. Stability of chlorides decreases from CCl_4 to $PbCl_4$. Thus $PbCl_4$ decomposes to give $PbCl_2$.



Stability of +4 oxidation state decreases down the group so C and Si forms only CCl_4 , $SiCl_4$ while Pb often forms $PbCl_2$.

CCl_4 does not react with water as water cannot reach to carbon as carbon is a small atom and four big Cl atoms are around it. $SiCl_4$ to $PbCl_4$ reacts violently with water producing their oxides.



(Brown)

$PbCl_2$ is ionic so it just gets dissolves in water. $PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$

Oxides:

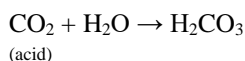
Group IV-A elements make two type of oxides i.e. monoxides (CO , SnO and PbO) and dioxides (CO_2 , SnO_2 and PbO_2).

Nature of oxides:

Carbon and Silicon are non-metals so their oxides are covalent in nature. Whereas Tin and Lead are metals so their oxides are ionic in nature.

Acid base behaviour of oxides:

As metallic character increases down the group so acidic behaviour decreases down the group. Thus among dioxides CO_2 and SnO_2 are acidic while GeO_2 , SnO_2 and PbO_2 are amphoteric oxides. Among monoxides CO is neutral oxide while GeO , SnO and PbO are amphoteric.



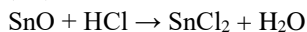
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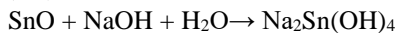
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(acid)



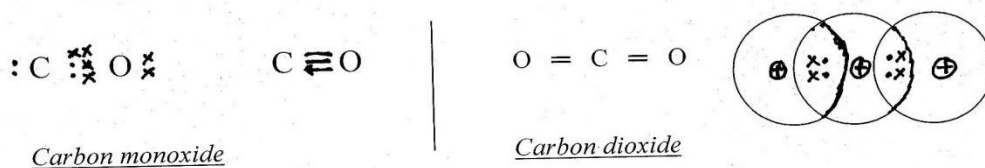
(base)



(acid)

Structure of carbon monoxide CO:

Carbon monoxide is a divalent molecule. Carbon and oxygen contributes unequal number of electrons in the bond formation. There is a triple bond between the two atoms including two covalent and a coordinate covalent bond.

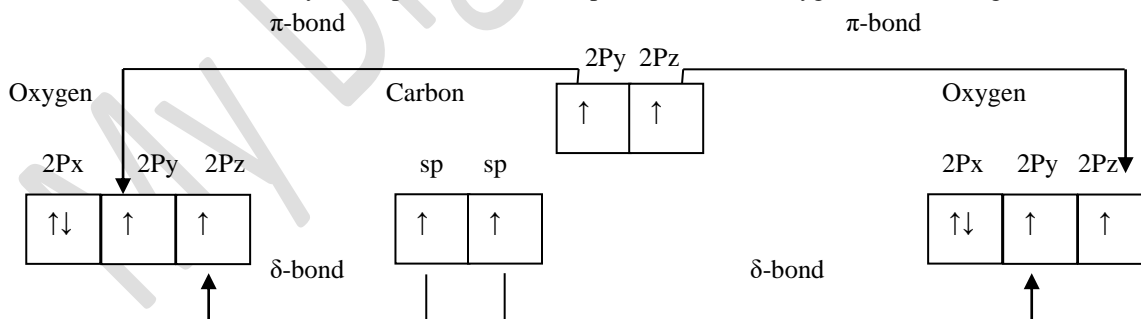


Structure of carbon dioxide (CO₂)

It is most stable oxide of carbon. It has linear structure having two carbon-oxygen double covalent bonds. It has linear structure. The bond length is 1.15 Å or 1.15×10^{-10} m. Carbon dioxide molecule is non-polar due to its linear structure having zero dipole moment.

In solid state (i.e. dry ice) carbon dioxide has face-centered cubic structure.

Carbon in CO₂ is sp hybridized. One of half-filled sp hybrid orbital of carbon overlaps with one of the half-filled p-orbital of one oxygen atom. This overlapping take place on bond axis hence sigma bond is formed. The other half filled sp hybrid orbital of carbon overlaps with one of the half-filled p-orbital of other oxygen atom. This overlapping also take place on bond axis hence sigma bond is formed. Remaining two half-filled unhybridized p-orbitals of carbon each laterally overlaps with half-filled p-orbital of each oxygen atom forming Pi-bonds with them.



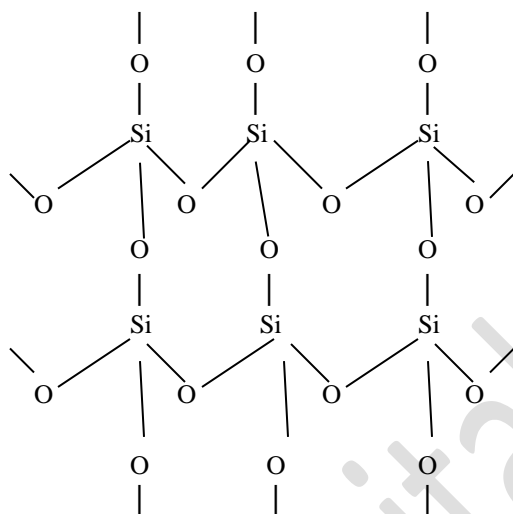
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Structure of Silicon dioxide (SiO_2):

Silicon atoms are bigger than carbon atoms so silicon oxygen bond length is more than that of carbon oxygen bond length. Hence in this case lateral overlapping of orbitals will not be effective so only sigma bonds are formed. Silicon dioxide has giant molecular structure in which each silicon atom is bonded to four oxygen atoms and each oxygen atom is bonded to two silicon atoms.



Structure of Silicon dioxide (SiO_2)

Group VII-A Elements

The word halogen means salt former. Halogens belong to group VII-A. This group consists of the elements which are given in the following table.

Group VII-A		
${}_{9}\text{F}$	$1s^2, 2s^2, 2p^5$	$[\text{He}]2s^2, 2p^5$
${}_{17}\text{Cl}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$	$[\text{Ne}]3s^2, 3p^5$
${}_{35}\text{Br}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^5$	$[\text{Ar}]3d^{10}, 4s^2, 4p^5$
${}_{53}\text{I}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^5$	$[\text{Kr}]4d^{10}, 5s^2, 5p^5$
${}_{85}\text{At}$	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6, 5s^2, 4d^{10}, 5p^6, 6s^2, 4f^{14}, 5d^{10}, 6p^5$	$[\text{Xe}]4f^{14}, 5d^{10}, 6s^2, 6p^5$

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General Properties:

- (i) Their general electronic configuration is ns^2, np^5 .
 (ii) All halogens are *non-metals*.
 (iii) They exist as *discrete diatomic molecules* $F_2, Cl_2, Br_2, I_2, At_2$.
 (iv) Their *atomic radii* increase down the group.
 (v) Their *electronegativities* are high and decrease down the group. Fluorine has highest electronegativity which is four.

Element	F	Cl	Br	I	At
Electronegativity (Pauling scale)	4.0	3.0	2.8	2.5	2.2

- (vi) *Electron affinity* is the energy released or absorbed when an electron is added to gaseous atom or ion. It is the measure of attraction between incoming electron and nucleus. Higher is the attraction higher will be the electron affinity.

Trend of electron affinity $F < Cl > Br > I > At$ or $At < I < Br < F < Cl$

Element	F	Cl	Br	I	At
Electron Affinity (kJ/mol)	328	349	325	295	270

Trend is not regular. Fluorine is showing exceptionally low value than chlorine. Due to its very smaller atomic size valence shell is smaller so electrons present in it repel the incoming electron. Thus difference between energy released due to attraction by nucleus and energy absorbed during repulsion by the electrons is less and therefore, electron affinity of fluorine is less than chlorine.

- (vii) Their *melting and boiling* points increase down the group. Thus from top to bottom they change from gas to solid. Astatine is radioactive and its half life is 8.3hrs.

(viii)

Element	State	M.P	B.P	Colour
Fluorine	gas	-219.6°C	-188.2°C	pale yellow
Chlorine	gas	-101.0°C	-34.7°C	yellowish green
Bromine	liquid	-7.2°C	59°C	dark red (vapours reddish brown)
Iodine	solid	113.7°C	184°C	dark crumbly (vapours violet)
Astatine	solid	300°C	380°C	black (vapours dark)

- (ix) *Bond Enthalpy* is the energy required to break one mole chemical bonds in gaseous molecules to form gaseous atoms.

	$Cl_{2(g)} \rightarrow 2Cl_{(g)}$	$\Delta H = 242 \text{ kJ/mol}$		
Element	F	Cl	Br	I
Bond Enthalpy (kJ/mol)	158	242	193	151

F_2 has abnormally low bond enthalpy than chlorine due to its smaller atomic size. Due to smaller size distance between nuclei of two atoms will be less and hence repulsion between nuclei will be more. As a result bond will be weaker.

- (x) Halogens are good *oxidizing agents*; however their oxidizing power decreases down the group. Their oxidizing power depends upon

- (a) Dissociation energy more is dissociation energy less is oxidizing power.
 (b) Electron affinity more is electron affinity more is oxidizing power.
 (c) Reduction potential more is reduction potential more is oxidizing power.
 Dominating factor is reduction potential.

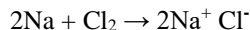
Order of oxidizing power is	$F_2 > Cl_2 > Br_2 > I_2$
Standard reduction potential (V)	2.87 1.36 1.06 0.54

Halogens take electrons from other elements and thus oxidize them.

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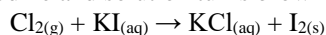
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e.g. (i) Fluorine and chlorine can oxidize coloured dyes to colourless. Thus they are used as bleaching agents.

e.g. (ii) Chlorine water oxidizes KI to iodine and solution turns brown due to formation of iodine.

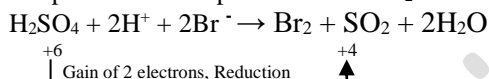


In this reaction Cl_2 has oxidized I^- to I_2 . Similarly Cl_2 can oxidize Br^- to Br_2 .

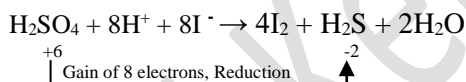
(xi) *Reducing power* of halide ions depend upon their sizes. Larger is the size of halide ion more is its reducing power. Larger ions can easily donate electron and thus can easily reduce other substances.

Order of reducing power is $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$
 Ionic radius (nm) 0.216 0.195 0.181 0.136

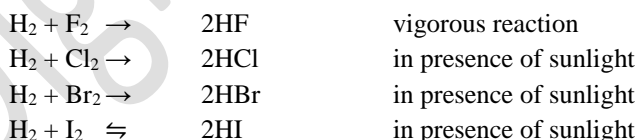
e.g. (i) Br^- ion reduces sulphate ion of sulphuric acid to SO_2 .



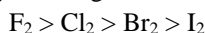
e.g. (ii) I^- ion is larger than Br^- ion so it is stronger reducing agent than Br^- ion. It reduces sulphate ion of sulphuric acid to S^{2-} ion.



- (xii) Halogens have irritating odours and they attack skin. Bromine causes burns that heal slowly
- (xiii) They have high ionization energies, electron affinities and electronegativities.
- (xiv) Common oxidation state for halogens is -1, but they also show +1, +3, +5, and +7 oxidation states in their compounds. However fluorine does not show positive oxidation state as it has highest electronegativity.
- (xv) They form ionic compounds with group I-A and group II-A elements.
- (xvi) Halogens directly react with hydrogen under different conditions to produce their hydrides (*Hydrogen halides*).



The order of reactivity of halogens towards this reaction is



As the size of halogen increases, the bond energy of H – X bond decreases and thus stability of halide decreases also polarity of the bond decreases.

- (a) The order of stability and polarity is $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$
- (b) While order of reactivity of halogen acids is $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

(c) Acidic strength of hydrogen halides increases down the group. As stability of halogen acids decrease down the group accordingly their acidic strength increases down the group.

Order of acid strength $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

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All halogen are highly soluble in water and are stronger acids. HF is also highly soluble in water but it is weak acid.

(d) Bond enthalpies of hydrogen halides decrease down the group.

As down the group size of halogen increases so bond length increases and hold of nuclei decreases on shared electrons so bond enthalpy decreases.

Also polarity of molecule decreases down the group so bond become weaker and thus bond enthalpy decrease.

Hydrogen halide	H – F	H – Cl	H – Br	H – I
Bond Enthalpy (kJ/mol)	568	432	366	298

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