GROUP 1

MODULE ONE

These are also referred to as **ALKALI METALS**. The members of this group are

Lithium	Li (3)	[He]$2s^1$	$1s^2$, $\mathbf{2s^1}$
Sodium	Na (11)	[Ne]$3s^1$	$1s^2$, $2s^2$, $2p^6$, $\mathbf{3s^1}$
Potassium	K (19)	[Ar]$4s^1$	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $\mathbf{4s^1}$
Rubidium	Rb (37)	[Kr]$5s^1$	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $\mathbf{5s^1}$
Caesium	Cs (55)	[Xe]$6s^1$	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^6$, $\mathbf{6s^1}$
Francium	Fr (87)	[Rn]$7s^1$	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^6$, $6s^2$, $4f^{14}$, $5d^{10}$, $6s^2$, $6p^6$, $\mathbf{7s^1}$

- Elements of this group have ground state valence electronic configuration $\mathbf{ns^1}$**.**
- They conduct electricity and heat.
- They are soft and have low melting point. The softness and low melting point is a result of weak metallic bonding arising from the fact that each atom provides only one electron.
- They adopt a body centre cubic (bcc) structure and because this structure is not closed-packed they have low densities.
- All the elements have to be stored under a hydrocarbon solvent to prevent reaction with atmospheric oxygen.
- They do not exist in the elemental state because they are very reactive

OCCURRENCE

Na and K occurs in the earth as mineral salts (2.6% and 2.4% respectively) a. These elements are extracted from the following:

a. Rock salt almost pure NaCl
b. Natural brine and sea water NaCl
c. Sylvite KCl
d. Sylvinite KCl/NaCl
e. Carnelite $KCl.MgCl_2.6H_2O$
f. Borax $Na_2[B_4O_5(OH)_4].8H_2O$
g. Chile salt petre $NaNO_3$
h. Potash KOH
i. Lepidolite $K_2LiAl_4Si_7O_{21}(F, OH)_3$
j. Pollucite $Cs_4Al_4Si_9O_{26}.H_2O$

Li, Rb and Cs occur in very small amounts, smaller than Na and K (% abundance Rb > Li > Cs). They often occur as silicate minerals e.g. spodumene ($LiAlSi_7O_6$), pollucite, carnallite, leucite ($KAlSi_2O_6$) and lepidolite. Only artificial isotopes to francium are know $^{223}_{87}Fr$

EXTRACTION

Lithium is extracted by electrolysis of LiCl similar to that of NaCl. LiCl is also obtained from the reduction of spodumene by heating it with CaO. This reaction produces LiOH which is converted to LiCl.

$$LiAlSi_7O_6 \xrightarrow[\Delta]{CaO} LiOH \xrightarrow[NH_3]{CaCl_2} LiCl \xrightarrow{electrolysis} Li$$

Sodium is extracted by electrolysis of molten NaCl and this is called Downs process

$$\text{At the cathode: } 2Na^+_{(l)} + 2e \longrightarrow 2Na_{(l)}$$

$$\text{At the Anode: } 2Cl^-_{(l)} \longrightarrow Cl_{2(g)} + 2e$$

$$\text{Overall reaction: } 2Na^+_{(l)} + 2Cl^-_{(l)} \longrightarrow 2Na_{(l)} + Cl_{2(g)}$$

Because pure NaCl melts at 1073K, $CaCl_2$ is added to reduce the operating temperature to about 870K

$$NaCl_{(l)} \xrightarrow{\text{electrolysis}} Na_{(l)} + Cl_{2(g)}$$

Potassium can be extracted by electrolysis but it is a hazardous process. Another method uses molten Na and molten KCl which are heated together to yield potassium and NaCl.

$$Na_{(l)} + KCl_{(l)} \rightleftharpoons NaCl_{(l)} + K_{(g)}$$

The temperature of the reaction is so high that K is in the vapour state. It is collected as the reaction is on-going as this drives the equilibrium to the right.

Rubidium is extracted as a minor constituent during the extraction of Li from Lepidolite. Frist Lepidolite is reacted with conc H_2SO_4 for a long time to form alums of the alkali metal for example $Rb_2SO_4.Al_2(SO_4)_3.nH_2O$. The alums are then separated by multiple fractional crystallization and then converted to the hydroxide by reacting with $Ba(OH)_2$. It afterward converted to the chloride by ion exchange process. The molten chlorides are then reduced to the meal with calcium or barium.

$$2RbCl_{(l)} + Ca_{(l)} \longrightarrow CaCl_{2(l)} + 2Rb_{(l)}$$

$$\begin{tikzcd}
\text{Lepidolite} \arrow[r, "\text{conc } H_2SO_4"] & \text{alum} \arrow[r, "\text{fractional}", "\text{crystallization}"'] & Rb_2SO_4 \arrow[r, "Ba(OH)_2"] & RbOH \arrow[d, "\text{ion exchange}"] \\
& & Rb & RbCl \arrow[l, "Ca/Ba"']
\end{tikzcd}$$

Caesium occurs in the mineral Pollucite and is extracted by treatment with conc H_2SO_4 to form an alum $Cs_2SO_4.Al(SO4)_3.24H_2O$. This is converted to the sulphate by roasting with carbon. Again it is converted to the chloride by ion exchange and then reduced with barium and calcium.

$$\begin{tikzcd}
\text{Pollucite} \arrow[r, "\text{conc } H_2SO_4"] & \text{alum} \arrow[r, "C", "\Delta"'] & Cs_2SO_4+Al_2(SO_4)_3 \arrow[r, "\text{ion exchange}"] & CsCl \arrow[d, "Ca/Ba"] \\
& & & Cs
\end{tikzcd}$$

$$2CsCl_{(l)} + Ba_{(l)} \longrightarrow BaCl_{2(l)} + 2Cs_{(l)}$$

USES OF THE GROUP 1 ELEMENTS AND THEIR COMPOUNDS

1. Lithium with it low density is used as alloy for air crafts, glasses and ceramics.
2. Li_2CO_3 is used in the treatment of bipolar disorder.
3. Li is used in the manufacture of Li battery.
4. Lithium stearate is used as a lubricant in automobile industries.

5. Sodium and potassium play important roles in biological systems.
6. Sodium is used in the extraction of some rare metals such as titanium.
7. NaCl is used in food and production of baking soda.
8. NaCl is used in de-icing.
9. NaCl is also used in the manufacture of NaOH and this is made in large quantities.
10. Na is used in sodium light.
11. NaOH is used in the manufacture of soap and detergents.
12. KOH is used in the making of soft liquid soups.
13. KCl and K_2SO_4 is used in fertilizers.
14. $KClO_3$ and KNO_3 are used in fireworks.
15. KBr is used as anti-aphrodisiac, it reduces libido.
16. Rb and Cs are used interchangeably in the same application. They are used in manufacture of glass for fibre optics used in telecommunication.
17. Rb and Cs are used in the manufacture of night vision equipment.
18. They are also used in the manufacture of photoelectric cells.
19. Cs is in the Caesium clock which is used for the international standard measure of time.

MODULE TWO

GENERAL PROPERTIES

Properties	**Li**	**Na**	**K**	**Rb**	**Cs**
Atomic radius (pm)	152	186	231	244	262
Ionic radius (pm)	60	95	133	148	169
ΔH°_{IE} kJ/mol	519	494	418	402	376
$E_{M^+/M}$ (V)	-3.04	-2.71	-2.94	-2.92	-2.93
Density (g/cm^3)	0.53	0.97	0.86	1.53	1.90
Mp (°C)	180	98	64	39	29
Bp (°C)	1341	883	756	686	669
ΔH°_{sub} kJ/mol	161	109	90	86	79
ΔH°_{hyd} kJ/mol	-519	-406	-322	-301	-276

1. Typically going down the group atomic number increases and hence atomic radius and ionic radius increases.

2. Increase in atomic radius results in decrease in metallic bonding hence melting and boiling points decrease down the group.

3. Down the group increase nuclear charge increase however due to increase in atomic radius, ionization energy (IE) decrease. Because the first ionization energy of these atoms is so low, it makes them very reactive e.g. Li reacts with water gently; Na reacts vigorously; K reaction is highly exothermic that the hydrogen produced is ignited; Rb and Cs react explosively.
$$M_{(s)} + 2H_2O_{(l)} \rightarrow MOH_{(aq)} + H_{2(g)}$$
However, the second IE of these groups are so high hence they do not form M^{2+} ions under normal reaction conditions.

4. The values of $E_{M^+/M}$ (standard reduction potential) are usually large and negative.

$$M^{+}_{(aq)} + e \rightarrow M_{(s)}$$

This means that metals are readily oxidized and therefore strong reducing agents. However, there is not much difference in the values moving from Li to Cs and several factors play a role.

Before the reduction process other processes occur.

Sublimation (atomization) $M_{(s)} \rightarrow M_{(g)} \quad \Delta H^{\circ}_{sub}$ (ΔH°_{sub} decreases down the group)

Ionization $M_{(g)} \rightarrow M^{+}_{(g)} \quad \Delta H^{\circ}_{IE}$ (ΔH°_{IE} decreases down the group)

Hydration $M^{+}_{(g)} \rightarrow M^{+}_{(aq)} \quad \Delta H^{\circ}_{hyd}$ (ΔH°_{hyd} decreases down the group)

$$\mathbf{E_{M^{+}/M} = \Delta H^{\circ}_{sub} + \Delta H^{\circ}_{IE} + \Delta H^{\circ}_{hyd}}$$

$$\mathbf{\therefore \Delta H^{\circ}_{sub} + \Delta H^{\circ}_{IE} > \Delta H^{\circ}_{hyd}}$$

From the table above we see that ΔH°_{sub} and ΔH°_{IE} are endothermic processes, but the exothermic ΔH°_{hyd} process makes provides the additional heat to facility the endothermic process above . This is why Li is a stronger reduction agent than Cs even though its ionization and sublimation energies are high and endothermic.

5. As stated earlier, the ions of members of this group are good conductors of electricity. However, conductivity decreases $Cs^{+} > Rb^{+} > K^{+} > Na^{+} > Li^{+}$ (in aqueous solution). This is as a result of ions being hydrated in solution. Conductivity is all about the movement of ions or electrons. Li is being heavily hydrated moves slowest while Cs is least hydrated moves faster. The extent of hydration decreases from Li to Cs. Because of it large charge density Li is able to attract more water molecules to it. The strength of the force of attraction is inversely proportional to the size of the metal ion.
6. There is a diagonal relationship between Li and Mg. In the periodic table first element in each group has a diagonal relationship with the element to the lower right of it. In a diagonal relationship the 2 elements have many similar chemical properties. This is because of the similarities in their atomic radius. Below are the similarities between Li and Mg:

a. Many Li and Mg salts have a high degree of covalent character in their bonding. This is due to the high polarization power caused by their high charge density i.e. small size and large charge. Recall that Fajan's rules state that covalent bonding is favoured by small +ve ions, large –ve ions and large charge on either ions.

b. Li and Mg form normal oxide whereas the other elements in Group 1 form peroxides and superoxides.

c. Li is the only Group 1 element that readily forms nitride and the others do not.

d. All the carbonates, phosphates and flourides of members of this group are soluble in water except those of Li. The corresponding compounds of Group 2 are also insoluble.

e. LiOH is sparingly soluble while other hydroxides of the Group 1 are very soluble. The insolubility of any compound is due to the fact the hydration energy is less than the lattice energy.

f. Li forms organomentallic compounds similar to those of Mg

g. The carbonates of Li and Mg decompose on heating to give the metal oxides and CO_2. The carbonates of other elements of Group 1 do not decompose on heating.

h. Unlike other Group 1 elements Li reacts directly with C to form anionic carbide and Group 2 elements react similarly with C.

i. Li has a greater tendency to form complexes than other the metal in its group e.g. Li ammoniate salt {$[Li(NH_3)_4]I$}.

j. Some reaction of Li

$$Li + C_2H_2 \rightarrow Li_2C_2 + H_2$$
$$9Li + 2CH_4 \rightarrow LiC_2 + 8LiH$$
$$Li + 4C \rightarrow Li_2C_2 + C_2H_2$$
$$Li_2C_2 + 2H_2O \rightarrow C_2H_2\ 2LiOH$$

HYDRIDES

Hydrides are compound that consist of hydrogen and another element only. Hydrides of Group 1 elements are ionic and contain the hydride H^- ion. They have rock salt structure. In the solid state they are non-conduction, and non-volatile but in liquid state they conduct electricity.

With these groups hydrogen acts the H^- ion that is accepts an electron and bond with these electropositive metals to yield the salts.

$$2E_{(s)} + H_{2(g)} \rightarrow 2EH_{(s)}$$

I. They are all white and high melting points solids LiH 953K, NaH 1073K.

II. They are very reactive e.g. reaction of LiH with Al_2Cl_6 and NaH with $B(OMe)_3$/ BCl_3

$$LiH + Al_2Cl_6 \rightarrow 6LiCl + \mathbf{2Li[AlH_4]}\ Lithium\ tetrahydridoaluminate)$$

$$4NaH + B(OMe)_3 \rightarrow \mathbf{Na[BH_4]} + 3NaOMe\ (Sodium\ tetrahydroborate)$$

$$4NaH + BCl_3 \rightarrow \mathbf{Na[BH_4]} + 3NaCl$$

III. These compounds are used as reducing agent, especially metal oxides.

IV. These hydrides react with water to produce hydrogen and corresponding hydroxide.

$$EH_{(s)} + H_2O \rightarrow EOH_{(aq)} + H_{2(g)}$$

These hydrides react violently with water.

$$NaH_{(s)} + H_2O_{(l)} \rightarrow Na(NH_2)_{am} + H_{2(g)}$$

am indicates in ammonia solution

V. They react with protic solvents such as H_2O, NH_3, EtOH, showing that H^- ion is a strong base. It abstracts a proton from the protic solvent to form hydrogen.

$$EH_{(s)} \rightarrow E^+_{(aq)} + \boldsymbol{H^-}$$
$$\boldsymbol{H_2O_{(l)}} \rightarrow OH^- + H^+$$
$$\boldsymbol{EH_{(s)} + H_2O \rightarrow EOH_{(aq)} + H_{2(g)}}$$

VI. They are used to remove a proton from reactive C – H bonds.

$$NaH + CH_3C \equiv CH \rightarrow CH_3C \equiv C^-Na^+ + H_2$$

HALIDES

All the elements react directly with halogen to form the corresponding halide. They adopt NaCl rock salt structure (co-ordination no of 6) but CsCl, CsBr, and CsI having the Cs-Cl type of structure with coordinator no of 8.

- **The more negative the value of ΔH_f° is, the more stable the halide.**

ΔH_f° kJ/mol	F^-	Cl^-	Br^-	I^-
Li	-616	-409	-315	-270
Na	-577	-411	-361	-288
K	-567	-436	-394	-328
Rb	-568	-435	-395	-344
Cs	-553	-443	-406	-347

$$\mathbf{\Delta H_f^\circ} = \underbrace{\Delta H_{sub}^\circ + \Delta H_{IE}^\circ}_{\boxed{\text{Depends on metal}}} + \underbrace{\Delta H_{dis}^\circ + \Delta H_{EA}^\circ}_{\boxed{\text{Depends on halogen}}} - \mathbf{\Delta H_L^\circ}$$

Generally, lattice enthalpy ΔH_L decrease moving down a group and this is due to increase in ionic radii going down the group.

$$\Delta H_{(L)} \propto \frac{1}{r_+ + r_-}$$

ΔH_L kJ/mol	F	Cl	Br	I
Li	-1030	-834	-788	-730
Na	-910	-769	-732	-682
K	-808	-701	-671	-632
Rb	-774	-680	-651	-617
Cs	-744	-657	-632	-600

- **For a given metal M $\Delta H_f^\circ(MX)$ always becomes less negative moving from MF to MI.**

$(\Delta H_{sub}^\circ + \Delta H_{IE}^\circ)$ will remain the same since it is the same metal. ΔH_f is largely dependent on the nature halogens i.e. their ΔH_{dis}° & ΔH_{EA}° and lattice energy (ΔH_L°).

Properties	**F (9)**	**Cl (17)**	**Br (35)**	**I (53)**
Ionic radius X^- (pm)	133	181	196	220
Enthalpy of atomization (kJ/mol^{-1})	79	121	112	107
Electron Affinity	-334	-355	-325	-295

- ΔH_{dis}° of X_2 is endothermic and increases from F_2 to I_2
- ΔH_{EA}° of X_2 is exothermic and decreases from F_2 to I_2
- ΔH_L° of MX is also exothermic and decreases from MF to MI

$$\mathbf{\Delta H_{dis}^\circ + \Delta H_{EA}^\circ < \Delta H_L^\circ}$$

For example LiF and LiCl (negative sign shows it and exothermic process)

$$LiF \quad (79 + (-334) < -1030$$
$$LiCl \ (121 + (-355) < -834$$

The effect of lattice energy outweighs the combined effect of dissociation energy and electron affinity of the halide and so enthalpy of formation moving from MF to MI also decreases as lattice energy decrease down the group of a specific metal halide.

- **For the Group 1 chlorides, bromides and iodides ΔH_f° becomes more negative going down the group.** The reverse is the case for the Group 1 fluorides.
  $\Delta H_{dis}^\circ + \Delta H_{EA}^\circ$ will remain the same since it is the same halide. ΔH_f is dependent now on (ΔH_{sub}° & ΔH_{IE}°) the variation in the metals and lattice energy (ΔH_L°).

Properties	**Li**	**Na**	**K**	**Rb**	**Cs**
ΔH_{IE}° kJ/mol	519	494	418	402	376
ΔH_{sub}° kJ/mol	161	109	90	86	79

  - ΔH_{sub}° of $M_{(s)}$ is endothermic and decreases from Li to Cs
  - ΔH_{IE}° of $M_{(g)}$ is also endothermic and decreases from Li to Cs
  - ΔH_L° of MX is exothermic and decreases from LiX to CsX

The ΔH_f° for all the halides are negative showing that the lattice energy has a major role to play. However due to the small ionic radius of the fluoride ion, it is more sensitive to the change in ionic radius as one moves from Li^+ to Cs^+. This is not the case with the other halides.

MODULE THREE

OXIDES

When Group 1 elements are heated in excess air or oxygen the following are produced:

Li forms simple oxides $4Li_{(s)} + O_{2(g)} \rightarrow 2Li_2O_{(s)}$ $[\mathbf{O^{2-}}]$

Na forms peroxides $2Na_{(s)} + O_{2(g)} \rightarrow Na_2O_{2(s)}$ $[\mathbf{O_2^{2-}}]$

K, Rb and Cs form superoxides $K_{(s)} + O_{2(g)} \rightarrow KO_{2(s)}$ $[\mathbf{O_2^-}]$

All the oxides are strong bases and basicity increases from Li to Cs. They also react with water to give hydroxides.

$$2Li_2O_{(s)} + 2H_2O_{(l)} \rightarrow 4LiOH_{(aq)}$$

$$Na_2O_{2(s)} + 2H_2O_{(l)} \rightarrow NaOH_{(aq)} + H_2O_{2(aq)}$$

$$KO_{2(s)} + 2H_2O_{(l)} \rightarrow 2KOH_{(aq)} + H_2O_{2(aq)} + O_{2(g)}$$

By heating Na, K, Rb and Cs with limited amount oxygen or thermal decomposition of the peroxide or superoxide would yield normal oxides.

$$4KO_2 \xrightarrow[\Delta]{} 2K_2O_{(s)} + O_{2(g)}$$

Stability of the peroxides and superoxides decrease down the group Na_2O_2 to Cs_2O_2. (Stability means high lattice energy). Lattice enthalpy is inversely proportional to the sum of the ionic radii, hence the lattice enthalpy of normal oxides are larger than the corresponding superoxide or peroxide ($O^- < O_2^{2-}$ or O_2^-). Descending the group as ionic radius of the cation increase the lattice enthalpy decrease whether oxide, peroxide or superoxide.

OZONIDES (O_3^-)

These exist for all members of the group however these compounds are unstable and explode violently.

$$2KO_{3(s)} \rightarrow 2KO_{2(s)} + O_{2(g)}$$

K, Rb and Cs ozonides are made by heating their peroxide or superoxide with ozone. While Li and Na ozonides are prepared by ion exchanger loaded with Li^+ or Na^+ and running CsO_3 in liquid ammonia through it.

$$K_2O_{2(S)} + 2O_3 \underset{\Delta}{\rightarrow} 2KO_{3(S)} + O_{2(g)}$$

HYDROXIDES

The hydroxides react with acids and acidic oxides to yield the corresponding salt.

$$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

$$NaOH_{(aq)} + SO_{2(aq)} \rightarrow NaSO_{3(aq)} + H_2O_{(l)}$$

When excess CO_2 is passed through an aqueous solution of metal hydroxide the bicarbonate is produced but in limit supply of CO_2 then carbonate is produced.

Reaction 1: $2NaOH_{(aq)} + CO_{2(g)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$

Reaction 2: $Na_2CO_{3(aq)} + H_2O_{(l)} + CO_{2(g)} \rightarrow NaHCO_{3(aq)}$

Overall reaction: $2NaOH_{(aq)} + CO_{2(g)} \rightarrow NaHCO_{3(aq)}$

They also produce metal methanoates when reacted with CO.

Some non-metals undergo disproportation when treated with hydroxide.

$P_{4(s)}$ yeilds PH_3 and $[H_2PO_2]^-$

$S_{8(s)}$ yeilds S^{2-} and oxoanions such as HSO_4^-, SO_3^{2-}, SO_4^{2-} etc

$Cl_{2(g)}$ yeilds OCl^- or ClO_3^-

Amphoteric metals react with MOH to yield hydrogen gas and oxoanions

$$2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O_{(l)} \rightarrow 2Na[Al(OH)_4] + 3H_{2(g)}$$

OXOACIDS

These include carbonates, hydrocarbonate, sulphates, nitrates, thiosulphate ($S_2O_3^{2-}$), etc. All the carbonates are soluble in water except Li_2CO_3 which is sparingly soluble. Solvay process is used to manufacture sodium carbonate from NaCl.

$$NaCl \quad + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$$

$LiHCO_3$ has not been isolated. $NaHCO_3$ is prepared by bubbling CO_2 through a saturated solution of Na_2CO_3.

$$Na_2CO_{3(aq)} + CO_{2(g)} + H_2O_{(l)} \rightarrow 2NaHCO_{3(s)}$$

$$2NaHCO_{3(s)} \underset{\Delta}{\rightarrow} Na_2CO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}$$

All the sulphates and nitrates Group 1 are soluble in water.

AQUEOUS SOLUTION CHEMISTRY

This aspect has to deal with solubility and how the ions can be separated in solution.

- LiF and Li_2CO_3 are sparingly soluble in water but large ions of Li are soluble e.g. ClO_4^-, $[PtCl_6]^{2-}$. Whereas for K, Rb and Cs salts they are sparingly soluble, ($MClO_4$, $M_2[PtCl_6]$).
- These group of metal can coordinate with $[EDTA]^-$ and $[P_2O_7]^{4-}$ to form insoluble complex. The order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ while using a ion exchange resin the order of strength of adsorption in the reverse $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$.

E XTRA INFO

Group 1 elements all have body-centred cubic structure (bcc). The rock-like structure is a crystal structure in which the cations have a face-centred cubic (fcc) arrangement with the anions occupying all he octahedral hole.

For the group 1 chlorides, bromides and iodides ΔH_f° becomes more negative going down the group. The reverse is the case for the group 1 fluorides.

$$\mathbf{\Delta H_f^\circ} = \underbrace{\Delta H_{sub}^\circ + \Delta H_{IE}^\circ}_{\boxed{\text{Depends on metal}}} + \underbrace{\Delta H_{dis}^\circ + \Delta H_{EA}^\circ}_{\boxed{\text{Depends on halogen}}} - \Delta H_L^\circ$$

This is because the variation in the value of $(\Delta H_{sub}^\circ + \Delta H_{IE}^\circ)$ for the fluorides is less than the variation in ΔH_L° . The significance of this variation is that the contribution of metals is not as significant as the effect of the lattice energy. We would make an attempt to explain this. Let us referred to the sum of $\mathbf{\Delta H_{sub}^\circ} + \mathbf{\Delta H_{IE}^\circ} = \mathbf{q}$ and for a particular halogen the values of $\Delta H_{dis}^\circ + \Delta H_{EA}^\circ$ is constant. In that case for a particular halide ion X^-, ∴ ΔH_f° depends largely on **q** and $\mathbf{\Delta H_L^\circ}$. The variation for the fluorides is as follow

$$q_{Li} - q_{Na} < \Delta H_L(LiF) - \Delta H_L(NaF)$$
$$q_{Na} - q_K < \Delta H_L(NaF) - \Delta H_L(KF)$$
$$q_K - q_{Rb} < \Delta H_L(KF) - \Delta H_L(RbF)$$
$$q_{Rb} - q_{Cs} < \Delta H_L(RbF) - \Delta H_L(CsF)$$

But for the chlorides, bromides and iodides the variation in the value of $\Delta H_{sub}^\circ + \Delta H_{IE}^\circ$ is more than the variation in their corresponding ΔH_L°.

$$q_{Li} - q_{Na} > \Delta H_L(LiCl) - \Delta H_L(NaCl)$$
$$q_{Na} - q_K > \Delta H_L(NaCl) - \Delta H_L(KCl)$$
$$q_K - q_{Rb} > \Delta H_L(KCl) - \Delta H_L(RbCl)$$
$$q_{Rb} - q_{Cs} > \Delta H_L(RbCl) - \Delta H_L(CsCl)$$

Hence their enthalpy of formation becomes more negative as you go down the group 1 of chlorides, bromides iodides. Whereas for the fluorides, the small ionic radius of fluorine ensures that the differences in ΔH_L° are greater than the corresponding value of $(\Delta H_{sub}^\circ + \Delta H_{IE}^\circ)$ and hence the enthalpy of formation of becomes less negative. *In summary we can say that the* ΔH_f° *of group 1 fluorides decreases down the group because the small ionic radius of the fluoride ion, the variation in* ΔH_L° *as we go down the group is greater than the corresponding values of the sum of* ΔH_{Sub}° *and* ΔH_{IE}°

Difference in Lattice Energy	F	Cl	Br	I
Li – Na	120	65	56	48
Na – K	102	68	61	50
K – Rb	34	21	20	15
Rb – Cs	30	23	19	17
Li – Cs	286	177	156	130

QUESTION: Lithium and Sodium belongs to the same group, however lithium carbonate is insoluble in water and sodium carbonate is, why?

QUESTION: The difference in atomic radius of group 1 and group 2 metals (in the same period) is responsible for the differences in certain physical and chemical properties they have. Discuss how atomic radius affects these properties

Group 1

1. Briefly explain why the lattice enthalpies of the halides of lithium are greater than the corresponding halides of other group 1 metals.
2. Write the correct products of the following reaction equations and balance them.
   - (i) $NaOH_{(aq)} + \underset{\textbf{excess}}{CO_{2(g)}} \longrightarrow$
   - (ii) $NaOH_{(aq)} + \underset{\textbf{limited}}{CO_{2(g)}} \longrightarrow$
   - (iii) $NaOH_{(aq)} + CO_{(g)} \xrightarrow{450\text{ K}}$
3. Below are the steps taken for the extraction of rubidium from its ore. Provide the correct answers to **i – v**.

$$\mathbf{i} \xrightarrow{\text{conc } H_2SO_4} \mathbf{alum} \xrightarrow{ii} \mathbf{Rb_2SO_4} \xrightarrow{iii} \mathbf{RbOH} \xrightarrow{iv} \mathbf{RbCl} \xrightarrow{v} \mathbf{Rb}$$

4. In not more than one sentence state why
   - i. Alkali metals are soft and have low melting points
   - ii. They have low densities.
   - iii. $Li^{+}_{(aq)}$ is a poor conductor of electricity?
5. Complete and balance the following reactions.
   - a) $Na + O_2 \rightarrow$
   - b) $KO_2 + H_2O \rightarrow$
   - c) $K_2O_2 + O_3 \rightarrow$
   - d) $NaOH + CO_2 \xrightarrow{450K}$
   - e) $Al + NaOH + H_2O \rightarrow$
   - f) $CsH + H_2O \rightarrow$
   - g) $NaH + BCl_3 \rightarrow$
6. Lithium reacts with water gently and sodium reacts vigorously. The reaction of potassium with water is very exothermic that it ignites the hydrogen produced while rhodium and cesium react explosively with water. Explain the reason for this reactivity.
7. Lithium has similarities with alkaline earth metals write any three of these similarities
8. Explain the following (in not more than 3 lines):
   - a. The stability of Group 1 superoxides decreasing down the group.
   - b. The conductivity of cesium is greater than lithium
9. Write the name (or chemical formula) of one of the ore which lithium is extracted from and one of the uses of lithium.
10. Write the products and balance the following reaction equations;
    - i. $NaCl + CaCO_3 \rightarrow$
    - ii. $Cs + O_2 \rightarrow$
    - iii. $Ba + N_2 \xrightarrow[\Delta]{}$
    - iv. $K + O_2 \rightarrow$
    - v. $Li + O_2 \rightarrow$
11. Give two uses of sodium or any of it compounds.
12. The enthalpy of sublimation, lattice enthalpy, and ionization energy affect the enthalpy of formation of group 1 metal halides. Explain why the enthalpies of formation of group 1 fluorides decrease down the group while it is the reverse with the other group 1 halides.
13. Explain why Group 1 elements do not exist in the +2 oxidation state.
14. Explain why the lattice enthalpy of Group 1 bromides decreases down the group.

GROUP 2

Module one

The elements in this group are beryllium, magnesium, calcium, strontium, barium and radium. They are also referred to as alkaline earth metals.

Berylium	Be (4)	$[He]2s^2$	$1s^2$, $\mathbf{2s^2}$
Magnesium	Mg (12)	$[Ne]3s^2$	$1s^2$, $2s^2$, $2p^6$, $\mathbf{3s^2}$
Calcium	Ca (20)	$[Ar]4s^2$	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $\mathbf{4s^2}$
Strontium	Sr (38)	$[Kr]5s^2$	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $\mathbf{5s^2}$
Barium	Ba (56)	$[Xe]6s^2$	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^6$, $\mathbf{6s^2}$
Radium	Ra (88)	$[Rn]7s^2$	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^6$, $6s^2$, $4f^{14}$, $5d^{10}$, $6s^2$, $6p^6$, $\mathbf{7s^2}$

- The elements of this group have ground state valence electronic configuration **ns^2,** hence exist in the M(II) state in their compounds.
- They are silvery white metals
- They are harder than Group 1 metals indicating an increase in the strength of the metallic bond. This is due to the increase in the number of available electrons and hence stronger cohesive forces resulting in a closed packed arrangement of their atoms.
- The atomic radii of the elements in Group 2 are smaller than those of Group 1.
- They have higher charge density compared to Group 1 elements
- Their smaller atomic radii and stronger cohesion force gives rise to their closed packed arrangement of their atoms in their lattice.
- Reactivity and electropositivity increase down the group because ionization energy decreases down the group.

OCCURRENCE

These metals occur in the earth crust as minerals.

1. Beryl $Be_3Al_2(SiO_3)_6$
2. Dolomite $MgCa(CO_3)_2$
3. Magnesite $MgCO_3$
4. Olivine $(Mg,Fe)_2SiO_4$
5. Carnalite $MgCl_3.6H_2O/MgCl_2.6H_2O$
6. Chalk, limestone, marble $CaCO_3$
7. Gypsium $CaSO_4.2H_2O$
8. Stronitianite $SrCO_3$
9. Barytes $BaSO_4$
10. Kieserite $MgSO_4.H_2O$
11. Celesite $SrSO_4$
12. Phenacite $BeSiO_4$

EXTRACTION

Beryllium is extracted by heating beryl with sodium hexafluorosilicate Na_2SiF_6 to produced BeF_2 which is then reduced to Be by magnesium.

$$Be_3Al_2(SiO_3)_{6(s)} \xrightarrow[97°C]{Na_2SiF_6} BeF_{(s)} \xrightarrow[900°C]{Mg} Be$$

Magnesium is extracted by first thermal decomposition of dolomite to yield a mixture of MgO and CaO. MgO is reduced by ferrosilicon in a Ni vessel. Mg is removed by distillation under vacuum.

$$CaCO_3 \cdot MgCO_{3(s)} \underset{\Delta}{\rightarrow} CaO_{(s)} + MgO_{(s)} + 2CO_2$$

$$2CaO_{(s)} + MgO_{(s)} + FeSi_{(s)} \xrightarrow{1450K} 2Mg_{(s)} + CaSiO_{4(s)} + Fe_{(l)}$$

It can also be extracted from sea water ($MgCO_3$) by adding CaO (quicklime) or $Ca(OH)_2$ (slake lime) to precipitate $Mg(OH)_2$. $Mg(OH)_2$ is neutralized with HCl and water is evaporated leaving behind $MgCl_2.xH_2O$. This is then heated at 990K to yield anhydrous chloride and finally Mg is obtained by electrolysis of molten $MgCl_2$.

$$Mg^{2+}_{(aq)} + Ca(OH)_{2(aq)} \rightarrow Mg(OH)_{(s)} + Ca^{2+}_{(aq)}$$

$$Mg(OH)_{(s)} + HCl_{(aq)} \rightarrow MgCl_{(aq)} + H_2O_{(i)}$$

$$MgCl_2xH_2O_{(s)} \xrightarrow{990K} MgCl_{2(l)}$$

Cathode: $Mg^{2+}_{(aq)} + 2e^- \rightarrow Mg_{(s)}$ **Anode:** $2Cl^-_{(aq)} \rightarrow Cl_{2(aq)} + 2e^-$

Calcium is extracted by electrolysis of molten calcium chloride which is produced during the Solvay process for the production of Na_2CO_3. Strontium is obtained by the electrolysis of $SrCl_2$ or by reduction of SrO with Al.

$$6SrO_{(s)} + 2Al_{(s)} \rightarrow 3Sr_{(s)} + Sr_3Al_2O_{6(s)}$$

Barium is also obtained by electrolysis of its molten barium chloride. **Radium** is a radioactive spp and was first discovered by Pierre and Maria Curie. It was found in the mineral ore called pitch-blende (UO_2) which contains approximately 1g of Ra in 10t of ore

USES OF THE ELEMENT OF GROUP 2 AND THEIR COMPOUNDS

- Be is one of the lightest metal, being non-magnetic with high thermal conductivity, very high melting point (1596K) and inertness to oxidation. It is used to manufacture body parts of high speed aircrafts, missiles and communication satellites
- Be is a poor absorber of electromagnetic radiation, hence it is used in x-ray tube windows.
- Mg is alloy with aluminium to impact greater mechanical strength and resistance to corrosion. This is used in aircrafts, automobile body parts and light weight tools
- Mg is used in the manufacture of flares, fireworks, photographic flash lights, In medical application – milk of magnesia ($Mg(OH)_2$) and Epson salt ($MgSO_4.7H_2O$).
- Both Mg^{2+} and Ca^{2+} ions are catalyst for diphosphate-triphosphate transformation in biological systems. Mg^{2+} is also an essential part of chlorophyll in green plants
- CaO is the major component of mortar and cement and in the manufacture of steel and paper.
- $CaCO_3$ is used in Solvay process in the manufacture of Na_2CO_3
- CaF is used in making cells and windows for IR and UV spectrometers. This is because it is insoluble in most solvents and transparent over a wide range of wavelength.
- Strontium is pyrotechnics and in glass for colour and TV tubes.
- Barium compounds are effective in absorbing x-rays

- $BaSO_4$ is used in "barium meals" to investigate the intestinal tracts because it is sparingly soluble.
- $BaCO_3$ is used in the manufacture of glass and it is used as rat poison
- BaS is used in hair removal products
- Radium was used in the treatment of malignant tumour but it has been stopped and less hazardous compounds are used.

MODULE TWO

GENERAL PROPERTIES

Properties	Be	Mg	Ca	Sr	Ba	Ra
Atomic radius (pm)	112	160	197	215	224	-
Ionic radius (pm)	27	72	100	126	142	148
ΔH°_{IE} kJ/mol	900	737	590	548	502	510
$E_{M^{+}/M}$ (V)	-1.85	-2.37	-2.87	-2.89	-2.90	-2.92
Density (g/cm^3)	1.85	1.74	1.54	2.62	3.51	5.00
Mp (°C)	1280	650	850	768	714	700
ΔH°_{sub} kJ/mol	324	146	178	164	178	130
ΔH°_{hyd} kJ/mol	-2500	-1920	-1650	-1480	-1360	-

1. Generally, their melting point decreases down the group due to increase in atomic radius going down the group as this decreases the cohesive force bonding the atoms together. However, this does not vary regularly because the metals adopt different crystal structure. Be and Mg have hexagonal closed packed crystal structure (hcp). Ca and Sr have face-cantered cubic structure (fcc) while Ba has body-centred cubic structure (bcc).

2. They are most often divalent and ionic.

3. Due to smaller size their ionization energies are higher than those of Group 1. The second IE of the element of this group is very high. This arises from the fact that after the loss of the first electron the ratio of charge on the nucleus to the smaller size of the ion increase hence more energy is required to remove the second electron. This is usually almost twice that of required to remove the first.

4. The hydration energy of their ions are 4 or 5 times greater than those of Group 1. This is because of their smaller ionic radius and increase charged density, ΔH_{hyd} decreases down the group as the ionic radius increases (down group). Even their solid compounds are more hydrated than those of Group 1.

5. Their compounds are diamagnetic and colourless because the divalent ions have an inert gas structure.

6. The value of $E^{\circ}_{M^{2+}/M}$ is fairly constant (except for Be) and this is for the same reason as with Group 1.

7. Be and Mg are passivated and this makes them inert O_2 and H_2O at room temperature. *To become passivated means that a thin film of a protecting oxide is coating the metal surface, preventing further reaction on the inside. This oxide is formed when they react with atmospheric oxygen.*

$$2Be_{(s)} + O_2 \rightarrow 2BeO_{(s)}$$

8. Be reacts with steam at high temperatures (700 °C) or more. While Mg burn in steam to yield the oxide and hydrogen gas.

$$Be_{(s)} + H_2O_{(g)} \rightarrow BeO_{(s)} + H_{2(g)}$$

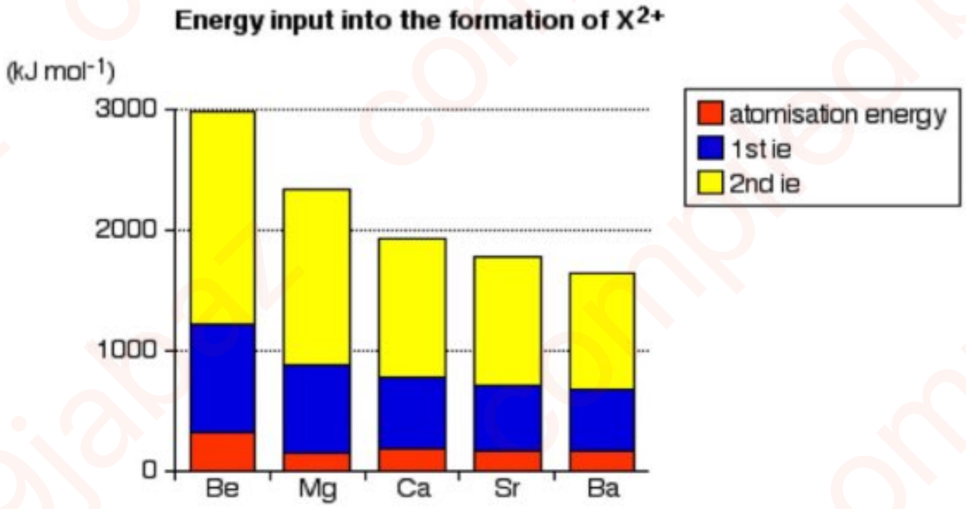
$$Mg_{(s)} + H_2O_{(g)} \rightarrow MgO_{(s)} + H_{2(g)}$$

If very clean magnesium ribbon is used, then it can react mildly with cold water to give the oxide and hydrogen. However, Mg reacts with hot water to form it hydroxide and liberate H_2. Ca, Sr, Ba reacts readily with cold water.

$$Mg_{(s)} + 2H_2O_{(g)} \underset{\Delta}{\rightarrow} Mg(OH)_{2(s)} + H_{2(g)}$$

$$M_{(s)} + 2H_2O_{(l)} \rightarrow M(OH)_{2(aq\ or\ s)} + H_{2(g)}$$

When Group 2 metals react to form their oxides or hydroxides, 2 stages are involved **(i.)** atomization of the metals (ΔH°_{sub}) **(ii.)** 1st & 2nd ionizations energies (ΔH°_{IE}) to convert the metal to the +2 oxidation states. The predominant factor is the very high second ionization energy. And this decreases down the group. This in turn affects the activation energy of the reaction.



9. All the metals in this group combine with O_2, N_2, S and halogen when heated.

$$2M + O_2 \underset{\Delta}{\rightarrow} 2MO$$

$$3M + N_2 \underset{\Delta}{\rightarrow} M_3N_2$$

$$8M + S_8 \underset{\Delta}{\rightarrow} 8MS$$

$$M + X_2 \underset{\Delta}{\rightarrow} MX_2 (X = F, Cl, Br, I)$$

10. There is a strong diagonal relationship between Be and Al.
    a. Be and Al form covalent hydride, halides and oxides where as other members of forms of ionic compounds of these.
    b. Oxides and hydroxides of Be and Al are amphoteric while all the rest are basic.

c. In the presence of excess OH^- ions Be and Al form $[Be(OH_2)_4]^{2-}$· and $[Al(OH_2)_4]^{-}$·. Mg does not react with OH ion.

d. Be^{2+} ion is hydrated in aqueous solution yielding $[Be(OH_2)_4]^{2+}$. Here Be^{2+} ion polarizes the O-H bond which is already a polar bond. This result in the loss of H^+ hence making the solution acidic. Similarly Al^{3+} forms $[Al(H_2O)_4]^{3+}$ with pKa of 5.0

e. $BeCl_2$ and $AlCl_3$ fume in moist air to produce HCl

f. They both form complex halides.

g. Both carbides of Be and Al contain C^{4-} ion

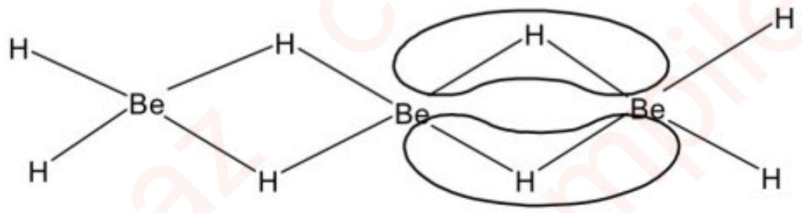
HYDRIDES

They all form ionic hydrides like Group 1 metals except for Be. This is because of the high polarizing power of Be, it forms covalent hydride. MH_2 of Ca, Sr and Ba are formed when heated with H_2. Mg only reacts with hydrogen at high pressure. BeH_2 is polymeric and is prepared from beryllium alkyl (R_1R_2Be). These ionic hydrides react violently with water to yield hydrogen but not as violet as Group 1 hydrides

$$Ca_{(s)} + H_2 \rightarrow CaH_{2(s)}$$

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

In BeH_2 Be has 2 valence electrons and H has only 1 and because the electron deficient centre of Be it forms a 3-center bond (Be….H….Be) which is a banana shaped molecular orbital having 2 electrons. This is referred to as 2-electron; 3-centre bond. Be is sp^3 hybridized hence the banana shaped molecular orbital is as a result of overlapping of sp^3-s-sp^3 orbitals containing 2 delocalized electrons.



CARBIDES

Be_2C is formed by the reaction of Be and carbon at high temperature. Carbides of Be contain the C^{4-} ion and when reacted with water form methane. While other members of the group contain C_2^{2-} ($[C \equiv C]^{2-}$) and liberates ethyn on reaction with water. Mg_2C_3 is a linear carbide that contains the linear $[C{=}C{=}C]^{4-}$ ion. Mg_2C_3 reacts with water to produce propyn.

$$Be_2C + 2H_2O \rightarrow 2Be(OH)_2 + CH_4$$

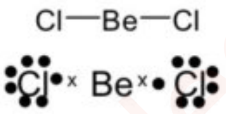
$$MC_2 + 2H_2O \rightarrow M(OH)_2 + HC \equiv CH\ (M = Mg, Ca, Sr, Ba)$$

$$Mg_2C_3 + 2H_2O \rightarrow 2(MgOH)_2 + H_3CC \equiv CH$$

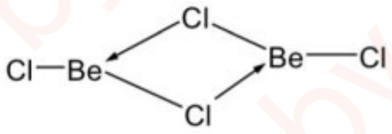
HALIDES

All the MF_2 are almost insoluble in water while the other Group 2 metal halides are ionic and readily soluble in water. Be halides are covalent. The solubility of these halides somewhat decrease down the group. The halides are hydroscopic and from hydrated salts. $CaCl_2$ is a drying agent and $BeCl_2$ acts as a Friedel–Crafts catalyst just like $AlCl_3$.

Monomeric or dimer of $BeCl_2$ exists in the vapour phase but in the solid state it exists in the polymeric form.

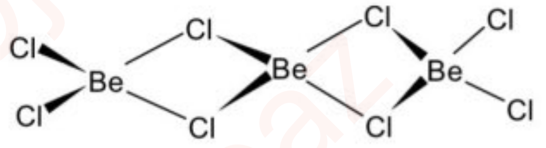


$BeCl_2$



$(BeCl_2)_2$

Be forms covalent bond with Cl and Cl dontes lone pair to Be.



Polymeric form $(BeCl_2)_n$

MODULE THREE

OXIDES

BeO is formed by burning Be or its compound in oxygen to yield an insoluble white solid.

$$Be_{(s)} + O_2 \xrightarrow[\Delta]{} BeO_{(s)}$$

Oxides of the other members of the group are prepared by thermal decomposition of their carbonates.

$$MCO_{3(s)} \xrightarrow[\Delta]{} MO_{(s)} + CO_{2(g)}$$

These oxides are high melting point solids and are therefore used as refractory materials. The oxides Mg reacts slowly with water to give $Mg(OH)_2$ which is also insoluble in water. While the CaO reacts rapidly and also absorbs CO_2 from the atmosphere.

$$CaO_{(s)} + H_2O \rightarrow Ca(OH)_{2(aq)}$$
$$Ca(OH)_{2(aq)} + CO_2 \rightarrow CaCO_{3(s)}$$

Peroxides of Group 2 metals are known (MO_2) for all members except Be and these are strong oxidizing agents

HYDROXIDE

$Be(OH)_2$ is amphoteric and the other hydroxides of other members are basic. The solubility in water and thermal stability (of Mg, Ca, Sr, Ba) increases down the group

$$M(OH)_2 \xrightarrow[\Delta]{} MO + H_2O$$

The basicity of the hydroxides also increases down the group. $Mg(OH)_2$ is a weak base.

SALTS OF OXOACIDS

1. Carbonates and hydrogencarbonates: all the carbonates are sparingly soluble in water with the exception of $BeCO_3$. $BeCO_3$ easily gets hydrolysed to $[Be(H_2O)_4]^{2+}$ because of the high charge density of Be. Hydrogencarbonates are more soluble than the corresponding carbonate. The solubility of $CaCO_3$ decreases with heating and so form precipitate on heating. Temporary hardness of water is caused by Mg and Ca hydrogencarbonates and the ions can be precipitated out as the carbonates by boiling.

   $$Ca(HCO_3)_{2(aq)} \xrightarrow[\Delta]{} CaCO_{3(s)} + 2H_2O$$

   Temporary hardness can also be removed by treating with $Ca(OH)_2$

   $$Ca(HCO_3)_{2(aq)} + Ca(OH)_2 \rightarrow CaCO_{3(s)} + 2H_2O$$

Thermal decomposition of the carbonates forms the oxides with the liberation of CO_2 gas.

$$CaCO_{3(s)} \underset{\Delta}{\rightarrow} CaO + CO_2$$

Thermal stability increases down the group, hence more heat is required to decompose the large metal carbonates.

2. Sulphates: Ca sulphate and Mg Sulphates are responsible for permanent hardness of water and cannot be removed by boiling but by passing water through ion-exchange resin. The solubility of sulphates decreased down the group. Because of small size of Be, Mg ions hence higher solvation energy. The thermal stability increases down the group and decompose to MO and SO_3.

$$MgSO_4 \underset{\Delta}{\rightarrow} MgO + SO_3$$

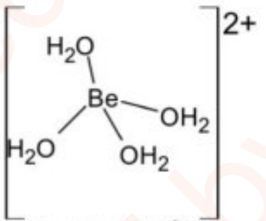
3. Nitrates: can be prepared in solution as hydrated salts by reacting HNO_3 with the carbonates, oxides or sulphates. All the nitrates of this group are soluble in water. Heating these hydrates solids decomposes to oxides.

$$CaCO_{3(s)} + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$$
$$Ca(NO_3)_{2(s)} \underset{\Delta}{\rightarrow} CaO_{(s)} + 4NO_{2(g)} + O_2$$

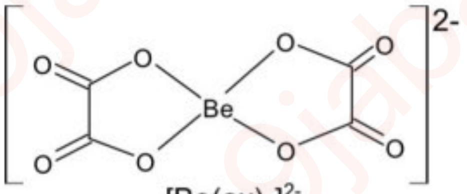
Just as with the carbonated of this group their thermal stability decrease down the group.

4. Solubility and hydration: Group 2 elements are generally less soluble in water than those of Group 1 elements even though ΔH_{hyd} is more negative. Mononegative anions are usually more soluble in water (except for fluorides) while the dinegative anions are sparingly soluble. Increase in lattice energy of dinegative anions e.g. CO_3^{2-} and SO_4^{2-} as a result of increased charge on the anion outweighs the effect of enthalpy of hydration. Fluorides are not soluble in water because of the small size of fluoride ion resulting in high lattice enthalpy. With the exception of BeF_2, it was high hydrate enthalpy due to high hydration enthalpy due to the high charge density of Be.

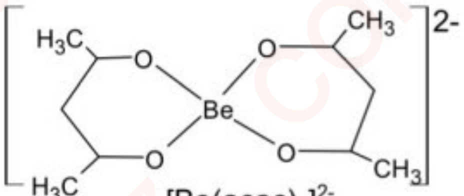
5. Coordination compounds: complex formation is favoured by small highly charged ions with suitable empty orbitals of the appropriate energy. BeF_2 coordinates with extra fluorides ion for $[BeF_3]^-$ or $[BeF_4]^{2-}$. They are usually tetrahedral complexes like $[Be(H_2O)_4]^{2+}$. Chelating ligand such as acetic acid, oxalate (ox), acetylacetone (acac) can be used to coordinate beryllium e.g. $[Be(ox)_2]^{2-}$, $Be(acac)_2$. Magnesium is inside porphyrin ring of chlorophyll. Ca, Ba, Sr for complex with strong complexing agents e.g. acetylacetone and EDTA. EDTA is used to remove Mg and Ca in water.



$[Be(H_2O)_4]^{2+}$



$[Be(ox)_2]^{2-}$



$[Be(acac)_2]^{2-}$

Group II

1. Provide an explanation each of the following trends.
   a. Sodium is more reactive than magnesium.
   b. Group 2 elements can form +2 oxidation state but group 1 cannot.

2. Mention 2 similarities between beryllium and aluminium.
3. Give a brief explanation to each of the following statements:
   a. The melting point of sodium is 98 ℃ and rubidium is 39 ℃ while of barium is 714 ℃
   b. The reactivity of alkaline metals increases down the group.
   c. Lithium and magnesium have similar properties however the enthalpy of hydration of magnesium is -1920 kJ/mole while that of lithium is -519 kJ/mole.
   d. Rubidium and strontium are next to each other in the periodic table, give reasons why strontium harder than rubidium.
4. $BeCl_2$ is a covalent compound while other elements in its group are ionic. Explain the reason for this. Draw the various forms in which $BeCl_2$ exist.
5. What compounds are responsible for temporary and permanent hardness and how can they be removed.
6. Explain why the ionization energies of Group II metals is greater than those of Group I
7. Write the name (or chemical formula) of one of the ore which beryllium is extracted from and one of the uses of beryllium.
8. Write the products and balance the following reaction equations;
   i. $S_8 + Mg \rightarrow$
   ii. $BaCO_{3(s)} \underset{\Delta}{\rightarrow}$
   iii. $Be_2C + H_2O \rightarrow$
   iv. $Sr + S_8 \rightarrow$
   v. $Ba + N_2 \rightarrow$
9. Explain the following trends:
   i. Group I metals have larger atomic radii than Group II
   ii. Group I metals are soft and have low melting points while Group II metals are harder and have much higher melting points.
   iii. Group I metals are stronger reducing agents than Group II metals
10. Group the following compound based on their solubility in water: MgF_2, $LiCO_3$, $BaBr_2$, BCl_3, Na_2SO_4, CaO, Rb_2CO_3, $Ca(HCO_3)$, $MgSO_4$, CaH_2
11. Explain why (i) magnesium higher melting point than sodium (ii) the ionization energy of magnesium is greater than sodium
12. The beryllium ion is hydrated in aqueous solution yielding $[Be(OH_2)_4]^{2+}$ but the solution is acidic. Explain the reason for this.
13. Explain why BeH_2 is the only covalent hydride in Group 2.
14. Explain the following
    a. Why the hydration energy of Be^{2+} is -2500 kJ/mol while that of Li^+ is – 519 kJ/mol
    b. $BeCO_3$ is the only soluble carbonate of Group 2 elements

GROUP 13 (3)

MODULE ONE

			Oxidation state	Coordination no
Boron	B (5)	$[He]\mathbf{2s^2 2p^1}$	III	3, 4
Aluminium	Al (13)	$[Ne]\mathbf{3s^2 3p^1}$	(I) III	3, 4, 6
Gallium	Ga (31)	$[Ar]3d^{10}\mathbf{4s^2 4p^1}$	I III	3, (4), 6
Indium	In (49)	$[Kr]4d^{10}\mathbf{5s^2 5p^1}$	I III	3, (4), 6
Thallium	Tl (81)	$[Xe]4f^{14}5d^{10}\mathbf{6s^2 6p^1}$	I III	3, 6

The oxidation state or complexes that are not stable are in brackets

- These elements have valence ground state electronic configuration of **ns^2, np^1**.
- Unlike s and d- block which are metallic in nature and these p-block elements range from non-metal (B), to metalloid (Al) to metals (Ga, In, Tl) and this results in wide range of chemical properties. Metallic character increases down the group.
- Amorphous boron is brown powder and the pure element is shiny, silver-grey crystals. Aluminium is white and hard; gallium is silver-coloured. Indium and thallium are white and soft metals.

OCCURRENCE

They are extracted from the ores listed below

a. Borax $Na_2[B_4O_5(OH)_4].8H_2O$
b. Kernite $Na_2[B_4O_5(OH)_4].2H_2O$
c. Gibbsite $Al(OH)_3$
d. Boehmite γ-AlO(OH) Bauxite
e. Dispur α-AlO(OH)
f. Aluminosilicate Al_2SiO_5
g. Cryolite $Na_3[AlF_6]$

Gallium, indium and thallium occur in trace amount in sulphide. Gallium oxides occur as impurities of bauxite.

EXTRACTION

Boron is extracted from borax by first treating it with acid to form boric acid and boric acid is heated to boron oxide.

$$[Na_2B_4(OH)_4]\cdot 8H_2O_{(s)} + H_2SO_{4(aq)} \rightarrow 4B(OH)_{3(aq)} + Na_2SO_{4(aq)} + 5H_2O_{(l)}$$

$$[Na_2B_4(OH)_4]\cdot 8H_2O_{(s)} + 2HCl_{(aq)} \rightarrow 4B(OH)_{3(aq)} + 2NaCl_{(aq)} + 5H_2O_{(l)}$$

Then,

$$2B(OH)_{3(aq)} \xrightarrow{300^\circ C} B_2O_{3(s)} + 3H_2O$$

Boron oxide is then reduced with magnesium and followed by washing with alkali, HCl, HOF.

$$B_2O_{3(s)} \xrightarrow{Mg} B_{(s)} + MgO_{(s)}$$

Pure boron is obtained by reduction of the vapour of BBr_3 with H_2.

$$BBr_{(g)} + 3H_{2(g)} \rightarrow 2B_{(g)} + 6HBr_{(g)}$$

Aluminium is extracted from bauxite. Bauxite is a mixture of impurities of Fe_2O_3, SiO_2 and TiO_2 and it purified by Bayers process. First the ore is added to hot NaOH solution under high pressure and this causes Fe_2O_3 to be separated. The solution is then seeded with $Al_2O_3.3H_2O$ and cooled or treated with a stream of CO_2. This will cause the precipitation of α-$Al(OH)_3$. Anhydrous Al_2O_3 is produced by heating $Al(OH)_3$. Molten Al_2O_3 (alumina) is subjected to electrolysis to yield pure aluminium at the cathode.

Gallium is extracted as a by-product of the manufacture of aluminium during electrolysis.

Indium is a by-product of the extraction of lead and zinc and isolated by electrolysis.

Thallium is also a by-product of smelting of Ca, Zn and Pb.

USES OF ELEMENTS AND THEIR COMPOUNDS

1. B is used in the manufacture of borosilicate glass
2. Borax has many domestic uses such as water softener, cleaner and mild pesticides
3. Boric acid is used as mild antiseptic
4. Aluminium used in construction, cans, foils, air crafts because it is light and resistant to corrosion as well as it is easily recyclable.
5. Gallium is used as high temperature thermometer because of its melting point just above room temperature.
6. Alloys of Ga and In are used safety devices in sprinkler system.
7. In_2O_3 and SrO_2 is used as transparent, conducting coating for electronic display and heat reflective coating for light bulb.
8. Tl compound is used in treating ringworm and as rat and ant poison.
9. Thallium sulphate is absorbed by tumour cell and used in imaging.
10. Alloy of aluminium have a wide of uses: Cu or Mg for increasing strength. Aluminium oxide mixed with oxides of Fe make is extremely hard and used as an abrasive.
11. Lithium borohydride and sodium borohydride are used as reducing agent for the reduction of aldehydes and ketone to the alcohols. Lithium aluminium hydride is used as a reducing agent of in organic compounds.

GENERAL PROPERTIES

Properties	B	Al	Ga	In	Tl
Atomic radius (pm)	85	143	135	166	171
Ionic radius (pm)	20	50	62	81	88
Covalent radius (pm)	80	125	125	150	155
ΔH°_{IE} kJ/mol	799	577	577	556	590
$E_{M^{3+}/M}$ (V)	-0.89	-1.68	-0.55	-0.34	+1.26
MP(°C)	2300	660	30	157	304

1. Descending the group there is change from being predominately covalent to becoming ionic. This is because as atomic radius increases down the group ionization energy decreases such that the metals have low ionization energy and so more readily form cation.
2. Electronegativity decreases down a group but for this group there is anomaly. This anomaly moving from Al to Ga as Ga is more electronegative than Al. The anomaly is known as **Alternation Effect** and it due to decrease in atomic radius due poor shielding the 3d electrons such that the 4p orbitals are more drawn to the nucleus, having a higher atomic mass the nuclear charge is stronger.
3. The covalent radii of the atoms do not increase regularly down the group because of the inner electronic configuration of Ga, In and Tl have the 10-d electrons (3d, 4d, 5d respectively). These orbitals are poorly shield the nuclear charge such that the outer electrons are held more firmly. Hence these atoms with the inner d^{10} orbitals are smaller in size and hence have higher IE than expected. This includes the 14-electrons in the f-orbitals which are even more poorly shielding and in turn affect the size and IE of Tl.
4. Some members of this group have 2 oxidation states +1 and +3. The heavier elements show this tendency and the stability of the univalent compound increases down the group. This is because the electrons in the outermost s-orbital being poorly shielded by the inner electrons are strongly held by the nuclear charge. As a result, it would require a large amount of energy to unpair them. This is referred to as **Inert Pair Effect**.
5. Boron has a diagonal relationship with Si.
   a. Boron and silicon form many polymeric oxides
   b. B and Si form flammable, gaseous hydrides while aluminium is a solid hydride.

MODULE TWO

HYDRIDES

Boron forms a wide range of neutral and anionic hydrides with cage-like structures. The compounds are often electron deficient and act as Lewis acid.

Boranes are analogous with alkanes. There are 7 well characterized boranes and they fall into 2 groups; B_nH_{n+4} and the less stable B_nH_{n+6}. Their nomenclature is such that the number of boron atoms provides the prefix and the number of H-atoms are included in the name.

B_nH_{n+4}	B_nH_{n+6}
B_2H_6 Diborane	B_4H_{10} Tetraborane-10
B_5H_9 Pentaborane-9	B_5H_{11} Pentaborane-11
$B_{10}H_{14}$ Decaborane-14	B_9H_{15} Nonaborane-15 or enneaborane-15
	$B_{10}H_{16}$ Decaborane-16

Other boranes include B_4H_8, B_6H_{10}, B_6H_{12}

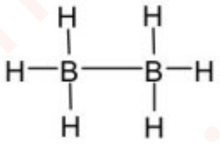
Diborane is the most studied of all the boranes. It is prepared by the following ways:

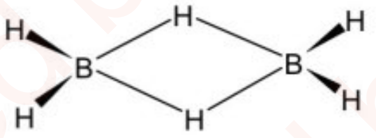
$$4BCl_{3(g)} + 3LiAlH_{4(s)} \rightarrow 2B_2H_{6(g)} + 3AlCl_{(s)} + 3LiCl_{(s)}$$

$$2BCl_{3(g)} + 6H_{2(s)} \xrightarrow[]{\substack{electric \\ discharge}} 2B_2H_{6(g)} + 6HCl_{(g)}$$

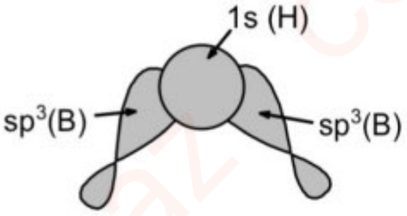
$$Mg_3B_{2(g)} + H_3PO_{4(aq)} \rightarrow \left(\substack{mixture \\ of\ boranes}\right) B_4H_{10} \underset{\Delta}{\rightarrow} B_2H_6$$

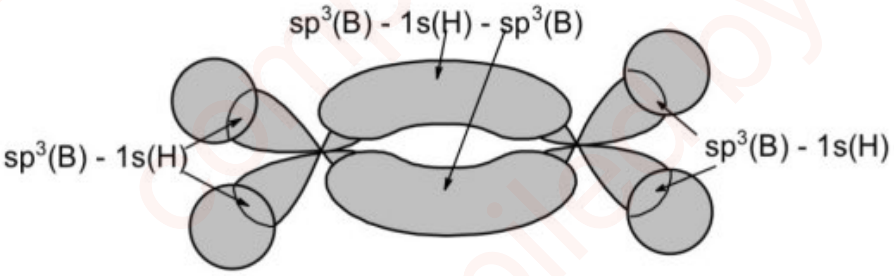
Diborane has 12 valence electrons 3 from each boron atom and a total of 6 from 6-H atoms. Diborane does not have B-B bond because this would mean that it has a valence of 4 and not 3. Instead it forms a bridge [B – H – B] that is a 2é-3 bond centre. The bridging H-atoms are planar and the 4 terminal H-atom perpendicular to the plane. The 2 bridges are formed by one electron from one B-atom and another electron from H-atom.



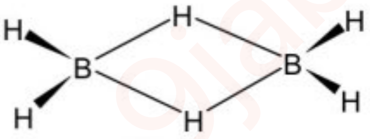


The hyrbidization of B is sp^3 and it overlaps the Is of H to form a delocalized molecular orbital covering all 3 nuclei but having only 2 electrons hence making the bridge.

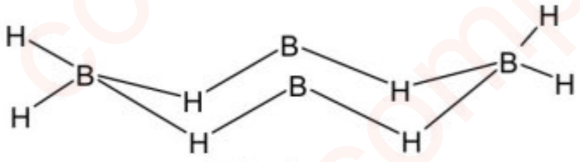




The higher boranes have an open cage structure which are multicentre covering B-atoms and B – H – B bridges.



Diborane



Tetraborane

Boranes burn or explode in air and decompose by water or aqueous alkali

$$B_2H_6 + 3O_2 \rightarrow B(OH)_{3(g)}$$

$$B_2H_6 + 6H_2O \rightarrow 2B(OH)_{3(aq)} + 6H_2$$

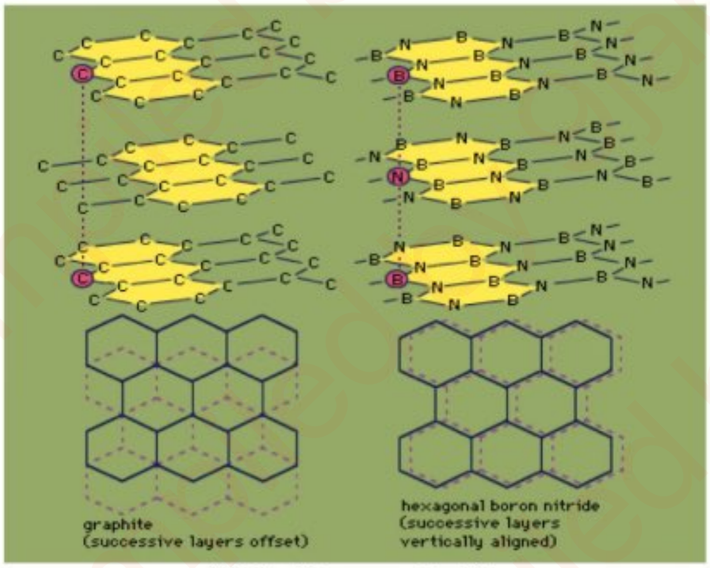
All boranes are colourless and diamagnetic. They range from gas (B_2H_6 and B_4H_8), volatile liquids (B_5H_9 B_6H_{10}) and to sublime solids ($B_{10}H_{14}$).

All boranes react with ammonia but yield different products under different conditions.

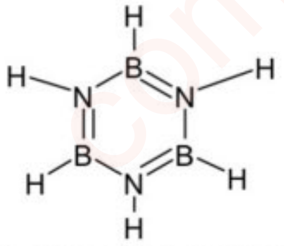
$$B_2H_6 + NH_3 \rightarrow \boldsymbol{B_2H_6 \cdot 2NH_3} \text{ (excess } NH_3, @\ low\ tempt)$$

$$B_2H_6 + NH_3 \rightarrow (\boldsymbol{BN})_{\boldsymbol{x}} + H_{2\uparrow} \text{ (excess } NH_3, @\ high\ tempt)$$

$$B_2H_6 + NH_3 \rightarrow \boldsymbol{B_3N_3H_6}\ (ratio\ 1:2, @\ high\ tempt)$$

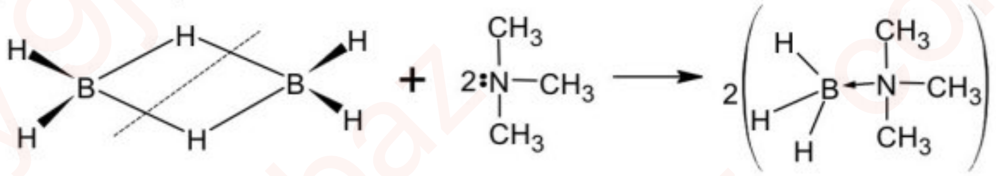


$(BN)_x$ Boron nitride

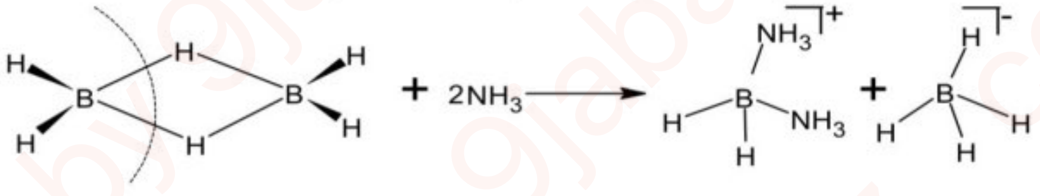


$B_3N_3H_6$ = Borazole (borazine)
is called the inorganic beneze

Diborane is a soft Lewis acid and reacts with soft and bulky Lewis bases which cleave diborane symmetrically.



Hard bases cleave diborane unsymmetrically leading to ionic product.



Diborane reacts with alkali metal hydrides to produce tetrahydroborate salt BH_4^-.

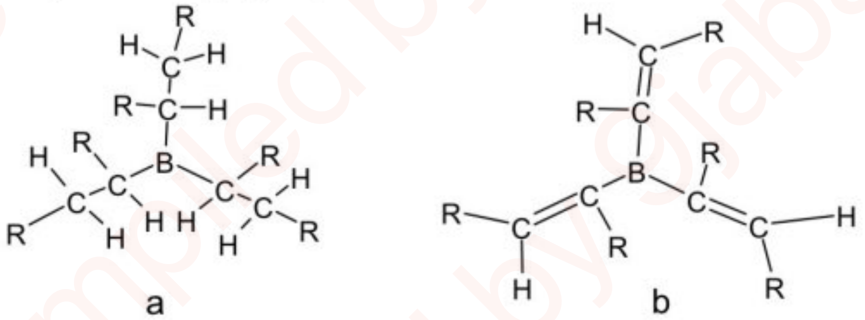
$$B_2H_6 + 2LiH \rightarrow 2LiBH_4$$

Hydroboration: these are reactions of diborane and alkenes and alkynes to yield alkylboranes and the reactions occur across the double/triple bond.

$$a.\quad B_2H_6 + 6RCH = CHR \rightarrow 2B(RCH - CH_2R)_3$$

$$b.\quad B_2H_6 + 6RC \equiv CR \rightarrow 2B(RC = CHR)_3$$

Where R = H or any other alkyl group



The reaction is carried out in dry ether under an atmosphere of nitrogen because B_2H_6 and the products are very reactive.

Where the alkene or alkyne is asymmetrical across the double or triple bond then the reaction follows an anti-Markovnikov pathway. This means that hydrogen atom (borane) adds to the more substituted carbon of the double/triple bond, while the boron attaches to the less substituted carbon.

The alkylboranes produced are converted to hydrocarbons by reacting with carboxylic acids;

$$BR_3 + 3CH_3COOH \rightarrow 3(RH) + B(CH_3COO)_3$$

Alkylboranes are converted to alcohols by reacting with alkali H_2O_2

$$B(CH_2R)_3 + 2H_2O_2 \rightarrow 3(RCH_2OH) + H_3BO_3$$

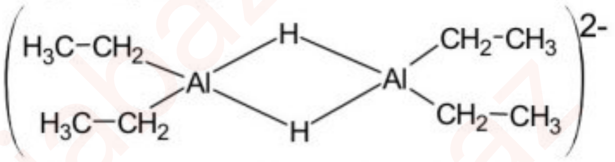
Alkylboranes are converted to ketone or carboxylic acid by reacting with chromic acids.

$$(RR'CH)_3B \overset{[O]}{\rightarrow} 3(RR'C = O)$$

$$(RCH_2)_3B \overset{[O]}{\rightarrow} 3(RHC = O) \overset{[O]}{\rightarrow} 3RCOOH$$

Hydrides of other members of the group

Alkyl aluminium hydride e.g. $Al_2(C_2H_5)_4H_2$ contain Al – H – Al bridges.



Metathesis of the halides of Al and Ga with LiH form lithium hydridoaluminate $LiAlH_4$ or tetrahydrogallate $LiGaH_4$.

$$LiH + \ ECl_3 \xrightarrow[\Delta]{} LiEH_4 + 3LiCl\ (in\ ether)$$

[E= Al, Ga]

Sodium borohydride is can also be prepared using NaH.

$$NaH + \ BCl_3 \rightarrow NaBH_4 + 3NaCl$$

NOTE:

- BH_4^- ion is isoelectronic with CH_4 and NH_4^+
- $BH_4^-$is hydridic i.e. it is a hydride donor H$^-$
- CH_4 is neither acidic or basic
- $NH_4^+$is protic i.e. it is a proton donor H$^+$

The tetrahydride ions of Al and Ga (AlH_4^- and GaH_4^-) are more hydridic than BH_4^-

$$[AlH_4]^- + SiCl_4 \xrightarrow{THF} [AlCl_4]^- + SiH_4$$

But unlike complex of BH_4^- those Al and Ga can add a second molecule to form 5-coordinate compound because they have the ability to expand their octet and form hypervalent compounds.

$$LiEH_4 + [(CH_3)_3NH]^+Cl^- \rightarrow (CH_3)_3N - EH_3 + LiCl + H_2$$
$$[\mathrm{E = B, Al, Ga}]$$

$$(CH_3)_3N - EH_3 + N(CH_3)_3 \rightarrow ((CH_3)_3N)_2 - EH_3$$
$$[\mathrm{E = Al, Ga}]$$

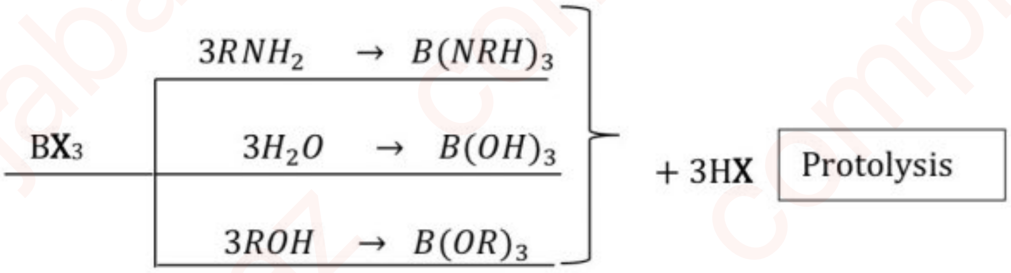
MODULE THREE

Halides

Trihalides: All the elements of this group form trihalides by direct reaction with halogen. Al, Ga and In react with hydrogen halides gas to yield their corresponding trihalide

$$2Al_{(s)} + 6HCl_{(g)} \rightarrow 2AlCl_{3(s)} + 3H_{2(g)}$$

Boron trihalides are covalent and gaseous. The chlorides, bromide and iodides a susceptible to protolysis (proton transfer) with mild protons donors like water, alcohols and amines.



$$BX_3 \begin{cases} 3RNH_2 \rightarrow B(NRH)_3 \\ 3H_2O \rightarrow B(OH)_3 \\ 3ROH \rightarrow B(OR)_3 \end{cases} + 3HX$$

Protolysis

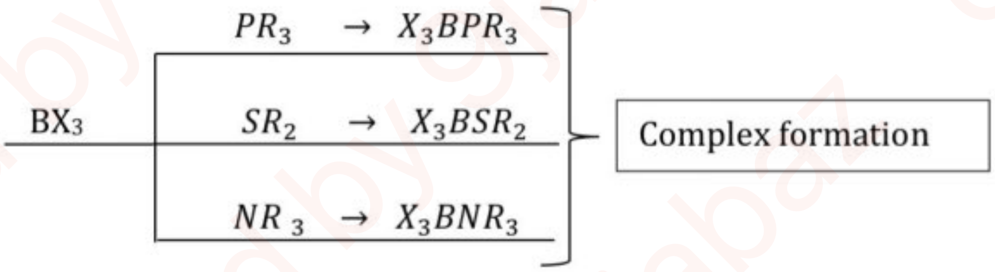
All the other halides are hydrolyzed to boric acid and the corresponding hydrogen halide.

$$BX_3 + H_2O \rightarrow B(OH)_3 + HX$$

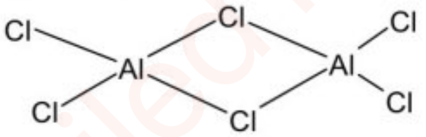
Except BF$_3$ that forms the tetrafluoroborate $[BF_4]^-$ and this is because BF$_3$ is a hard and a strong Lewis acid hence has a high affinity of for F^- ion.

$$4BF_3 + 6H_2O \rightarrow 3(H_3O)^+ + 3[BF_4]^- + B(OH)_3$$

Boron atom in BX$_3$ is sp^2 hybridized and the unhybridized p-orbital is available for coordination with molecules that have lone pair of electrons e.g. O, N, P or S.



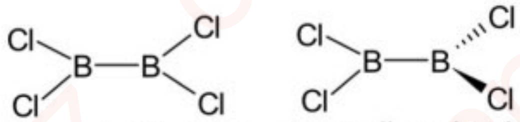
Only BX_3 can form a complete octet by accepting lone pair from a donor. The other halides of the group cannot because of their large sizes as a result the unhybridized p-orbital cannot overlap effectively with the orbital of the other molecule that has the lone pair so they rather polymerize to satisfy the octet.



Fluorides of Al, Ga, In and Tl are ionic with high melting point. The other halides are largely covalent when anhydrous. $AlCl_3$, $AlBr_3$, $GaCl_3$ exist as dimers. Their dimeric form is retained in non-polar solvent like benzene but it is lost in water due to high hydration energy to form the aquo complex ($[M(H_2O)_6]^{3+}$) and $3X^-$ ion.

Dihalides:

$$2BCl_3 + 2Hg \rightarrow B_2Cl_4 + Hg_2Cl$$



Planar (solid state) non eclipse (gas)

$$GaCl_3 + Ga \rightarrow Ga + GaCl_2$$
$$In_{(s)} + HCl_{(g)} \rightarrow InCl_{2(s)}$$

$Ga + GaCl_2$ is more properly written as $Ga^+[GaCl_4]^-$ containing Ga(I) and Ga(III) rather than Ga(II). The $GaCl_2$ and $InCl_2$ exist as a mixture of oxidation state Ga(I)/Ga(III) and In(I)/In(III).

Monohalides: The group will form monohalide in the gaseous phase at very high temperature.

$$AlCl_3 + Al \xrightarrow{high\ tempt} 3AlCl$$

The compounds are covalent. TlF is the only one that is ionic. Boron on the other hand form a number of polymeric monohalides $(BX)_n$ B_4Cl_4, B_8Cl_8, $B_{12}Cl_{12}$ etc.

Low oxidation state halide

The oxidation state of +1 increases in stability as you go down the group because of inert pair effect. AlX compounds and GaF and InF are unstable gaseous spp that will undergo disproporation in the solid state.

$$3AlX_{(s)} \rightarrow 2Al_{(s)} + AlX_{3(s)}$$

All other monohalides of Ga, In and Tl are stable.

Oxides/Hydroxides

Boron sesquioxide B_2O_3 is made by heating the element in oxygen or by dehydrating boric acid

$$B(OH)_3 \xrightarrow[100°]{} HBO_2 \rightarrow B_2O_3$$

B_2O_3 can react with metal oxide to give metaborate

$$CoO + B_2O_3 \rightarrow Co(BO_2)_2 \qquad (BO_2^-)$$

They can react with strong acidic oxides to form a salt.

$$B_2O_3 + P_2O_5 \rightarrow 2BPO_4$$

Boric acid behaves like a weak monobasic acid

$$B(OH)_3 + H_2 \rightleftharpoons H^+ + [B(OH)_4]^-$$

At high concentration of boric acid, a polymer metaborate is formed

$$B(OH)_3 + H_2 \rightleftharpoons H^+ + [B_3O_3(OH)_4]^- + 2H_2O$$

Reaction with NaOH yields ($Na[B(OH)_4]$ or ($NaBO_2$) and water.

$$B(OH)_3 + NaOH \rightarrow \begin{cases} Na[B(OH)_4] \\ \quad \uparrow \ \text{hydrolysis} \\ NaBO_2 + H_2O \end{cases}$$

A metaborate is a borate anion consisting of boron and oxygen, with empirical formula BO_2^-. Metaborate also refers to any salt or ester of such anion eg salt of sodium metaborate $NaBO_2$or esters such as methyl metaborate CH_3BO_2. Metaborates can be monomeric, oligomer or polymeric.

Al_2O_3 is made by dehydration of $Al(OH)_3$ or from oxides of other elements as Al has a high affinity for oxygen.

$$3MnO_4 + 8Al \rightarrow 4Al_2O_3 + 9Mn$$

$$Al(OH)_3 \xrightarrow[\Delta]{1100\ °C} Al_2O_3 + 3H_2O_{(g)}$$

$Al(OH)_3$ is precipitated as a white gelatinous ppt which is soluble in excess hydroxide to give $[Al(H_2O)_6]^{3+}$ ion. Ga like Al form amphoteric oxide and hydroxide. Tl and In form sesquioxides which are complete basic. Tl is strong base soluble in water thus different from the trivalent hydroxides. For elements that can exist in more than one oxidation state, the lower state is the most basic state.

EXTRA INFO

Fajan's Rule

If 2 ions A^+ and B^- are brought together to an equilibrium distance, the type of bond formed will depend on the effect they have on each other at this distance. The +ve ion A^+ will attract the electron on B^- and repel its nucleus. This will distort or polarize the B^- ion. If the polarization is small, then an ionic bond is formed.

If the extent of polarization is large then electron will be drawn from B^- ion to A^+ ion and a covalent character is generated.

Polarizing power is the power of an ion to distort another. Negatively charge ions are more easily polarized than the positively charged ion. That is because the electrons on the negatively charged spp are held less firmly due to lower charge density. Large ions are more polarizable than small ones.

Fajan's rule state that covalent bonding in favoured by (1) small +ve ion (2) large –ve ion (3) large charge (size) on either ion.

Diagonal relationship: means that even though elements are not in the same group but being diagonal to each other in the Periodic table exhibit similar properties.

Group 1	Group 2	Group 13	Group 14
Li	Be	B	C
Na	Mg	Al	Si

Group III

1. Mention any 2 uses of boron and its compounds.

2. Give one example of when you have (i) alternation effect (ii) inert pair effect (iii) 2-electron 3-bond centre (structure required for iii).

3. These chlorides of Group 13 below were treated with $\boldsymbol{N(C_2H_5)_3}$, in each case what product would you expect and why?
   a. BCl_3
   b. $GaCl_3$

4. Write the double decomposition reaction equation of gallium chloride with lithium hydride in ether.

5. What would be product(s) if the gallium product of 4 above is reacted with $\boldsymbol{[(CH_3)_3NH]^+Cl^-}$ and then with $\boldsymbol{(CH_3)_3N}$**?** (Reaction equations not required).

6. Give a brief explanation to each of the following statements:
   a. Boron can only form BF_3 but gallium can form both GaF_3 and GaF.
   b. BCl_3 can reacted with triethylamine yielding a complex but when $InCl_3$ is reacted with triethylamine In_2Cl_6 is formed.

7. Diborane has 12 valence electrons, give a brief explanation on how it is able to form a stable compound.

8. Write the name (or chemical formula) of one ore of boron and aluminium.

9. Explain the following (in not more than 3 lines):
   a. Boron forms only BF_3 while gallium form both GaF and GaF_3
   b. $LiAlH_4$ can form a 5-coordinate complex while $LiBH_4$ cannot

10. Write the name (or chemical formula) of one of the ore which boron are extracted from and one of the uses of boron

11. Write the products and balance the following reaction equations;
    i. $BBr_3 + CH_3CH_2OH \rightarrow$
    ii. $B_2H_6 + LiH \rightarrow$
    iii. $B_2H_6 + CH_3CH = CHCH_3 \rightarrow$
    iv. $AlBr_{(g)} \rightarrow$

12. Generally, electronegativity decreases down the group but in the case of Group 3 elements there is an anomaly going from aluminium to gallium. Briefly explain why this is so.

13. Predict the compounds A to E from the reaction equations below
    i. $B_2H_6 + CH_3CH = CHCH_3 \rightarrow A$
    ii. $A + HCOOH \rightarrow B + C$
    iii. $A + H_2O_2 \rightarrow D + E$

14. Define the following and give an example of each (i) alternation effect (ii) inert pair effect.

15. Write the expected product of the reactions below
    a. $B_2H_6 + O_2 \rightarrow$
    b. $B_2H_6 + NH_3 \rightarrow$ (xs NH_3 and at high tempt)
    c. $B_2H_6 + LiH \rightarrow$

16. Write two uses of boron or any of its compounds

17. Classify the reactions below as wither protolysis or complex formation, then write the products and balance the equations.
    a. $BBr_3 + PPh_3 \rightarrow$
    b. $BBr_3 + (CH_3)_3N \rightarrow$
    c. $BBr_3 + (CH_3)_2CHOH \rightarrow$
    d. $BBr_3 + (CH_3)_2NH \rightarrow$

Dr Ayodabola

Group 14

Element	electronic configuration	Oxidation state
Carbon, C	[He] $2s^2 2p^2$	(IV)
Silicon, Si	[Ne] $3s^2 3p^2$	(II) (IV)
Germanium, Ge	[Ar] $3d^{10} 4s^2 4p^2$	(II) (IV)
Tin, Sn	[Kr] $4d^{10} 5s^2 5p^2$	(II) (IV)
Lead, Pb	[Xe] $4f^{14} 5d^{10} 6s^2 6p^2$	(II) (IV)

physical properties

The general configuration of group 14 elements is n^2np^2. The group oxidation state is 4. However, down the group, oxidation state of 2 becomes more state. This is attributed to inert pair effect. The electron pair in ns orbital remains inert and does not participate in bonding. But in oxidation state of 2 and 4 are almost equally state

However, tetravalent state is strongly oxidizing. The energy required to remove all four valence electron is extremely high, Hence, simple ionic compound in tetravalent state are rare.

Although Sn and Pb are metals, their melting and boiling points are lower than the non-metals occupying higher positions in the group. This shows that both Pb and Sn do not use all the four valence electrons for metallic bonding.

②
COVALENT RADIUS

The covalent radii increases down the group. The difference in size between Si and Ge is less than might be expected, because Ge has a full 3d shell which shields the nuclear charge rather ineffectively. In a similar way, the small difference in size between Tin and Lead is because of the filling of the 4f shells

③
- IONIZATION ENERY

This decreases from Carbon to Silicon, then changes in an irregular way because of the effect of the filling of the d and f shells

ALLOTROPES OF CARBON

They are various allotropes of carbon. This includes

(i) Graphite (ii) Diamond (iii) Chaoite (iv) Fullerenes

(v) lonsdaleite (vi) carbon vi

(i) Graphite: It is composed of planar two dimensional sheet of Sp^2 hydridized carbon atoms. Each sheets is a network of fused hexagonal rings of carbon atom. The layers are held together by relatively weak vander waal forces of attraction. Due to the weak bonding between the layers, graphite is soft and cleaves easily.

The layers easily slide over each other, therefore, graphite is used as a lubricant as well as additives for motor oil and in lead pencil.

In graphite, only three of the carbon 4 valence electrons are involved in sigma bonding. The 4th one is involved in pi bonding The pi electrons are delocalized over the all structure. This are mobile and hence, graphite can conduct electricity

(ii) Diamond: In diamond, each Sp^3 hybridized carbon is tetrahedrally coordinated to four equidistant neighbours. The tetrahedral are arranged to give a cubic unit cell. This results in a three-dimensional closed packed arrangement as a result of which diamond has a high melting point and it is one of the hardest substance known.

CATENATION

Carbon possess a unique ability to bond to itself. This self linkage is called catenation.

Catenation is also shown by other element of group 14, but to a limited extent. The tendency of catenation decreases down the group

The tendency of carbon to catenate originates because of the high C-C bond strength. The variation in element to element bond energy follows the order;

$C-C > Si-Si > Ge-Ge > Sn-Sn > Pb-Pb$

The reason

① The size of carbon atom is smallest in the group, therefore the C-C bond length is also small. The smaller the bond length, the stronger is the bond, there is better overlap

② The nuclear charge increases down the group, this means that proton-proton repulsion on C-C bond are relatively small as compared to the corresponding repulsion of Pb-Pb bond

REACTIVITY

(1) Reaction with water: carbon, silicon and Germanium are unaffected by water. Tin reacts with steam to give SnO_2 and hydrogen gas.

Pb is unaffected by water. This is probably because of the protective oxide film that it forms

② Reaction with air: carbon bonds in limited quantity of air to give CO

$$2C + O_2 \rightarrow 2CO$$ - limited

In excess air, to give CO_2

$$C + O_2 + CO_2 \rightarrow$$ excess.

~~S~~ Si, Ge and Sn at high temperature combines with air to give corresponding oxides

$$Si + O_2 \xrightarrow{\geq 1200K} SiO_2$$

$$Ge + O_2 \xrightarrow{\text{red heat}} GeO_2$$

$$Sn + O_2 \xrightarrow{1800K} SnO_2$$

Pb forms a corresponding mono-oxides when heated in air at about 1000K

$$2Pb + O_2 \rightarrow \cancel{2}PbO$$ (because the +2 oxidation state of lead is more stable)

③ Reation with halogen: Carbon as graphite combines with flouring~~e~~, Si and Ge reacts readily with all the halogens, forming volatile halides

$$C + F \rightarrow CF$$

SiX_4, GeX_4

Sn and Pb are less reactive. Sn reacts with Cl and Br in cold and with F and I on warming give TnX_4

Pb reacts with F in cold to give PbF_2 and the chlorine give $PbCl_2$

④ Reaction with Acid: C, Si, and Ge are unaffected by dil acids. Sn liberates hydrogen when treated with dil H_2SO_4. It however give Sulphur dioxide when treated with Conc. H_2SO_4

Pb does not dissolve in dil. H_2SO_4 because of a surface coating of $PbSO_4$ it forms. It However dissolves slowly in dil. acid.

CARBIDES

The compounds of carbon and less electronegative elements are called carbides. This excludes compounds with N, P, O, S. & halogens

There are three major types;

(i) Ionic carbides
(ii) Covalent carbide
(iii) Intertestial carbide

SILICIDES

Similar to the carbides, silicides is a group of compound ~~carbon~~ that has silicon with more electropositive elements

This bonding varies from essentially metallic to ionic and covalent.

SILICATE

They are compounds in which silicons ~~is~~ coordinated tetrahedrally by four oxygen atom, ~~oxidation state~~ to form silicate units, are called silicate

The SiO_4 unit may exist are discrete tetrahedral of a compound with each oter by pairing oxygen atom to form chains, ring or sheet

Examples includes;

(i) ortho silicate. (ii) cyclic silicate (iii) chain silicate

(iv) pyro silicate (v) sheet silicate

HYDRIDES

All the elements form covalent hydrides but the number of bonds formed and the ease to which they are formed differs

(I) Carbon: Carbon forms a versed number of chains and ring compounds; (i) alkane (ii) alkenes (iii) alkynes (iv) aromatic compounds

② Silicon: Silicon forms a limited number of saturated hydrides called silanes. This may exist as straight chain, branched, containing up to 8 silicon atoms. Ring compounds are very rare. Compounds with Si-H bonds undergo are important ionsilation reaction

$$RCH \equiv CH_2 + SiHCl_3 \rightarrow RCH_2CH_2SiCl_3$$

The difference in behaviour between alkene and silanes is attributed to various factors.

① Pauli's electronegativity values: C = 2·5, Si = 1·8, H = 2·1. Thus, the bonding electrons between C-H, or Si-H are not equally shared leaving δ^- on carbon and positive δ^+ on silron

$$\overset{\delta^-}{C} - H^{\delta+} \qquad \overset{\delta+}{Si} - H^{\delta-}$$

Thus, Si is vulnerable to attack by nucleophile reagents

② The large size of silicons makes it easier to attack

③ Silicon has low energy d-orbitals which may be used to form an intermediate compounds, and thus lowers the oxidation energy of the process;

Read on hydrides formed by Ge, Sn, and Pb

Carbon forms more oxide than the other element and these oxides differ e

(1) CO : It is a poisonous gas $HCOOH + H_2SO_4 \rightarrow CO + H_2O$

Lab Preparation

1. Dehydration of formic acid with conc. H_2SO_4

<u>Characteristics</u>: (i) It burns with a blue flame.

(ii) It reduces PCl_3 solution to Pd

(iii) It liberates I_2 from a solution of Iodine pentoxide.

CO is toxic because it forms a complex with haemoglobin in the blood, and this complex is more stable than oxyhaemoglobin. This prevents the haemoglobin in the red blood corpuscle from carrying oxygen round the body.

Thus, causing an oxygen deficiency, leading to unconsciousness and then, death.

CO_2:

Preparation:

① It is the byproduct from the manufacture of hydrogen for making ammonia. $CO + H_2O \rightleftharpoons CO_2 + H_2$

② Fermentation processes ~~[illegible]~~ in breweries $CH_4 + 2H_2O \rightleftharpoons$

③ Action of dil. acid on carbonate

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

(4) By burning carbon in excess of air

$C + O_2 \Rightarrow CO_2$

Recovery of CO_2

$Na_2CO_3 + CO_2 + H_2O \rightleftharpoons 2NaHCO_3$

Properties

① It is an odourless, colourless gas

② It reacts with bases forming salt

(3) It reacts with lime water ($Ca(OH)_2$) to give white insoluble ppt. of $CaCO_3$. However, when more CO_2 is passed to the mixture, the cloudiness disappears. This is because soluble bicarbonate is formed:

$Ca(OH)_2 + CO_2 \rightarrow \underset{\text{white ppt}}{CaCO_3} + H_2O$

$CaCO_3$

Oxides of Silicon

Two oxides of silicon has been reported
Silicon mono oxide SiO
Silicon di oxide (silica) (SiO_2).

Preparation of SiO

This formed by high temperature reduction of SiO_2 with Si. However, it existence at room temperature is in doubt.

SiO forms an infinite 3D structure. It has high melting point. It exists in at least 12 different forms, this includes quartz.

It is unreactive, it is an acidic oxide ...

Group 14 of elements typically form bonds. Carbon can form pπ - pπ double bonds and hence, CO_2 is a discrete molecule and is a gas.

Silicon cannot form double bonds in this way, i.e, using pπ - pπ orbitals, for bonding. The SiO_2 forms infinite 3D structure (although silicon compound pπ - pπ bonds in which silicon atom appears to use the d-orbital for bonding are known).

Oxides of Ge, Sn, Pb

The dioxides GeO_2, SnO_2 and PbO_2 normally have ~~six~~ 6:3 coordination. The basicity of the oxides increases down the group, thus CO_2, SiO_2 are purely acidic, GeO_2 is not as strongly acidic as SiO_2.

SnO_2 and PbO_2 are amphoteric, the lower Oxides GeO, SnO, and PbO have layer lattices rather than the typical ionic structure. They are Slightly more basic and ionic than the corresponding higher oxides.

GeO is distinctively acidic, SnO and PbO are amphoteric. The increased stability of the lower valence state on descending a group is illustrated by the fact that Ge^{2+} and Sn^{2+} are quite strong reducing agent. Whereas, Pb^{2+} is Stable.

Ni

Group 15

Chemical properties

Nitrogen and phosphorus essentially forms covalent bonds

Write Group 5 electronic configuration, element

N - Nitrogen	[He] $2s^2 2p^3$	III	V
P - Phosphorus	[Ne] $3s^2 3p^3$	III	IV
As - Arsenic	[Ar] $3d^{10} 4s^2 3p^3$	III	IV
Antimony	[Kr] $4d^{10} 5s^2 5p^3$	III	IV
Bi - Bismuth	[Xe] $4f^{14} 5d^{10} 6s^2 6p^3$	III	IV

Chemical properties

N and P essentially forms covalent compound, As, Sb and Bi shows increasing tendency to cationic behaviour due to its small size, N tends to form pπ - pπ bond. No such bonds exists with the corresponding phosphorus compound.

Allotropy

All the element except Bismut show allotropy. Nitrogen exists in two allotropic forms i.e, α-nitrogen and β-nitrogen

Phosphorus exist in three allotropic forms, i.e white, black and violent phosphorus

Arsenic exist in three allotropic forms while Antimony exists as yellow, black, β- antimony

Physical State and Elemental Structure (Bond Strength)

In its natural state, nitrogen is a gas, while other elements of this group are solids.

Gaseous nitrogen is inert since extremely high energy is required to break the triple bond holding the constituent atoms.

The symmentrical electron distribution, also contributes to the stability and hence the inertness of nitrogen. Due to its non-reactive nature, Nitrogen has high natural abundance (78.1% in the atmosphere.

Nitrogen exists as diatomic molecule, N_2, while Phosphorus, arsenic and Antimony exists as tetratomic molecule (P_4, As_4, Sb_4).

This is because it is not possible for Phosphorus and arsenic atoms to form pπ-pπ bond, because this atoms cannot come close to each other to form $p\pi - p\pi$ bonds due to the increased repulsion from the non-bonding electron on penultimate shells.

However, nitrogen atoms do not encounter such repulsion, since they contain $1s^2$ electrons in the penultimate shell. Thus, nitrogen atoms can form N_2 species.

(B) Metallic character: The metallic character of group 15 element increases down the group. N and P are non metals, As, Sb are metalloid and Bi is a metal.

(C) Melting and Boiling point: The melting point and b.p, except for Sb and Bi, increases down the group. The melting point of Bi is usually low. The low mp of Bi suggests that there is little possibility of the availability of the pair of electrons in s-orbital.

The element of this group are more volatile than their immediate neighbours, this is because of the fact that this element have 5 electrons in their valence shells.

I) Oxidation state and Valency: formation of M^{3+} and M^{5+} cations (where M = elements of the group. M^{3+} cation are formed only when all 3 elements of Sp orbitals use in forming ns^2p^3 configuration are lost and ns^2 electrons remain inert. Since the inert-pair effect increases the group, the heavier element, i.e Sb, and Bi lose their 3 electrons from np orpital and form ~~and~~ M^{3+} cation.

. In order to get noble gas configuration, it is not possible for N and P to lose its five ns^2p^3 electrons to form M^{5+} cations.

Thus, in the case of N and P M^{5+} cations, do not exist.

II. Formation of M^{3+} anion:

In order to achieve noble gas configuration, these element accept 3 electrons from strongly electropositive element and form M^{3-} anions. As the size of the atoms increases down the group, the attraction of the nucleus for the newly added electrons decreases.

Thus, on moving down the group, the tendency of the element to give M^{3-} ions decreases, therefore Nitrogen atom has its strongest tendency to give M^{3-} ions

P forms P^{3-} ions less readily. While other members of the group show little tendency to form M^{3-} ions.

(C) Covalency of 3 and 5:

The element forms 3 covalent bonds and thereby attains the noble gas electronic configuration of ns^2p^6 when they use all their key electrons, except N, all other elements have d-orbitals as well. As a result, one of the ns electrons maybe promoted to the vacant nd orbitals to have 5 unpaired electrons in the valence shell.

This 5 unpaired electrons can be used in forming 5 covalent bonds, thus; P, AS, Sb show 5 covalent states

This is not possible for N atom since it has no d-orbital

Due to the presence of lone pairs of electron on N and P ~~molecules~~ atoms in ammonia and PH_3 molecules, this molecules can act as lewis base towards

H^+ and PF_3 to form NH_4^+ and BF_3H^+

$$NH_3 + H^+ \rightarrow NH_4^+$$

Chemical Reactivity

(1) Reaction with air: N form ~~NO_2~~ nitric oxide when heated with air

$$N_2 + O_2 \rightarrow 2NO$$

P yield phosphorus (III) oxide

$$P_4 + 3O_2 \rightarrow P_4O_6$$

forms phosphorus (V) oxide when heated in excess air

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

$$As_4 + 3O_2 \rightarrow 2As_2O_3$$

$$4Sb + 3O_2 \rightarrow 2Sb_2O_2$$

(2) Reaction with halogen: This element form two types of halides (i) trihalides (ii) pentahalides With the exception of Bimuth trihalides, Other trihalides have covalent character down the group.

The structure of the trihalide is similar to ammonia. In this molecule, the central atom is sp^3 hybridized.

out of the 4 sp^3 hybridized orbitals. One contains a lone pair, therefore, the shape of the MX_3 molecule becomes trigonal pyrimidal

b Pentahalides

N and Bi cannot ~~f~~ form pentahalides. N cannot form pentahalides, because it cannot expand its octet due to the non availability of the d-orbital.

Bismuth cannot form pentahalides because of the electron pair present in 6S orbital (inert pair effect) an hence, does not participate in bond formation

The pentahalides are trigonal bipyramidal in shape and this as a result of the sp^3d^2 hybridization of the central atom.

(3) Reaction with Sulphur: P, As, Sb, reacts with sulphur to give a number of products. BiS_3 cannot be prepared by direct combination of element but by reaction of hydrogen sulphide with aq Bi^{3+} ions.

Oxide formation : All the elements of this group forms oxides. M_2O_3 trioxides, tetra oxide and penta oxides (~~M_2O_4~~) (M_2O_4, M_2O_5).

Thermal stability and acidic character of M_2O_3 decreases from N to P trioxides. Thus, NO_3 and PO_3 are completely acidic.

AsO_3 and SbO_3 are amphoteric (they form salts with acids as well as bases)

BiO_3 is predominantly basic and forms salts with acid. It also shows feeble.

The decrease in the acidic character from NO_3 and BiO_3 is accounted for by the suggestion that the N^{3+} ion is smaller in size than Bi^{3+} interacts with water more strongly and thus, gives an acidic oxide, while Bi^{3+} ion forms basic BiO_3.

~~NO_3~~ (This also explains the fact that an oxide in lower oxidation state is less acidic than that in higher oxidation state).

Oxides of Nitrogen

① Nitrous oxide - N_2O , Oxidation state of 1

N_2O is a stable, relatively unreactive colourless gas. It is prepared by thermal decomposition of molten ammonium nitrate.

It is a neutral oxide, It is used as anaesthetic especially dental. It is a linear triatomic molecule

② Nitric oxide (NO) oxidation state of 2

NO is a colourless gas and it is also neutral. It readily forms coordination complexes with transition metal ions.

③ Nitroge di oxide (NO_2). -

It is an odd electron molecule and is paramagnetic and very reactive. It dimerises to N_2O_4

Group 16

Oxygen	O	[Ne] $2s^2\ 2p^4$	(-2), (-1)
Sulphur.	S	[Ne] $3s^2\ 3p^4$	6, -2, 2, 4
Selenium	Se	[Ar] $3d^{10}\ 4s^2\ 4p^4$	4, 2, 6
Tellurium	Te	[Kr] $4d^{10}\ 5s^2\ 5p^4$	4, 6.
Pollonium	Po	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$	4

The first four elements are non-metals, the elements exhibits an increasing metallic character on descending down the group. Oxygen and sulphur are non-metallic. Non metallic character is weaker in Se and Te. Po is metallic and is also radioactive and short lived.

The elements all have the electronic structure of ns^2p^4. They may attain a noble gas configuration either by gaining two electrons forming M^{2-} anion or by sharing two electrons, thus forming two covalent bonds.

~~React~~ ALLOTROPY

All the elements except Te exhibits/exists in more than one allotropic form

Oxygen

O occurs as two non-metallic forms, dioxygen, O_2 and ozone (O_3)

O_2 Dioxygen is stable as a diatomic molecule which accounts for it being a gas. Liquid dioxygen is pale blue in colour and the solid is also blue

Ozone (O_3) is the triatomic allotrope of oxygen. It is unstable and decomposes readily to oxygen gas (O_2). The structure is described as a central atom, Oxygen using sp^2 hybrid orbitals to bind to the terminal oxygen atoms. The central atom has one lone pair and the terminal oxygen atom.

This gives four electrons for π bonding. The pz atomic orbitals from the three atoms (3 delocalized molecular orbital) covering all 3 atoms. One molecular orbital (MO) is bonding, one, non-bonding and one, antibonding. The first pi electron fills the bonding and non-bonding (MO). And this contributes on delocized π-bonding to the molecule in addition to the sigma bond.

~~In addition to the sigma bond~~

SULPHUR

(1) Alpha- Rhombic sulphur

(2) Beta - monoclinic sulphure

Reactivity

Chemical properties

① Reactions with air: On heating with air, the element from the respective dioxides

$M + O_2 \rightarrow MO_2$ (M= S, Se, Te, Po)

(2) Reaction with Hydrogen

$O_2 + 2H_2 \rightarrow 2H_2O$

$S + H_2 \rightarrow H_2S$

$Se + H_2 \rightarrow H_2Se$

The volatility of the hydrides formed is of the order I the thermal stability with respect to dissociation of the element decreases in the order II they.

I: $H_2O <<< H_2S \geq H_2Se > H_2Te$

II: $H_2O >> H_2S > H_2Se > H_2Te > H_2Po$

They are weak acids and the acidity increase as the group is descended.

Oxides

Oxides can be described or classified based on the acidic or basic properties

(1) Basic Oxides: metallic oxides are generally basic. They mostly contain O_2^- ion. A large amount of energy is required to form an ionic oxide. This oxides typically have high melting points.

(2) Amphoteric Oxides: This reacts with both strong acids and

bases.

③ Acidic oxides: Non-metallic oxides are usually covalent. They are all acids, they generally low melting and boiling points.

In cases where the elements exists as more than one oxidation state, then the highest oxidation state is the most acidic

Question

① Account for the following;

(i) Graphite conducts electricity

(ii) It is used in lead pencil

② Discuss the metallic properties of the group 4 elements

③ What makes Sn and Pb poor metals?

④ Why is phosphorus relatively reactive compared to Nitrogen

07-03-2023

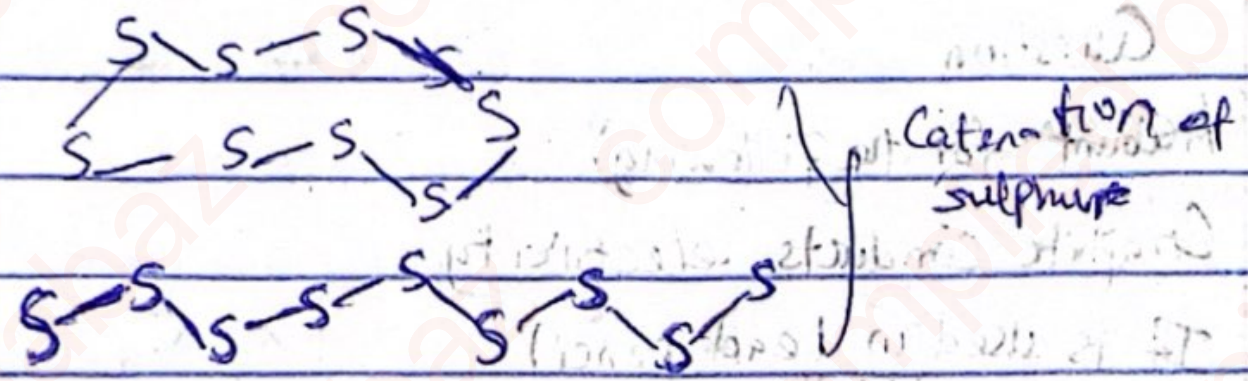
Group 6

Atomic No	Element			
8	Oxygen	O	[He] $2s^2\ 2p^4$	
16	Sulphur	S	[Ne] $3s^2\ 3p^4$	
34	Selenium	Se	[Ar] $3d^{10}\ 4s^2\ 4p^4$	semi conductor
~~54~~	Tellurium	Te	[Kr] $4d^{10}\ 5s^2\ 5p^4$	semi conductor
84	Pollonium	Po	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 5p^4$	

becomes more metallic

Group 6: $ns^2\ p^4$

S_8



All the elements in Groups 6 are polymorphic

Selenium: red (non-metallic), green (metallic)

Oxidation State

n^2p^4 in their outermost orbital. To form a complete octet, they share 2 electrons

* electronegativity of S, Se, Te are low

The formation of S^{2-}, Se^{2-} and Te^{2-} ions are less Probable

The least electronegative element Po does not form Po^{2-}, but it forms Po^{2+}

Positive Oxidation State

Oxygen shows −2 oxidation state, in its compound. Electronegativity decreases down the group and the tendency to show + oxidation state increase, S, Se, Te, Po shows +2 oxidation state, and in addition shows +4 and +6 oxidation state. It is due to the availability of d-orbitals in this elements.
O has no d orbital hence cannot show +4 or +6 oxidation state.

Incase of S, unpairing of electrons can take place if the promotion of 3p and 3s electrons is made to 3d orbitals therefore having +2, +4 and +6 oxidation state

Oxygen is therefore more divalent, while more members can be divalent, tetravalent and hexavalent. For Pollonium +4 oxidation state is more important than +6 oxidation state, due to inert pair effect

Some of the chemical properties;

(1) Formation of hydrides: All elements of the group forms hydrides of the type

~~Hoo~~ H_2S, H_2Se and H_2Te are prepared by action of acids on metal sulphides, metal selenides, metal tellurium

$FeS + H_2SO_4 \longrightarrow H_2S + FeSO_4$

$K_2Se + H_2SO_4 \rightarrow H_2Se + K_2SO_4$

H_2Po has been prepared in traces by dissolving Mg foil plated with Po in HCl

Properties of the Hydrides

H_2O is colourless liquid while the hydrides of other elements are colourless, poisonous.

They are flammable gases which burns with blue flame

Group VI Elements

8 Oxygen O [He] $2s^2 2p^4$
16 Sulphur S [Ne] $3s^2 3p^4$
34 Selenium Se [Ar] $3d^{10} 4s^2 4p^4$
52 Tellurium Te [Kr] $4d^{10} 5s^2 5p^4$
84 Polonium Po [Xe] $4f^{14} 5d^{10} 6s^2 6p^4$

All the elements have ns^2p^4 configuration in the outer-most shell. The four electrons in p-orbitals are distributed in ~~the outermost shell~~ as $p_x^2 p_y^1 p_z^1$ in accordance with Hund's ru
The penultimate shell in oxygen atom contains s^2 ga
(saturated)

~~Oxygen occupies S contrast~~ There is decrease in non-mettallic character down the group and this is see in

⇒ Oxygen exists only as two gaseous allotropes (O_2 & O_3
→ Sulphur has many allotropes are all which are insulat
→ the stable forms of selenium and tellurium are semiconductors.
→ Polonium is metallic conductors.

Some Physical pptIes of these elements:

Density, atomic volume, melting and boiling pts:

With increase in atomic no, the density, the atomic volume, melting pt and b.pt all show steady increase. Polonium shows exception when we consider m.pt & b.pt. Knowledge of the chemistry of polonium and its compds is limited becos of absence of a stable isotope.

The m.pt ~~and~~ and b.pt of Po are less ~~than~~ than those of Te
There is a large difference btw melting & boiling point of O & ~~S~~ S becos Oxygen exists in form of O_2 molecules whereas Sulphur exist as S_8 molecules

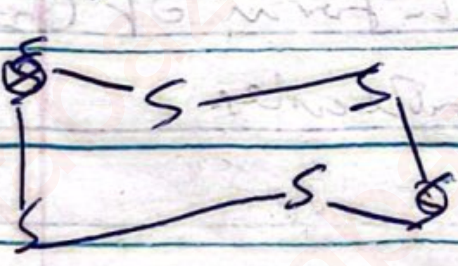
Ionisation energies: Due to the increased lear charge, the first & subsequent ionisation energies ese elements are higher than that of corresponding p of ~~group~~ group V. ~~A~~ As the size of the atoms increases lues of ionisation energies decrease down the group.

Atomicity (Molecular Structure). All the elements polymeric. Oxygen is diatomic (O_2) while the cules of other elements are more complex.

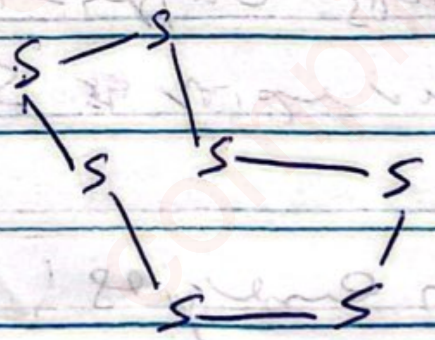
e.g Sulphur, Selenium and Polonium are octatomic molecules ie S_8, Se_8 and Po_8 with Puckered ring structures

Puckered rings of sulphur.

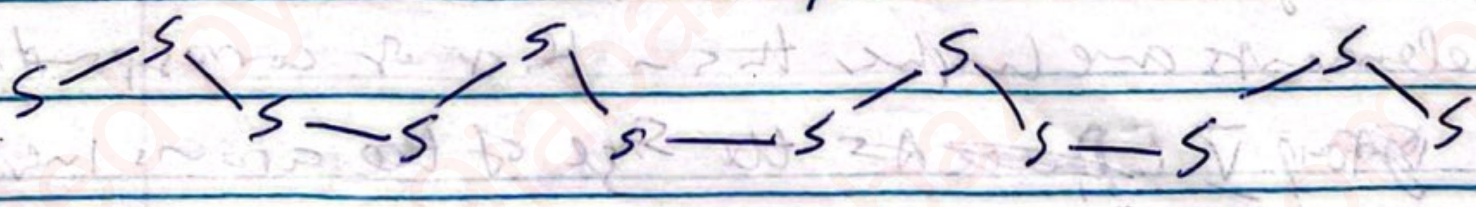
Infact, allotropy of sulphur is complicated, The tendenc for ~~form~~ catenation is high and leads to the formation of S rings and chains of various sizes. Allotropes of Sulphur includ Cyclic S_6, S_7, S_8, S_{10}, S_{11}, S_{12}, S_{18} and S_{20}, catena S_∞



S_6



S_7



S_∞ (the chain continues at each e

These rings give molecular crystal in which the rings are together by relatively weak polar forces. Consequently SulPh (rhombic or monoclinic) have low melting points.

Polymorphism (Allotropy): All the elements are Polymorph ~~i.e. show allotropy~~ Oxygen exists in two non-metallic forms viz O_2 & O_3. Sulphur has several allotropic forms which are non-metallic e.g. rhombic, monoclinic, & Plastic Sulphur. Se has two forms: red (non-metallic) & grey (metallic). Te exists in two forms non-metallic & metallic (stable)

Oxidation States: they all have ns^2p^4 configuration in their outermost orbit, they therefore attain noble gas config either by gaining or by sharing two electrons. They therefore show 2 types of oxidation States:

ⓐ negative oxidation states: Oxygen tends to complete its octet by gaining electrons. Oxygen form the electronegative atoms in its compounds giving oxygen an oxidation state equal to -2 in most of ~~the~~ compounds except in OF_2 molecule in which oxygen is as O^{2+} ion.

The electronegativities of S, Se, & Te are low, ~~the~~ forma of S^{2-}, Se^{2-} and Te^{2-} ions are less probable. Po least electronegative element Po does not form Po^{2-} but it form Po^{2+}.

ⓑ Positive Oxidation states: Oxygen shows −2 oxidation state in its compds. Down the group, electronegativities decreases and the tendency to show Positive Oxidation states increases. S, Se, Te, & Po show +2 oxidation state and in addition show +4 & +6 oxidation states. This is due to the availability of d-orbitals in these ~~atoms~~ elements. Oxygen has no d-orbital and hence cannot show +4 and +6 oxidation states. In case of Sulphur, unpairing of electrons can take place if the promotion of 3p & 3s electrons is made to 3d orbitals, therefore giving +2, +4, +6 oxidation states. Oxygen is therefore never more than divalent, while other members may be divalent, tetravalent, and hexavalent. For polonium, +4 oxidation state is more important than +6 oxidation state due to the Inert Pair effect.

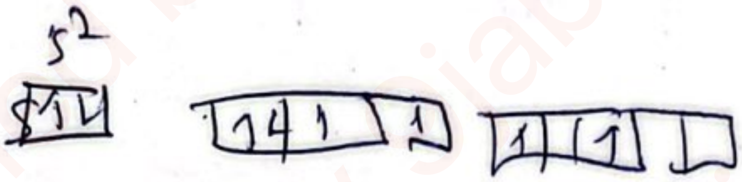
Chemical properties

① Formation of hydrides: All the elements of this group form the hydrides of type H_2A, A = O, S, Se, Te & Po.

H_2O is prepared by burning H_2 in the atmosphere of O_2 while H_2S, H_2Se and H_2Te are prepd by action of acids on metal sulphides, selenides and tellurides e.g.

$$FeS + H_2SO_4 \rightarrow FeSO_4 + H_2S$$

$$K_2Se + H_2SO_4 \rightarrow K_2SO_4 + H_2Se$$



H_2Po has been prepared in traces by dissolving Mg foil plated with Po in ~~0.2N~~ HCl.

properties of the hydrides: Water is colorless, odourless liquid while the hydrides of other elements are colourless, poisonous gases with unpleasant odour. They are inflammable gases which burn with a blue flame.

The volatility of these hydrides increases from H_2O to H_2S and then decreases. Abnormal low volatility of H_2O is due to presence of hydrogen bonding in solid & liquid states. Water has the highest b.pt & m.pt among the hydrides
m.pt b.p m.pt b.pt b.pt
H_2O = 100°, 0.0° H_2S = −60.3°, −85.50. H_2Se = −41.3°, −
Pt
H_2Te = −2.3°, −51.0°. Due to low electronegativity of S-atom, H-bonding in H_2S is rare and hence the association of H_2S molecules does not exist, thereby H_2S is more volatile than H_2O. In going down the group, the volatility of H_2M hydrides decreases from $H_2S \longrightarrow H_2Se \longrightarrow H_2Te$ due to the increase in molecular weights of the hydrides.

The thermal stability of the hydrides decreases from H_2O to H_2Te, thereby, water dissociates at about 2000°c, H_2S at 400 − 600°c, H_2Se at 150°c while H_2Te decomposes even at ordinary temp. The decrease in thermal stability ~~of~~ from H_2O to H_2Te is becos the size of M^{2-} ion in H_2M hydrides increases from O^{2-} to Te^{2-} ion and hence the charge is distributed ove a large volume and this makes the H_2M hydride thermally unstable. The decrease in thermal stability from H_2O to H_2Te is also becos of an increase in M—H bond length as we move from H_2O to H_2Te.

H_2O; O—H = 0.96 A°
H_2S ~~S~~—H = 1.32A°
H_2Se Se—H = 1.47 A°
H_2Te Te—H = 1.73A°

The increase of M—H bond length from O—H (in H_2O) to Te—H (in H_2Te) weakens the M—H bond and hence the hydride becomes thermally unstable. With the decrease of thermal stability of these hydrides from H_2O to H_2Te, ~~the~~ reducing power of these hydrides gradually increase in the same direction.

Covalent character: Since the electronegativity of O, S, Se and Te decreases from O to Te, the electronegativity diff between M (M = O, S, Se, Te) and H decreases and hence ionic character of M—H bond also decreases from O—H to Te—H bonds in H_2M hydrides. That is, the covalent character of these hydrides increases from H_2O t H_2Te.

The increase in covalent character from H_2O to H_2Te can also be explained by Fajans rules, as the size of M^{2-} ion in H_2M hydrides increases from O^{2-} to Te^{2-} the tendency of these ions to form covalent hydrides increases.

Acidic Character: aqueous solutions of the hydrid of these elements behave as weak, diprotic acids and hence ionise as

$$H_2M \rightleftharpoons H^+ + HM^-$$
$$HM^- \rightleftharpoons H^+ + M^{2-}$$
$$H_2M \rightleftharpoons 2H^+ + M^{2-}$$

The acidic character of these acids increases in th sequence from H_2O to H_2Te. The increase in acidic character from H_2O to H_2Te is also confirmed by the fact that the value of dissociation constant of these hydrides also increases in the same direction as shown

$H_2O = 1.0 \times 10^{-11}$

$H_2S \Rightarrow 1.1 \times 10^{-7}$

$H_2Se = 2.0 \times 10^{-4}$

$H_2Te = 2.3 \times 10^{-3}$

As the charge density on the conjugate bases i.e. OH^-, SH^-, SeH^- and TeH^- decreases from OH^- to TeH^-, the proton is less tightly held with higher members and hence the acidic character increases from H_2O to H_2Te.

Formation of Halides : All the elements of this group form binary halides. Since fluorine is more electronegative than oxygen, fluorine compounds with oxygen are called fluorides of oxygen rather than oxide of fluorine e.g. OF_2 is called oxygen difluoride and not difluorine dioxide. On the other hand, since oxygen is more electronegative than Cl, Br and I, oxygen compds with Cl, Br and I are called oxides of halogens rather than halides of oxygen. e.g ClO_2 is chlorine dioxide.

Examples of halides Hexafluorides (MF_6)

except oxygen, all other elements form hexafluoro
The element (S, Se, or Te) shows its maximum covalen
of six by using its d-orbitals.

Hexahalides can be prepared by direct combinat
of the elements.

Hexafluorides are relatively stable and their stabilit
decreases from SF_6 to TeF_6 due to the increase i
size from S to Te atoms. Thus SF_6 is extremel
stable and inert both thermally and chemically.

SeF_6 is less stable and quite reactive while TeF_6
is still more reactive as is evident from the fact that
TeF_6 is completely hydrolysed by H_2O and adds F^-
ion and lewis bases like $(CH_3)_3N$ to form
8 coordinated complex.

$$TeF_6 + 6H_2O \longrightarrow 6HF + H_2TeO_6$$

$$TeF_6 \xrightarrow{+F^-} [TeF_7]^- \longrightarrow [TeF_8]^{2-}$$

$TeF_6 + 2(CH_3)_3N \rightarrow TeF_6 \cdot 2(CH_3)_3N$
Adduct

All the hexafluorides are colourless gases. All have low boiling points and hence show a degree of covalency. All the hexafluorides have regular octahedral geometry resulting from sp^3d^2 hybridisation of the central atom, M (M = S, Se or T
All the M–F bonds are σ-bonds. All the FMF bond angles and M–F bond lengths are equa

Tetrahalides:) (MX_4)

Tetrahalides of these elements are obtained by indirect methods like:

$S + 4CoF_3 \rightarrow SF_{4(g)} + 4CoF_2$

$SeCl_4 + 4AgF \rightarrow SeF_{4(l)} + 4AgCl$

$TeO_2 + 2SeF_2 \rightarrow TeF_{4(s)} + 2SeOF_2$

2. **Reaction with halides**: Nitrogen forms only trihalides, NX_3 of which only NF_3 is stable, NCl_3 is explosive while NBr_3 is non-existent. All the other elements form stable trihalides which are readily hydrolysed to the acid by water (see Equations 2.75 and 2.76).

$$4AsCl_3 + 6H_2O \longrightarrow 12HCl + As_4O_6 \quad \text{......(2.75)}$$

$$SbCl_3 + H_2O \longrightarrow 2HCl + SbOCl \quad \text{......(2.76)}$$

3. **Reaction with oxygen**: They all form oxides with the empirical formula, M_2O_3 which react readily with water to form acid anhydrides (for example, Equation 2.77) except for Bi_2O_3 which forms the hydroxide (Equation 2.78).

$$As_4O_6 + 6H_2O \longrightarrow 4H_3As_4O_3 \quad \text{......(2.77)}$$

$$Bi_2O_3 + 3H_2O \longrightarrow 2Bi(OH)_3 \quad \text{......(2.78)}$$

4. **Reaction with sulphur:** As, Sb and Bi form the trisulphides, As_2S_3, Sb_2S_3 and Bi_2S_3 respectively. As_2S_3 and Sb_2S_3 react with sulphides to form trithioarsenate (III) (equation 2.79) and trithioantimonate (III) (Equation 2.80) respectively.

$$As_2S_3 + 3Na_2S \longrightarrow 2Na_3AsS_3 \quad \text{......(2.79)}$$

$$Sb_2S_3 + 3Na_2S \longrightarrow 2Na_3SbS_3 \quad \text{......(2.80)}$$

2.6 Physical and Chemical Properties of the Group VI^A Elements (The Oxygen Group)

Physical Properties

These are summarized in Table 2.13.

Table 2.13: Summary of the physical properties of the group VI^A elements

Element (At. No.)	At. Rad.(Å)	Ionic Rad. (Å)	M.pt (°C)	B.pt (°C)	1st I.E^Y (kJmol^{-1})	Electro-negativity	Density (gmcm^{-3})
O(8)	0.74	1.40	53	-	1318	3.5	1.27 (solid)
S(16)	1.04	1.84	392 (monoclinic)	718	1001	2.5	2.06
Se(34)	1.40	1.98	490	958	940	2.4	4.80(grey)
Te(52)	1.60	2.20	725	1263	870	2.0	6.24(metal)
*Po(84)	1.64	2.30 (varies)	527	1235	813	1.8	9.51 (β^-)

*Radioactive

Size of the elements increases down the group with increase in atomic number which explains the observed increase in radii, density, melting point and boiling point (except for radioactive polonium) as well as the decrease in ionization energy and electronegativity down the group. Increase in size down the group increases the number of electronic shells shielding the nuclear positive charge, thus reducing the tendency to attract electrons.

Electronegativity of an element is the ability of the element to attract electrons forming the X^{n-} ions (n = 2 here). Ionization energy is the ease by which an electron is knocked off from the outermost shell of the gaseous atom. This value will obviously decrease with increasing size of the atom down the group due to increased shielding of the nuclear positive charge from attracting the electron. Increase in melting point and boiling point down the group is due to increasing van-der-waals forces with increasing availability of orbitals as the atomic number increases. The anomalous values of melting point and boiling point found for polonium is due to its radioactivity which also accounts for its variable ionic radii. Increase of orbitals maximizes overlap between bonding orbitals leading to extensive delocalization of electrons and consequently stability of the atom. This may explain why oxygen is a gas at room temperature while other members of the group are solids.

Chemical Properties

Oxygen is soluble in water (30 cm^3 per 1000 cm^3 H_2O at 20°C) and reacts readily with many elements to form the corresponding oxides (Equations 2.81 and 2.85).

$$C + O_2 \xrightarrow{\text{High Tempt.}} CO_2 \quad \text{......(2.81)}$$

$$2H_2 + O_2 \xrightarrow{\text{High Tempt.}} 2H_2O \quad \text{......(2.82)}$$

$$4Na + O_2 \xrightarrow[\text{Highly exothermic}]{\text{Fast}} 2Na_2O \quad \text{......(2.83)}$$

$$\underset{\text{(white)}}{P_4} + 3O_2 \xrightarrow{\text{in the cold}} P_4O_6 \quad \text{......(2.84)}$$

$$2NO + O_2 \xrightarrow{\text{in the cold}} 2NO_2 \quad \text{......(2.85)}$$

Formation, structure and properties of ozone

1. **Formation:** Ozone is formed in the stratosphere (upper atmosphere) by the action of U/V light on oxygen (Equations 2.86 and 2.87).

$$O_2 \xrightarrow{\text{Ultraviolet light}} 2O \quad \text{.......... (2.86)}$$

$$O + O_2 \longrightarrow O_3 \text{ (Ozone)} \quad \text{.......... (2.87)}$$

2. **Structure**: Ozone exists in canonical forms (Figure 2.4). It is a bent molecule, being isoelectronic with SO_2 and NO_2^-.

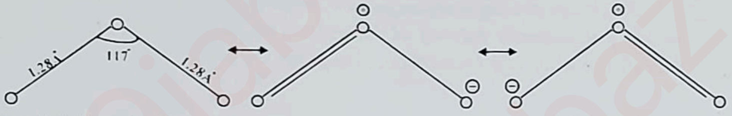
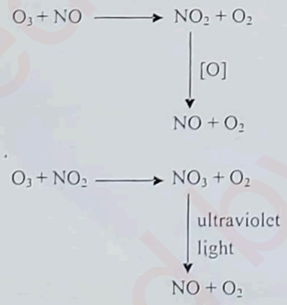


Figure 2.4: Canonical forms of ozone

3. **Properties:** Ozone is another form of existence of oxygen. It is a triatomic allotrope of oxygen and it is an unstable, blue, diamagnetic gas with a characteristic pungent smell. It has a strong absorption in the ultraviolet region of the spectrum between 220 and 290 nm, thus protecting the surface of the earth and its inhabitants from the otherwise intensive ultraviolet radiation of the sun. It thus acts as a shield to human beings in its capacity as an important natural constituent of the atmosphere, being concentrated (27% by weight of the atmosphere) between altitudes 15 and 25 km. Destruction of the ozone layer in the upper atmosphere (stratosphere) particularly by supersonic aircrafts flying in the ozone layer could cause dramatic increase in surface temperature and consequently, cancer of the skin. This is because such aircrafts discharge NO and NO_2 from their exhausts and these gases react with ozone (Scheme 2.5) causing its depletion.



Scheme 2.5: Depletion of ozone by aircrafts flying in the stratosphere

Ozone is much more powerful oxidizing agent than oxygen and reacts with most substances at temperatures as low as 25°C. It oxidizes Fe^{2+} salts to Fe^{3+} and sulphides to sulphates. It adds to unsaturated compounds in organic chemistry to form ozomides. The formation of iodine from the reaction of ozone with aqueous KI allows the quantitative determination of ozone with ease (Equation 2.88).

$$\underset{\text{(acidified)}}{O_3 + 2KI + H_2O} \longrightarrow I_2 + 2KOH + O_2 \quad \text{.......... (2.88)}$$

Compounds of oxygen

These include, H_2O_2, ionic peroxides, super oxides and ozonides. Hydrogen peroxide is prepared by the addition of ice-cold dilute H_2SO_4 to hydrated barium peroxide (Equation 2.89) or sodium peroxide (Equation 2.90).

$$H_2SO_4 + BaO_2.8H_2O \longrightarrow BaSO_4 + 8H_2O + \underset{\text{(15\% solution)}}{H_2O_2} \quad \text{.......... (2.89)}$$

$$H_2SO_4 + Na_2O_2 \longrightarrow Na_2SO_4 + H_2O_2 \quad \text{.......... (2.90)}$$

Sodium peroxide is a colourless liquid, boiling point 150°C and melting point -0.43°C (density = 1.44 $gmcm^{-3}$ at 25°C). Pure H_2O_2 is a viscous, polar liquid and has hydrogen bonding. It is more acidic than water and its solution readily decomposes to H_2O and O_2 (Equation 2.91).

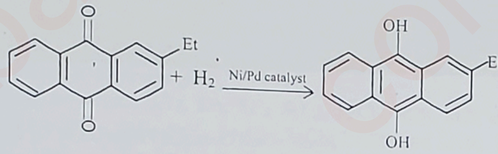
$$2H_2O_2 \xrightarrow{\text{decomposition}} 2H_2O + O_2 \quad \text{.......... (2.91)}$$

The enthalpy of decomposition, ΔH, is -99 $kJmol^{-1}$. The decomposition is catalysed by traces of heavy metals such as Pt, Ag and Au. H_2O_2 is used as a bleaching agent for textiles, paper pulp, oils, fats etcetera. It also finds domestic use as a hair bleach and as a mild disinfectant for domestic and industrial effluents and as a germicide in toothpastes and in mouth wash. It is also used in the manufacture of drugs.

A recent[7] synthetic technique for H_2O_2 production involves the dissolution of 2-ethylanthroquinone in ester/hydrocarbon or alcohol/hydrocarbon solvent followed by reduction with H_2 in the presence of Ni/Pd catalysts to give the corresponding alcohol (Equation 2.92).

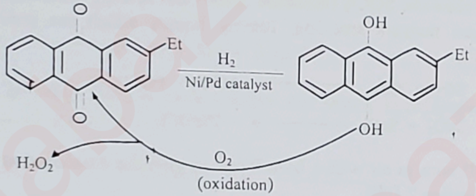
---

[7] C.A. Crampton, G. Faber, R. Jones, J.P. Leaver and S. Schelle (1977), "The manufacture, properties and uses of hydrogen peroxide and other inorganic peroxy compounds" in R. Thompson (Ed.). The Modern Inorganic Chemicals Industry, published by the Chemical Society, London.



.... (2.92)

This alcohol is rapidly oxidized by air (O_2) to give H_2O_2 and the regeneration of 2-ethylanthroquinone to commence the catalyst cycle (Scheme 2.6).



Scheme 2.6: Catalytic cycle for the production of H_2O_2 from 2-ethylanthroquinone

1. **Structure of H_2O_2:** Hydrogen peroxide has a skew, chain structure as shown in Figure 2.5.

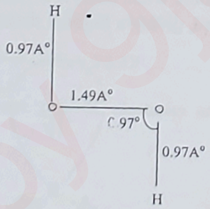


Figure 2.5: Skew structure of H_2O_2

2. **Chemical properties of H_2O_2**
   (a) It liberates iodine from acidified KI (Equation 2.93)
   $2I^- + 2H^+ + H_2O_2 \longrightarrow I_2 + 2H_2O$ ....(2.93)
   (b) It oxidizes Fe^{2+} to Fe^{3+} (Equation 2.94)
   $2Fe^{2+} + 2H^+ + H_2O_2 \longrightarrow 2Fe^{3+} + 2H_2O$ .... (2.94)

   (c) It oxidizes sulphides (Equation 2.95) and sulphites (Equation 2.96) to sulphates
   $S^{2-} + 4H_2O_2 \longrightarrow SO_4^{2-} + 4H_2O$ .... (2.95)
   $SO_3^{2-} + H_2O_2 \longrightarrow SO_4^{2-} + H_2O$ .... (2.96)
   (d) It reduces ammoniacal silver nitrate to silver metal (Equation 2.97)
   $2Ag(NH_3)_2^+ + H_2O_2 \longrightarrow 2Ag + 4NH_3 + 2H^+ + O_2$ .... (2.97)
   (e) It reduces acidified $KMnO_4$ to Mn^{2+} salt (Equation 2.98)
   $2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$ ...... (2.98)

Other compounds of oxygen include ionic peroxides, superoxides and ozonides.

3. **Ionic Peroxides:** These contain the peroxide ion, $(O\ O)^{2-}$ and react with water or dilute acids to produce H_2O_2, thus demonstrating their powerful oxidizing properties (Equations 2.99 and 2.100).

$Na_2O_2 + 2H_2O \longrightarrow H_2O_2 + 2NaOH$ .... (2.99)

$Na_2O_2 + 2HCl \longrightarrow H_2O_2 + 2NaCl$ .... (2.100))

Ionic peroxides include M_2O_2 (M = group I^A metals) and MO_2 (M = group II^A metals).

4. **Superoxides:** These contain the ion $(O\ O)^-$ and are paramagnetic, that is, they have one unpaired electron per two oxygen atoms. They are also powerful oxidizing agents and readily produce oxygen on treatment with water (Scheme 2.7).

$$\begin{tikzcd}
2O_2^- + H_2O \arrow[r, "\text{fast}"] & HO_2^- + OH^- + O_2\uparrow \arrow[d, "\text{slow}"] \\
 & {}^-OH + \tfrac{1}{2}O_2\uparrow
\end{tikzcd}$$

Scheme 2.7: Hydrolysis of superoxides

5. **Oxonides:** These contain the ozonide ion, O_3^- which has one unpaired electron and consequently paramagnetic. They are formed from the reaction of ozone with the hydroxides of alkali metals (Equation 2.101).

$$2O_3(g) + 3MOH(s) \longrightarrow 2MO_3(s) + 2MOH.H_2O(s) + ½O_2\uparrow \text{......} (2.101)$$

Their thermal stabilities decrease along the sequence, $CsO_3 > KO_3 > NaO_3 > LiO_3$, that is, with decreasing atomic number of the elements.

Chemical Properties of S, Se and Te

1. All the elements dissolve readily in C. HNO_3 to form the corresponding acids (Equations 2.102 and 2.103).

$$S + 6HNO_3 \longrightarrow H_2SO_4 + 2H_2O + 6NO_2 \text{ ......} (2.102)$$

$$Se + 4HNO_3 \longrightarrow \underset{\text{(selenious acid)}}{H_2SeO_3} + H_2O + 4NO_2 \text{ ......} (2.103)$$

2. They form colourless, poisonous and pungent hydrides by direct interaction with hydrogen above 350°C (Equation 2.104) or by the reaction of their metal chalconides with acids (Equation 2.105).

$$Se + H_2 \xrightarrow{>350°C} H_2Se \text{ ......} (2.104)$$

$$FeSe + 2HCl \longrightarrow H_2Se + FeCl_2 \text{ ......} (2.105)$$

The stability of these hydrides follows the sequence $H_2S > H_2Se > H_2Te$, that is stability decreases with increasing atomic number of the group VI^A elements.

3. They all interact with the group VII^A elements to form the corresponding halides in which the oxidation state of the group VI^A elements vary from less than 1 to 6 (no +3 halide is known till date) (Table 2.14).

Table 2.14: Variation of oxidation states with known halides of the group VI^A elements

Oxidation State	Known Halides
<1	Te_2Cl, Te_2Br, Te_2I, Te_3Cl_2
+1	S_2F_2, S_2Cl_2, S_2Br_2, Se_2Cl_2, Se_2Br_2, Te_4I_4
+2	SCl_2, SeF_2, $SeCl_2$, $SeBr_2$
+4	SF_4, SCl_4, SeF_4, $SeCl_4$, $SeBr_4$, TeF_4, Se_4Cl_{16}
+5	S_2F_{10}, Te_2F_{10}
+6	SeF_6, TeF_6

4. S and Se form oxohalides called thionyl-(S) and selenyl-(Se) halides. Examples include thionyl chloride, $SOCl_2$ (Equation 2.106) and selenyl chloride, $SeOCl_2$ (Equation 2.107). These are pungent smelling, fuming liquids which are used extensively in organic synthesis.

$$SO_2 + PCl_5 \longrightarrow SOCl_2 + POCl_3 \text{ ......} (2.106)$$

$$SeO_2 + SeCl_4 \longrightarrow 2SeOCl_2 \text{ ......} (2.107)$$

5. They all burn in air with a blue flame to give the dioxide, that is, SO_2, SeO_2 and TeO_2 (see Equation 2.108).

$$S + O_2 \longrightarrow SO_2 \text{ ......} (2.108)$$

Structures of SO_2 and SeO_2

SO_2 is a gas at room temperature while SeO_2 is a white solid at room temperature. In SO_2, the sulphur atom is sp^2 hybridized, giving a trigonal structure (Figure 2.6).

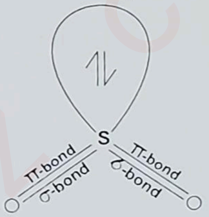


Figure 2.6: Trigonal structure of SO_2

The π-bond results from overlap of d-orbitals on sulphur atom and P-orbitals on oxygen atom (that is, $P\pi - d\pi$ overlap).

SeO_2 is a white solid at room temperature but turns gaseous at high temperatures, assuming the trigonal structure of SO_2. However, in the solid state, it forms chains of SeO_2 molecules (Figure 2.7).

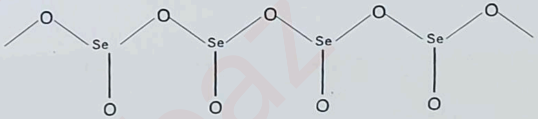


Figure 2.7: Solid structure of SeO_2

Polysulphides: These are compounds containing more than one sulphur atom. Examples are H_2S_2, H_2S_3 and H_2S_4. Other sulphides of hydrogen are unstable.

Halides and Hexahalides of S, Se and Te

Stable halides of sulphur include S_2F_2, SF_4, SF_6, S_2F_{10}, $SeCl_2$, SCl_2, SCl_4 and S_2Br_2. Stable halides of selenium are Se_2F_2, SeF_4, SeF_6, Se_2Cl_2, $SeCl_4$, Se_2Br_2 and $SeBr_4$. Stable halides of tellurium are TeF_4, Te_2F_{10}, TeF_6, $TeCl_2$, $TeCl_4$, $TeBr_2$, $TeBr_4$ and TeI_4. The known hexahalides are the fluorides, that is, SF_6, SeF_6 and TeF_6. They are prepared by direct fluorination of the elements. For example, the reaction of S_8 with excess fluoride gives SF_6 and traces of SF_4 and S_2F_{10} (Equation 2.109).

$$\tfrac{1}{2}S_8 + 10F_2 \longrightarrow SF_6 + SF_4 + S_2F_{10} \;\ldots\ldots\ldots\ldots (2.109)$$

SF_6 and SeF_6 are inert while TeF_6 is more reactive and slowly hydrolyzed to telluric acid (Equation 2.110).

$$TeF_6 + 6H_2O \longrightarrow H_6TeO_6 + 6HF \;\ldots\ldots\ldots\ldots (2.110)$$

The tetrafluorides can only be produced by controlled fluorination of the elements (Equations 2.111 to 2.113) since the direct fluorination is very difficult.

$$S + 4CoF_3 \longrightarrow SF_4 + 4CoF_2 \;\ldots\ldots\ldots\ldots (2.111)$$

$$SeCl_4 + 4AgF \longrightarrow SeF_4 + 4AgCl \;\ldots\ldots\ldots\ldots (2.112)$$

$$TeO_2 + 2SeF_4 \longrightarrow TeF_4 + 2SeOF_2 \;\ldots\ldots\ldots\ldots (2.113)$$

All the tetrafluorides possess a lone pair of electrons and exhibit trigonal bipyramidal structure (Figure 2.8).

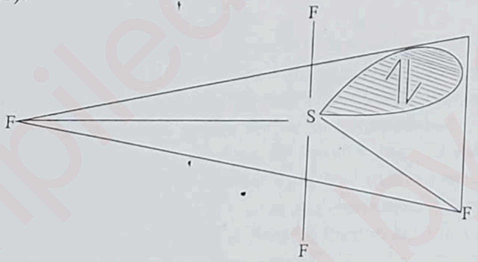
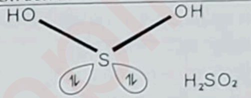
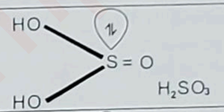
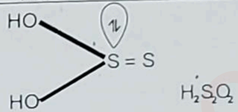
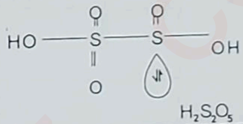
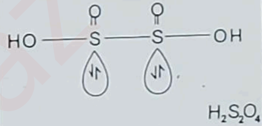


Figure 2.8: Trigonal bipyramidal structure of SF_4

Oxo Acids[8,9] *of Sulphur, Selenium and Tellurium*

The Oxo acids of sulphur are more numerous than those of Se and Te but many, of them are unstable and can only be isolated as their anions or salts (Table 2.15).

Table 2.15: Oxo- and peroxo-acids of sulphur

Name of Acid	Structure	Comment
I. Sulphotylic acid (Dioxosulphate(II) acid)		Only isolable as the Zn or Co salt
II. Sulphurous acid (Trioxosulphate(IV) acid)		Not isolable
III. Thiosulphurous acid (Dioxosulphate(I) acid)		Not isolable
IV. Pyrosulphurous acid (Pentaoxosulphate(IV) acid)		Not isolable
V. Dithionous acid (Tetraoxosulphate(III) acid)		Not isolable

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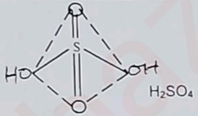
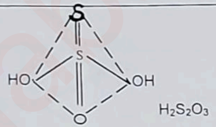
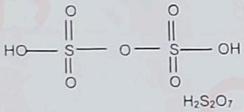
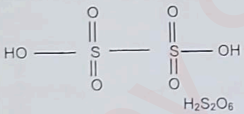
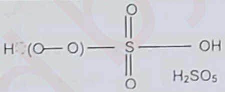
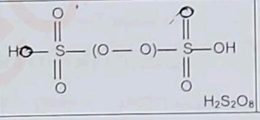
[8] M. Schmidt and W. Siebert, "Oxyaxids of Sulphur" in Comprehensive Inorganic Chemistry, Vol. 2, Chapter 23.

[9] N.N. Greenwood and A. Earnshaw (1986), "Chemistry of the Elements" Pergamon Press Ltd, UK.

VI. Sulphuric acid (Tetraoxosulphate (VI) acid	 H_2SO_4	Stable known acid
VII. Thiosulphuric acid (Trioxosulphate(II) acid)	 $H_2S_2O_3$	Stable known acid
VIII. Pyrosulphuric acid (Heptaoxosulphate(VI) acid)	 $HO-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-O-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-OH$ $H_2S_2O_7$	Stable known acid
IX. Dithionic acid (Hexaoxosulphate(V) acid)	 $HO-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-OH$ $H_2S_2O_6$	Stable known acid
X. Peroxosulphuric acid (Pentaoxosulphate(VIII) acid)	 $H(O-O)-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-OH$ H_2SO_5	Stable known acid
XI. Peroxodisulphuric acid (Octaoxosulphate(VII) acid)	 $HO-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-(O-O)-\overset{\overset{O}{\parallel}}{\underset{\underset{O}{\parallel}}{S}}-OH$ $H_2S_2O_8$	Stable known acid

Oxo acids of Se and Te are very few. Examples are selenious acid (Equation 2.114) and selenic acid (Equation 2.115).

$$SeO_2 + H_2O \longrightarrow H_2SeO_3 \quad \text{.................................} \quad (2.114)$$

$$H_2SeO_3 + H_2O_2 \longrightarrow H_2SeO_4 + H_2O \quad \text{..........................} \quad (2.115)$$

Telluric acid, H_6TeO_6 or $Te(OH)_6$ is produced by reacting H_2O_2 with TeO_2 (Equation 2.116a).

$$3H_2O_2 + TeO_2 \longrightarrow Te(OH)_6 + O_2 \quad \text{.........................} \quad (2.116a)$$

2.7 Physical and Chemical Properties of the Group VII^{A} Elements (The Halogens)

Physical Properties

These are summarized in Table 2.16.

Table 2.16: Summary of the physical properties of the group VII^{A} elements

Element (At. No.)	At. Rad. (Å)	Ionic Rad. (Å)	Ionization E^{Y} ($kJmol^{-1}$)	M.pt (°K)	B.pt (°K)	Electron Affinity ($kJmol^{-1}$)	Electro-negativity
F(9)	0.71	1.20	1682	43	153	330	3.9
Cl(17)	0.99	1.75	1252	170	238	350	3.0
Br(35)	1.14	1.90	1140	266	332	325	2.8
I(53)	1.33	2.14	1008	387	457	298	2.5

In their physical states, fluorine is a pale yellow gas, chlorine is a greenish yellow gas, bromine is a red liquid and iodine is a violet black solid. All the elements have the ns^2np^5 electronic configuration, that is, seven electrons in their outermost shells. This means that they can complete the octet configuration by acquiring one electron, that is

$$X(g) + e^- \longrightarrow X^- \quad \text{...} \quad (2.116b)$$

They can also form single covalent bonds by overlap either between 2p-orbitals (for example (Cl–Cl) or between a p-orbital and an s-orbital (e.g. H–Cl).

The atomic radii, ionic radii, melting point and boiling point of the elements increase down the group from fluorine to iodine owing to increasing size of atoms resulting from increased number of shells around the nucleus. The decrease in ionization energy down the group is also a size effect. Ionization energy is the energy required to remove an electron from the isolated gaseous atom. Increasing size of atoms from F to I implies that the electron to be removed from the outermost shell is shielded from the positively charged nucleus by the increased number of shells, explaining why iodine has the least ionization energy. The electron affinity of the elements decreases from F to I except for the anomalous value of 330 $kJmol^{-1}$ found[10,11] for fluorine. Electron affinity is defined as the energy released when an electron is added to the valence shell of an atom. The lower value of fluorine compared with chlorine may be attributed to its small size. The truth is that it has greater capacity to accept

---

[10] J. Berkowitz and A.C. Wahl (1973), "The Dissociation Energy of Fluorine", Adv. Fluorine Chem., 7, 147-174.

[11] P. Politzer (1969), "Anomalous Properties of Fluorine", J. Am. Chem. Soc., 91, 6235-6237.

GROUP VII ELEMENTS
(THE HALOGENS)

Group VII comprises of non-metals, namely, fluorine-F_2, chlorine-Cl_2, bromine-Br_2 and astatine-At_2.

General valence shell:-
ns^2np^5

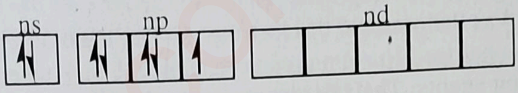
Table 1: Some physical properties of halogens

Property	F(9)	Cl(17)	Br(35)	I(53)
Electronic configuration	$[He]2s^22p^5$	$[Ne]3s^23p^5$	$[Ar]3d^{10}4s^24p^5$	$[Kr]4d^{10}5s^25p^5$
1st IE ($kJmol^{-1}$)	1681	1255	1142	1007
Electronegativity	4.0	3.2	3.0	2.7
Melting pt. (°C)	-220	-101	-7	113
Boiling pt. (°C)	-188	-34	59	189
Density(liquid) (gm^{-3})	1.11	1.56	3.1	4.94
Electron affinity of X^{-1} ($kJmol^{-1}$)	338	348	340	297
Ionic radius M^{-1}/A°	1.36	1.81	1.96	2.16
Covalent radius of X A°	0.64	0.99	1.14	1.33
Bond dissociation energy.X_2($kJmol^{-1}$)	158	243	193	151
Oxidation states	-1	-1, 1, 3, 5, 7	-1, 1, 3, 5	-1, 1, 3, 5, 7
Lattice energy ($kJmol^{-1}$) (Potassium salt)	817	718	656	615
Physical state	Gas pale yellow	Gas. Yellowish green	Liquid dark brown	Solid black with shiny metallic lustre.

Occurrence:
Fluorine constitutes nearly 0.054% of earth's crust, where it occurs as fluorspar (CaF_2), cryolite ($AlF_3.3NaF$) and fluorapatite [$CaF_2.3Ca_3(PO_4)_2$]. Small amounts of fluorides occur in sea water and in some mineral springs. Bones also contain small amounts of fluorine.
Chlorine, which forms 0.013% of earth's crust, occurs mainly as chlorides of sodium and other alkali and alkaline earth metals in salt mines as well as in sea water. Sea water is almost a 3% solution of various salts, of which sodium chloride forms ~83%.
Bromine as bromides, occurs in sea water and dry salt lakes and constitutes about $2.0x10^{-4}$% of the earth's crust. Iodine forms only $4.6x10^{-5}$% of earth's crust. It is mostly extracted from brine. Astatine is a radioactive element. Its longest half-life (7.21 hrs) isotope, is made by bombarding bismuth with α particles.

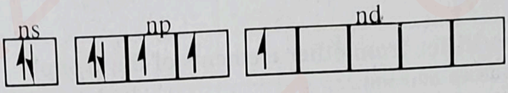
oxidation states of +3, +5 and +7 due to availability of vacant d-orbitals as shown below:

(i) Oxidation state +1: Halogen (except F) in Ground state



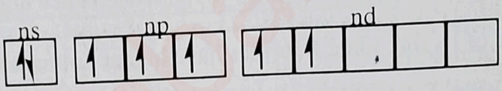
E.g., Oxdn state=-1: HCl, HBr & HI
Oxdn state=+1: HClO, HBrO & HIO

(ii) Oxidation state +3: Halogen in 1st excited state



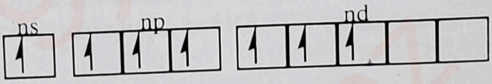
E.g., ClF_3, BrF_3, $HClO_2$

(iii) Oxidation state +5: Halogen atom in the 2nd excited state



E.g., $HClO_3$, $HBrO_3$, HIO_3

(iv) Oxidation state +7: Halogen atom in the 3rd excited state



E.g., $HClO_4$, HIO_4

Chlorine and bromine also exhibit oxdn state +4 (ClO_2 andBrO_2) and +6 (Cl_2O_6 and BrO_3).
Iodine exhibits an oxdn state +4 in I_2O_4.

The power of the halogen to bring about the highest oxdn states of other elements bonded to them decreases in the order F>Cl>Br>I. Thus fluorine forms compounds like SiF_4, SF_6, BrF_5, etc.which have no analogues with Cl. Compare also the oxdn states of iodine in IF_7 Vs ICl_3 and IBr. It is fluorine which brings about the highest oxdn state i.e. +7 in iodine.(Cl =+3, while Br=+1).

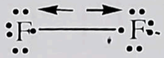
- Coordination number:-
  Fluorine can never have more than one covalent bond and in addition a hydrogen bond (H—F----H—F) thus; it can have a maximum of two coordination number. Other halogens can reach higher coordination numbers because they can extend their octet by using the low lying d-orbitals.

- Oxidizing power:-
  Oxidation is regarded as the removal of electrons, so that the oxidizing agent gains electrons. Since halogens have a greater tendency to pick up electrons, they act as strong oxidizing agents. Their oxidizing power, however, decreases on moving down the group (from F to I).

- The ionic character of metal halides decreases on descending the group. E.g., AlF_3 is mainly ionic whereas $AlCl_3$ is covalent.

Why do Fluorine properties differ from other elements of the group?

1. Small size of the fluorine atom and ion.
   - Results to better overlap of atomic orbitals and hence shorter and stronger bonds.
   - Results in higher coordination numbers to other elements (hence higher oxidation states).
   - Due to the small size of its ion, ionic fluorides have higher Lattice energies than other ionic halides.
2. Low dissociation energy of F_2 molecule.
   Because of the small size of its atoms, the lone pairs in F-F molecules are very close and repel each other strongly thus fluorine has the lowest bond dissociation energy among the halogen molecules.



   This results in lower activation energy of most of its reactions. Thus, they are faster and often more vigorous than those of other halogens.
3. Fluorine valence shell is restricted to an octet while other halogens have d-orbitals to expand their octet. Thus, many fluoro compounds are quite inert.
4. Fluorine has high oxidizing power
   It has the greatest tendency among all halogens to pick up electrons.
   It oxidizes the elements to their highest oxidation state, e.g., IF_7 has oxidation number seven.
5. Has the highest electronegativity.
   - Thus the fluorides are more ionic than other halides.
   - And AgF is soluble in water while the other silver halides are not.
   - The bond between fluorine and other elements is very strong so its compounds are more stable.
6. Fluorine fumes in moist air and decomposes water to give oxygen, whereas other halogens are sparingly soluble in water and react partly to give hydrohalic and hypohalous acids.

$$2F_2 + 2H_2O \rightarrow 4HF + O2$$

$$X_2 + H_2O \rightleftharpoons HOX + HX$$

HYDROGEN HALIDES

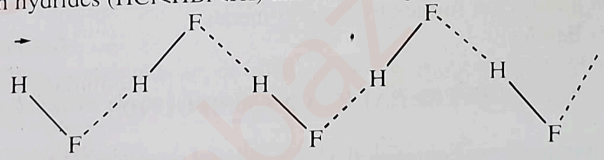
Halogens combine with hydrogen and form volatile hydrides of the type HX, which are also known as hydrogen halides. The reaction of fluorine with hydrogen is very violent whereas bromine and iodine react with hydrogen only at elevated temperatures and in the case of iodine the reaction does not proceed to completion.

Table 2: Some properties of hydrogen halides

Property	**HF**	**HCl**	**HBr**	**HI**
Physical state	liquid	gas	gas	gas
Colour	colourless	colourless	colourless	colourless
Melting pt (°C)	-83.0	-114.6	-88.5	-50.9
Boiling pt (°C)	19.5	-86	-67	-35.4
% dissociation at 373 K	Very slight	0.0014	0.5	33
% ionic character	44	17	11	5
Reactivity	→ Acidity increases Reducing power increases Thermal stability decreases			

Due to strong hydrogen bonding in HF molecule:-

- Under ordinary conditions HCl, HBr and HI are gases while HF is a liquid.
- HF does not follow the trend of the melting and boiling points shown by other halogen hydrides (HCl<HBr<HI) and has unexpectedly higher values.



Percent ionic character:-

- Hydrogen compounds are covalent compounds with varying degrees of polarity of the H-X bond depending upon the electronegativity of the halogen atom. Thus, H-F bond is most polar and the decreasing order of polarity is H-F>H-Cl>H-Br>H-I as shown by percent ionic character in these bonds.
- Due to its polarity HF is readily soluble in water. The solution is a weak acid. This is due to high H-F bond dissociation energy. HCl, HBr and HI dissolve in non-polar solvents; here no chemical reaction is involved. Aqueous solutions of these hydrides are called hydrochloric, hydrobromic and hydoiodic acid.

Acidity:-
In aqueous solutions they ionize and, HCl. HBr and HI act as strong acids.

$$\begin{array}{ll} \mathrm{HF} + \mathrm{H_2O} \longrightarrow \mathrm{H_3O^+} + \mathrm{F^-} & \text{- slightly ionize} \\ \left.\begin{array}{l} \mathrm{HCl} + \mathrm{H_2O} \longrightarrow \mathrm{H_3O^+} + \mathrm{Cl^-} \\ \mathrm{HBr} + \mathrm{H_2O} \longrightarrow \mathrm{H_3O^+} + \mathrm{Br^-} \\ \mathrm{HI} + \mathrm{H_2O} \longrightarrow \mathrm{H_3O^+} + \mathrm{I^-} \end{array}\right\} & \text{completely ionize} \end{array}$$

acid strength increases from HF to HI ↓

Reducing power increases down the group, in such reactions the halides are oxidized to the halogens. Therefore:-

- HCl does reduce strong oxidizing agents
- HBr reduces strong oxidizing agents
- HI reduces even mild oxidizing agents

HALIDES

Binary halogen compounds:-
Halogens form compounds with all elements except the three noble gases- He, Ne and Argon. Nature of the bonds varies from completely ionic to nearly completely covalent.

- Ionic halides are sometimes called salt-like halides
- Covalent halides are formed by the non-metals
- Complex halides.

INTREHALOGEN COMPOUNDS

Interhalogen compounds are compounds formed by the interaction of one halogen with the other halogen.
Such compounds are either binary, formed by a combination of two halogens or ternary, formed by a combination of three halogens.
The binary interhalogen are of the general formular:-

XY'_n Where A is a halogen with low electronegativity
Y' is a halogen with high electronegativity and
n is always an odd integer.

They are of four types:- XY'; XY'_3; XY'_5 and XY'_7.
Interhalogen compounds are named as the halides of less electronegative halogen. Thus, for example ClF is called chlorine monofluoride and not fluorine monochloride.

Ternary compounds were unknown until recently except as polyhalide anions or polyhalonium cations, but now some compounds, e.g., $IFCl_2$ and IF_2Cl have been prepared.
The interhalogen compounds with fluorine are more common.

Table 3: some physical properties of interhalogen compounds.

Type	Compound	Mpt (°C)	Bpt (°C)	Appearance
XY’	ClF (Chlorine fluoride)	-156	-100	Colourles gas
	BrF (Bromine fluoride)	-33	-20	Pale brown gas
	BrCl (Bromine chloride)	~-66	~5	Redish yellow liq.
	ICl (Iodine chloride)	27.2 (α)	97	Ruby red solid
		13.9 (β)	-	Brown red solid
	IBr (Iodine bromide)	36	116	Black solid
XY’$_3$	ClF$_3$ (Chlorine trifluoride)	-76	12	Colourless gas
	BrF$_3$ (Bromine trifluoride)	8.8	126	Colourless liquid
	BrCl$_3$ (Bromine trichloride)	374K (decomposes)	-	Orange solid
	ICl$_3$ (Iodine trichloride)	101/16 atm	64(sub)	Orange solid
	IF$_3$ Iodine trifluoride)	-28(decomposes)	-	Yellow powder
XY’$_5$	ClF$_5$.(Chlorine pentafluoride)	>-196	-	Colourles gas
	BrF$_5$ (Bromine pentafluoride)	-61.3	41	Colourless liquid
	IF$_5$ (Iodine pentafluoride)	9.6	98	Colourless liquid
XY’$_7$	IF$_7$ (Iodine heptafluoride)	45	5	Colourless gas

The stability of interhalogen compounds depends on the electronegativity difference of the two halogens. Greater the difference, more polar is the bond and therefore, greater is the thermal stability and higher their melting and boiling points.

General properties:

- Interhalogen compounds are covalent. However, they are generally more reactive than the halogens except fluorine, since X-Y’ bond is more polar than the Y-Y bond.
- They exist as diamagnetic volatile solids, ~~liquids or gases~~ since all of them contain an even number of halogen atoms.
- They are hydrolysed by water;
  $$ClF + H_2O \rightarrow HF + HOCl$$
- They react with alkenes and add across the double bond (C=C).
- They are strong oxidizing agents and they are used to prepare metal halides. They convert metal into metal halides.
  $$XY' + 2M \rightarrow MX + MY'$$
- Iodine trichloride (ICl$_3$) and bromine trifluoride (BrF$_3$) autoionize (self ionization) like water and ammonia to give polyhalides ions such as ICl$_4^-$.
  $$2ICl_3 \rightleftharpoons ICl_2^+ + ICl_4^-$$
  $$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$
  Thus, the substances which furnish ICl$_2^+$ and BrF$_2^+$ behave as acids and those

furnishing ICl_4^- and BrF_4^- behave as bases in ICl_3 and BrF_3 solvent systems, respectively.

- Their mpts and bpts are higher than expected from interpolation of the melting and boiling pts of the constituent halogens.
- Other properties like colour are intermediate between those of the constituent elements.

Structure of Interhalogen compounds:

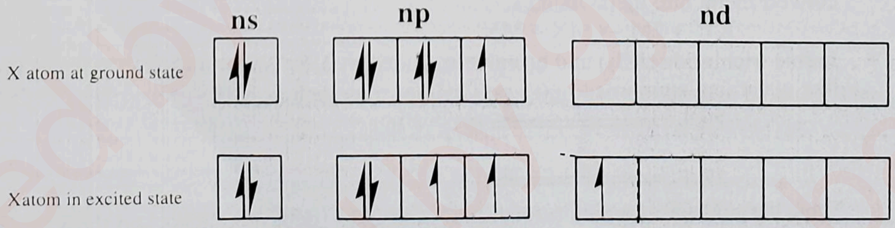
The larger atom lies in the center. Their structures can be explained with the help of Valence Bond Theory.

Molecule	Total number of electron pairs around X	Bond pairs	Lone pairs	Shape	Hybridization
XY'	4	1	3	Linear	sp
XY'_3	5	3	2	T-shaped	sp^3d
XY'_5	6	5	1	Square pyramidal	sp^3d^2
XY'_7	7	7	0	Pentagonal bipyramidal	sp^3d^3

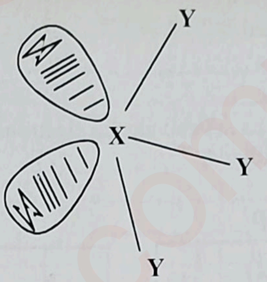
1. Type XY': As expected, the compound of the type XY' are linear. Thus ClF, BrF, BrCl, IBr and ICl all have a linear structure.

X—Y

2. Type XY'_3: The central halogen atom X undergoes sp^3d hybridization. Three of the hybrid orbitals having an electron each are used in making three covalent bonds with three atoms of the other halogen atom. The remaining two orbitals accommodate the two lone pairs of the central atom. In order to minimize lone pair-lone pair and lone pair-bond pair repulsions, the lone pairs occupy the two equatorial sites around the central halogen atom, thereby giving a T-shape to the molecule. Thus ClF, BrF and ICl have a T-shaped structure.

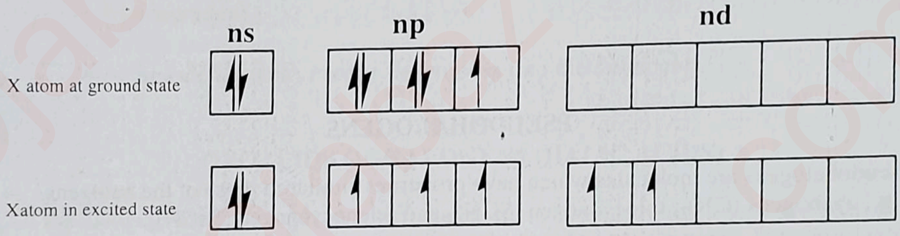


sp^3d hybridisation

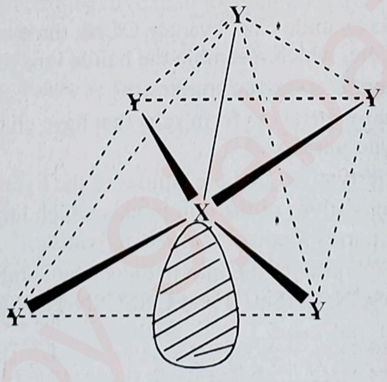


T-shaped structre of XY'$_3$

3. Type XY'$_5$: The central atom X uses five of its seven valence electrons in forming five bonds with Y' and two electrons remain as lone pair. Thus X-atom in XY'5 molecule is sp^3d^2 hybridized.

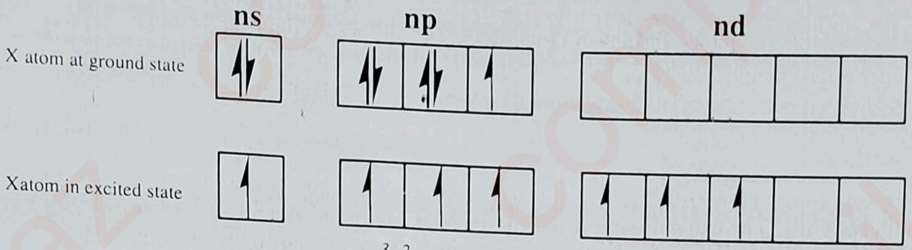


sp^3d^2 hybridisation



square pyramidal structure of XY'$_5$

4. Type XY'_7: The central atom uses all its seven valence electrons in forming seven X-Y bonds. The X atom is sp^3d^3 hybridized.



sp^3d^3hybridisation

PSEUDOHALOGENS

Pseudohalogens are molecules which have properties similar to those of the halogens. E.g., cyanogens $(CN)_2$, thiocyanogen $(SCN)_2$ and selenocyanogen $(SeCN)_2$.

The pseudohalogens in general exhibit physical and chemical properties characteristic of the halogens. E.g.:-

- They form ions such as cyanide CN^-, cyanate OCN^-, thiocyanate SCN^-, selenocyanate $SeCN^-$, etc. which resemble the halide ions to some extent.
- They are oxidizing agents.
- They combine with many metals to form salts that have characteristics similar to those formed by the halogens.
- They form hydrogen derivatives that are similar to the hydrogen halides.
- They form covalent derivatives of the non-metals which have properties very similar to those of the corresponding halogen derivatives.
- They form compounds similar to the interhalogens by combining with each other.(e.g., CNN_3, CSSCN, CNSeCN and $CNSCSN_3$) and with the halogens.

OXIDES OF HALOGENS

All halogens form binary oxygen derivatives although many of them are unstable. Halogen-oxygen bonds are largely covalent because of the similarities in electronegativity of halogens and oxygen.
The oxygen compounds formed with all the halogens except fluorine are called oxides because oxygen is the most electronegative of these elements.
Fluorine is more electronegative than oxygen, hence compounds of fluorine with oxygen are considered as fluorides of oxygen (are named oxygen fluorides) rather than oxides of fluorine.

Table 4: Oxides of halogens.

Fluorides		Oxides					
Compound	**Oxidation Number (O.N)**	**Chlorine compound**	**O.N**	**Bromine compound**	**O.N**	**Iodine compound**	**O.N**
OF_2	-1	Cl_2O	+1	Br_2O	+1	I_2O_5	+5
O_2F_2	-1	ClO_2	+4	BrO_2	+4		
		Cl_2O_6	+6	BrO_3	+6		
		Cl_2O_7	+7				

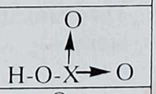
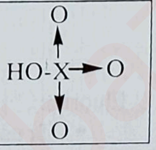
Fluorine:-
Forms several oxygen compounds with general formula O_nF_2 (where n=1-6).
The compounds with n=3-6 are unstable at room temperature and decompose to OF_2 and oxygen. (OF_2 is a stable gas).
Properties:

- All are covalent, having discrete molecules (gases or volatile liquids at room temperature).
- They are acidic
- They are unstable, readily decompose into their elements.

OXOACIDS OF HALOGENS (HALIC ACIDS)

All the halogens form oxoacids in which the halogens have acquired a formal positive oxidation state. The oxoacids have oxygen attached to the halogen atom. They have the general formula $HOX(O)_n$ where n = 0, 1, 2 and 3.
Fluorine being more electronegative than oxygen does not form oxoacids except the unstable HOF (hypofluorous acid).

Table 5: Important oxoacids of halogens

Names of the acids	Oxidation State of halogen In the acid	Oxoacids of			Structure
		Cl	**Br**	**I**	
Hypohalous [Halic (I) acid]	+1 (HXO)	HOCl Hypochlorous acid	HOBr Hypobromous acid	HOI Hypoiodous acid	H-O-X
Halous [Halic (III) acid]	+3 (HXO_2)	HOClO Chlorous acid	HOBrO Bromous acid	-	H-O-X→O
Halic [Halic (V) acids]	+5 (HXO_3)	$HOClO_2$ Chloric acid	$HOBrO_2$ Bromic acid	$HOIO_2$ Iodic acid	 $\text{H-O-}\overset{\overset{O}{\uparrow}}{X}\rightarrow O$
Perhalic [Halic (VII) acid]	+7 (HXO_4)	$HOCl_3$ Perchloric acid	$HOBrO_3$ Perbromic acid	$HOIO_3$ Periodic acid	 $\text{HO-}\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{X}}\rightarrow O$

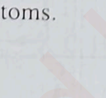
Properties:

$$\xrightarrow[\substack{\text{Thermal stability increases} \\ \text{Acidity increases}}]{HOX;\ HXO_2;\ HXO_3;\ HXO_4}$$

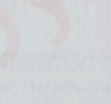
- The oxoacids containing higher number of oxygen atoms are thermally more stable. Since the sp^3 orbitals form relatively weak σ-bonds, the thermal stability is due to the strong (p-d)π bonds of filled 2p-orbitals of oxygen with empty d-orbitals of the halogens which increase with the number of oxygen. However, the thermal stability decreases with increase in the atomic number of the halogen. Thus, HOCl is the most stable and HOI the least stable among the hypohalous acids.
- Acid strength of oxoacids increases with increase in the oxidation number of the halogen. This is because oxygen is more electronegative than halogens (consider only Cl, Br and I), the terminal oxygen atom pulls the electron of the O-X bond towards itself, leaving a slight positive charge on the halogen atom. The halogen atom then draws the electrons of X-OH bond towards itself. This oxygen atom in turn pulls the electrons of O-H bond towards itself, leaving hydrogen atom slightly positively charged and making the O-H bond more easily ionisable. This makes the compound more acidic.

$$H\rightarrow O\rightarrow Cl\rightarrow\rightarrow O$$

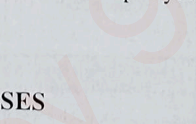
Structures of oxoacids



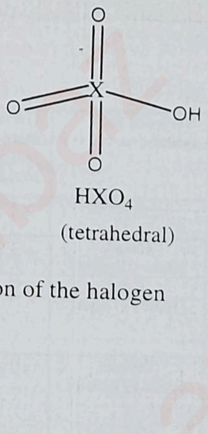
HOX
(linear)



HXO_2
(angular)



HXO_3
(trigonal pyramid)



HXO_4
(tetrahedral)

Their structures are all based on the tetrahedron of the sp^3 hybridization of the halogen atoms.

USES

Fluorine:

- Is used in toothpaste to prevent tooth decay by dental caries.
- Used for the production of uranium hexafluoride, the compound used for the separation of ^{235}U and ^{238}U isotopes by gaseous diffusion method.
- Teflon, in the form of its coating on kitchenware is used to make them nonstick. It is a polymer of fully fluorinated ethylene.

- Chlorofluorocarbons (CFCs) are used as refrigerants, in aerosol sprays and in micro-electrons.
- Freons, e.g., CCl_2F_2 (Freon-12) and CCl_3F (Freon-11) used as refrigerants also contain fluorine.

Chlorine:

- Is used in the manufacture of Polyvinylchloride (PVC), which because of its non-inflammability and insulating properties is used as an electrical insulator, for covering electric wires, making conduit pipes, etc.
- Dichlorodiphenyltrichloroethane (DDT) is used widely as an insecticide.
- Bleaching powder or liquid chlorine is used for disinfection of water on a large scale.
- Bleaching powder ($CaOCl_2$) is used for bleaching paper pulp and textiles.

Bromine:

- Methyl bromine is the most effective nematocide known. It is also used as a general pesticide.
- Silver bromide is used for making photographic plates or films.

Iodine:

- Tincture of iodine (iodine dissolved in alcohol) is used as an antiseptic.
- Iodine is present in the thyroid hormone.
- A deficiency of iodine causes goiter and leads to stunted growth and cretinism. To prevent this, common salt is routinely iodised.

GROUP VIII ELEMENTS
(THE NOBLE GASES)

Elements of this group are: - Helium-He; Neon-Ne; Argon-Ar; Krypton-Kr; Xenon-Xe; Radon-Rn.

Valence shell: ns^2np^6 (except He-ns^2)

- They have the most stable valence shell electronic configuration.
- They exist as single atoms.

Table 1: Some properties of the noble gases.

Property	He(2)	Ne (10)	Ar (18)	Kr (36)	Xe(54)	Rn(86)
Electronic configuration	$1s^2$	$[He]2s^22p^6$	$[Ne]3s^23p^6$	$[Ar]3d^{10}4s^24p^6$	$[Kr]4d^{10}5s^25p^6$	$[Xe]4f^{14}5d^{10}6s^26p^6$
Van der Waals radius (pm).	-	131	174	189	210	215
Boiling pt.(K)	4.2	27.2	87.2	119.6	165.1	211
Melting pt. (K)	1 at 26 atm	24	84	116	161	202
Density of liq at bpt (gm^{-3})	0.126	1.20	1.40	2.6	3.06	4.4
IE ($kJmol^{-1}$)	2372	2081	1520	1350	1170	1037
Elec affinity ($kJmol^{-1}$)	54	99	-	-	-	-
Abundance in dry air (ppm by volume)	5.2	18.2	93.40	1.14	0.087	0
Polarizability ($x10^{-24}cm^3$)	0.202	0.392	1.629	2.460	4.000	5.419

Physical properties:

- All noble gases are colourless, odourless and tasteless monoatomic gases. They are the only elements that exist as uncombined gaseous atoms at room temperature and one atm pressure. Each atom, behaves as if it is effectively isolated.
- Since there are no usual electron pair interactions between the noble gas atoms, the only interaction are the weak van der Waals forces. Therefore, have very low melting and boiling points in comparison with those of other elements of comparable atomic or molecular weights.
- Since they have the stable $1s^2$ *or* ns^2np^6 configuration, they have the highest ionization energies compared to other elements in their periods. And as we go down the group the IE decreases.
- Analogously, the electron affinity of these elements is either zero or a small positive value.
- Solubility of heavier noble gases in water is large (Ar-Rn).
- Noble gases are insoluble in metals and fused metals.

Chemical properties:

Lack of chemical reactivity of the noble gases can be understood from the following facts:-

- They have the highest 1st ionization energies in each period; hence they do not easily form cations or donor co-ordinate bonds.
- They possess positive electron affinities (i.e. low EAs) and exhibit the least attraction for further electrons in their periods. Thus, they don't easily form anions or accept electrons in coordinate bonds. For the same reasons they don't easily form normal covalent bonds.

Compounds formation

True chemical bonding in the noble gases seems to be restricted to krypton, xenon and radon with fluorine or oxygen ligands. None, however, combines with oxygen directly. The oxides are made from the fluorides when they react with water.

Krypton chemistry is limited to the difluorides, KrF_2, and one or two complexes with fluorine bridges between krypton and another element.

There should be an extensive chemistry of radon but it is radioactive, therefore short lifetime makes it impossible. However, at least one radon fluoride is known, but its formula has not yet been established.

One compound with a Xe-N bond is also known.

Compounds of Xenon:

The chemistry of xenon is the most extensive in this group and the known oxidation states of Xe range from +2 to +8.

Ionic derivatives:

Neil Bartlett observed that Platinum hexafluoride was able to oxidise oxygen molecule to form a stable compound.

$$O_{2(g)} + PtF_{6(g)} \rightarrow O_2^+PtF_6^-{}_{(s)}$$

He realized that Xenon should also form a similar compound because:-

- Xe 1st ionization energy is close to that of O_2, (IE_{xe}=1170kJmol^{-1} and IE_{O2}=1180kJmol^{-1})
- Size of Xe^+ and O_2^+ is similar.

Hence, the lattice energy and their enthalpy of formation of the compounds should not be too different

So when Xe and PtF6 were mixed an orangish solid was formed.

$$Xe(g) + PtF_{6(g)} \rightarrow Xe^+PtF_6^-{}_{(s)}$$

Fluoride derivatives:

Xe reacts directly with fluorine on heating. The products depend upon the amount of fluorine present and the reaction conditions:

$$Xe + F_2 \xrightarrow[400^\circ\text{C, sealed vessel}]{2:1\ \text{mixture}} XeF_2$$

$$Xe + 2F_2 \xrightarrow[400^\circ\text{C, 6 atmosphere}]{1:5\ \text{mixture}} XeF_4$$

$$Xe + 3F_3 \xrightarrow[>250^\circ\text{C, 50-60 atmosphere}]{1:20\ \text{mixture}} XeF_6$$

Properties:

1. The compounds XeF_2, XeF_4 and XeF_6 are white solids which can be sublimed at room temperature.
2. The lower fluorides react with fluorine on heating under pressure forming higher fluorides.
3. They react quantitatively with hydrogen.

$$XeF_2 + H_2 \longrightarrow 2HF + Xe$$

$$XeF_4 + 2H_2 \longrightarrow 4HF + Xe$$

$$XeF_6 + 3H_2 \longrightarrow 6HF + Xe$$

4. They oxidize chlorides to chlorine, iodides to iodine, cerium(III) to cerium(IV), Ag(I) to Ag(II), Cr(III) to Cr(VI) and Br(V) to Br(VII):

$$XeF_2 + 2HCl \longrightarrow Xe + 2HF + Cl_2$$

$$XeF_4 + 4KI \longrightarrow Xe + 4KF + 2I_2$$

$$XeF_2 + BrO_3^- + H_2O \longrightarrow Xe + BrO_4^- + 2HF$$

5. They fluorinate many compounds as well as elements:

$$XeF_4 + 2SF_4 \longrightarrow Xe + 2SF_6$$

$$XeF_4 + Pt \longrightarrow Xe + PtF_4$$

$$XeF_4 + 2C_6H_6 \longrightarrow Xe + 2C_6H_5F + 2HF$$

Oxygen derivatives:

- Reaction of Xe fluorides with water gives xenon oxygen compounds-XeO_3.
  $6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 3O_2 + 24HF$
  $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$
- With small quantities of water, partial hydrolysis occurs giving a colourless liquid **xenon oxofluoride**, $XeOF_4$.

$XeF_6 + H_2O \rightarrow XeOF_4$. The same product is formed when XeF_6 reacts with silica or glass. Because of the stepwise reaction which finally produces the dangerous XeO_3, XeF_6 cannot be handled in glass or quartz apparatus.

$2XeF_6 + SiO_2 \rightarrow 2XeOF_4 + SiF_4$
$2XeOF_4 + SiO_2 \rightarrow 2XeO_2F_2 + SiF_4$
$2XeO_2F_2 + SiO_2 \rightarrow 2XeO_3 + SiF_4$

- In alkaline solution XeO_3 forms **xenate ion** $HXeO_4^-$
  $XeO_3 + NaOH \rightarrow \underset{\text{Sodium xenate}}{Na^+HXeO_4^-}$
- Xenates slowly disproportionate in alkaline solution to form **perxenates** and gas:
  $2HXeO_4^- + 2OH^- \rightarrow XeO_6^{4-} + Xe + O_2 + 2H_2O$.
  Alkaline hydrolysis of XeF_6 also forms perxenates
  $2XeF_6 + 16OH^- \rightarrow XeO_6^{4-} + Xe + 12F^- + 8H_2O$
- Perxenates react with concentrated H_2SO_4 to give **xenon tetroxide**, XeO_4, which is volatile and explosive:
  $Ba_2XeO_6 + 2H_2SO_4 \rightarrow XeO_4 + 2BaSO_4 + 2H_2O$

Complex derivatives of xenon fluorides:

- XeF_2 acts as a fluoride donor and reacts with pentafluorides such as , PF_5, AsF_5, SbF_5, NbF_5, PtF_5, etc. to form salts of the types $[XeF]^+[MF_6]^-$, $[XeF]^+[M_2F_{11}]^-$ and $[Xe_2F_3]^+[MF_6]^-$.
- XeF_4 is much less reactive in this respect and reacts only with the strongest F^- acceptors such as SbF_5 and BiF_5.
- XeF_6 combines with pentafluorides to yield 1:1 complexes such as, $[XeF_5]^+[AsF_6]^-$ and $[XeF_5]^+[PtF_6]^-$.

Structure and bonding in some xenon compounds

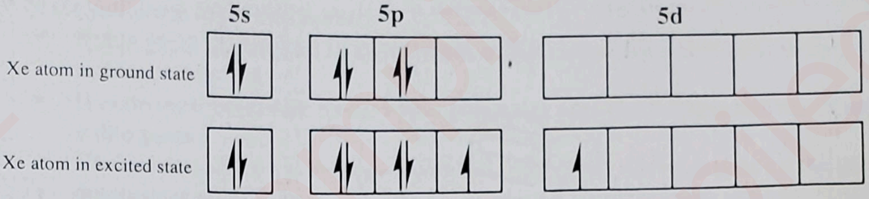
Bonding in these compounds can be explained by the help of Valence Bond Theory.

1. Xenon difluoride XeF_2

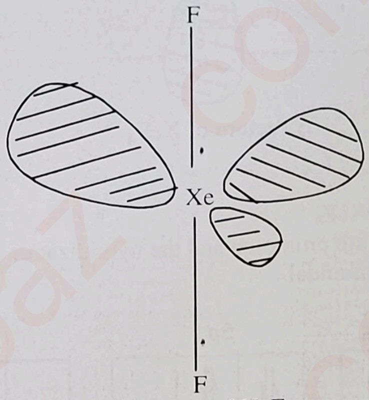
An electron from the 5*p* level of Xe is promoted to the 5*d* level, followed by sp^3d hybridisation.

The two unpaired electrons in axial orbitals form bonds with two fluorine atoms And three lone pairs occupy the equatorial positions of the trigonal bipyramid giving rise to a linear molecule.

The objection is that the 5*d* orbital of Xe appears to be too large and too high in energy to participate in hybridisation. However, it has been suggested that the highly electronegative atoms like fluorine cause a large contraction in the size of the d orbitals enabling them to participate in bonding.



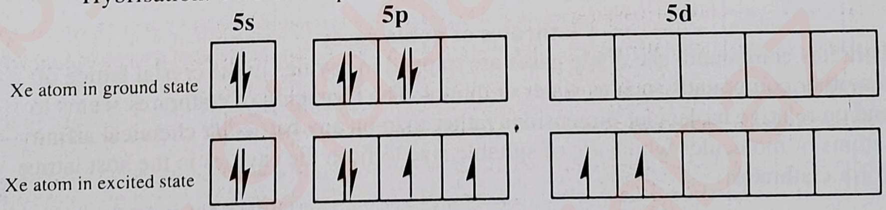
sp^3d hybridisation



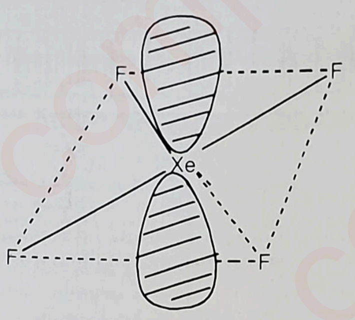
Structure of XeF_2

2. Xenon Tetrafluoride XeF_4

The structure of XeF_4 is square planar. Promotion of two electrons reslts in sp3d2 Hybrisation. Two of the positions are occupied by two lone pairs.



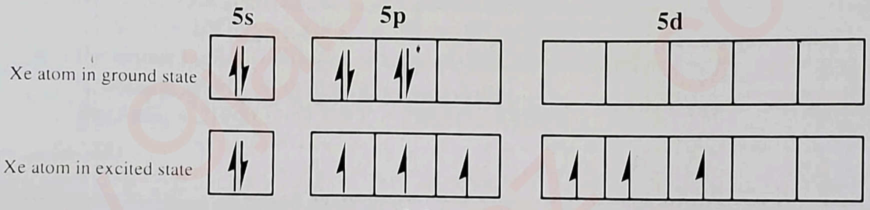
sp^3d^2 hybridisation



Structure of XeF_4

3. Xenon Hexafluoride XeF_6

Three electrons are promoted and the hybridization is sp3d3 which predicts a Pentagonal bipyramidal.



sp^3d^3 hybridisation

Clathrates of noble gases

In clathrates compounds the noble gases are trapped in cavities in the crystal lattice of certain other compounds such as water or quinol. The formation of clathrares seems to depend on relative molecular dimensions rather than on any particular chemical affinity. The atoms or molecules which are of suitable size to fit in the cavities in the host lattice can form clathrates.

Hydrates:

When water is allowed to freeze in the presence of Ar, Kr or Xe under pressure, atoms of noble gas get trapped in the crystal lattice of ice giving clathrates of composition $Ar.6H_2O$, $Xe.6H_2O$, $Kr.6H_2O$.

Quinol (or1,4-Dihydroxybenzene):

When quinol is crystallized from its aqueous solution in the presence of heavier noble gases like Ar, Kr or Xe under a pressure of 10-40 atmospheres, crystals of clathrates are formed.

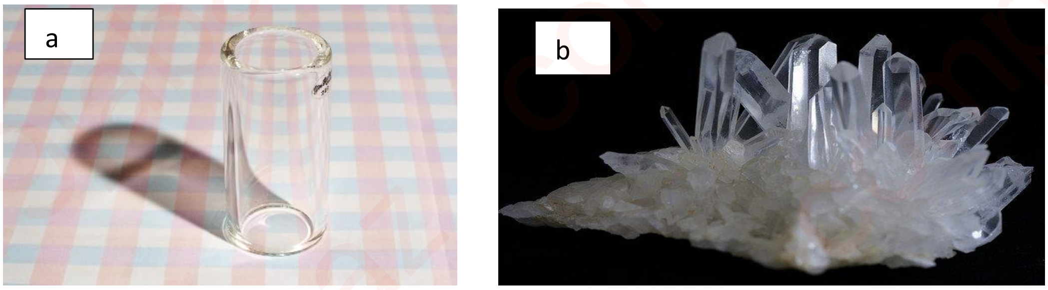
Note the following important points:

- Noble gases are trapped in the network of H_2O or quinol which is fixed by hydrogen bonding.
- No chemical bonds are formed only polarising effect of the host molecules on noble gases.
- Clathrates compounds are non-stoichiometric; cavity filling depends o the partial pressure of noble gases.
- Tendency to form clathrares and the thermal stability increase down the group.
- He and Ne don't form such compounds due to their small size hence very low polarizability.

CHM 302 NOTES BY DR FAMOJURO (First lecture)

1.0 SOLID STRUCTURES

All substances have the ability to form solid phases when the temperature is low enough. It should be noted that **<u>the nature of solid</u>** depends on the **<u>type of bonds</u>** that hold the atoms, ions, or molecules together in a tightly-packed arrays. Solid can be classified broadly as **CRYSTALLINE** or **AMORPHOUS. A crystalline solid** is a solid in which the constituent atoms, ions or molecules lie in an **ORDERLY ARRAY** for example, quartz (Fig.1.0), diamond etc**. An amorphous solid** is one in which the constituent atoms, ions, or molecules lie in a **RANDOMLY/DISORDERLY ARRANGEMENT,** for example glass, butter, rubber etc**.**



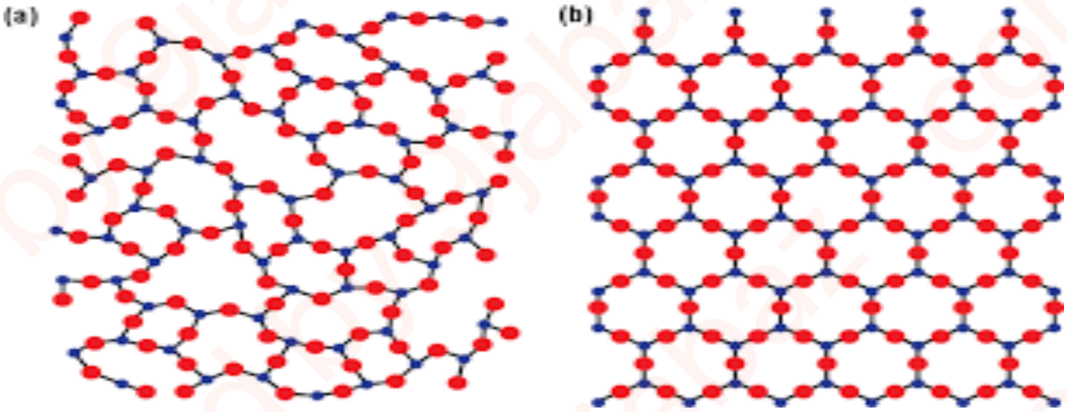


Figure1.0 : (a) Glass- amorphous form of Silica SiO_2; the atoms are arranged disorderly

(b) Quartz- crystalline form of Silica SiO_2, the atoms are arranged orderly.

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1.2 CHARACTERISTICS OF CRYSTALLINE AND AMORPHOUS SOLIDS

Crystalline solids or crystals, typically have flat, well-defined surfaces called FACES (Figure 2.0), which have definite angles at their edges. They exhibit **sharp melting points** and well-resolved X-ray diffraction patterns. In contrast, amorphous have irregular/curved surfaces, it does not give a well-resolved single crystal x-ray diffraction pattern and **melt over a wide range of temperature**.

Figure 2.0 : Galena crystal structure showing faces

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1.3. CRYSTALLINE SOLIDS

Many substances form crystals and these includes **metallic elements**, such as, copper, iron, **alloys** such as steel, **solid forms of non-metallic elements** (such as sulphur, phosphorous, iodine); ionic compunds (such as sodium chloride, potassium mitrate, hydrated copper sulphate); network molecules such as transition complexes, and many others. **Crystalline solids are classified according to the bonds that hold their atoms,**

ions, or molecules in place. Importantly, the atoms, ions, or molecules of a particular substances can adopt more than one arrangement, depending on the conditions under which they formed. These different arrangements are the different **solid phases** of a particular solid; alo known "Allotropes". Thus, diamond and graphite are two different phases of carbon; the carbon atoms are arranged differently in each phase. Different solid phases have different physical properties such as melting point and density. The specific arrangement of atoms, ions, or molecules within a crystal an be determined by X-ray diffraction.

1.4 Classification of Crystals

Crystals are classified based on the bonds that hold their constituent atoms, ions, or molecules together. On the basis of bond, there are four types of crystals, these are, metallic crystals, ionic, network/covalent and molecular solids.

1.4.1 Bonding types in crystals

(a) Metallic crystals: metal cations surrounded by sea of mobile valence electrons, thus metals are good conductors of electricity, examples are metals in the periodic table

(b) Ionic crystals : this consist of alternating positively charged cations bonded electrostatically to negatively charged anions.These structure formed generally from the bonding of metallic with non-metallic atoms. Examples are NaCl, KCl, $CaCl_2$ among others.

© Network/Covalent crystals : this consist of atoms covalently bonded to neighbouring atoms. This structure is in three dimensional and consist of large number of atoms. Example includes diamond, quartz, metalloids solids like Silicon, oxides of transition metals among others. They have high melting points, brittle and do not conduct electricity because they are composed of atoms not ions

(d) Molecular crystals : this consist of molecules at lattice points and are held together by weak intermolcular bonds such as hydrogen bonds, examples are iced water, supramolecules, among others. They could have low melting and boiling points due to the weak intermolecular forces.

METALLIC CRYSTALS

These are s- and d-block elements, such as sodium and magnessium metals (s-block), iron and copper (d-orbitals). A particular metallic crystal is homogeneous, because all the atoms present in the metallic element have the similar electronic configuration. The constituent atoms in the element are held together by a metallic bond. Metallic bond implies positive charges ions are held together by a sea of electrons, which are negatively charge. Metallic solids contain equal amount of positive and negative charges. Thus, metals are malleable, ductile, lustrous, eletrically and thermally conductive due to the free flow of electrons through the crystal lattice.

The arrangement of the atoms in a mettalic crystals is in a **Close-packed structure /arrangement**. Close-packed implies minimum wastage of space; the atoms are packed in such a way that minimum empty space is available. There are three main ways that metallic atoms are closely-packed together to form a crystals. These **are hexagonal close-packed (hcp), cubic close-packed (ccp) and body centred cubic(bcc)** structures. Cubic closed-oacked could also be referred to as **face- centred cubic (fcc)** structure.

Atomic arrangements in metallic crystals

The arrangement of atoms in mettalic crystals could be in three forms, these are hexagoanl close-packed, cubic close packed or face centred closed packed, or body-centred cubic structures. These atoms are arranged in such a way as to minimize unused spaces. It should be noted that, **the type of close-packed structure a metal adopts depend on which arrangement gives the lower energy, and that depends on details of its electronic structure.** In addition, **hcc and ccp are based on closest packing of spheres,** assuming each atom is represented as a sphere.

Close-packing

i. In one dimensional (direction) : First, It is important to understand the arrangement of atoms in one direction (figure 3.0), there is only one way to arrange atoms closely in one dimensional. Each atom (sphere) is in close contact with two of its neighbours and this determine its coordination nunmber. Coordination number is the number of atoms surrounding one atom. In this case, the coordination number is 2.

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Figure 3.0: Images showing arrangement in one direction

ii. **In two dimensional (direction) :** A two dimensional close-packing can be arranged in two forms. In Figure 4.0, the atoms in second row are placed directly on the atom of the first row, subsequently, the third row are placed directly on the atom of the second row. This gives rise to **Square Close packing**, and generated the system of AAAA arrangement. All the rows are the same, and the Coordination number of an atom here is four (4 neighbouring atoms).

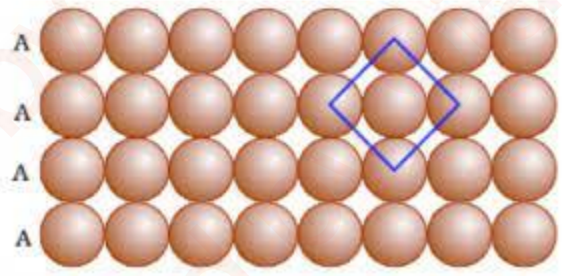


Figure 4. 0: images showing arrangement in two dimention resulting in Square close-packing (void is tetrahedral)

The second arrangement is shown in Figure 5.0, in which athe atoms of the second row are place in the dip of the first row, and subsequent row follow that of the first row giving rise to an ABABAB arrangement. This type of arrangement result in coordination number of six, thus hexagonal close-packing in two dimension is formed

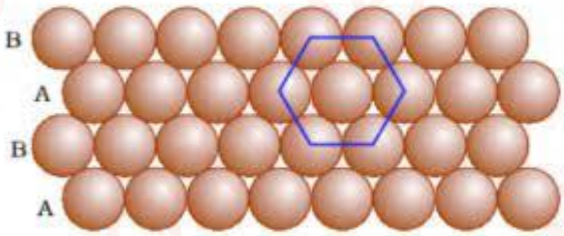


Figure 5.0 : Images showing six atoms surrounding an atom in an hexagonal close packing in two dimension. (void is tri-angle)

It is important to note that, the spaces called void that were available in square packing are larger than that of hexagonal packing. This imples that, the atoms in hexagonal close packing are much more closely packed, decreasing wastage of space and at lower energy, lots of metallic crystals adopt this kind of arrangement.

Crystal arrangement in three dimensional 3D

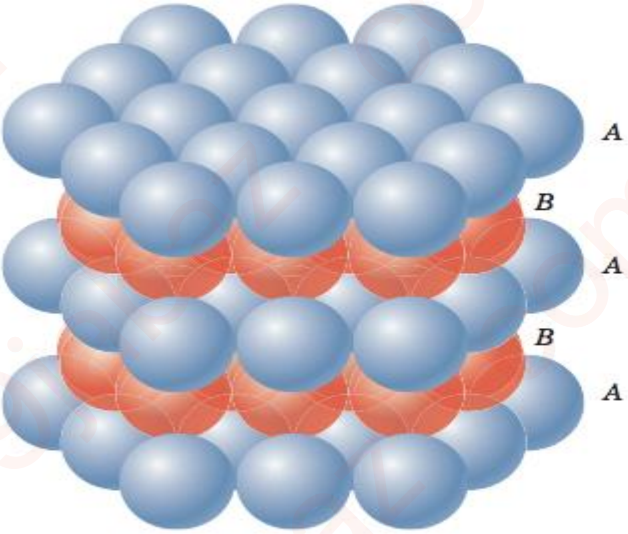
Metallic crystals could be arranged in three dimensional in three ways, namely (i) hexagonal closed packed (hcp) (ii) cubic closed-packed (ccp), also known as face-centred closed packing (fcc) (iii) body-centred closed packed (bcc).

The first two packing arrangements hcp and ccp are based on the closest packing of spheres, thus the atoms are tighly held in a closed packed. This is similar to the way the fruits are arranged in Figure 6.0

Figure 6.0: Fruits arranged in 3D hexagonal closed packing

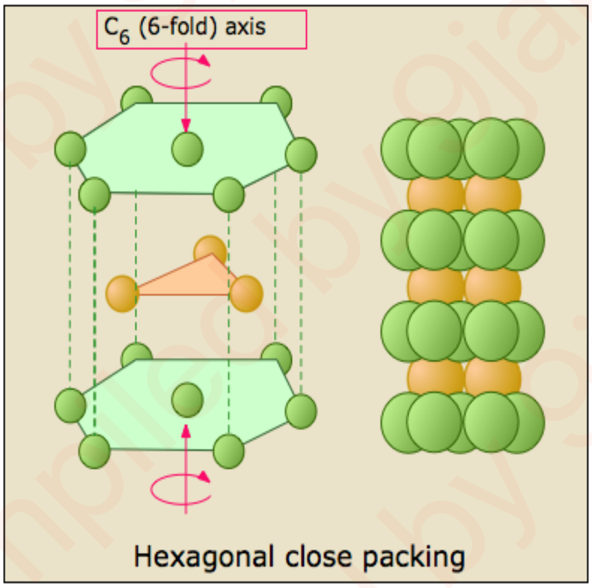
Hexagonal closed-packing (hcp)

In hcp, the first layer is arranged closely as in two dimensional hexagonal close- packin in figure 5.0, the second layer is placed in the depression of the first layer, and it keeps alternating until a solid 3D crystal is obtained. The first layer and the third layer are arranged the same way, while the second layer and fourth layer are the same, thus leading to a ABABAB pattern of layers (Figure 7.0) . In this hcp, each atom is surrounded by twelve neighbours; three nearest in the layer below, six in its own layer and three in the layer above (Figure 9.0). In hcp, the coordination number is twelve. It has the close packing density of approximately 74%. The hcp structure is very common for the crystals of beryllium, cadmium, magnesium, titanium, zinc and Zirconium



HCP.png (335×322) (psu.edu)

Figure 7.0: 3D image of hexagonal closed packing showing ABABABAB



hex_close_packing.png (395×354) (chem1.com)

Figure 8.0: image showing the coordination number of hexagonal closed packing

Cubic closed-packing (ccp)/ face-centred closed packing (fcc)

The atoms are closely packed together, and denser, the first layer 'A' of atoms are packed as closely packed as possible, the second layer 'B' settles into the crevices of first layer, the third layer 'C' could be placed on to layer B in two possibilities. One possibility is to place the atoms directly over the atoms of layer "A". The other possibility is to place the atoms over the second set of crevices in layer "A" forming a third layer, C. The repeating layer for 'ccp' is ABCABCABC, Figure 10. The coordination number of ccp is 12, three in above and below, and six in the same layer.

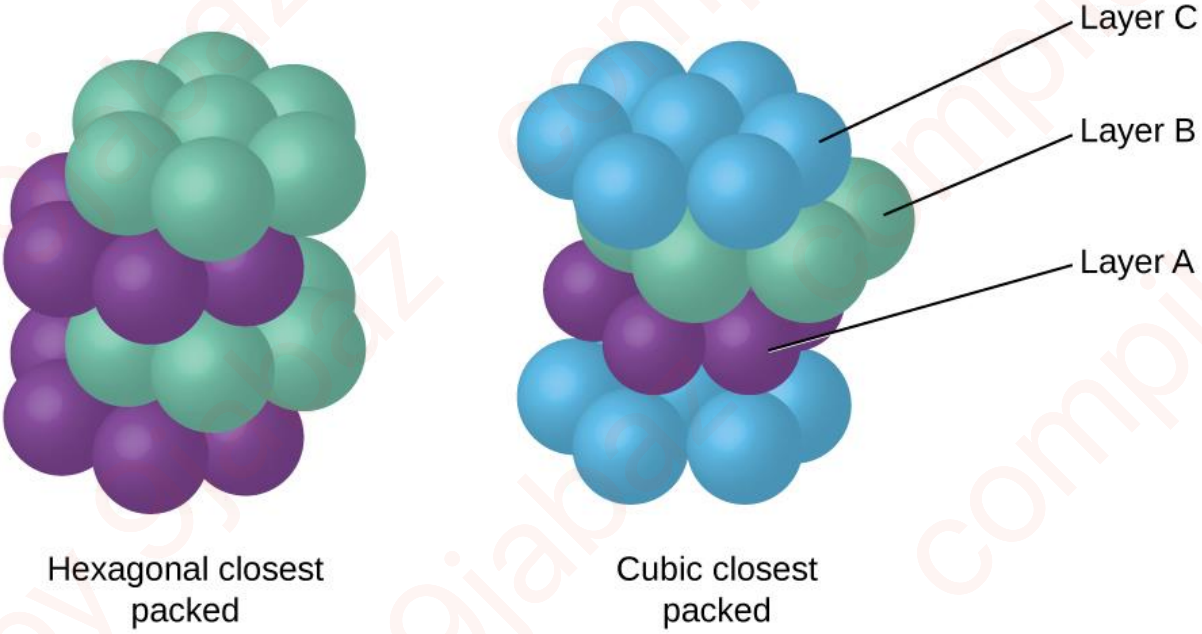


Figure 10: Hexagonal and Cubic packed Structure

Body centred close-packed (bcc)

In body centred close-packing (bcc), the atoms are packed side by side in the first layer (Figure 11). The second layer is placed directly in the depression of the first layer (Figure

12). The third layer is directly above the first layer. This form of packing is less efficient at filling the spaces, than ccp or hcp. The sphere/atoms occupy 64% (0.64 Atomic packing efficiency), of the total space. The coordination number is eight (Figure 13), each atom is surronded by eight neighbouring atoms, four from the upper layer and four from lower layer. Examples of metallic crystals with bcc structure are tungsten, alpha iron, chromium, beta titanium.

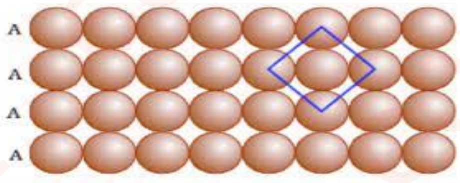


Figure 11: The first layer in bcc packing structure

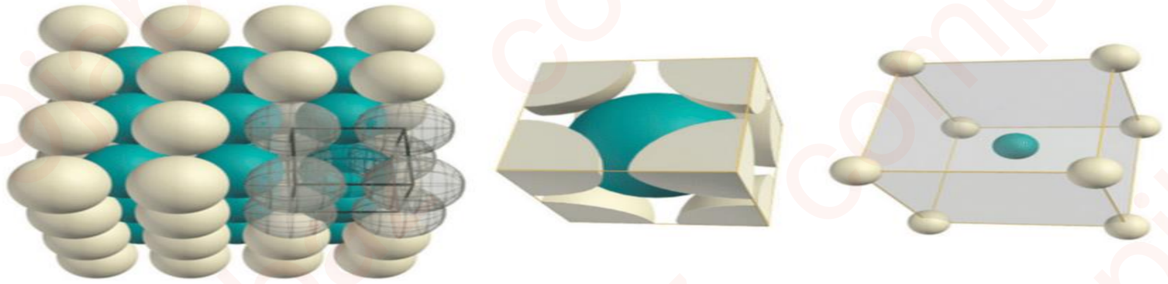


Figure 12: The 3D image of Body centred closed packing structure (bcc)
https://www.researchgate.net/profile/SlavicaGrdanovska/publication/309355490/figure/fig23/AS:669075927740416@1536531540164/2-Representation-of-a-body-centered-cubic-structure-collection-of-multiple-unit-cells.png

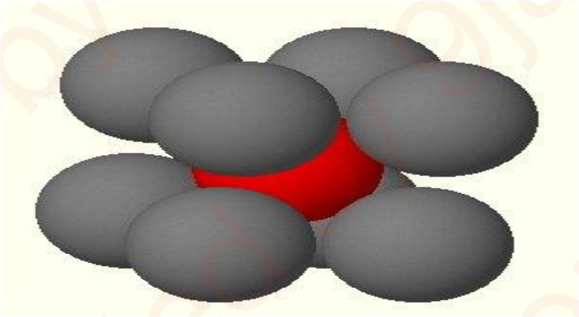
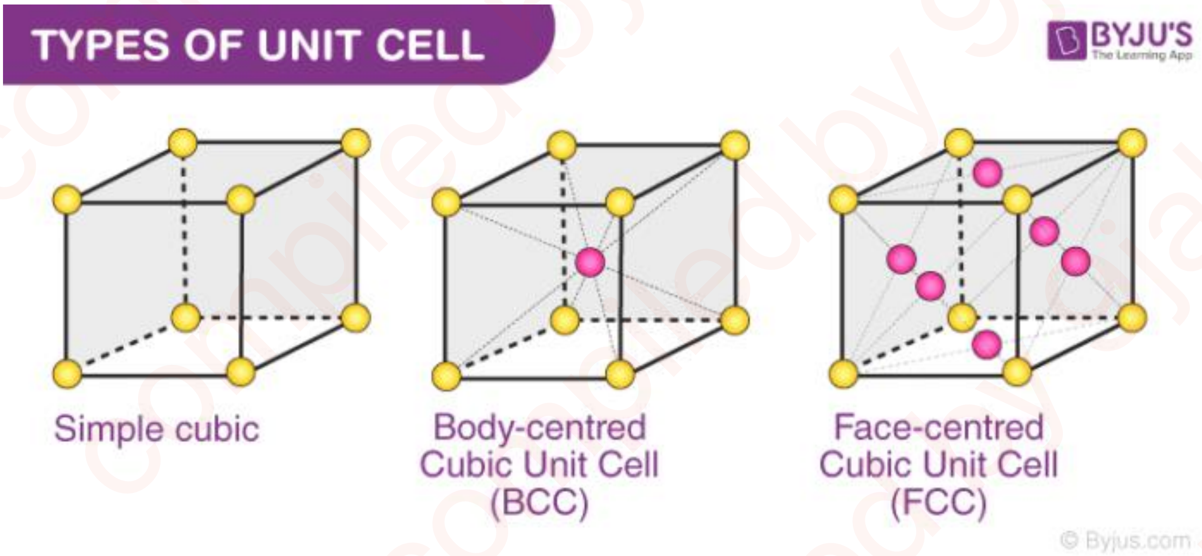


Figure 13: Image showing the coordination number of 8 in Body-centred cubic packing

https://lh3.googleusercontent.com/proxy/fGFiSFi9v8BTon35Mip9c_hWqTB_baKhbdRJaH27Vs2jCQ3uGqoOLbaaRKX_e6T9_0JgK8C3WJ1DNi3Ujkk3YqDh3o8GJhPISkB50jl8KP9eYCmuJY44ILqQ4m0o03G3wq0Qv1zYJClGx3dSzBV62WnSoUacXL-iEylrEjPJP5DprQbr7pFlF9q9dED9c5-GRvkTg



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IONIC CRYSTALS/SOLIDS (2nd lecture)

(DR FAMOJURO)

Ionic crystals are made up of positive and negative ions, bound by electrostatic attraction. The electrostatic force is the same in all the three-dimension; this is responsible for the high melting and boiling points of ionic compounds. This is due to the fact that considerable energy is needed to break the lattice in all directions for the solid to melt. On melting, ionic solids conducts electricity by the movement of ions, when they are placed in an electric potential. **Although when in solid forms, they do not conduct electricity easily, however due to defects in their crystal lattices, ions may move from one point to another in the solid state, thus behaving like a semiconductor.** Other properties of ionic solids includes, the ability to react speedily and their solubilities in polar solvents. Examples of ionic solids include metallic salts (NaCl, KCl, among others), oxides, sulphides, hydroxides and many inorganic compounds.

Crystal packing arrangement in ionic crystals

The crystal packing arrangement in ionic solids are dependent on the relative sizes of the constituent ions (positive and negative) and their numbers. Also, the coordination numbers can also be predicted from their relative sizes. Few ionic solids constitute both positive and negative ions of almost equal sizes, while majority have relatively smaller positive ions with larger negative ions. It is possible to predict the coordination number and shape of the unit cells by the ratio of the positive ionic radius to that of the negative ionic radius, this is known as limiting radius ratio rules “r^+/r^-.

The table below summarizes the relationship between limiting radius ratio rules “r^+/r , coordination number and shape of the unit cell.

limiting radius ratio rules “r^+/r	coordination number	Shapes
<0.155	2	Planar
0.155 -0.255	3	Trigonal
0.225 – 0.414	4	Tetrahedral
0.414 – 0.732	4	square planar
0.414 – 0.732	6	Octahedral
0.737 – 0.999	8	body-centred cubic

The maximum coordination number in ionic solid is 8, and the unit shape resembled Body-centred cubic, though not regular due to the vibration of the ions throughout the crystal lattice.

Ionic crystal packing arrangement could be described in terms of hexagonal or close-packed arrangement. In these two types of closed packed arrangements, 74% of the space is filled, while 26% remain unfilled, and this space is regarded as holes in the crystal lattices. There are two different types of holes, namely tetrahedral and octahedral holes. Tetrahedral and octahedral holes are bound by four and six ions respectively. The octahedral are larger than tetrahedral holes. An ion occupying a tetrahedral hole has coordination number of 4, while that of octahedral is six (figure 1.0)

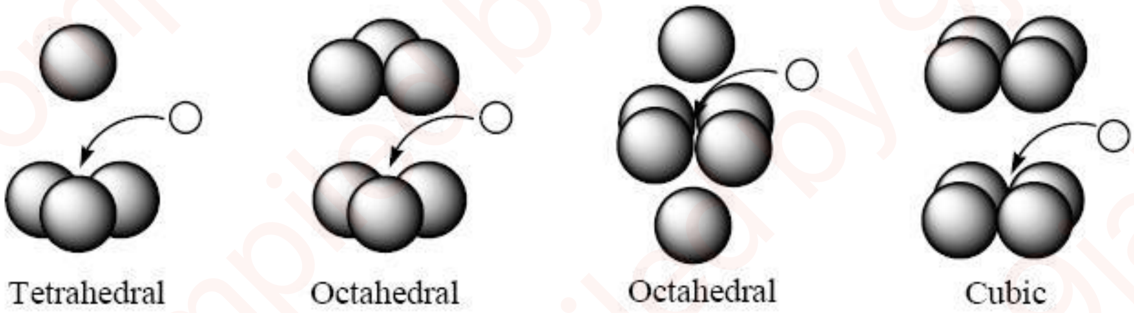


Figure 1.0: Crystal holes

It is important to note that, in most ionic solid the anions are much larger than the cations, and it is the anions that form the crystal arrays (Figure 2.0). The smaller ions, cations, reside in the holes between the anions.

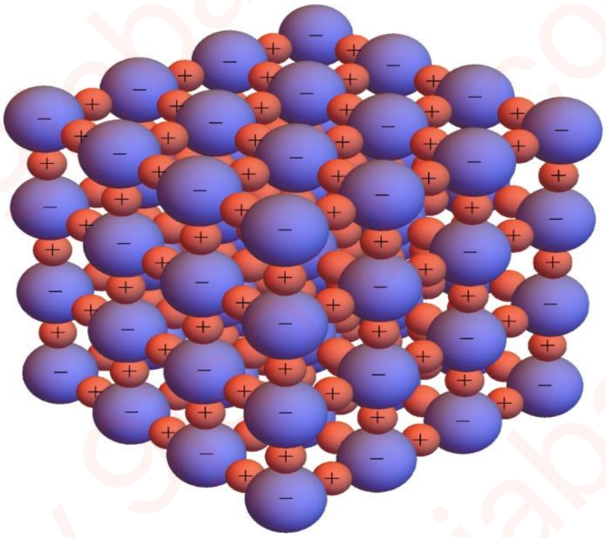
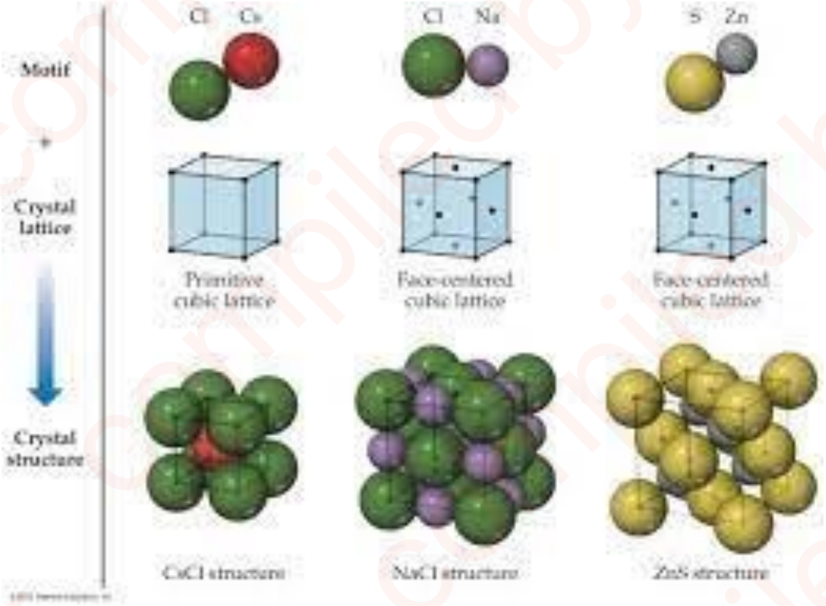


Figure 2.0: Typical Ionic crystal (small cations embedded in between anions)



https://encryptedtbn0.gstatic.com/images?q=tbn:ANd9GcSayiKhEEHqWTg0aVsC51XI7N8sx5R7pupgHlgjTpIUVxFAq6tM9264xGbEBKpR10NtpVU&usqp=CAU

Figure 3.0: Crystal packing arrangement of some ionic crystals with different radius ratios

Classification of Ionic crystal packing into AB, AB$_2$ and AB$_3$

CHM 302 NOTES (Dr Famojuro's part)

The importance of Solid State Crystal Packing

The importance of knowing the crystal packing (or crystal structure) of solid materials lies in understanding how atoms, ions, or molecules are arranged in a three-dimensional lattice. This knowledge is crucial because **the atomic arrangement directly determines the material's physical, chemical, electronic, and mechanical properties**.

This arrangement determination the material properties in terms of the followings

(1) Material's property

(a) Mechanical Properties:

Crystal packing affects hardness, ductility, and strength. For example, diamond (sp^3 carbon) is extremely hard due to its tightly bonded 3D network, while graphite (layered structure) is soft and slippery.

- (b) Electrical Conductivity:

Metals like copper have close-packed structures allowing free electron movement, whereas insulators like diamond have tightly bound electrons.

- (c) Optical Properties

The arrangement influences light absorption and refraction (e.g., transparency in quartz vs. opacity in metals).

- (d) Magnetic Properties

Ferromagnetic materials like iron have specific atomic alignments enabling magnetic ordering.

2. Phase Stability and Polymorphism

Different packing arrangements (polymorphs) can lead to varying stability and properties. For examples, the two allotropes of carbon, diamond (hard) vs. graphite (conductive). Also, for TiO_2, its allotropes Rutile, anatase, and brookite have different photocatalytic efficiencies. By understanding packing helps predict phase transitions under temperature/pressure (e.g., ice's multiple crystalline forms).

3. Chemical Reactivity and Catalysis

Surface atomic arrangements influence reactivity. For example: Platinum (Pt) catalysts* have active sites dependent on crystal facets (e.g., Pt(111) vs. Pt(100)), Zeolites* have porous structures critical for molecular sieving and catalysis.

4. Thermodynamic and Thermal Properties

Packing density affects *melting point, thermal expansion, and heat capacity, example: Tungsten's *body-centered cubic (BCC)* structure contributes to its high melting point.

5. Defects and Engineering Applications

Crystal defects (vacancies, dislocations) depend on the packing, influencing:

- *Semiconductor doping* (Si crystals with controlled impurities).
- *Alloy strength* (dislocation movement in FCC vs. BCC metals).

6. Drug Design and Pharmaceuticals

Different crystal forms (*polymorphs) of a drug can have varying solubility and bioavailability (e.g., ritonavir, an HIV drug, failed initially due to unexpected polymorph formation).

7. Predictive Modeling and Material Design

Computational methods (DFT, molecular dynamics) rely on crystal structure to predict new materials (e.g., *high-entropy alloys, perovskites for solar cells*).

Key Techniques to Study Crystal Packing

- X-ray Diffraction (XRD) – Determines atomic positions.
- Electron Microscopy (TEM/SEM) – Visualizes lattice arrangements.
- Neutron Diffraction – Locates light atoms (e.g., hydrogen).
- Computational Modeling – Predicts stable structures.

Understanding crystal packing is fundamental to materials science, chemistry, physics, and engineering because it bridges atomic-scale structure to macroscopic properties. This knowledge enables the design of better metals, semiconductors, batteries, pharmaceuticals, and nanomaterials with tailored functionalities.

IONIC CRYSTALS (2ND PART, DR FAMOJURO), Third lecture

Classification of ionic crystals

The whole ionic crystal is electrically neutral and each unit cell reflect the stoichiometry of the compound. The arrangement of the ions in a regular geometric structure is called **CRYSTAL LATTICE,** this is also true for metallic crystals. The ionic crystals are classified based on the relative numbers of positive and negative ions. They are classified as AX, AX_2 and AX_3, where A represent the cations, while X is the anions. It is important to clarify that in ionic crystal, the coordination number means the number of ions of opposite charge immediately surrounding it.

“AX” TYPE OF IONIC CRYSTAL

The AX type of ionic crystal means the oxidation states of both the cations and anions are the same but with opposite charges, for example, NaCl, ZnS, CsCl among others. The AX ionic crystals generally follow three broad ways of crystal packings. These are called (i) the Rock-salt structure/sodium chloride structure (ii) Cesium chloride-like structure (iii) Zinc sulphide-like structure (Zinc blende and Wurtzite)

(i) The Rock-salt structure/NaCl-like structure

This type of crystal arrangement derived its name from the mineral form of sodium chloride. In this arrangement, **(Figure 1.0)** taking NaCl as an example, the chloride ions Cl^-, lie at the corners (edges) and centre of the faces of a cube, forming **FACE-CENTRED CUBIC UNIT CELL. The smaller sodium cation (Na^+) fit snugly into the octahedron hole between the anions.** Each anion is surrounded by six cations, and each cations by six anions, thus the coordination number is denoted as **(6, 6)-coordination.** This means that the coordination of the cations is six (6 anions is surrounding one cations), and the coordination of the anions is six (6 cations is surrounding one anions). The three-dimensional array of NaCl crystal showed that each Na^+ is surrounded by 6 Cl^-, and vice versa.

This rock-salt structure is found for a number of other ionic compounds of the same charge type such as KBr, RbI. MgO, CaO and AgCl. It is commonly adopted by ionic crystals of the same oxidation state with opposite charges, and different ionic radii. The Rock salt arrangement is expected when the radius ratios is the range of 0.4 - 0.7. For sodium chloride, the Na^+ radius is 102pm, while that of Cl^- is 181pm, the radius ratio is 102/181, which is 0.564.

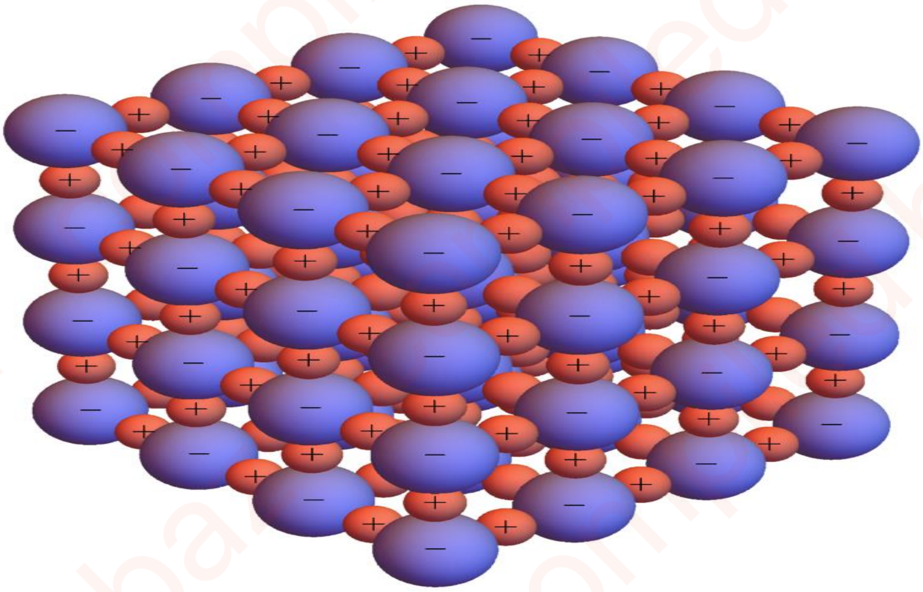


Figure 1.0: Rock salt type/Sodium chloride like AX crystal arrangement

(ii) Cesium Chloride-like structure

When the atomic radii of the cations and anions are similar and the radius ratio is greater than 0.7, the cations cannot fit into spaces between the anions as that of rock-salt, the cations lie the middle of the anions layer, adopt something similar to body-centred cubic unit (Figure 2.0), denoted as Cesium chloride structure. The crystal packing is not exactly body-centred cubic, because it has different ions in the centre unlike what makes for real body-centred. This is the structure for CsCl and it showed the chloride ions at the eight corners with Cesium ion Cs^+ at the centre. The coordination number is (8,8)-coordination. The ionic radius of Cs^+ and Cl^- are 174 and 181 pm respectively. This structure is also shared by CsBr and CsI

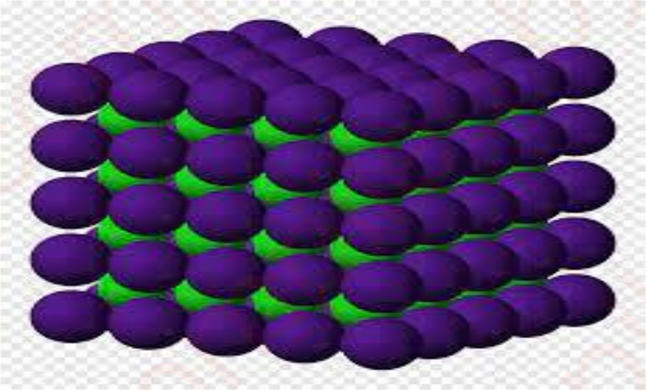


Figure 2.0: Cesium chloride-like structure

(iii) Zinc Blende and Wurtzite (ZnS-like structures)

Ionic crystals usually adopt these two types when the radius ratio is around less or equal to 0.4. The ionic radii of Zn^{2+} and S^{2-} are 74 and 190 pm, and it can adopt two types of crystal packing, namely Zinc blende or Wurtzite. By regarding these two as forms of closed-packed arrangement of S^{2}- ions, the Zinc blende is similar to face-centred cubic closed packing (ABCABC) in which the Zn^{2+} ions only fill the tetrahedral holes/voids. On the other hand the Wurtzite is similar to hexagonal closed packing (ABABAB) with the Zn ions filling the tetrahedral holes also. However, only half of the tetrahedral holes in the crystal lattice are occupied by Zn ions. The coordination number of both cations and anion is four, (4,4)-coordinations.

THE AX_2 TYPE OF IONIC CRYSTALS

The two major crystal packing for this type are fluorite such as CaF_2 and Rutile such as TiO_2. Many difluorides and dioxides adopt one or two structures.

(i) Calcium fluorite-like structure (CaF_2)- this fluorite crystal packing is adopted by ionic compound of the type AX_2, with the radius ratio of is greater or equal to 0.73. In this, each Ca^{2+} is surrounded by eight F^- giving something similar to body-centred cubic packing. Also, the F^- is surrounded by four Ca^{2+}, since there are twice as many F^- ions as Ca^{2+} ions. Thus, the coordination number is (8, 4)-coordination.

(ii) The Rutile (TiO2-like structure)

Titanium oxide has been found to exist in three different crystal packing, namely rutile, brookite and anatase, however many crystals of the type AX2 with radius ratios of 0.41 – 0.73 adopt the Rutile crystal packing. Here, each oxygen ion (O^{2-}) is trigonally surrounded by three Titanium ions (Ti^{4+}), while each titanium ion is surrounded by six Oxygen ions in a distorted body-centred closed packing. Thus, the coordination number is (6, 3)-coordination.

DEFECTS IN IONIC CRYSTAL LATTICES AND IMPORTANCE (DR FAMOJURO)

Theoretically, crystal models depicting the crystal packing always presented a perfect arrangement, however experimentally, this is not so. This is due to the fact that atoms, ions or molecules in crystals are not static, they possess thermal vibration and could be knocked off in a crystal lattice by appropriate external stimuli. In addition, there are defects and presence of impurities in crystal lattices. Ironically, many of the properties of solids are due to these defects, impurities and thermal vibrations.

Defects

There are mainly two types of defects that could present in crystal lattices. These are Stoichiometric and non-stoichiometric defects. At absolute zero, it is assumed that crystal lattice contains perfect arrangement of ions, however as the temperature increases, so also the thermal vibrations of each ion. If the vibration of an ion is large enough, it could jump out of its lattice sites. This is called POINT DEFECT, the higher the temperature the greater the chances of point defect in the crystal lattice (unoccupied spaces increases). This is a thermodynamic effect since it is dependent on **temperature**.

(A) Stoichiometric defects

Stoichiometric crystals are compounds that have the same number of different ions present, as indicated in their chemical formulae. This type of crystal obeys the law of constant composition, which states that, "*The same chemical compound always contains the same elements in the same composition by weight*". For instance, NaCl crystal which has 1:1 arrangement of Na ion to Cl ion is a stoichiometric crystal. Defects in stoichiometry could be present in two ways, these are (i) Schottky (ii) Frenkel

(i) Schottky defects- This is when there a positive ion and a negative ion are absent in the crystal lattice, leading to the formation of a pair of holes (Figure 1.0). The is always present in ionic crystal that have coordination number of 6 or 8. Examples are KCl, CsCl, NaCl among others. The number of Schottky defects formed per cm^3 can be calculated using this equation 1.0

$n_s = N \exp(- W_s/2kT)$ ………………(1.0)

Where, N_s is the number of sites per cm^3 that could be left vacant, W_s is work necessary to form a Schottky defects, k is the gas constant and T is the absolute temperature.

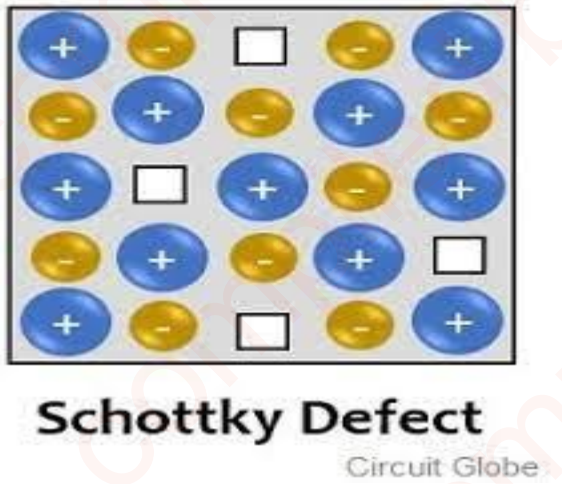


Figure 1.0: Schottky Defect

(ii) Frenkel defects:

This is when there is a vacant site (a hole) in the crystal lattice and the ion that was supposed to occupy the vacant site, is occupying an interstitial position (Figure 2.0). Since metal ions are usually smaller than the anions, it is easier to squeeze a metallic ion into alternative interstitial spaces. Thus, it is more common to find positive ions in the interstitial spaces. The presence of ions in the interstitial spaces will distort the whole crystal lattice and the closeness of like charges lead to a high dielectric constant. This defect is favoured by small positive ions and large negative ions; thus, the coordination number will be 4 or 6.

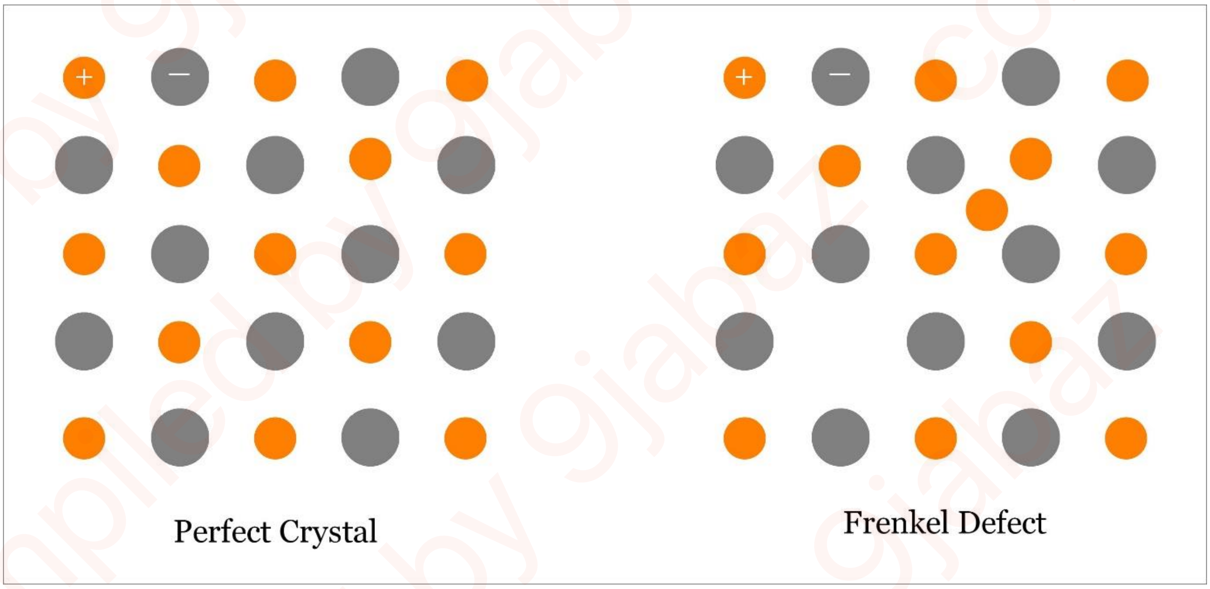


Figure 2.0: Frenkel Defect

The energy needed for the formation of either Schottky or Frenkel defects depend on two factors, temperature and work needed to be done. The fascinating consequence of these defects in a crystal lattice is that, the crystal may conduct electricity to a small degree. This type of conductivity when induced in a chemically pure stoichiometric semiconductor is called "intrinsic semiconduction". This is induced by ionic mechanism due to the movement of ion from its lattice site, to another hole, thereby creating another hole from where it left. If this mechanism is repeated throughout the crystal, then there is movement of holes, which is equivalent to moving a charge in the opposite direction. This phenomenon is responsible for the unwanted background noise produced by transistor.

It is important to note that, crystal with Frenkel defect has one type of hole, which is from positive ions, while crystal with Schottky defect has holes from both positive and negative ions. The presence of holes should lower the density of the crystal, however too much holes will lead to partial or complete distortion of the crystal lattice.

NON-STOICHIOMETRIC DEFECTS

Non stoichiometric crystals are called Berthollide crystals, and the chemical composition of this type of crystal varies. It does not obey the law of constant composition and the ionic compositions that are present, do not correlate to its chemical formulae. Exanples of this are oxides and sulphides of transition metals, such as FeO, FeS and CuO. The ionic ratios depict 1:1 in the chemical formulae, it is not so experimentally, $Fe_{0.9}S$, $Fe_{0.84}O$ are the non-stochiometric compositions. Overall electrical conductivity is maintained by having an extra electron in the structure or having to change the charge on some metal ions. There are two types of non-stoichiometric defects, these are Metal excess and Metal deficient.

Metal excess: this is when there is excess of positive ions in the crystal lattice. This could also be of two types, namely (i) F-centres (ii) interstitial ions and electrons

(i) F-centres defects

When crystals such as NaCl, KCl and LiH are heated with excess of their metallic vapour, bombarded with high radiation energy, they become deficient in the negative ions. This result in changes in their formulae and could be written as $AX_{1-\sigma}$, where σ is a small fraction. This means that a negative ion is absent from its lattice site, leaving a hole, which is now occupied by an electron in order to maintain electrical balance (Figure 3.0). Note, the mechanism is similar to Schottky defect but only one hole is present here.

Anion sites occupied by electrons are called F-centres (F means Fabre in German, translated as "colour" in English). The more the F centres the more the intensity of the colouration of the crystal. NaCl with F-centres are yellowish in colour, while that of KCl is lilac-purple. These colours are similar to the colour of the flames of these metallic ion. These crystals are paramagnetic (presence of unpaired electron), and when irradiated with light they become photoconductors. These means they are n-type semiconductors, since conductivity is by movement of the F-centred electrons from valence to conduction bands.

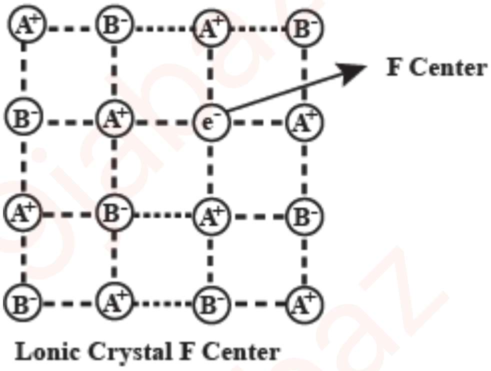


Figure 3.0: F-centre Defect

(ii) Interstitial ions and electrons defect

Metal excess defect is observed when there is an extra cation occupying an interstitial position in the crystal lattice, and the electrical neutrality is maintained by an inclusion of an interstitial electron (Figure 4.0). There is no vacant sites unlike Frenkel defect, only interstitial electron and positive ions. This type of defect is much more common than Frenkel defect, and generally found in crystals that have ions of different radii and with low coordination number. Examples include ZnO and CdO among others. Since these crystals have free electrons, they can conduct electricity, thus, are n-type semiconductors.

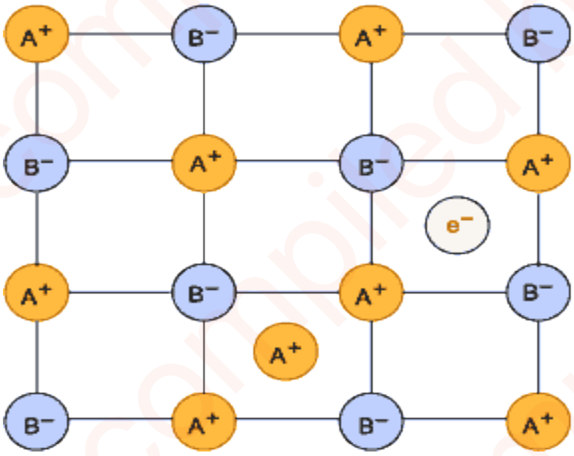
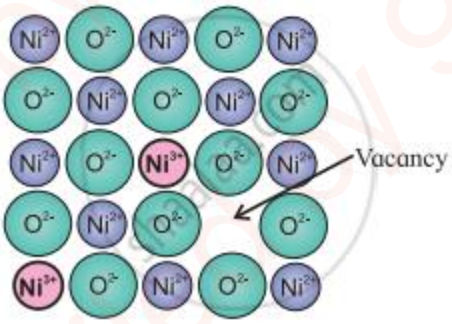


Figure 4.0: Interstitial ion and electron Defect

(iii) Metal Deficiency Defect

Metal deficiency defect occurs in two ways, (i) positive ion absent (ii)extra interstitial negative ions (extremely rare)

(a) Positive ions absent Defect:
This occurs majorly in some transition metal oxides such asNiO, FeO, FeS, CuI among others. These crystals possess metal ions that are in two different oxidation states, for instance, NiO, have both Ni^{2+} and Ni^{3+} in the crystal lattice. Positive ion absent defect occurs if a positive ion A^+ is missing from its crystal site, the charges are balanced by having positive ions with extra charges. If Ni^{2+} is missing from its crystal lattice site, there must be two Ni^{3+} ions that will balance the charges. Also, these types of crystals are p-type semiconductors (movement of holes, movement of positive ions)



CRSTAL LATTICE, UNIT CELLS AND CRYSTAL SYSTEMS (Dr. Famojuro)

WHAT IS A CRYSTAL LATTICE?

A crystal lattice is a graphical representation of constituent group of atoms, ions or/molecule of a crystal as points in three dimensional, and these points are joined together by lines (Figure 1.0). It is a geometrical concept that takes into account how the well-arranged points are related to each other in a translational symmetry. It is important to emphasize that, these points do not tell the position of an atom in a crystal. They are points in space oriented in such a way to build a crystal lattice (Figure 1.0). Note that crystal lattice is an aggregation of unit cells.

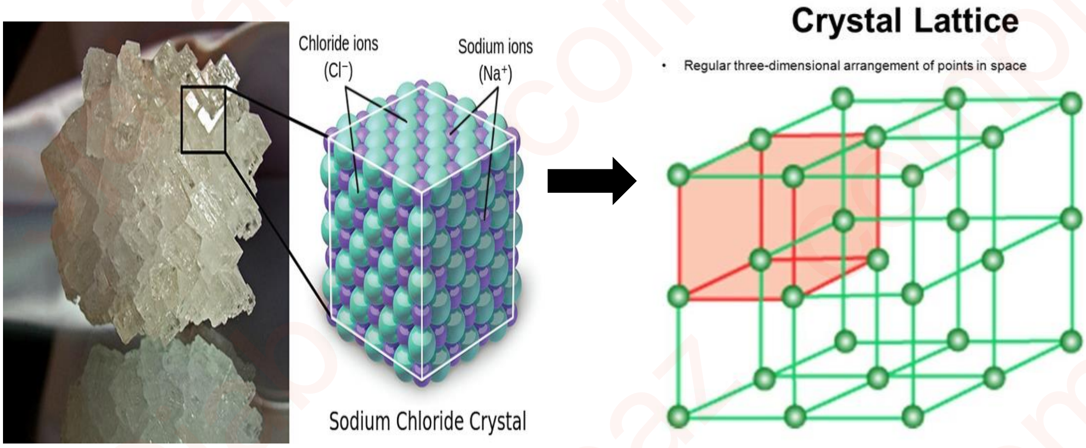


Figure 1.0: Group of ions representing a lattice point forming unit cell of the crystal lattice

Characteristics of Crystal Lattice

- In a crystal lattice, each atom, molecule or ions (constituent particle) is represented by a single point.
- These points are called lattice site or lattice point.
- Lattice sites or points are together joined by a straight line in a crystal lattice.
- When we connect these straight lines we can get a three-dimensional view of the structure. This 3D arrangement is called Crystal Lattice also known as Bravais Lattices.

Crystalline solid could fit into one of the fourteen well-defined lattice arrangements called **BRAVAIS LATTICES, also known as unit cells**

UNIT CELLS A CRYSTAL

The smallest unit that can represent a whole crystal is called unit cell. Unit cell is the smallest hypothetical unit that when stacked together can repeatedly without any gaps in three dimensional directions, can reproduce the entire crystal. A unit cell is to a crystal in three dimensions, what a tile is to a tiled floor in two dimensions (fig 2.0). Each unit cell is defined in terms of **lattice points** — the points in space about which the particles are free to vibrate in a crystal.

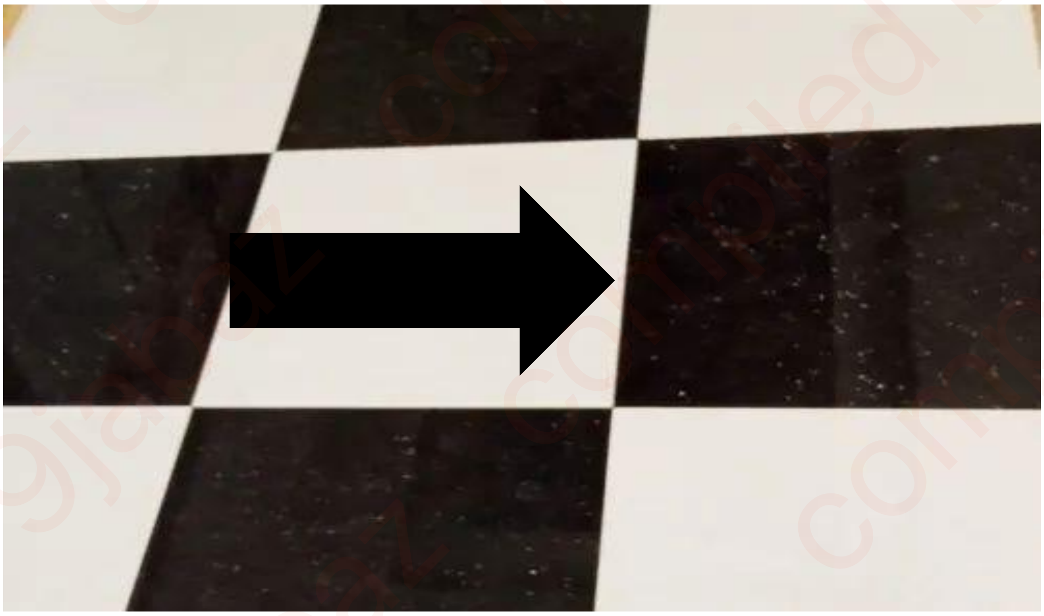


Figure 2.0: A panel of tiles (inset showing a unit cell of tiles)

In 1850, Auguste Bravais showed that crystals could be divided into 14-unit cells, (Fig 3.0) which meet the following criteria namely

(i) The unit cell is the simplest repeating unit in the crystal

(ii) (ii) Opposite faces of a unit cell are parallel

(iii) (iii) The edge of the unit cell connects equivalent points.

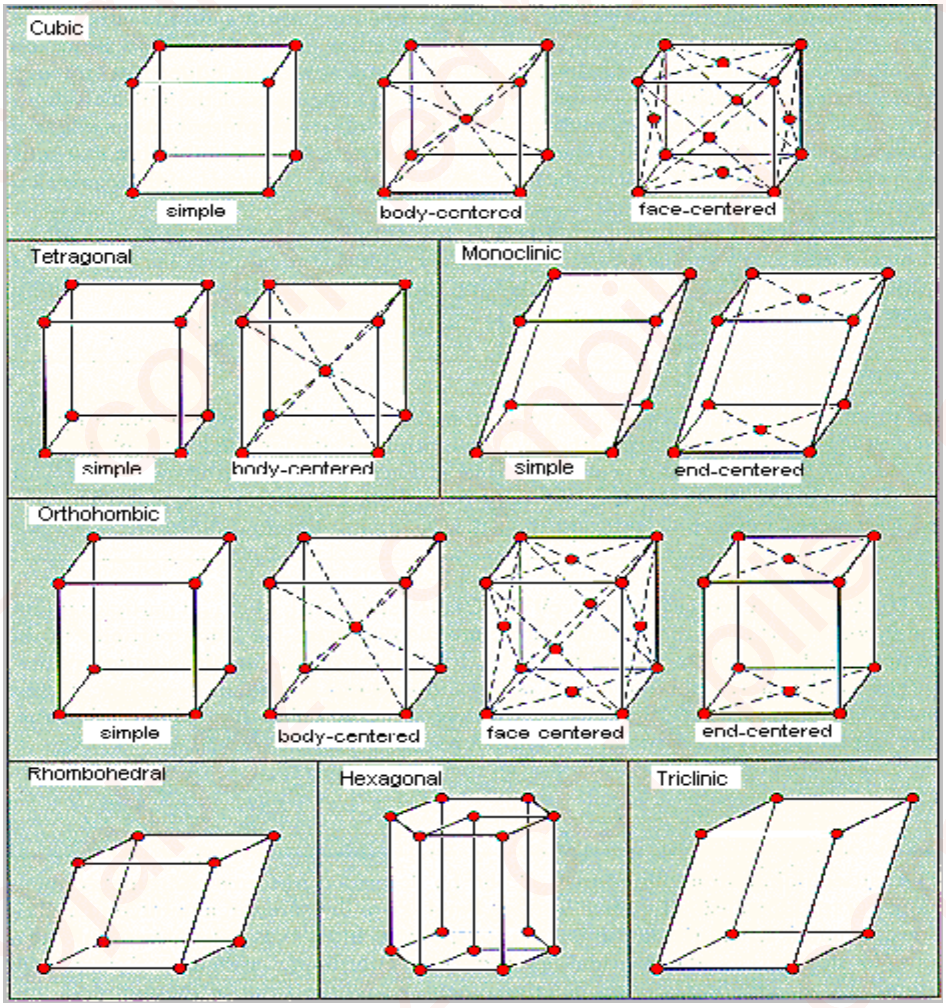


Figure 3.0 : The 14 units cells which makes up the each14 Bravais lattices

In a unit cell, each atom/ion/molecule is sometimes represented by a dot that marks the location of its centre. The number of atoms in a unit cell is counted by noting how they are shared between neighbouring cells. For example, an atom at the centre a cell belongs entirely to that cell, (Fig. 4.0) but one on a face is shared between two cells and counts as one-half an atom. For instance, in fcc unit cell (face-centred cubic unit cell), each of the eight corner atoms is shared by eight cells, so overall they contribute 8 * 1/8 = 1 atom to the cell, each ato at the centre of each of the six faces contribute one-half an atom, so they jointly contribute 6* 1/2 = 3 atoms, the total number of atoms in a fcc unit cells is four. This means that the mass of a unit cell in fcc is four times the mass of an atom (Fig. 5.0)

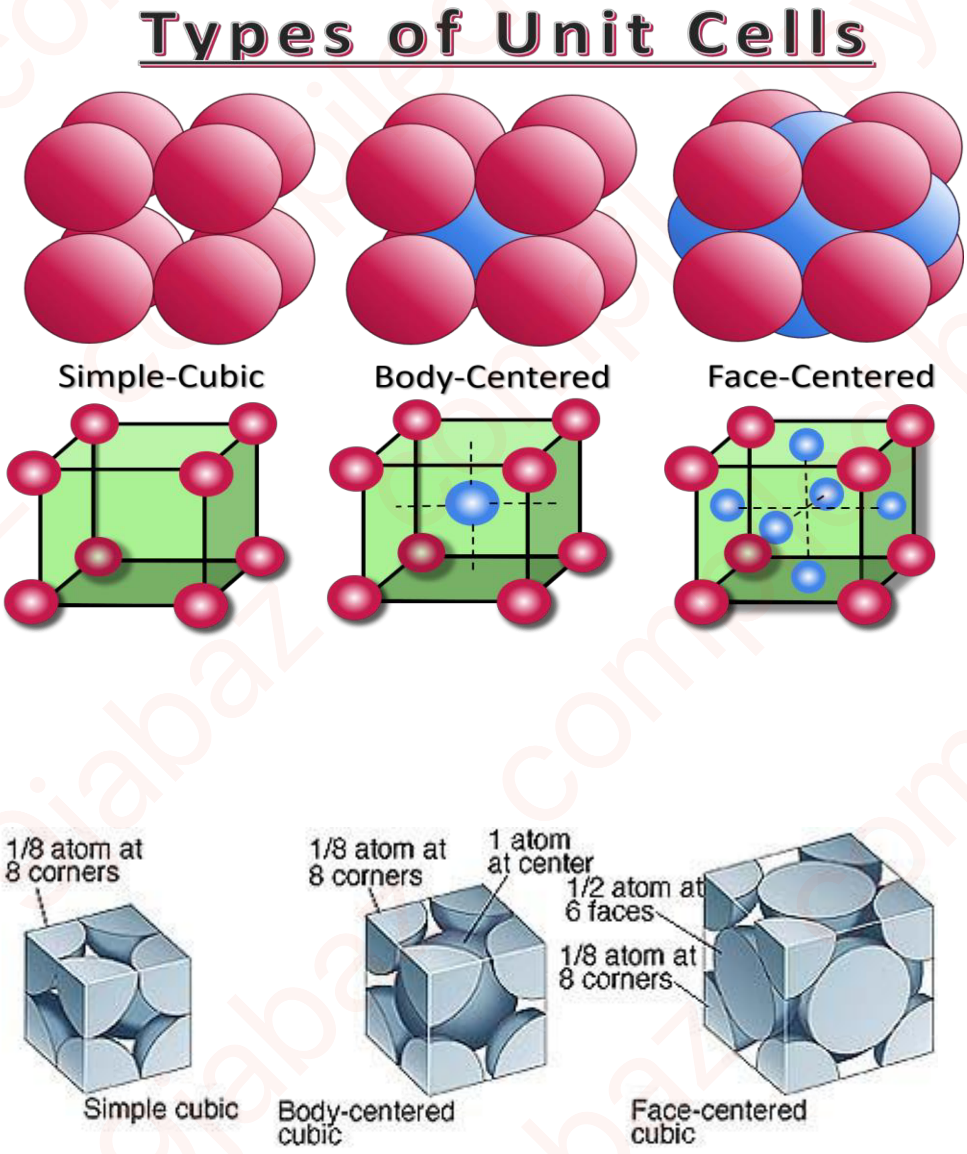
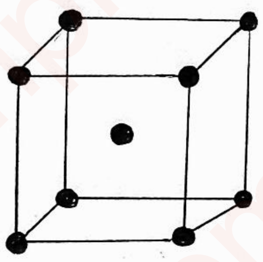


Figure 4.0: Three Unit cells present in Cubic crystal system

The body centred cubic arrangement can be represented as -



Contribution of body centre = 1.

Contribution of corners = 1/8

∴ Total no. of atoms = $1 \times 1 + 8 \times \frac{1}{8} = \underline{2}$

(a) fcc: 8 corner atoms × 1/8 = 1 atom
6 face atoms × ½ = 3 atoms
Total of 4 atoms per unit cell

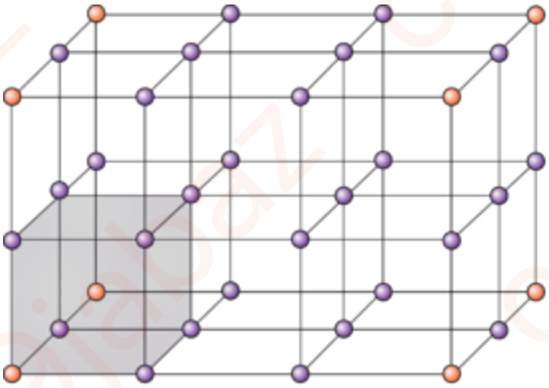
(b) bcc: 8 corner atoms × 1/8 = 1 atom
1 enclosed atom = 1 atom
Total of 2 atoms per unit cell

(c) Diamond: 8 corner atoms × 1/8 = 1 atom
6 face atoms × ½ = 3 atoms
4 enclosed atoms = 4 atoms
Total of 8 atoms per unit cell

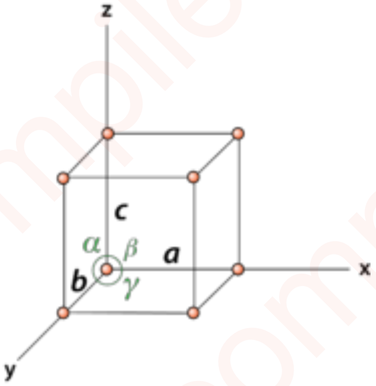
Figure 5.0: Number of atoms present in a unit cell

CRYSTAL SYSTEM

Crystal system is a concept that completely described a crystal in terms of its geometrical arrangement of its lattices. It could be classified into one of the seven systems shown in Figure 4.0, according to the shape of its lattice unit cells. Each systems depict the translation symmetrical orientation of the crystal lattice, denoted as a, b and c, and the angle each of these made with each other α, β, and γ (fig. 6.0). These unit cells (fig. 4.0) fall into seven categories (Fig. 7.0) which differ in the three unit-cell edge lengths (*a*, *b*, and *c*) and three internal angles (α, β, and γ.),



Crystal Lattice



Unit Cell

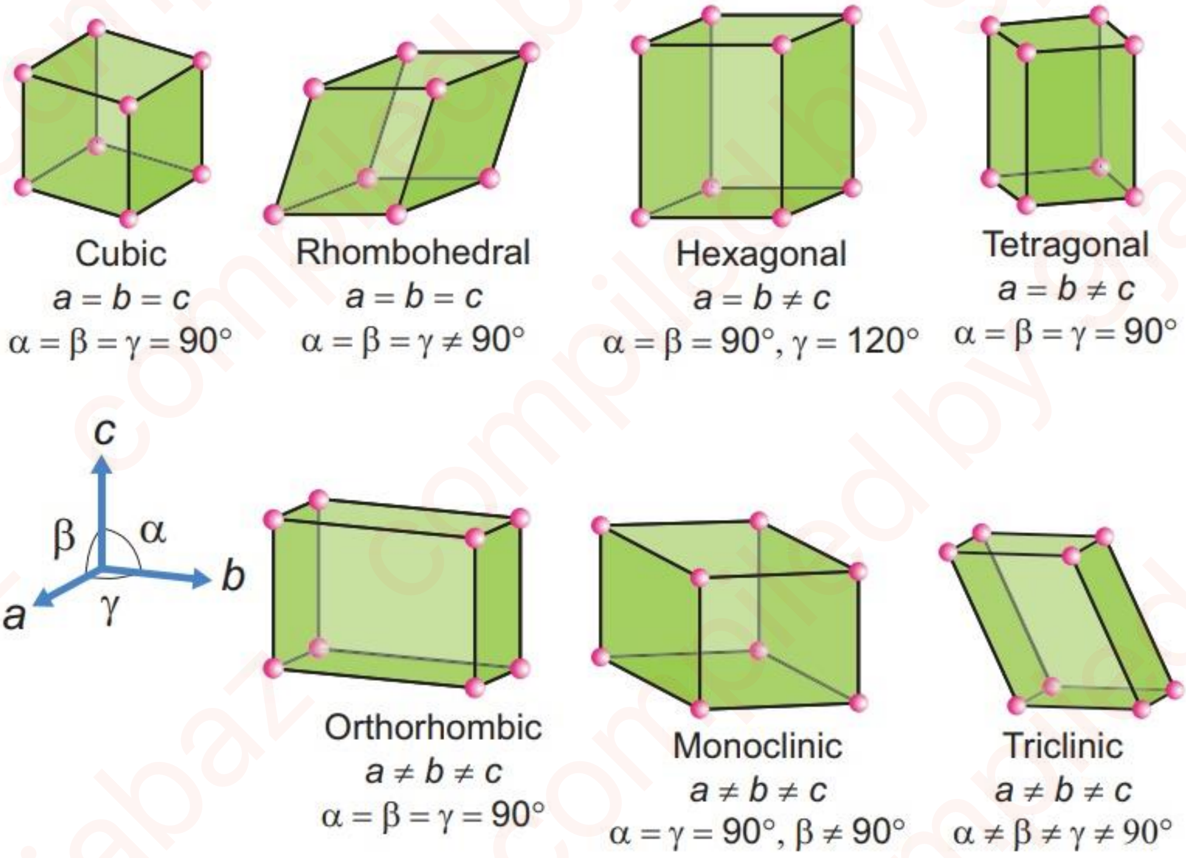


Figure 7.0: The seven crystal systems (3 in cubic, 2 in tetragonal, 2 in monoclinic, 4 in orthorhombic, 1 in hexagonal, rhombohedral and triclinic – the 14 Bravais unit cells

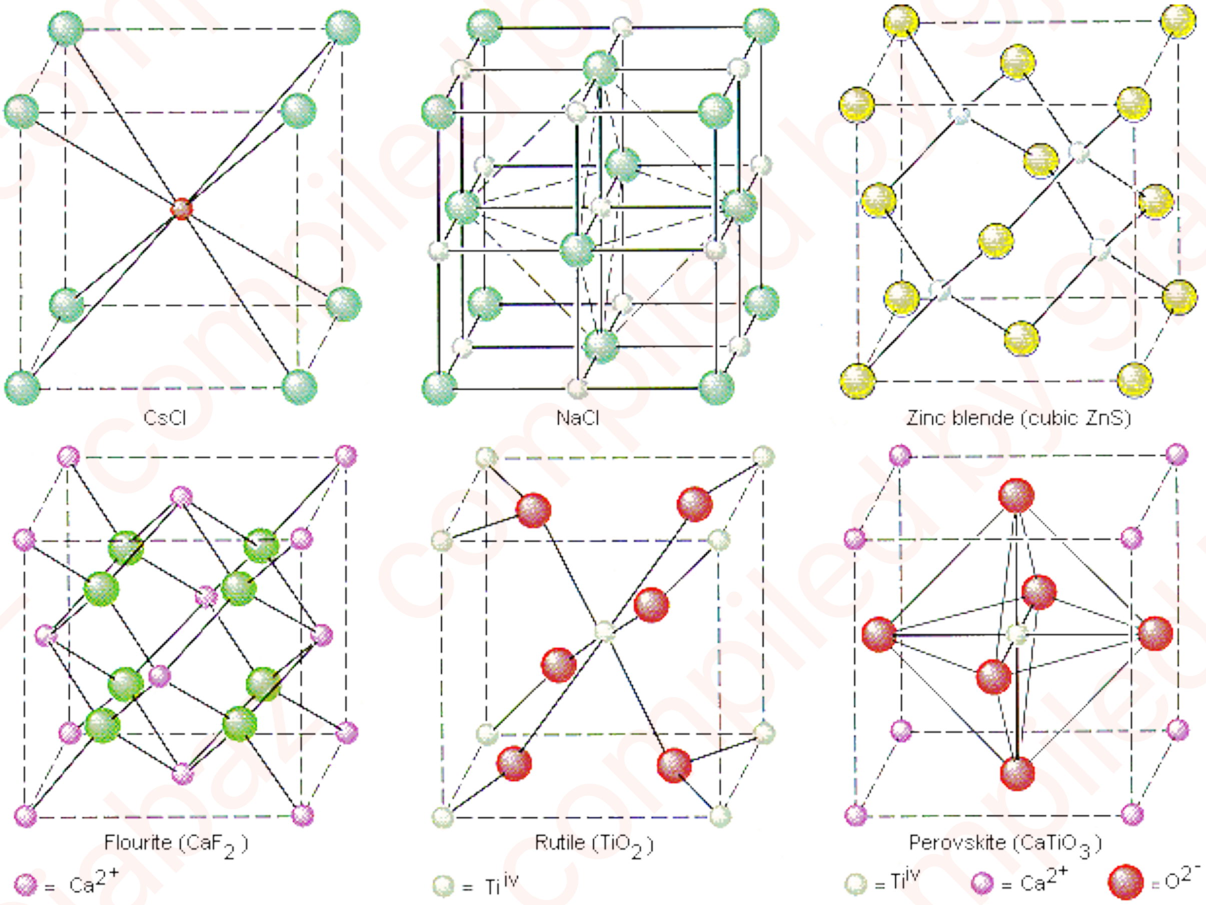


Figure 8.0: The crystal unit cells of some common ionic compounds