s - BLOCK ELEMENTS

1 HYDROGEN

1.1 ATOMIC AND MOLECULAR PROPERTIES OF HYDROGEN

Atomic Properties		Molecular Properties	
Ionisation enthalpy, (kJ mol^{-1})	1312	Melting point, (K)	13.8
Electron gain enthalpy (earlier electron affinity), (kJ mol^{-1})	–72.8	Boiling point, (K)	20.4
Electronegativity	2.1	Density, (g/cm^3)	0.0899
Atomic radius, (pm)	37	Bond length, (pm)	74.2
Ionic radius (H^-), (pm) H^+, (pm)	210 $\approx 1.5 \times 10^{-3}$	Bond enthalpy, (kJ mol^{-1})	435.9

Hydrogen in the gaseous state exist as a diatomic species H_2. The diatomic H_2 molecule is also termed as dihydrogen to distinguish it from the hydrogen atom.

1.2 RESEMBLANCE WITH ALKALI METALS

Hydrogen resembles alkali metals in the following respects.

(i) Electronic configuration:

The hydrogen atom has one electron in the outermost shell like the alkali metals.

Element	H	Li	Na
Atomic number	1	3	11
Electronic configuration	$1s^1$	$1s^2, 2s^1$	$1s^2, 2s^2, 2p^6, 3s^1$

(ii) Cation formation:

Hydrogen like alkali metals forms singly charged cation by losing the outermost electron.

$$H(1s^1) \longrightarrow H^+ + e^-$$

$$Na(1s^2, 2s^2, 2p^6, 3s^1) \longrightarrow Na^+(1s^2, 2s^2, 2p^6) + e^-$$

(iii) Affinity for non–metals:

Both hydrogen and alkali metals combine with halogens to form halides, with oxygen to give oxides and with sulphur to give sulphides. For example,

HCl	H_2O	H_2S
$NaCl$	Na_2O	Na_2S

(iv) Electropositive nature:

Hydrogen is displaced from acids by metals. In this reaction hydrogen behaves as an electropositive element. For example,

$$Zn + \text{dil. } H_2SO_4 \longrightarrow ZnSO_4 + H_2(g)$$

It is further supported by the fact that when an aqueous solution of hydrogen chloride or a molten alkali metals halide is electrolysed, both hydrogen and alkali metals are liberated at the cathode.

$$HCl \longrightarrow H^+ + Cl^- \qquad NaCl \longrightarrow Na^+ + Cl^-$$

At cathode: $H^+ + e^- \longrightarrow \frac{1}{2} H_2(g) \qquad Na^+ + e^- \longrightarrow Na$

(v) Reducing character:

$$CuO + H_2 \longrightarrow Cu + H_2O$$

$$B_2O_3 + 6K \longrightarrow 2B + 3K_2O$$

potassium
(an alkali metal)

1.3 RESEMBLANCE WITH HALOGENS

Hydrogen resembles halogens in the following respects

(i) Electronic configuration:

Both hydrogen and halogens are one electron short of saturation in their outermost shell. After gaining one electron they acquire stable configuration of the nearest noble gas. Thus, both behave as univalent non–metals as shown below.

$H + e^- \longrightarrow H^-$ (This corresponds to He)
$1s^1$ $1s^2$
$Cl + e^- \longrightarrow Cl^-$ (This corresponds to Ar)
$1s^2, 2s^2 2p^6, 3s^2 3p^5$ $1s^2, 2s^2 2p^6, 3s^2 3p^6$
$Br + e^- \longrightarrow Br^-$ (This corresponds to Kr)
2, 8, 18, 7 2, 8, 18, 8

(ii) Hydrides and halides:

Hydrogen combines with alkali and alkaline earth metals to form hydrides similar to halides.

$H_2 + 2Na \longrightarrow 2NaH$ $Cl_2 + 2Na \longrightarrow 2NaCl$
$H_2 + Ca \longrightarrow CaH_2$ $Cl_2 + Ca \longrightarrow CaCl_2$

The fused hydrides on electrolysis produce hydrogen at anode, like chlorine from fused chlorides.

$H^- \xrightarrow{\text{at anode}} \frac{1}{2} H_2(g) + e^-$ $Cl^- \xrightarrow{\text{at anode}} \frac{1}{2} Cl_2(g) + e^-$

(iii)Ionisation enthalpy:

The ionisation enthalpy of hydrogen is closer to halogens and much different from alkali metals.

	Hydrogen	Alkali metals					Halogens			
Element	H	Li	Na	K	Rb	Cs	F	Cl	Br	I
Ionisation enthalpy / kJ mol^{-1}	1301	520	496 375	419	408		1680	1256	1142	1008

(iv)Formation of covalent compounds:

Like halogens, hydrogen readily combines with non–metals such as carbon, silicon, nitrogen etc. to form covalent compounds.

With hydrogen:	CH_4 Methane	SiH_4 Silane	NH_3 Ammonia
With halogens:	CCl_4 Carbon tetrachloride	$SiCl_4$ Silicon tetrachloride	NCl_3 Nitrogen trichloride

2 ALKALI METALS

All elements of group 1 are typical metals. These are referred to as alkali metals since they react with water to form highly alkaline substances. Francium is a radioactive element and its longest isotope has a half–life of 21 minutes. So very little is known about this element but in its properties it resembles with Cs and therefore has been placed in group I.

2.1 PHYSICAL PROPERTIES

We shall confine our discussion to only first five members of the family of alkali metals as very little is known about the last member, namely Francium.

A correlation between atomic and physical properties are discussed. Attempt has been made to explain the physical properties of alkali metals on the basis of two facts:

(a) Size of the alkali metal atoms and ions.
(b) Loose binding of electrons.

I. MELTING POINT AND BOILING POINT

All these elements are soft and have low melting point. This is due to the fact that they have only one valence electron per metal atom. Hence, the energy binding the atoms in the crystal lattice of the metal is relatively low. The melting points invariably decrease in moving down the group from Li to Cs. Thus, the melting point decreases with increase in size.

The boiling point also decreases in the same order as the melting point.

II. IONIZATION ENERGY

The first ionisation energies for the atoms in this group are appreciably lower than those for any other group in the periodic table. The atoms are very large so the outer electrons are only held weakly by the nucleus hence the amount of energy needed to remove the outer electron is not very large. On descending the group from Li to Cs, the size of the atoms increases, the outermost electrons become less strongly held and so the ionisation energy decreases.

The second ionisation energy, that is, the energy to remove a second electron from the atoms is extremely high. The second ionisation energy is always larger than the first, often by a factor of two, because in involves removing an electron from a smaller positive ion, rather than from a larger neutral atom. The difference between first and second ionisation energies is much larger in this case since in addition it corresponds to removing an electron from a closed shell. A second electron is never removed under normal conditions, as the energy required is greater than that needed to ionise the noble gases. The elements commonly form M^+ ions.

III.ELECTRONEGATIVITY

The electronegativity values for the elements in this group are very small, in fact the smallest values of any element. Thus, when these elements react with other elements to form compounds, a large electronegativity difference between the two atoms is probable and ionic bond is formed. However, *these elements also show covalent bonding* in certain cases. For example, the vapour of alkali metals contain diatomic molecules such as Na_2, Cs_2, which are covalently bonded. The strength of covalent bond in diatomic molecules decreases down the group.

IV. PHOTOELECTRIC EFFECT AND COLOURATION TO THE FLAME

A result of the low ionisation energies is that when these elements are irradiated with light, the light energy absorbed may be sufficient to make an atom lose an electron. Electrons emitted in this way are called photoelectrons and this explains the use of caesium and potassium as cathodes in photoelectric cells.

Electrons may also be quite readily excited to a higher energy level, for example in the flame test. To perform this test, a sample of the metal chloride, or any salt of the metal moistened with concentrated HCl, is heated on a platinum or nichrome wire in a Bunsen burner flame. In general chlorides are more volatile than most of other solids.

$$\text{M–Chlorides} \xrightarrow{\Delta} \text{dissociate to atoms (not ions)}$$

When an alkali metal or any of its compounds is heated in burner flame, the e^-s get excited to higher energy levels. When these electrons return to their original (ground level), the excitation energy which had been absorbed by then is released in the form of light, in the visible region of the spectrum. Now for the same excitation energy, the energy level to which the electron in Li rises is lower than that to which the electron in Na rises and this in turn, is lower than the level to which the electron in K rises and so on. These differences are on the account of differences in ionisation energy emitted in the bunsen flame will be minimum in the case of Li. It increases in the order from lithium to Cs. Thus, the colour of the flame is crimson red in the case of Li, yellow in the case of Na, violet in the case of K and almost same in the case of Rb and Cs. The colours are specific as they correspond to the definite frequency.

V. COLOUR OF COMPOUNDS

Colour arises because the energy absorbed or emitted in electronic transitions corresponds to a wavelength in the visible region. The group I metal ions all have noble gas configurations in which all the electrons are paired. Thus promoting an electron requires some energy to unpair an electron, some to break a full shell of electrons and some to promote the electron to a higher level. The total energy is large: hence there are no suitable transitions and the compounds are typically white. Any transitions, which do occur, will be of high energy, will appear in the ultraviolet region rather than in the visible region and will be invisible to the human eye. Compounds of Group I metals are typically white except those where the anion is coloured, for example sodium chromate $Na_2[CrO_4]$ (yellow), potassium dichromate $K_2[Cr_2O_7]$ (orange) and potassium permanganate $K[MnO_4]$ (deep purple). In these cases the colour comes from the anions $[CrO_4]^-$, $[Cr_2O_7]^{2-}$ or $[MnO_4]^-$ and not from the group I metal ion.

VI. HIGH LUSTRE

This can also be explained due to the presence of highly mobile electrons of the metallic lattice. When the light wave interacts with the electrons of the metal and gets these in oscillatory motion. Like any other moving charged object, these moving electrons radiate electromagnetic energy as light. In other words, the beam of light is reflected from the metal surface.

TRENDS IN PHYSICAL PROPERTIES OF Gr–IA ELEMENTS

Some physical constants of alkali metals are listed in given table

Property	**Element**				
	Li	Na	K	Rb	Cs
Atomic (metallic) radius, (pm)	155	190	236	248	267
Covalent radius, (pm)	123	154	203	216	235
Ionic radius, M^+ (pm)	60	95	133	148	169
Melting point, (K)	453.6	370.9	336.8	312.0	301.8
Boiling point, (K)	1603	1165	1033	961	943
Ionization enthalpy, (kJ/mol)	520.3	495.5	418.9	403.0	375.7
Density, (kg/L)	0.534	0.972	0.859	1.525	1.903
Electronegativity	1.0	0.9	0.8	0.8	0.7
E°, (V)	–3.05	–2.71	–2.92	–2.92	–2.92
Flame colour	Crimson red	Golden yellow	Violet	Violet	Violet
Oxidation state	+1	+1	+1	+1	+1
Hydration enthalpy, (kJ mol^{-1})	–520	– 405	– 321	– 300	– 277

VII. LATTICE ENTHALPY OF ALKALI METAL COMPOUNDS

Lattice enthalpies ($\Delta_L H°$) of alkali metal salts are very high. The lattice enthalpy decreases (in magnitude) down the group from Li to Cs.

Salt	**Lattice enthalpy (kJ mol^{-1})**	**Salt**	**Lattice enthalpy (kJ mol^{-1})**
LiCl	840	NaF	914
NaCl	770	NaCl	770
KCl	701	NaBr	728
RbCl	682	NaI	680
CsCl	630		

The change in enthalpy when one mole of any crystalline solid is completely separated into its constituent units (ions if the solid is ionic and molecule if the solid is molecular) in the gaseous form under standard conditions is called lattice enthalpy ($\Delta_L H°$). For example, the enthalpy change for the reaction,

$$M^+X^-(s) \longrightarrow M^+(g) + X^-(g) \quad \Delta_rH = \Delta_LH°$$

is called the lattice enthalpy of $M^+X^-(s)$. As per definition lattice enthalpy is a positive quantity. Compounds of alkali metals are ionic in nature. These compounds consist of cations and anions arranged in space around each other, which are held together by strong columbic forces. Therefore, lattice enthalpies of alkali metal salts are very high.

Lattice enthalpy of any salt depends directly upon the product of the charges on the cation and anion and inversely on the sum of ionic radii ($r_+ + r_-$). So, for a salt of particular type, the lattice enthalpy will be lower for bigger ions. That is why, the magnitude of the lattice enthalpy decreases in going from Li to Cs.

2.2 CHEMICAL PROPERTIES

We shall confine our discussion to only first five members of the family of alkali metals as very little is known about the last member, namely Francium.

Alkali metals are highly reactive. This is due to,

(a) their low ionisation enthalpies

(b) their low enthalpy of atomisation.

The reactivity of alkali metals increases down the group, i.e. from Li to Cs. Some typical chemical reactions of alkali metals are described below.

Action of air:

Alkali metals react with air or oxygen rapidly and get tarnished due to the formation of oxide layer on the surface. Lithium when burnt in oxygen gives lithium monoxide.

$$4Li + O_2 \xrightarrow{\Delta} 2Li_2O$$

lithium monoxide

$$2Na + O_2 \xrightarrow{\Delta} Na_2O_2$$

sodium peroxide

$$M\ (= K, Rb, Cs) + O_2 \xrightarrow{\Delta} MO_2$$

superoxide

The peroxides (O_2^{2-}) and superoxides (O_2^-) are strong oxidising agents and react with water to give H_2O_2 and O_2.

COMPOUNDS OF ALKALI ELEMENTS

I. OXIDES, PEROXIDES AND SUPEROXIDES

The nature of the alkali metal plays an important role when they are burnt in O_2.

(i) Li when burnt in Cs forms mainly lithium monoxide (O^{-2}).

$$4Li + O_2 \longrightarrow 2Li_2O \text{ (ionic)}$$

(Lithiummonoxide)

Tiny lithium ion has a strong positive field around it, which on combination with oxide anion restricts the spread of negative charge towards another oxygen atom and thus prevents the formation of higher oxide.

(ii) Na forms peroxide $(O_2)^{-2}$ on burning in O_2.

$$2Na + O_2 \longrightarrow Na_2O_2$$

The positive field around Na^+ is too weak to prevent the conversion of the oxide anion (O^{2-}) to a peroxide ion (O_2^{2-}) but is strong enough to prevent further oxidation to a superoxide ion.

(iii) Other alkali metals react with O_2 to form superoxides of the type $MO_2 (O_2^-)$

$$K + O_2 \longrightarrow KO_2$$

Potassium superoxide

The weak field around larger unipositive ions of potassium, rubidium and cesium allow the superoxide ion O_2^- to be formed.

The superoxide have the tetrahedral lattice of calcium carbide in which anion containing $3e^-$ bonds makes it paramagnetic and coloured. These oxides are usually basic.

$$Li_2O + H_2O \longrightarrow 2LiOH$$
$$Na_2O + H_2O \longrightarrow 2NaOH$$
$$K_2O + H_2O \longrightarrow 2KOH$$

Two factors are, for the responsible of hydroxide ion formation.

(a) Polarity of bond:

Greater the polarity of bond, greater is the ease of ionisation. The alkali metal hydroxides M–OH don't greatly differ in polarity. This factor is not of much significance here.

(b) The internuclear distance between the oxygen of the hydroxide and metal ion.

Since the cation size increases from Li to Cs, hence internuclear distance increases with increasing atomic number of the metal. This results in greater separation of hydroxide ion from the metal ion. The strength of the bases increases from LiOH to Cs–OH.

$$Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$$

Superoxides are even stronger oxidizing agents than peroxides and give both H_2O_2 and O_2 with either water or acids.

$$KO_2 + 2H_2O \longrightarrow KOH + H_2O_2 + \frac{1}{2}O_2$$

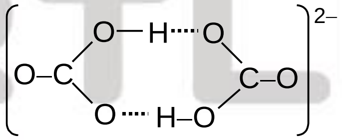
KO_2 is used in space capsules, submarines and breathing masks, because both of it produces oxygen and removes carbon dioxide. Both functions are important in life support systems.

II. OXOSALTS – CARBONATES, BICARBONATES

Group I metals are highly electropositive and thus very strong bases and have quite stable oxosalts. The carbonates are remarkably stable and will melt before they eventually decompose into oxides at temperatures above 1000°C. Li_2CO_3 is considerably less stable and decomposes more readily.

Because group I metals are so strongly basic, they also form solid bicarbonates (also called hydrogen carbonates). No other metals form solid bicarbonates, though NH_4HCO_3 also exists as a solid. Bicarbonates evolve carbon dioxide and turn into carbonates on gentle warming. This is one test for bicarbonates in qualitative analysis. The crystal structures of $NaHCO_3$ and $KHCO_3$ both show hydrogen bonding, but are different.

In $NaHCO_3$ the HCO_3^- ions are linked into an infinite chain, whilst in $KHCO_3$ a dimeric anion is formed.



Lithium is exceptional in that it does not form a solid bicarbonate, though $LiHCO_3$ can exist in solution. All the carbonates and bicarbonates are soluble in water.

III. HALIDES

Alkali metals react vigorously with halogens to form metal halides of the general formula MX. Alkali metal halides are ideal ionic compounds i.e. their physical and chemical properties can be interpreted with reasonable accuracy on the assumption that ions are present in solid state. Therefore, the structure and stability of alkali metal halides are determined in part by the lattice energies and radius ratio effects as discussed below:

SOLUBILITY

LiF is insoluble in water where as other alkali metals are soluble. This is because very small Li^+ is in combination with F^-. This results in high lattice energy of Li–F and thus it does not dissolve in H_2O. The solubility of most of the salts of Group I elements in water decreases on descending the group. For a substance to dissolve the energy evolved when the ions are hydrated (hydration energy) must be larger than the energy required to break the crystal lattice (lattice energy). Conversely, if the solid is insoluble, the hydration energy is less than the lattice energy. Strictly in the two cycles shown in given figure we should use Gibbs free energy ΔG values. In particular, the lattice energy is an enthalpy $\Delta H°$ term and we should use $\Delta G°$ the standard free energy for converting the crystalline salt into gaseous ions an infinite distance apart. However, the two terms differ only by a small term for the entropy of vaporization of the ions. It should in principle be possible to predict solubilities from lattice energies and hydration energies. In practice there are difficulties in predicting solubilities because the values for the data are not known very accurately and the result depends on a small difference between two large values.

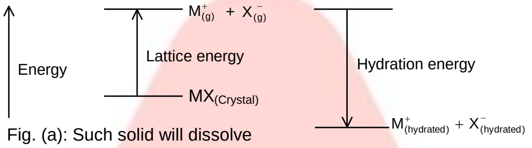


Fig. (a): Such solid will dissolve

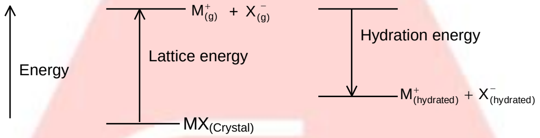


Fig. (b): Such solid will be insoluble

The reason why the solubility of most group I metals decreases on descending the group is that the lattice energy only changes slightly, but the free energy of hydration changes rather more. For example, the difference in lattice energy between NaCl and KCl is 67 kJ mol^{-1} and yet the difference in $\Delta G_{(hydration)}$ for Na^+ and K^+ is 76 kJ mol^{-1}. Thus KCl is less soluble than NaCl.

The group I fluorides and carbonates are exceptional in that their solubilities increase rapidly on descending the group. The reason for this is that their lattice energies change more than the hydration energies on descending the group. The lattice energy depends on electrostatic attraction between ions and is proportional to the distance between the ions, that is proportional to $1/(r^+ + r^-)$. It follows that the lattice energy will vary most when r^- is small, that is with F^- and will vary least when r^+ is large (with I^-). The weight of solute dissolving does not provide a very useful comparison of the solubilities, because the molecular weights differ. The easiest way to compare the number of ions is to compare the solubilities as molar quantities.

IV. SODIUM HYDROXIDE, (NaOH)

Sodium hydroxide is commonly called caustic soda because of its corrosive action on animal and vegetable tissues. Large quantity of sodium hydroxide is now–a –days prepared by electrolytic process. There are two electrolytic methods commonly used for preparing sodium hydroxide.

Castner–Kellner Cell

Cathode: $Na^+ + e^- \xrightarrow{Hg} Na(Hg)$
(sodium amalgam)
Anode: $Cl^- \longrightarrow \frac{1}{2} Cl_2 + e^-$

Castner–Kellner Cell

Some typical chemical reaction given by sodium hydroxide are given below:

NaOH:

with amphoteric oxides $2NaOH + Al_2O_3 \longrightarrow 2NaAlO_2 + H_2O$
with metals $Zn + 2NaOH \longrightarrow Na_2ZnO_2 + H_2$
with non–metals $Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$

SOLUTION OF METALS IN LIQUID AMMONIA

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

1. Its colour, which is independent of the metal.
2. Its density, when is similar to that at pure NH_3.
3. Its conductivity, which is in the same range as those of other electrolytes in NH_3.
4. Its paramagnetism indicating unpaired electrons.
5. Its reversible nature.
6. Its strong reducing nature. This has been interpreted in terms of ionisation of alkali metal to form alkali metal cations and electrons which are solvated by ammonia.

$$M \xrightarrow[(x+y)NH_3]{\text{dissolve in}} M^+(NH_3)_y + [e(NH_3)_x]^-$$

The dissociation into cation and electron accounts for the electrical conductivity. The dilute solutions thus consist of free e^-s (thus showing reducing behaviour); such solutions are metastable and when catalysed give hydrogen and amide.

The bronze solutions show the following characters.

1. Bronze colour with a metallic lustre.
2. Very low densities
3. Conductivities in the range of metals

SODIUM

EXTRACTION OF SODIUM

Alkali metals are strong reducing agents and therefore, cannot be extracted by reducing their oxides or other compounds. Sodium and potassium are therefore, obtained by electrolytic reduction of their molten hydroxides or chlorides. The extraction of sodium metal is described below.

(a) Castner's process:

By the electrolysis of fused caustic soda.

The various reactions taking place during electrolysis are represented below:

$$NaOH \xrightarrow{\text{melting}} Na^+ + OH^- \ \text{(dissociation)}$$

At cathode: $Na^+ + e^- \longrightarrow 2Na$

At anode: $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

(b) Down's process:

By the electrolysis of fused sodium chloride. Sodium chloride melts at higher temperature (1085 K). To lower the melting temperature of sodium chloride generally a mixture of $NaCl$ (40%) and $CaCl_2$ (60%) or a mixture containing sodium chloride, potassium chloride and potassium fluoride ($NaCl + KCl + KF$) is employed. These mixtures melt at about 850–875 K.

$$2NaCl \xrightarrow{\text{melting}} 2Na^+ + 2Cl^-$$

At cathode: $2Na^+ + 2e^- \longrightarrow 2Na$

At anode: $2Cl^- \longrightarrow Cl_2 + 2e^-$

CHEMICAL PROPERTIES OF SODIUM

Action of air:

Sodium remains unaffected by dry air but gets readily tarnished in moist air forming a film of oxide, which reacts with moisture giving sodium hydroxide and finally carbonate

$$4Na + O_2 \longrightarrow 2Na_2O \xrightarrow{+2H_2O} 4NaOH \xrightarrow{+2CO_2} 2Na_2CO_3 + 2H_2O$$

Sodium hydroxide is a strong alkali

Action with non–metals

Sodium combines directly with hydrogen, sulphur, halogens and other non–metals on heating.

With hydrogen: $2Na + H_2 \xrightarrow{365^\circ C} 2NaH$

sodium hydride (an ionic hydride)

Action with mercury

With mercury, sodium forms amalgams of varying composition, e.g. $NaHg$, Na_2Hg, Na_3Hg etc.

Solubility in liquid ammonia

Sodium dissolves in liquid ammonia to give conducting, blue–coloured solution. Blue colour of the solution is due to the presence of ammoniated electrons in solutions.

$$Na + (n + m)\, NH_3 \longrightarrow Na^+(NH_3)_m + e^-\,(NH_3)_n$$

Some important compounds of sodium

- Sodium peroxide
- Sodium carbonate
- Sodium bicarbonate
- Sodium hydroxide

Oxidising property

Sodium peroxide is a very powerful oxidising agent. It oxidises SO_2 to SO_3, manganese(II) salts to manganates, chromium(III) salts to chromates etc.

(a) $4Na_2O_2 + 2Mn(OH)_2 \longrightarrow 2Na_2MnO_4 + 4NaOH$

(b) $3Na_2O_2 + 3H_2O \longrightarrow 6NaOH + 3O$

$$\begin{array}{l}
2Cr(OH)_3 + 4NaOH + 3O \longrightarrow 2Na_2CrO_4 + 5H_2O \\
\hline
2Cr(OH)_3 + 3Na_2O_2 \longrightarrow 2Na_2CrO_4 + 2NaOH + 2H_2O \\
\hline
\end{array}$$

Uses of sodium peroxide

Sodium peroxide is a very strong oxidising agent. It reacts with organic compounds violently.
Sodium peroxide is widely used as a bleaching agent for wool, silk, hair,
bones etc.

Sodium carbonate exists as anhydrous salt (Na_2CO_3) and also as a hydrated salt.
The decahydrate ($Na_2CO_3.10H_2O$) is known as washing soda. The anhydrous salt is called soda ash.

Manufacture of sodium carbonate

Sodium carbonate is manufactured by the Solvay or Ammonia–soda process.

Principle

When carbon dioxide is passed into a concentrated solution of brine saturated with ammonia, ammonium bicarbonate is produced,

$$NH_3 + H_2O \longrightarrow NH_4OH$$

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$NH_4OH + H_2CO_3 \longrightarrow \underset{\text{ammonium bicarbonate}}{NH_4HCO_3} + H_2O$$

The ammonium bicarbonate then reacts with common salt forming sodium bicarbonate,

$$NH_4HCO_3 + NaCl \longrightarrow \underset{\text{sodium bicarbonate}}{NaHCO_3} + NH_4Cl$$

Sodium bicarbonate being slightly soluble (in presence of sodium ions) gets precipitated. The precipitated sodium bicarbonate is removed by filtration and changed into sodium carbonate by heating.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$$

The mother liquor remaining after the precipitation of sodium bicarbonate contains ammonium chloride. This is then heated by steam with milk of lime to regenerate ammonia, which can be used as one of the raw materials.

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O + 2NH_3$$

(i) Saturating the ammoniating tank

In this tank, ammonia gas mixed with a little carbon dioxide gas (from ammonia recovery tower) is bubbled through a 20% sodium chloride solution (brine). Impurities of calcium and magnesium salts present in brine are precipitated as carbonates or hydroxides.

$$2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3$$
$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3\downarrow + 2NH_4Cl$$
$$MgCl_2 + 2NH_4OH \longrightarrow Mg(OH)_2\downarrow + 2NH_4Cl$$
$$MgCl_2 + (NH_4)_2CO_3 \longrightarrow MgCO_3\downarrow + 2NH_4Cl$$

The ammonia that escapes absorption in the saturating tank is absorbed by ammonia absorption tower fitted at the top of the saturating tank.

(ii) Carbonating tower

In this tower carbonation of ammoniacal brine is carried out on the principle of counter–current. The clear ammoniacal brine solution is pumped to the top of the tower which flows downward and meets a current of carbon dioxide (obtained from a lime kiln) introduced from the bottom of the tower at a pressure of 1–2 atmosphere. As a result of reaction shown below, ammonium chloride and crystals of sodium bicarbonate are formed.

$$NH_3 + CO_2 + H_2O \longrightarrow NH_4HCO_3$$
$$2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 + H_2O + CO_2 \longrightarrow 2NH_4HCO_3$$
$$NH_4HCO_3 + NaCl \longrightarrow \underset{\text{white crystal}}{NaHCO_3} + NH_4Cl$$

These crystals remain suspended in the mother liquor giving rise to thick milky liquid.

3 ALKALINE EARTH METALS

The elements are known as alkaline earth metals because:

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

(ii) The name "earth" was given by chemists to substance like alumina, which remained unchanged even on heating. Calcium and barium oxides could stand very high temperatures and hence they were also called "earths". Thus, the metal Ca, Ba and Sr come to be known as alkaline earth metals. The name is now applied to all elements of group II A.

The oxides and hydroxides are less basic than those of group I, hence their oxosalts (carbonates, sulphates, nitrates) are less stable to heat.

Loose binding of 's' electrons are responsible for the following properties:

(i) Formation of bipositive ions
(ii) Reducing agents
(iii) Colouration to the flame.

3.1 REDUCING AGENTS

The high negative value of standard electrode potential indicate that in aqueous solution these elements are good reducing agents quite comparable to alkali metals and this is due to their great hydration energies. The high negative E° values of these elements mean that all react vigorously with water also.

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

3.2 COLORATION TO THE FLAME EXCEPT Be AND Mg

The chlorides of these elements produce characteristic flames due to easy excitation of electrons to higher energy levels.

In case of Be and Mg, the excitation energy is very high (because of their high I.E) and their salts don't impart any colour to the flame. The flame spectra of alkaline earth metals are more complex than those of the alkali metals because their atoms have two 's' electrons, which are "excitable" at flame temperatures where as alkali metals have only single 's' electron which is "excitable" at flame temperature.

3.3 CONDUCTORS OF HEAT AND ELECTRICITY

In the metallic state, the two 's' electrons resonate and thus form covalent bonds between each atom and its nearest neighbour (roughly 12 in number) in the crystal lattice. These electrons can move through the crystal lattice under the influence of electrical potential. Consequently, elements are good conductors of heat and electricity.

3.4 SIZE OF ATOMS AND IONS

Group II atoms are large, but are smaller than the corresponding group I elements as the extra charge on the nucleus draws the orbital electrons in. Similarly the ions are large, but are smaller than those of group I, especially because the removal of two orbital electrons increases the effective nuclear charge even further. Thus, these elements have higher densities than group I, metals.

Group II metals are silvery white in colour. They have two valency electrons that may participate in metallic bonding, compared with one electron for Group I metals. Consequently Group II metals are harder, have higher cohesive energy and have much higher melting points and boiling points than Group I elements, but the metal are relatively soft. The melting points do not vary regularly, mainly because the metals adopt different crystal structures.

The metal bond strength (as is evident from heat of atomisation) diminishes with increasing atomic

Property	**Element**					
	Be	Mg	Ca	Sr	Ba	Ra
Covalent radius, (pm)	90	136	174	191	198	–
Melting point, (K)	1550	923	1111	1036	987	973
Boiling point (K)	1773	1380	1713	1653	1810	–
Ionisation enthalpy $\Delta_I H_1$,	899.5	737.7	590.2	547.5	502.9	509.4
(kJ mol^{-1}) $\Delta_I H_2$	1757.1	1450.7	1145.4	1064.3	965.2	979.1
Density, (kg L^{-1})	1.84	1.74	1.55	2.54	3.75	6.00
Electronegativity	1.5	1.2	1.0	1.0	0.9	0.9

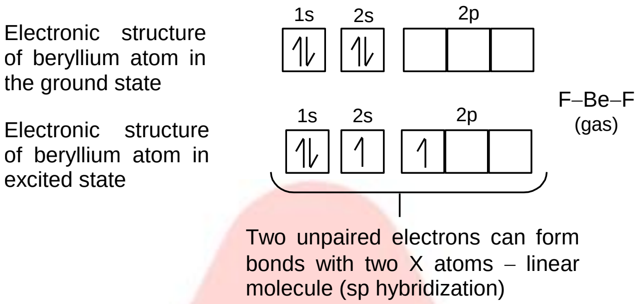
3.5 ANOMALOUS BEHAVIOUR OF BERYLLIUM

Be differs from the rest of the group for three reasons.

1. It is extremely small and Fajan' rules state that small highly charged ions tend to form covalent compounds.
2. Be has a comparatively high electronegativity. Thus when beryllium reacts with another atom, the difference in electronegativity is seldom large, which again favours the formation of covalent compounds. Even BeF_2 (electronegativity difference 2.5) and BeO (electronegativity difference 2.0) show evidence of covalent character.
3. Be is in the second row of the periodic table and the outer shell can hold a maximum of eight electrons. (The orbitals available for bonding are one 2s and three 2p orbitals. Thus Be can form a maximum of four conventional electron pair bonds and in many compounds the maximum coordination number of Be is 4. The later elements can have more than eight outer electrons and may attain a coordination number of 6 using one 's', three 'p' and two 'd' orbitals for bonding. Exceptions occur if multi–centre bonding occurs, as for example in basic beryllium acetate,

when higher coordination numbers are obtained.

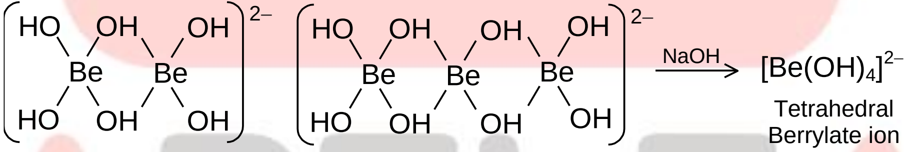
Thus, we should expect Be to form mainly covalent compounds and commonly have a coordination number of 4. Anhydrous compounds of Be are predominantly two–covalent and BeX_2 molecules should be linear.



In fact linear molecules exist only in the gas phase, as this electronic arrangement has not filled the outer shell of electrons. In the solid state four fold coordination is always achieved. There are several ways by which this can be achieved.

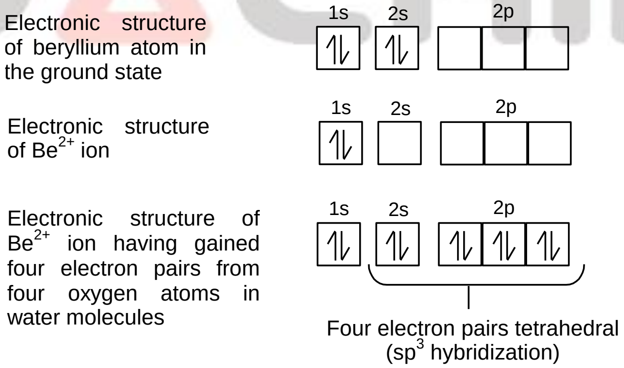
1. Two ligands that have a lone pair of electrons may form coordinate bonds using the two unfilled orbitals in the valence shell of Be. Thus two F^- ions might coordinate to BeF_2, forming $[BeF_4]^{2-}$. Similarly diethyl ether can coordinate to Be(+II) in $BeCl_2$, forming $[BeCl_2(OEt)_2]$.
2. The BeX_2 molecules may polymerise to form chains, containing bridging halogen groups, for example $(BeF_2)_n$, $(BeCl_2)_n$. Each halogen forms one normal covalent bond and uses a lone pair to form a coordinate bond.
3. $(BeMe_2)_n$ has essentially the same structure as $(BeCl_2)_n$, but the bonding in the methyl compound is best regarded as three–centre two electron bonds covering one Me and two Be atoms.
4. A covalent lattice may be formed with a zinc blende or wurtzite structure (coordination number 4), for example by BeO and BeS.

In water beryllium salts are extensively hydrolysed to give a series of hydroxo complexes of unknown structure. They may be polymeric and of the type:



If alkali is added to these solutions, the polymers break down to give the simple mononuclear berrylate ion $[Be(OH)_4]^{2-}$, which is tetrahedral. Many beryllium salts contain the hydrated ion $[Be(H_2O)_4]^{2-}$, which is tetrahedral. Many beryllium salts contain the hydrated ion $[Be(H_2O)_4]^{2+}$ rather than Be^{2+} and the hydrated ion too is a tetrahedral complex ion. Note that the coordination number is 4. Forming a hydrated

complex increases the effective size of the beryllium ion, thus spreading the charge over a larger area. Stable ionic salts such as $[Be(H_2O)_4]SO_4$, $[Be(H_2O)_4](NO_3)_2$ and $[Be(H_2O)_4]Cl_2$ are known.



Beryllium salts are acidic when dissolved in pure water because the hydrated ion hydrolyses producing H_3O^+. This happens because the Be–O bond is very strong and so in the hydrated ion this weakens the O–H bonds and hence there is a tendency to lose protons. The initial reaction is

$$H_2O + [Be(H_2O)_4]^{2+} \rightleftharpoons [Be(H_2O)_3(OH)]^+ + H_3O^+$$

but this may be followed by further polymerization, involving hydroxobridged structures.

In alkaline solutions $[Be(OH)_4]^{2-}$ is formed. The other group II salts do not interact so strongly with water and do not hydrolyse appreciably.

Beryllium salts rarely have more than four molecules of water of crystallization associated with the metal ion, because there are only four orbitals available in the second shell of electrons, whereas magnesium can have a coordination number of 6 by using some 3d orbitals as well as 3s and 3p orbitals.

3.6 SOLUBILITY AND LATTICE ENERGY

The solubility of most salts decreases with increased atomic weight, though the usual trend is reversed with the fluorides and hydroxides in this group. Solubility depends on the lattice energy of the solid and the hydration energy of the ions. With most compounds, on descending the group, the hydration energy decreases more rapidly than the lattice energy; hence the compounds become less soluble as the metal gets larger. However, with fluorides and hydroxides the lattice energy decreases more rapidly than the hydration energy and so their solubility increases on descending the group.

3.7 SOLUTIONS OF THE METALS IN LIQUID AMMONIA

These metals, all dissolve in liquid ammonia as do the group I metals. Dilute solutions are bright blue in colour due to the spectrum from the solvated electron. These solutions decompose very slowly, forming amides and evolving hydrogen, but the reaction is accelerated by many transition metals and their compounds.

$$2NH_3 + 2e^- \longrightarrow 2NH_2^- + H_2$$

Evaporation of the ammonia from solutions of group I metals yields the metal, but with group II metals evaporation of ammonia gives hexammoniates of the metals. These slowly decompose to give amides.

$$M(NH_3)_6 \longrightarrow M(NH_2)_2 + 4NH_3 + H_2$$

Concentrated solutions of the metals in ammonia are bronze coloured, due to the formation of metal clusters.

3.8 OXIDES AND PEROXIDES

All the elements in this group burn in O_2 to form oxides MO. Be metal is relatively unreactive in the massive form and does not react below 600°C, but the powder is much more reactive and burns brilliantly. The elements also burn in air, forming a mixture of oxide and nitride.

The oxosalts are less stable to heat than the corresponding group I salts because the metals and their hydroxides are less basic than those of group I.

(i) Action of oxygen/air

All the metals of this group (except Be and Mg) are easily oxidised by the atmospheric oxygen. Barium readily inflames in air. All alkaline earth metals have affinity towards oxygen.

$$2M(Be, Mg, Ca) + O_2 \xrightarrow{\text{heat}} \underset{\text{monoxide}}{2MO}$$

$$M(Ba, Sr) + O_2 \xrightarrow{\text{heat}} \underset{\text{peroxide}}{MO_2}$$

(a) Nature of oxides

BeO is amphoteric, MgO is weakly basic, CaO is more basic while SrO and BaO are extremely basic.

(b) Solubility

BeO and MgO are insoluble in water, while the other oxides react with water to give corresponding hydroxides of the type $M(OH)_2$, viz,

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

BeO and MgO are insoluble in water due to their large lattice enthalpies.

$Be(OH)_2$ $Mg(OH)_2$ $Ca(OH)_2$ $Sr(OH)_2$ $Ba(OH)_2$
amphoteric strongly basic

Base strength increases ⟶

Be and Al dissolve in strong alkalies liberating hydrogen and forming beryllates and aluminates.

$$Be + 2NaOH \longrightarrow \underset{\text{sodium beryllate}}{Na_2BeO_2} + H_2$$

$$2Al + 2NaOH + 2H_2O \longrightarrow \underset{\text{sodium aluminate}}{2NaAlO_2} + 3H_2$$

3.9 SULPHATES

The sulphates of alkaline earth metals are less soluble than the sulphate of corresponding alkali metal. The solubility of the sulphates of alkaline earth metals decreases in going down the group. The solubilities of these sulphates in water follow the order,

$BeSO_4$ $MgSO_4$ $CaSO_4$ $SrSO_4$ $BaSO_4$ $RaSO_4$
readily soluble slightly soluble almost insoluble

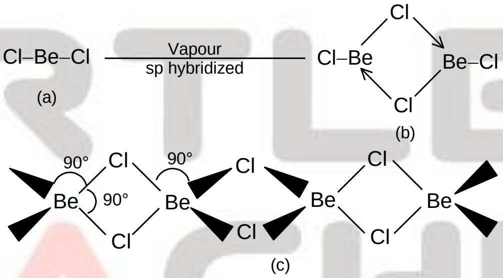
——— Base strength increases ⟶

The lattice enthalpies of alkaline earth metal sulphates are higher than those of the alkali metal sulphates. This is why the sulphates of alkaline earth metals are less soluble than those of alkali metals.

On moving down the group, the hydration energy becomes smaller and therefore, the solubility of sulphates of alkaline earth metals decreases down the group.

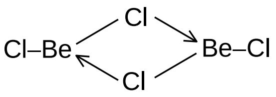
3.10 HALIDES

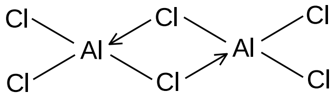
The anhydrous halides are polymeric. Beryllium chloride vapour contains $BeCl_2$ and $(BeCl_2)_2$, but the solid is polymerised. Though the structure of the $(BeCl_2)_n$ polymer is similar to that for $(BeH_2)_n$, the bonding is different. Both show clustering, but the hydride has three–centre bonding. Whereas the halides have halogen bridges, in which a halogen atom bonded to one beryllium atom uses a lone pair of electrons to form a coordinate bond to another beryllium atom.



Beryllium fluoride is very soluble in water, owing to the high solvation energy of Be in forming $[Be(H_2O)_4]^{2+}$. The other fluorides MF_2 are all almost insoluble.

Both $BeCl_2$ and Al_2Cl_6 are covalent and have a bridged polymeric structure. Both these chlorides are soluble in organic solvents and act as strong Lewis acid.





$BeCl_2$ can also polymerise in two dimensional plane an $(BeCl_2)_n$.

If magnesium chloride hydrate is heated strongly, it hydrolyses to yield magnesium oxide (magnesia) which is a refractory material and not the anhydrous magnesium chloride.

$$MgCl_2.6H_2O \xrightarrow{heat} MgO + 2HCl + 5H_2O$$

$$MgO + C + Cl_2 \xrightarrow{\Delta} MgCl_2 + CO(g)$$

Magnesium chloride upon electrolysis gives magnesium metal at the cathode.

3.11 CARBIDES

The carbides of beryllium (Be) and aluminium (Al) react with water to give

$$Be_2C + 2H_2O \longrightarrow 2BeO + CH_4$$

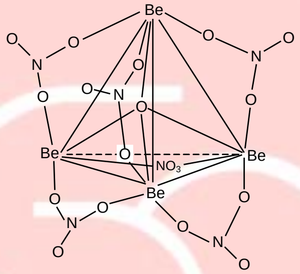
$$Al_4C_3 + 6H_2O \longrightarrow 2Al_2O_3 + 3CH_4$$

3.12 NITRATES

Nitrates of the metals can all be prepared in solution and can be crystallized as hydrated salts by the reaction of HNO_3 with carbonate oxides or hydroxides. Heating the hydrated solids does not give the anhydrous nitrate because the solid decomposes to the oxide. Anhydrous nitrates can be prepared using liquid dinitrogen tetra oxide and ethyl acetate. Beryllium is unusual in that it forms a basic nitrate in addition to the normal salt.

$$BeCl_2 \xrightarrow{N_2O_4(NO_2)_2} Be(NO_3)_2.2N_2O_4 \xrightarrow[\text{under vacuum}]{\text{warm to } 50^\circ C} Be(NO_3)_2 \xrightarrow{125^\circ C} [Be_4O(NO_3)_6]$$

Normal Be nitrate



3.13 COMPLEX FORMATION

Due to similar charge/radius ratio (i.e. cation) both Be^{2+} and Al^{3+} ions form complexes.

For example, beryllium forms tetrahedral complexes, such as BeF_4^{2-}, $[Be(C_2O_4)_2]^{2-}$ and Al forms octahedral complexes such as AlF_6^{3-} and $[Al(C_2O_4)_3]^{3-}$ in solution.

3.14 TEST FOR Mg^{2+} ION

To a solution of any magnesium salt add ammonium hydroxide until it smells of ammonia. Add disodium hydrogen phosphate and scratch the sides of the test tube with a glass rod. Formation of white crystalline magnesium ammonium phosphate confirms the presence of Mg^{2+} in the given solution.

$$MgSO_4 + Na_2HPO_4 + NH_4OH \longrightarrow \underset{\text{white ppt.}}{MgNH_4PO_4\downarrow} + Na_2SO_4 + H_2O$$

3.15 PLASTER OF PARIS $[(2CaSO_4.H_2O)]$

Calcium sulphate with half a molecule of water per molecule of the salt (hemi–hydrate) is called plaster of paris.

Preparation

It is prepared by heating gypsum $CaSO_4.2H_2O$

$$\underset{\text{hemihydrate}}{CaSO_4.\tfrac{1}{2}H_2O} \xrightarrow[\text{setting}]{H_2O} \underset{\text{orthorhombic dihydrate}}{CaSO_4.2H_2O} \xrightarrow[\text{hardening}]{} \underset{\text{gypsum monoclinic dihydrate}}{CaSO_4.2H_2O}$$