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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 $Cs_4Al_4Si_9O_{26}.H_2O$

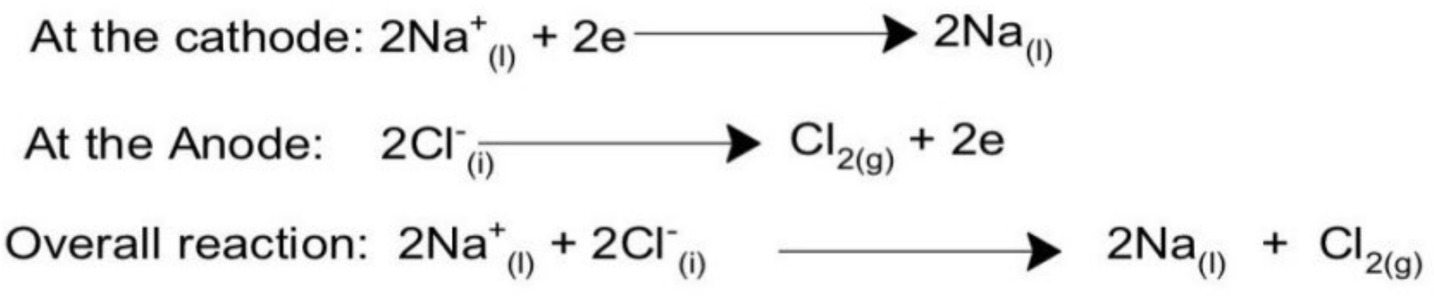
Li, Rb and Cs occur in very small amounts, smaller than Na and K (% abundance Rb > Li > Cs). They often occur as silicate minerals e.g. spodumene ($LiAlSi_7O_6$), pollucite, carnallite, leucite ($KAlSi_2O_6$) and lepidolite. Only artificial isotopes to francium are know $^{223}_{87}Fr$

EXTRACTION

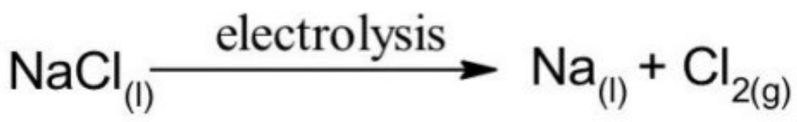
Lithium is extracted by electrolysis of LiCl similar to that of NaCl. LiCl is also obtained from the reduction of spodumene by heating it with CaO. This reaction produces LiOH which is converted to LiCl.

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

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



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



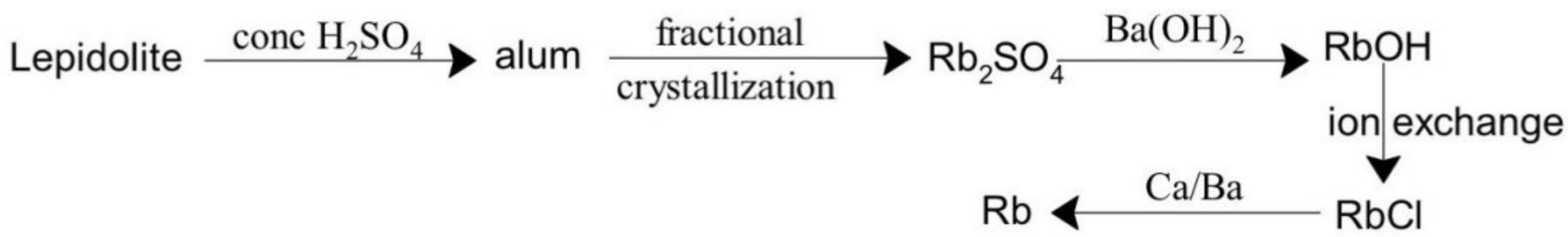
Potassium can be extracted by electrolysis but it is a hazardous process. Another method uses molten Na and molten KCl which are heated together to yield potassium and NaCl.



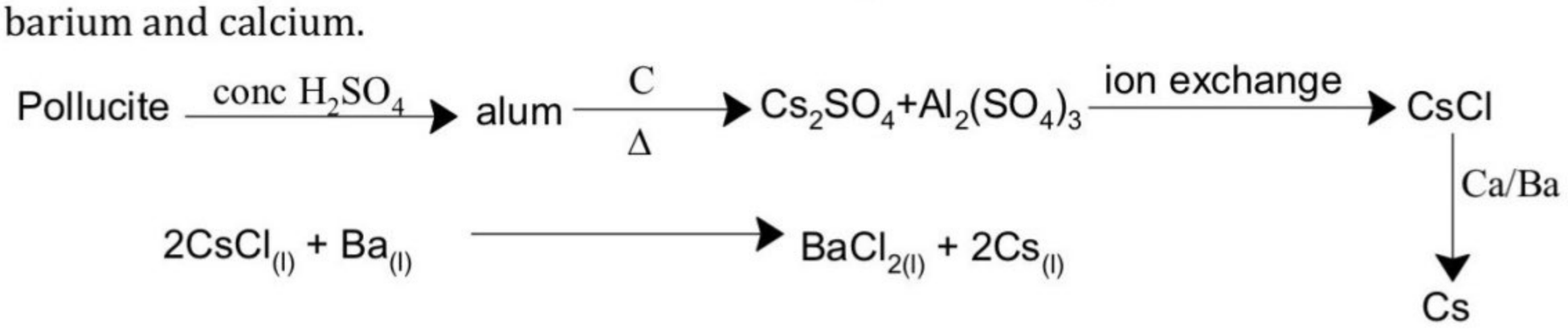
The temperature of the reaction is so high that K is in the vapour state. It is collected as the reaction is on-going as this drives the equilibrium to the right.

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.





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.



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 (^oC)	180	98	64	39	29
Bp (^oC)	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) $M_{(s)} \rightarrow M_{(g)}$ ΔH°_{sub} (ΔH°_{sub} decreases down the group)

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

Hydration $M^{+}_{(g)} \rightarrow M^{+}_{(aq)}$ ΔH°_{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

$$\Delta H_f^\circ = \Delta H_{sub}^\circ + \Delta H_{IE}^\circ + \Delta H_{dis}^\circ + \Delta H_{EA}^\circ - \Delta H_L^\circ$$

Depends on metal

Depends on halogen

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

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

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

$$LiF \quad (79 + (-334) < -1030$$

$$LiCl \quad (121 + (-355) < -834$$

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 $(\Delta H_{sub}^\circ \ \& \ \Delta H_{IE}^\circ)$ 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 $\quad 4Li_{(s)} + O_{2(g)} \rightarrow 2Li_2O_{(s)} \quad [\mathbf{O^{2-}}]$

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

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

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 $(\mathbf{O_3^-})$

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.

$$K_2O_{2(S)} + 2O_3 \xrightarrow[\Delta]{} 2KO_{3(S)} + O_{2(g)}$$

HYDROXIDES

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

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

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

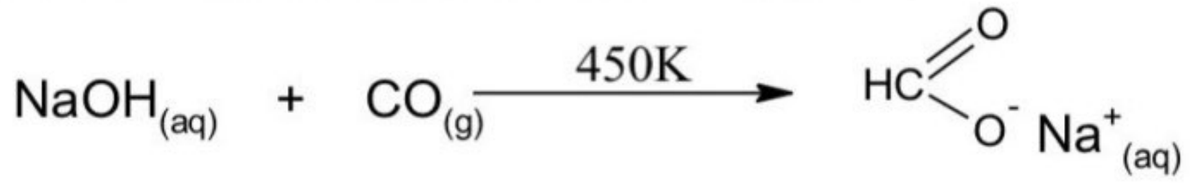
When excess CO_2 is passed through an aqueous solution of metal hydroxide the bicarbonate is produced but in limit supply of CO_2 then carbonate is produced.

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.

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

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

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

$$2NaHCO_{3(s)} \xrightarrow[\Delta]{} Na_2CO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}$$

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.

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

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 $\Delta \mathbf{H_{sub}^\circ} + \Delta \mathbf{H_{IE}^\circ} = \mathbf{q}$ 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^-, $\therefore \Delta H_f^\circ$ depends largely on $\mathbf{q}$ and $\Delta \mathbf{H_L^\circ}$. The variation for the fluorides is as follow

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

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°.

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

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) $NaOH_{(aq)} + CO_{2(g)} \longrightarrow$
   (ii) $NaOH_{(aq)} + \underset{\text{excess}}{CO_{2(g)}} \longrightarrow$
   (iii) $NaOH_{(aq)} + \underset{\text{limited}}{CO_{(g)}} \xrightarrow{450\ K}$
3. Below are the steps taken for the extraction of rubidium from its ore. Provide the correct answers to **i – v**.

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

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

- 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.

$$CaCO_3 \cdot MgCO_{3(s)} \xrightarrow[\Delta]{} CaO_{(s)} + MgO_{(s)} + 2CO_2$$

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

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 (^oC)	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.

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

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

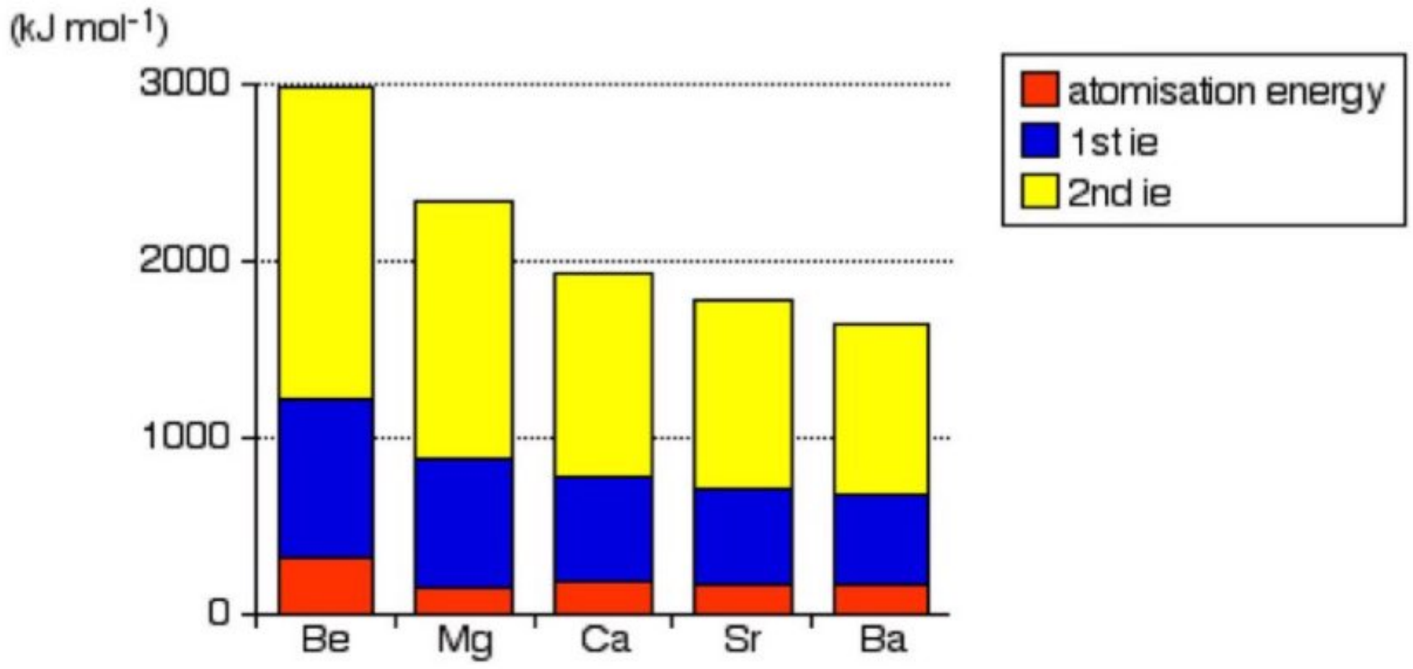
If very clean magnesium ribbon is used, then it can react mildly with cold water to give the oxide and hydrogen. However, Mg reacts with hot water to form it hydroxide and liberate H_2. Ca, Sr, Ba reacts readily with cold water.

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

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

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.

Energy input into the formation of X^{2+}



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

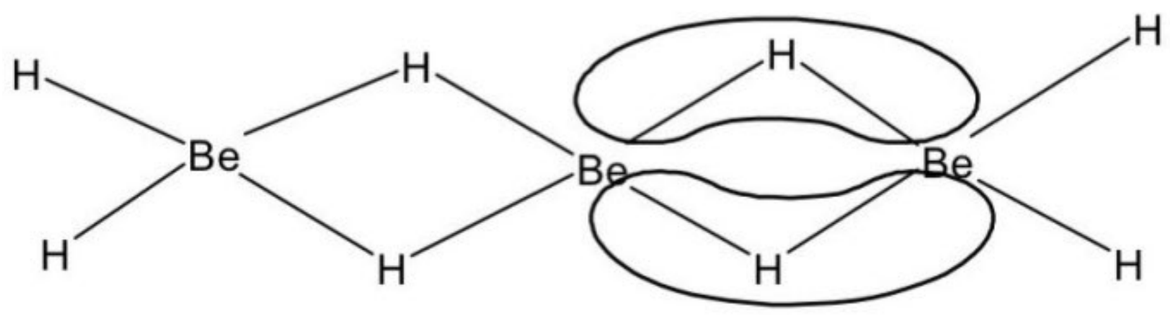
HYDRIDES

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.

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

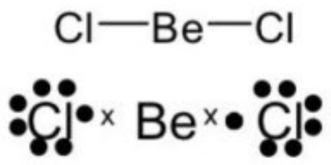
$$MC_2 + 2H_2O \rightarrow M(OH)_2 + HC \equiv CH\ (M = Mg, Ca, Sr, Ba)$$

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

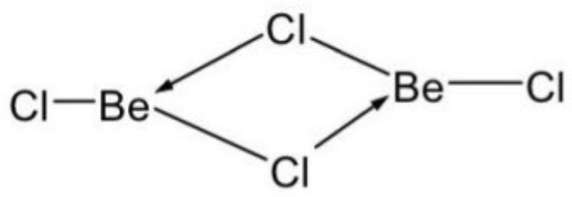
HALIDES

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.

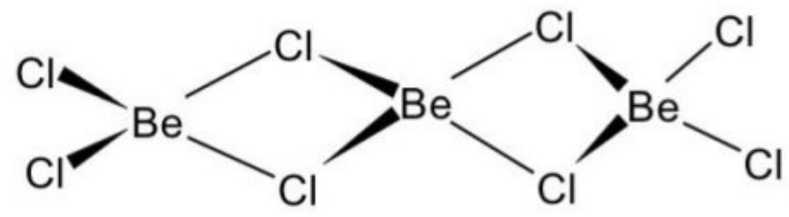


$BeCl_2$



$(BeCl_2)_2$

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.

$$CaCO_{3(s)} \xrightarrow[\Delta]{} CaO + CO_2$$

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.

$$MgSO_4 \xrightarrow[\Delta]{} MgO + SO_3$$

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.

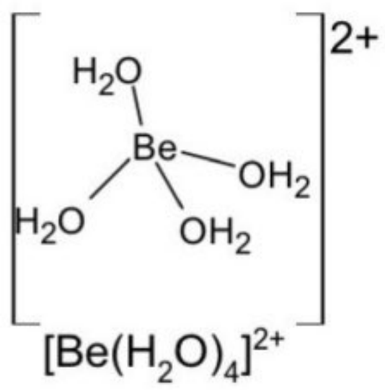
$$CaCO_{3(s)} + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$$

$$Ca(NO_3)_{2(s)} \xrightarrow[\Delta]{} CaO_{(s)} + 4NO_{2(g)} + O_2$$

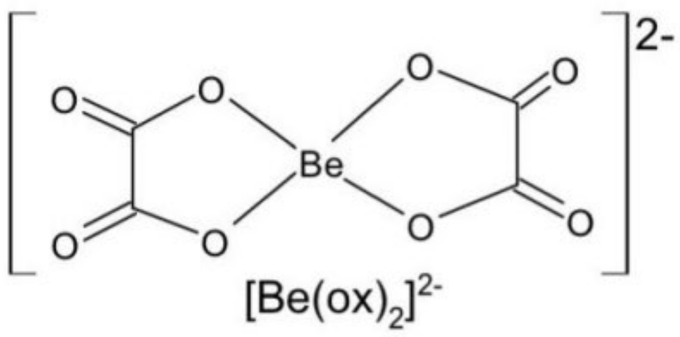
Just as with the carbonated of this group their thermal stability decrease down the group.

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.

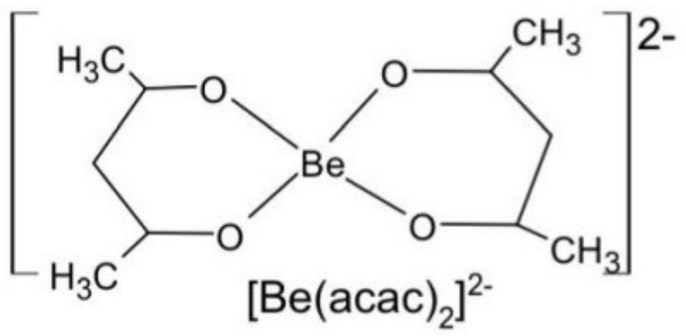
5. Coordination compounds: complex formation is favoured by small highly charged ions with suitable empty orbitals of the appropriate energy. BeF_2 coordinates with extra fluorides ion for $[BeF_3]^-$ or $[BeF_4]^{2-}$. They are usually tetrahedral complexes like $[Be(H_2O)_4]^{2+}$. Chelating ligand 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.



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



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



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

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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 °C and rubidium is 39 °C while of barium is 714 °C
   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. $BaCO_{3(s)} \xrightarrow[\Delta]{}$
   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-$AlO(OH)$
e. Dispur α-$AlO(OH)$

(c, d, e: Bauxite)

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.

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

1

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

2

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}

3

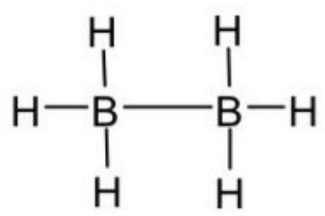
Diborane is the most studied of all the boranes. It is prepared by the following ways:

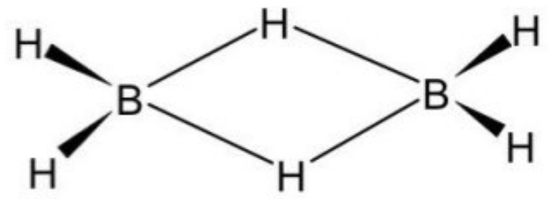
$$4BCl_{3(g)} + 3LiAlH_{4(s)} \rightarrow 2B_2H_{6(g)} + 3AlCl_{(s)} + 3LiCl_{(s)}$$

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

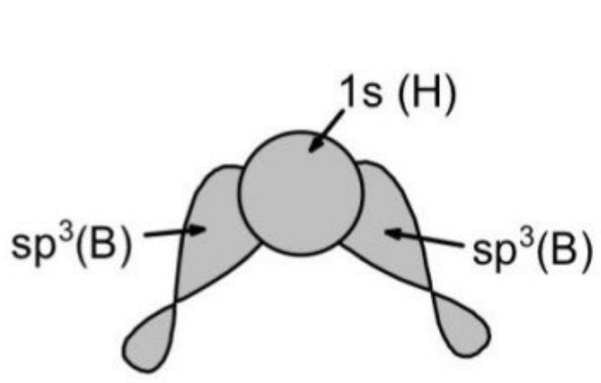
$$Mg_3B_{2(g)} + H_3PO_{4(aq)} \rightarrow (\underset{of\ boranes}{mixture}) B_4H_{10} \xrightarrow[\Delta]{} B_2H_6$$

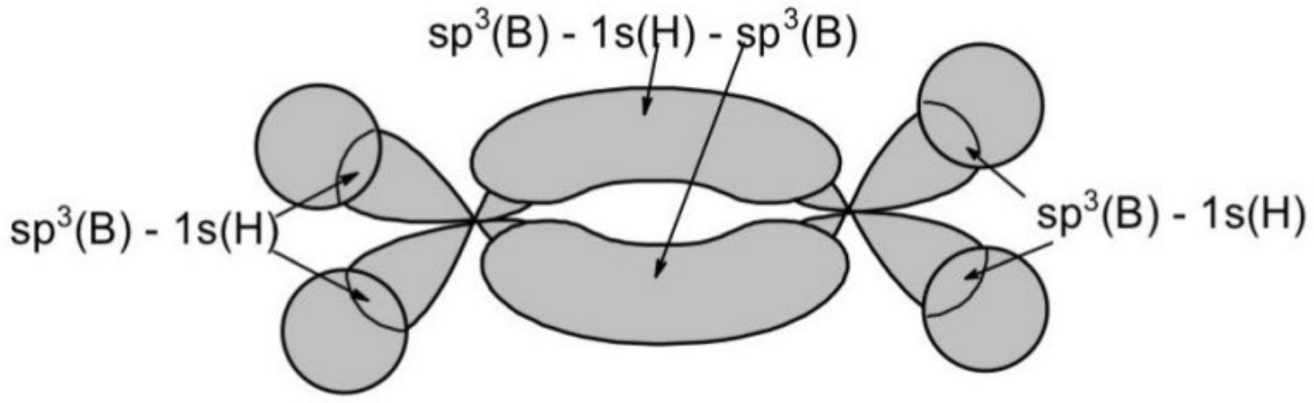
Diborane has 12 valence electrons 3 from each boron atom and a total of 6 from 6-H atoms. Diborane does not have B-B bond because this would mean that it has a valence of 4 and not 3. Instead it forms a bridge [B – H – B] that is a 2é-3 bond centre. The bridging H-atoms are planar and the 4 terminal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



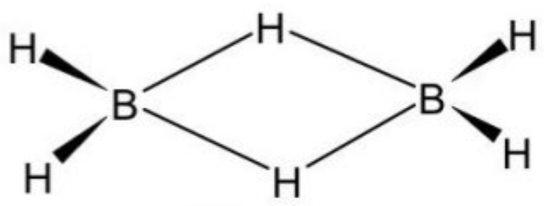


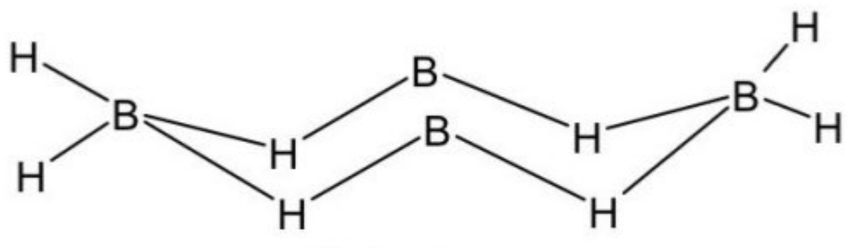
The hyrbidization of B is sp^3 and it overlaps the Is of H to form a delocalized molecular orbital covering all 3 nuclei but having only 2 electrons hence making the bridge.





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





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

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

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

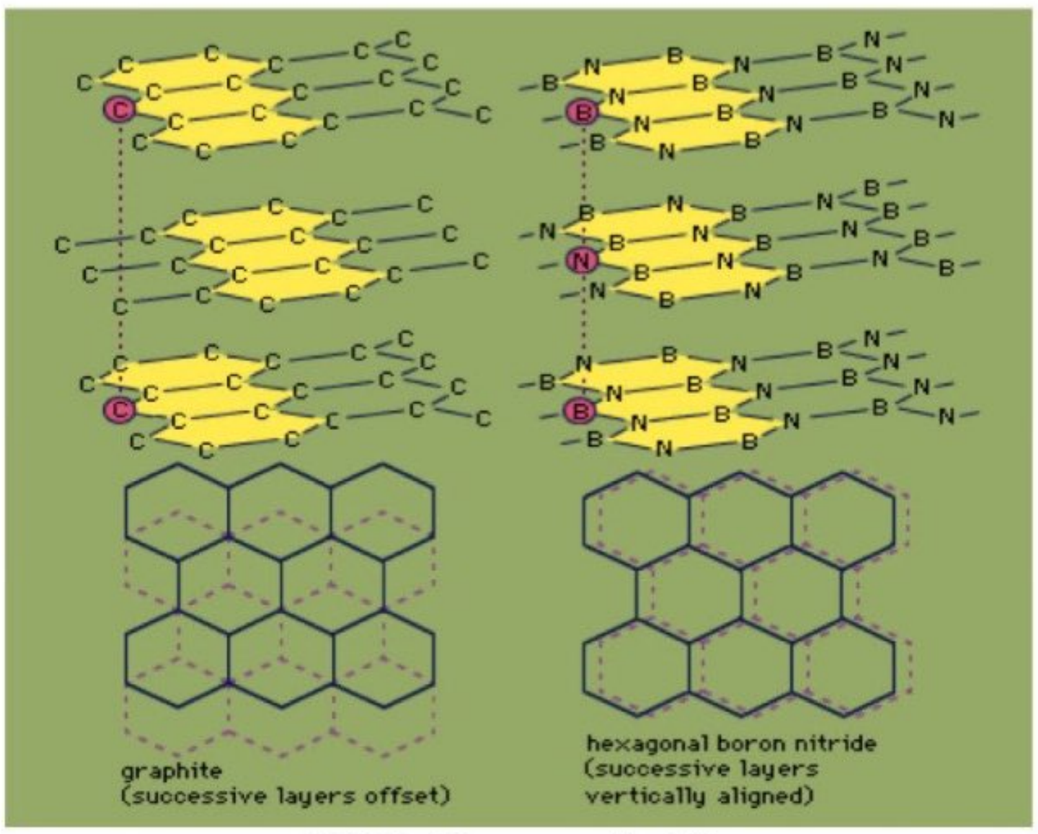
All boranes are colourless and diamagnetic. They range from gas (B_2H_6 and B_4H_8), volatile liquids (B_5H_9 B_6H_{10}) and to sublime solids ($B_{10}H_{14}$).

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

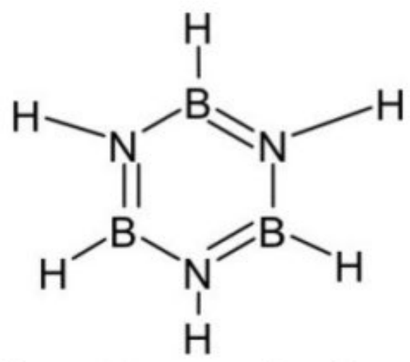
$$B_2H_6 + NH_3 \rightarrow \boldsymbol{B_2H_6 \cdot 2NH_3}\ (\text{excess } NH_3, @\ low\ tempt)$$

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

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

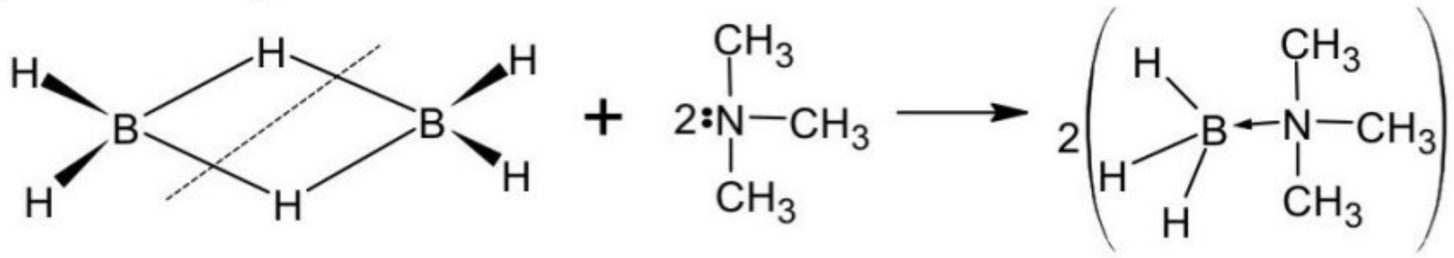


$(BN)_x$ Boron nitride

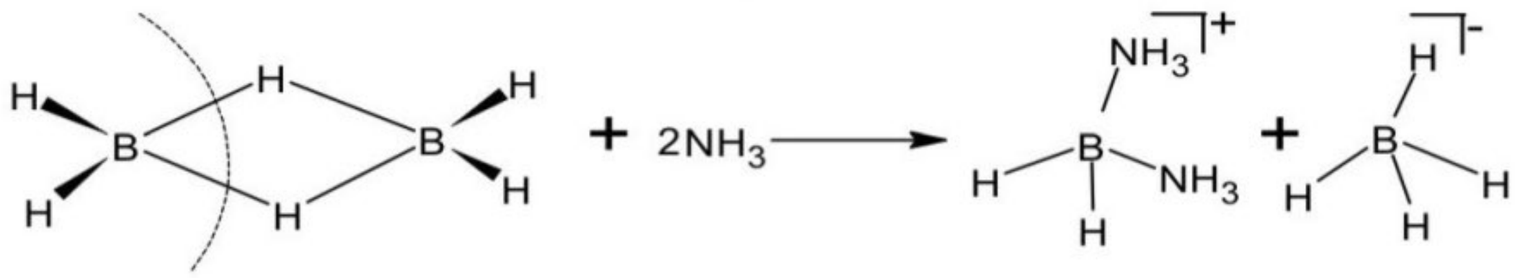


$B_3N_3H_6$ = Borazole (borazine)
is called the inorganic beneze

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^-.

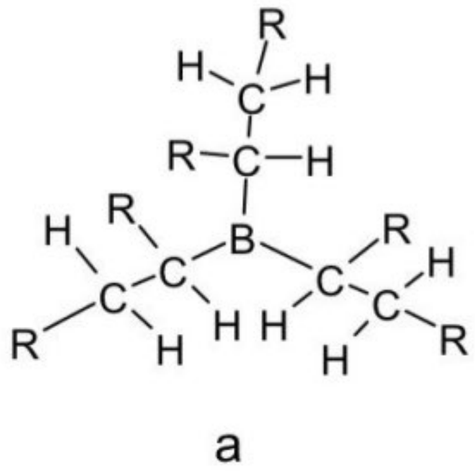
$$B_2H_6 + 2LiH \rightarrow 2LiBH_4$$

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

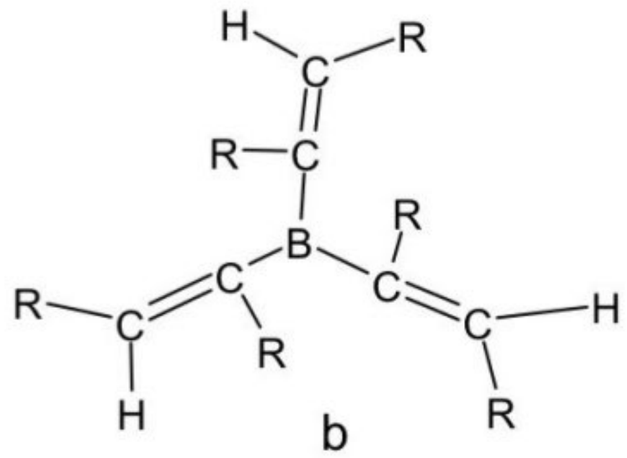
$$a. \quad B_2H_6 + 6RCH = CHR \rightarrow 2B(RCH - CH_2R)_3$$

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

Where R = H or any other alkyl group



a



b

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

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

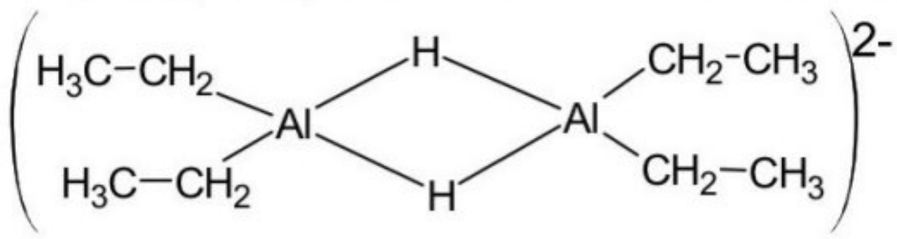
Alkylboranes are converted to ketone or carboxylic acid by reacting with chromic acids.

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

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

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.

$$LiEH_4 + [(CH_3)_3NH]^+Cl^- \rightarrow (CH_3)_3N - EH_3 + LiCl + H_2$$

[E = B, Al, Ga]

$$(CH_3)_3N - EH_3 + N(CH_3)_3 \rightarrow ((CH_3)_3N)_2 - EH_3$$

[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 + $\left\{\begin{array}{l} 3RNH_2 \rightarrow B(NRH)_3 \\ 3H_2O \rightarrow B(OH)_3 \\ 3ROH \rightarrow B(OR)_3 \end{array}\right.$ $+ 3HX$ Protolysis

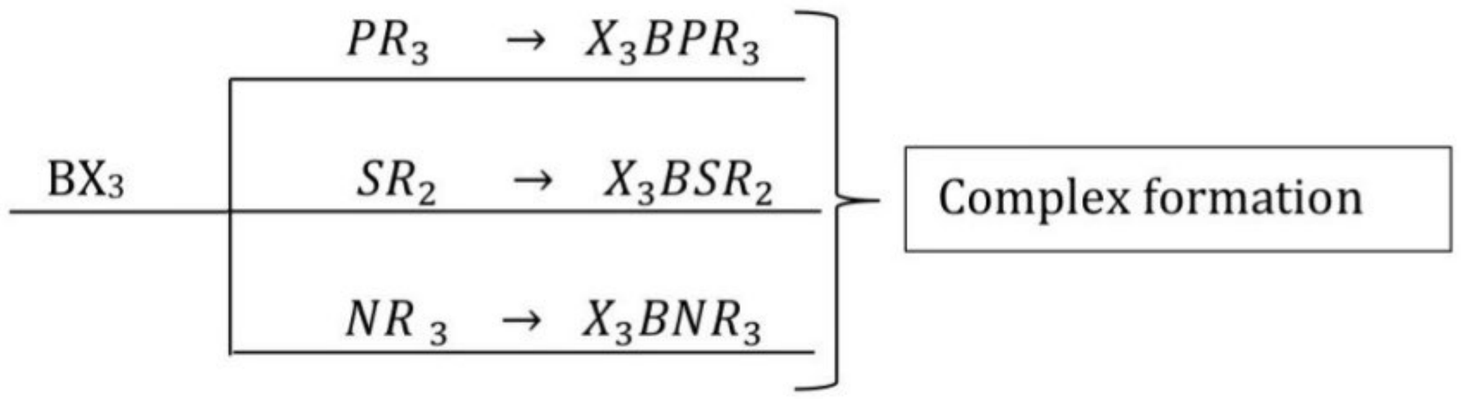
All the other halides are hydrolyzed to boric acid and the corresponding hydrogen halide.

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

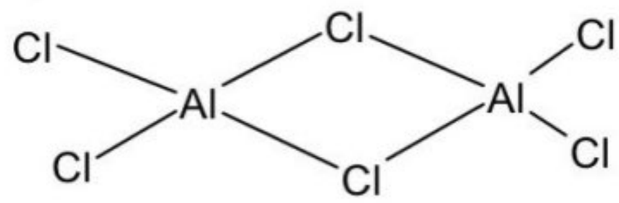
Except BF_3 that forms the tetrafluoroborate $[BF_4]^-$ and this is because BF_3 is a hard and a strong Lewis acid hence has a high affinity of for F^- ion.

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

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.



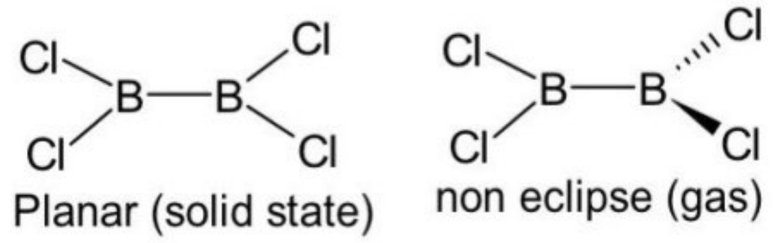
Only BX_3 can form a complete octet by accepting lone pair from a donor. The other halides of the group cannot because of their large sizes as a result the unhybridized p-orbital cannot overlap effectively with the orbital of the other molecule that has the lone pair so they rather polymerize to satisfy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

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



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

$Ga + GaCl_2$ 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

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

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.

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

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.

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

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

$Al(OH)_3$ 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 Adeyemi Adebola

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 $n^2 np^2$. The group oxidation state is 4. However, down the group, oxidation state of 2 becomes more stable. This is attributed to inert pair effect. The electron pair in As 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 ENERGY

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) Chaorite (iv) Fullerenes

(v) Ionsdaleite (vi) carbon VI

(1) 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

(2) 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 burns in limited quantity of air to give CO

$$2C + O_2 \rightarrow 2CO + \text{limited}$$

In excess air, to give CO_2

$$C + O_2 + CO_2 \rightarrow \text{excess}$$

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

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

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

$$Sn + O_2 \xrightarrow{1600K} SnO_2$$

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

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

(3) Reaction with halogen: Carbon as graphite combines with flourine, Si and Ge reacts readily with all the halogens, forming volatile halides

$$C + F \longrightarrow CF$$

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 SnX_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) Interstitial carbide

SILIGIDES

Similar to the carbides, silicides is a group of compound 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 co-ordinated tetrahedrally by four oxygen atom, to form silicate units, are called silicate

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

Examples includes;

(i) orthosilicate (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 Paulis 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 silicon

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

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

(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

Characteristics : (i) It burns with a blue flame.

(ii) It reduces $PdCl_2$ 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 in breweries $C_6H_{12}O_6 \rightleftharpoons 2C_2H_5OH + 2CO_2$

(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:

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

white ppt

$CaCO_3$

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 of elements typically form bonds. Carbon can form $p\pi - p\pi$ 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 $p\pi - p\pi$ orbitals, for bonding. The SiO_2 forms infinite 3D structure (although silicon compound $p\pi - p\pi$ 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 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.

Group 15

Chemical properties

Nitrogen and phosphorus essentially forms covelent bonds

Write Group 5 electronic Configuration, element

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

Chemical properties

N and P essentially forms covelent compound, As, Sb and Br shows increasing tendency to cationic behaviour due to its small size, N tends to form $p\pi - p\pi$ 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

4. 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 symmetrical 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 ~~tetra~~atomic molecule (P_4, As_4, Sb_4).

This is because it is not possible for phosphorus and arsenic atoms to form pp-pπ

bond, because the 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 of 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 5p 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 orbital and form 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 bond and thereby attains the noble gas electronic configuration of ns^2p^6 when they use all their ~~four~~ 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.

Thus 5 unpaired electrons can be used 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 PH_3 to form NH_4^+ and BF_3H^+

$NH_3 + H^+ \rightleftharpoons NH_4^+$

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 Bismuth 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 pyramidal

(b) Pentahalides

N and Bi cannot 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 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 (MO_2, M_2O_5).

Thermal stability and acidic character of M_2O_5 decreases from N to P trioxides. Thus, NO_3 and PO_3 are completely acidic.

As_2O_3 and Sb_2O_3 are amphoteric (they form salts with acids as well as bases)

Bi_2O_3 is predominantly basic and forms salts with acid. It also shows feeble.

The decrease in the acidic character from NO_3 and Bi_2O_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.

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 gass.. It is prepared by thermal decomposition of molten ammonium nitrate.

It is a neutral oxide, It is used as anaestwtic 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) Nitrogen dioxide (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.
Polonium Po	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$	4

The first four elements are non-metals, the element 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 electons forming M^{2-} donion or by sharing two electrons, thus forming two covalent bonds.

~~Reacti~~ 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 p_z 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 Sulphur

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. The thermal stability with respect to dissociation of the element decreases in the order. They:

I: $H_2O \ll H_2S \gg H_2Se > H_2Te$

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

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 ~~bone~~ metallic properties of the group 4 elements

(3) What makes Sn and Pb poor metals?

(4) Why is phosphorus relatively reactive compared to Nitrogen

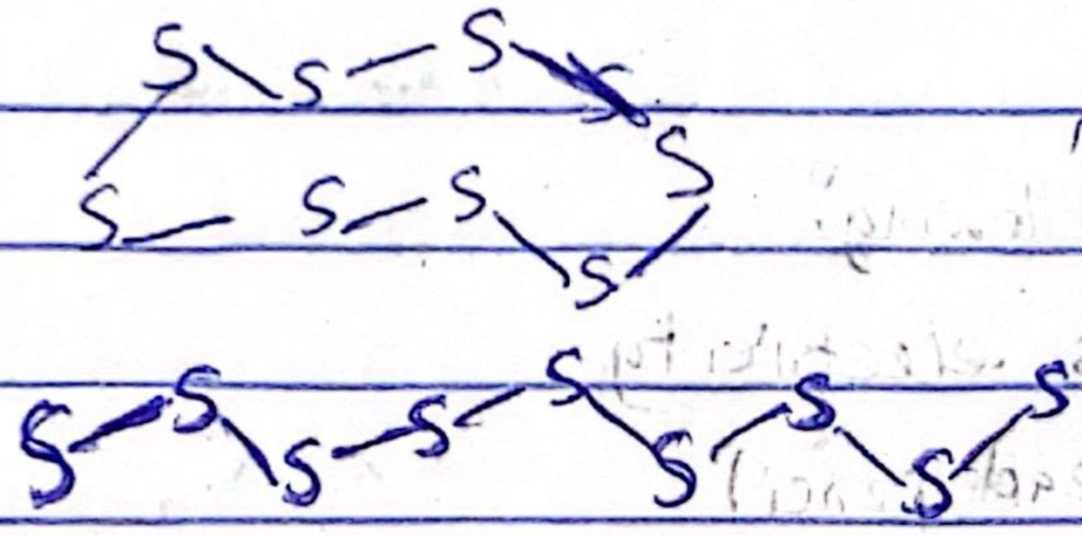
Group 6

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 conductors
52	Tellurium	Te	$[Kr]\ 4d^{10}\ 5s^2\ 5p^4$	
84	Polonium	Po	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 5p^4$	

becomes more metallic

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

S_8



Catenation of sulphur

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 & 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

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

$FeS + H_2SO_4 \rightarrow H_2S + FeSO_4$

$K_2Se + H_2SO_4 \rightarrow H_2Se + K_2SO_4$

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

Properties of the Hyarides

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

They are flammable gases which burns with blue flame