Study of Representative Elements (spdf blocks)

Revision Notes on s-Block Elements:

Alkali Metals (Group I elements of modern periodic table):

Poperty		Elements					
		Li	**Na**	**K**	**Rb**	**Cs**	**Fr (Radioactive)**
Atomic Number		3	11	19	37	55	87
Electronic Configuration		2s’	3s’	4s’	5s’	6s’	7s’
Atomic Mass		6.94	22.99	39.10	85.47	13.91	223
Metallic radius (pm)		152	186	227	248	265	375
Ionic radius (M$^+$/pm)		76	102	138	152	167	180
Ionization enthalpy (kJ mol^{-1})	I	520	496	419	403	376	–
	II	7298	3562	3051	2633	2230	–
Electro negativity (Pauling Scale)		0.98	0.93	0.82	0.82	0.79	
Density/g cm^{-3} (at 298K)		0.53	0.97	0.86	1.53	1.90	
Melting point/K		454	371	336	312	302	
Boiling point/K		1615	1156	1032	961	944	
E°(V) at 298K for M$^+$(aq) + e$^-$ → M(s)		–3.04	–2.714	–2.925	–2.930	–2.927	
Occurrence in Atmosphere		18*	227**	1.84**	78.12*	2.6*	

*ppm (parts per million)

** percentage by weight

Physical Properties of Alkali Metals:

- These are soft in nature and can be cut with the help of knife except the lithium.
- The atoms of alkali metals have the largest size in their respective periods.
- The first ionization energy of the alkali metals are the lowest as compared to the elements in the other group.
- The alkali metals show +1 oxidation state.
- The alkali metals have low values of reduction potential (as shown in table-I) and therefore have a strong tendency to lose electrons and act as good reducing agents.
- The melting and boiling points of alkali metals are very low because the intermetallic bonds in them are quite weak.
- ll the alkali metals form ionic (electrovalent) compounds.
- The alkali metals are good conductors of heat and electricity.
- Alkali metals (except Li) exhibit photoelectric effect
- The alkali metals and their salts impart a characteristic colour to flame

	Li	Na	K	Rb	Cs
Color	Crimson Red	Golden Yellow	Pale Violet	Violet	Sky Blue
l/nm	670.8	589.2	766.5	780.0	455.5

Hydroxides of Alkali Metals:

a) All the alkali metals, their oxides, peroxides and superoxides readily dissolve in water to produce corresponding hydroxides which are strong alkalies.

- $2Na + 2H_2O \rightarrow 2NaOH + H_2$
- $Na_2O + 2H_2O$ $2NaOH$
- $Na2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$
- $2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$

b) The basic strength of these hydroxides increases as we move down the group Li to Cs.

c) All these hydroxides are highly soluble in water and thermally stable except lithium hydroxide.

d) Alkali metals hydroxides being strongly basic react with all acids forming salts.

- $NaOH + HCl \rightarrow NacI + H_2O$
- $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

Halides of Alkali metals:

$M_2O + 2HX \rightarrow 2MX + H_2O$

$MOH + HX \rightarrow MX + H_2O$

$M_2CO_3 + 2HX \rightarrow 2MX + CO_2 + H_2O$ (M = Li, Na, K, Rb or Cs)

(X = F, Cl, Br or I)

a) **Standard enthalpies of formation in (kJ/mol^{-1})**

Element	MF	MCl	MBr	MI
Li	-612	-398	-350	-271
Na	-569	-400	-360	-288
K	-563	-428	-392	-328
Rb	-549	-423	-389	-329
Cs	-531	-424	-395	-

b) **Covalent Character:**

- Small cation and large anion favors covalency.
- Order: LiCl > NaCl > KCl > RbCl > CsCl & . LiI > LiBr > LiCl > LiF
- Greater the charge on the cation greater is its polarizing power and hence larger is the covalent character: $Na^+Cl^- < Mg^{+2}Cl_2 < Al^{+3}\ Cl_3$
- Greater the charge on the anion, more easily it gets polarized thereby imparting more covalent character to the compound formed eg covalent character increase in the order. $NaCl < Na_2SO_4 < Na_3PO_4$

c) **Lattice Energies:** Amount of energy required to separate one mole of solid ionic compound into its gaseous ions.

Greater the lattice energy, higher is the melting point of the alkali metals halide and lower is its solubility in water

d) **Hydration Energy:** Amount of energy released when one mole of gaseous ions combine with water to form hydrated ions.

- $M^+ (g) + aq \rightarrow M^+ (aq)$ + hydration energy
- $X^- (g) + aq \rightarrow X^- (aq)$ + hydration energy

Higher the hydration energy of the ions greater is the solubility of the compound in water.

The solubility of the most of alkali metal halides except those of fluorides decreases on descending the group since the decrease in hydration energy is more than the corresponding decrease in the lattice energy.

Due to high hydration energy of Li^+ ion, Lithium halides are soluble in water except LiF which is sparingly soluble due to its high lattice energy.

For the same alkali metal the melting point decreases in the order

fluoride > chloride > bromide > iodide

For the same halide ion, the melting point of lithium halides are lower than those of the corresponding sodium halides and thereafter they decrease as we move down the group from Na to Cs.

The low melting point of LiCl (887 K) as compared to NaCl is probably because LiCl is covalent in nature and NaCl is ionic.

Anomalous Behavior of Lithium and diagonal relationship with Magnesium:

Li has anomalous properties due to

- Very small size
- High polarizing Power

Lithium show diagonal relationship with magnesium because both elements have almost same polarizing power.

- The melting point and boiling point of lithium are comparatively high.
- Lithium is much harder than the other alkali metals. Magnesium is also hard metal.
- Lithium reacts with oxygen least readily to form normal oxide whereas other alkali metals form peroxides and superoxides.
- LiOH like $Mg(OH)_2$ is weak base. Hydroxides of other alkali metals are strong bases.
- Due to their appreciable covalent nature, the halides and alkyls of lithum and magnesium are soluble in organic solvents.
- Unlike elements of group 1 but like magnesium. Lithium forms nitride with nitrogen.$6Li + N_2 \rightarrow 2Li_3N$
- LiCl is deliquescent and crystallizes as a hydrate, $LiCl2H_2O$. Other alkali metals do not form hydrates. also forms hydrate, $MgCl_2.8H_2O$.
- Unlike other alkali metals lithium reacts directly with carbon to form an ionic carbide. Magnesium also forms a similar carbide.

- The carbonates, hydroxides and nitrates of lithium as well as magnesium decompose on heating.
    - $Li_2CO_3 \rightarrow Li_2O + CO_2$
    - $MgCO_3 \rightarrow MgO + CO_2$
    - $2LiOH \rightarrow Li_2O + H_2O$
    - $Mg(OH)_2 \rightarrow MgO + H_2O$
    - $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$
    - $2Mg(NO_3)_2 \rightarrow 2Mg + 4NO_2 + O_2$
- The corresponding salts of other alkali metals are stable towards heat.

Lithium nitrate, on heating, decomposes to give lithium oxide, Li_2O whereas other alkali metals nitrate decomposes to give the corresponding nitrite.

- $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$
- $2NaNO_3 \rightarrow 2NaNO_2 + O_2$
- $2KNO_3 \rightarrow 2KNO_2 + O_2$
- Li_2CO_3, $LiOH$, LiF and Li_3PO_4 are the only alkali metal salts which are insoluble in water. The corresponding magnesium compounds are also insoluble in water.
- Hydrogen carbonates of both lithium and magnesium can not be isolated in solid state. Hydrogen carbonates of other alkali metals can be isolated in solid state.

Sodium Hydroxide (NaOH):

a. Properties

- NaOH is stable towards heat but is reduced to metal when heated with carbon

  $2NaOH + 2C \rightarrow 2Na + 2CO + H_2$
- $FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 + 3NaCl$
- $NH_4Cl + NaOH \rightarrow NaCl + NH_3$ (pungent smell) $+ H_2O$
- $HgCl_2 + 2NaOH \rightarrow HgO$ (yellow powder) $+ 2NaCl + H_2O$
- $Zn(OH)_2 \uparrow + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2Oh$
- $Al_2O_3 \uparrow + 2NaOH \rightarrow 2NaAlO_2 + H_2O$
- $SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$
- $3P + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$
- $2Al + 2NaOH + 2H_2O \rightarrow 3H_2 + 2NaAlO_2$

b. Uses

- It is used in the manufacture of paper, soap and artificial silk.
- It is used in petroleum refining.
- It is used for mercerizing cotton.
- It is used for the preparation of sodium metal and many salts of sodium.

Sodium Carbonate (Washing soda) (Na_2CO_3):

a. Preparation:

Solvay process:

Carbon dioxide gas is bubbled through a brine solution saturated with ammonia and it results in the formation of sodium hydrogen carbonate.

- $NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$
- $NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl$

Sodium hydrogen carbonate so formed precipitates out because of the common ion effect caused due to the presence of excess of NaCl. The precipitated $NaHCO_3$ is filtered off and then ignited to get Na_2CO_3.

$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

b. Properties

1. The aqueous solution absorbs CO_2 yielding sparingly soluble sodium bicarbonate.
    - $Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$
2. Dissolves in acids with an effervescence of carbon dioxide and is causticised by lime to give caustic soda.
    - $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
    - $Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$
3. Fusion with silica, sodium carbonate yields sodium silicate.
    - $Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$
4. Hydrolysis – being a salt of a strong base (NaOH) and weak acid (H_2CO_3), when dissolved in water sodium carbonate. Undergoes hydrolysis to form an alkaline solution
    - $Na_2CO_3 + 2H_2O \rightarrow H_2CO_3 + 2NaOH$

c. Uses

- It is used for softening hard water.
- A mixture of sodium carbonate & potassium carbonate is used as fusion mixture.
- As an important laboratory reagent both in qualitative and quantitative analysis.
- It is used in paper, paints and textile industries.
- It is used for washing purposes in laundry.
- It is used in the manufacture of glass, borax, soap and caustic soda.

Alkali Earth Metals (Group II elements of modern periodic table):

Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra).

- **Physical Properties of Alkali Earth Metals:**

1. **Alkali earth metals are almost similar in properties to the corresponding alkali metals.**
    - Higher melting points than alkali metals
    - Higher boiling points alkali metals
    - Higher densities alkali metals
    - Harder than the corresponding alkali metals

2. **Atomic and ionic radii**

    The atomic radii as well as ionic radii of the members of the family are smaller than the corresponding members of alkali metals.

3. **Ionization energy:** The alkaline earth metals owing to their large size of atoms have fairly low values of ionization energies as compared to the p – block elements. However with in the group, the ionization energy decreases as the atomic number increases. It is because of increase in atomic size due to addition of new shells and increase in the magnitude of screening effect of the electrons in inner shells. Because their $(IE)_1$ is larger than that of their alkali metal neighbours, the group IIA metals trend to the some what less reactive than alkali metals. The general reactivity trend is Ba > Sr > Ca > Mg > Be.

4. **Oxidation state:** The alkaline earth metal have two electrons in their valence shell and by losing these electrons, these atoms acquire the stable noble gas configuration. Thus, unlike alkali metals, the alkaline earth metals exhibit +2 oxidation state in their compounds.

    $M \rightarrow M^{+2} + 2e^-$

    [noble gas]

5. **Characteristic flame colouration:**

Ion	**Colour**
Ca^{2+}	Brick-red
Sr^{2+}	Crimson
Ba^{2+}	Apple green
Ra^{2+}	Carmine – red

Difference between alkali metals and alkali earth metals:

	Properties	Alkaline earth metals	Alkali metals
1.	Electronic configuration	Two electrons are present in the valency shall. The configuration is ns^2 (bivalent)	One electron is present in the valency shell. The configuration is ns^1 (monovalent) more electropositive
2.	Valency	Bivalent	Monovalent
3.	Electropositive nature	Less electropositive	More electropositive
4.	Hydroxides	Weak bases, less soluble and decompose on heating.	Strong bases, highly soluble and stable towards heat.
5.	Bicarbonates	These are not known in free state. Exist only in solution.	These are known in solid state.
6.	Carbonates	Insoluble in water. Decompose on heating.	Soluble in water. Do not decompose on heating ($LiCO_3$ is an exception)
7.	Action of nitrogen	Directly combine with nitrogen and form nitrides	Do not directly combine with nitrogen except lithium
8.	Action of carbon	Directly combine with carbon and form carbides	Do not directly combine with carbon
9.	Nitrates	Decompose on heating evolving a mixture of NO_2 and oxygen	Decompose on heating evolving only oxygen
10.	Solubility of salts	Sulphates, phosphates fluorides, chromates, oxalates etc are insoluble in water	Sulphates, phosphates, fluorides, chromates, oxides etc are soluble in water.
11.	Physical properties	Comparatively harder. High melting points. Diamagnetic.	Soft, low melting points paramagnetic.
12.	Hydration of compounds	The compounds are extensively hydrated. $MgCl_2.6H_2O$, $CaCl_2.6H_2O$, $BaCl_2.2H_2O$ are hydrated chlorides.	The compounds are less hydrated. NaCl, KCl, RbCl form non – hydrated chlorides
13.	Reducing power	Weaker as ionization potential values are high and oxidation potential values are low.	Stronger as ionization potential values are low and oxidation potential values are high.

Chemical Properties of Alkali Earth Metals:

1. Reaction with water :

- $Mg + H_2O \rightarrow MgO + H_2$
- or, $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$
- $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$

2. Formation of oxides and nitrides

- Be + O_2 (air) +Δ→ 2BeO
- 3Be + N2 (air) +Δ → Be_3N_2
- Mg + air + Δ → MgO + Ng_3N_2

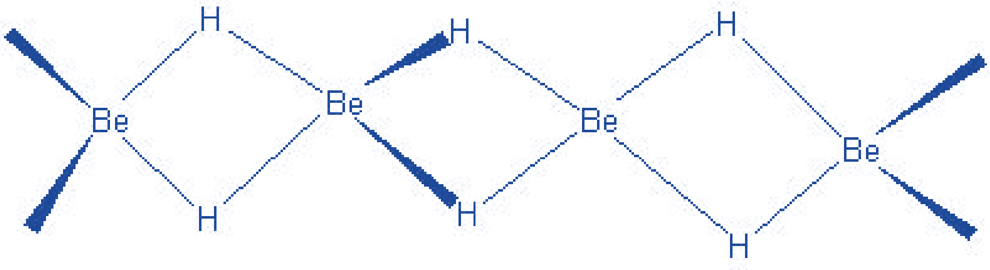
3. Formation of Nitrides

- 3M + N_2 + Δ → M_3N_2
- Be_3N_2 + Δ → 3Be + N_2
- Ba_3N_2 + $6H_2O$ + Δ → 3Ba $(OH)_2$ + $2NH_3$
- Ca_3N_2 + $6H_2O$ + Δ → 3Ca $(OH)_2$ + $2NH_3$

4. Reaction with hydrogen:

M + H_2 + Δ → MH_2

Both BeH_2 and MgH_2 are covalent compounds having polymeric structures in which H – atoms between beryllium atoms are held together by three centre – two electron (3C - 2e) bonds as shown below:



5. Reaction with carbon – (Formation of carbides)

When BeO is heated with carbon at 2175 – 2275 K a brick red coloured carbide of the formula Be_2C is formed

$$2BeO + 2C \xrightarrow{2175-2275K} Be_2C + 2CO$$

It is a covalent compound and react water forming methane.

Be_2C + $4H_2O$ → 2Be $(OH)_2$ + CH_4

6. Reaction with Ammonia:

Like alkali metal, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solution from which ammoniates [M $(NH_3)_6$ $]^{2+}$ can be recovered.

Anamolous Behaviour of Beryllium:

- Be is harder than other members of its group.
- Be is lighter than Mg.
- Its melting and boiling points are higher than those of Mg & other members.
- Be does not react with water while Mg reacts with boiling water.
- BeO is amphoteric while MgO is weakly basic.
- Be forms covalent compounds whereas other members form ionic compounds.
- Beryllium carbide reacts with water to give methane whereas carbides of other alkaline earth metals gives acetylene gas.
  - $Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$
  - $Mg_2C_2 + 2H_2O \rightarrow Mg(OH)_2 + C_2H_2$
  - $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$
- Beryllium does not exhibit coordination number more than four as it has four orbitals in the valence shell. The other members of this group has coordination number

Diagonal relationship of Be with Al:

- Unlike groups – 2 elements but like aluminium, beryllium forms covalent compounds.
- The hydroxides of Be, [$Be(OH)_2$] and aluminium [$Al(OH)_3$] are amphoteric in nature, whereas those of other elements of group – 2 are basic in nature.
- The oxides of both Be and Al i.e. BeO and Al_2O_3 are high melting insoluble solids.
- $BeCl_2$ and $AlCl_3$ have bridged chloride polymeric structure.
- The salts of beryllium as well as aluminium are extensively hydrolysed.
- Carbides of both the metal reacts with water liberating methane gas.
  - $Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$
  - $Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4$
- The oxides and hydroxides of both Be and Al are amphoteric and dissolve in sodium hydroxide as well as in hydrochloric acid.
  - $BeO + 2HCl \rightarrow BeCl_2 + H_2O$
  - $BeO + 2NaOH \rightarrow Na_2BeO_2 + H_2O$
  - $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + H_2O$
  - $Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O$
- Like Al, Be is not readily attacked by acids because of the presence of an oxide film.

Calcium Carbonate ($CaCO_3$):

It occurs in nature as marble, limestone, chalk, coral, calcite, etc. It is prepared as a white powder, known as precipitated chalk, by dissolving marble or limestone in hydrochloric acid and removing iron and aluminium present by precipitating with NH_3, and then adding ammonium carbonate to the solution; the precipitate is filtered, washed and dried.

$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3 + 2NH_4Cl$
It dissolves in water containing CO_2, forming $Ca(HCO_3)_2$ but is precipitated from solution by boiling.

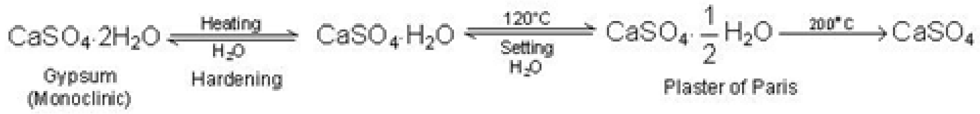
$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca(HCO_3)_2$

Plaster of Paris, $CaSO_4.1/2\ H_2O$ or $(CaSO_4)_2.H_2O$:

It occurs in nature as gypsum and the anhydrous salt as anhydride. It is prepared by precipitating a solution of calcium chloride or nitrate with dilute sulphuric acid.

The effect of heat on gypsum or the dihydrate presents a review of interesting changes. On heating the monoclinic gypsum is first converted into orthorhombic form without loss of water. When the temperature reaches 120°C, the hemihydrate or plaster of paris is the product. The latter losses water, becomes anhydrous above 200°C and finally above 400°C, it decomposes into calcium oxide.

$2CaSO_4 \rightarrow 2CaO + 2SO_2\uparrow + O_2\uparrow$



The addition of common salt accelerates the rate of setting, while a little borax or alum reduces it. The setting of plaster of paris is believed to be due to rehydration and its reconversion into gypsum.

$2CaSO_4.\ 1/2\ H_2O + 3H_2O \rightarrow 2CaSO_4.\ 2H_2O$
Plaster of Paris Gypsum

Uses

- Plaster of pairs is used for producing moulds for pottery and ceramics & casts of statues & busts.
- It is used in surgical bandages used for plastering broken or fractured bones.
- It is also used in dentistry

Industrial uses of lime and Limestone

Uses of lime

- Calcium oxide is called lime or quick lime. It main industrial uses are
- It is used in steel industry to remove phosphates and silicates as slag.
- It is used to make cement by mixing it with silica, alumina or clay.(iii) It is used in making glass.
- It is used in lime soda process for the conversion of Na_2CO_3 to NaOH & vice versa.
- It is used for softening water, for making slaked lime $Ca(OH)_2$ by treatment with water and calcium carbide CaC_2.

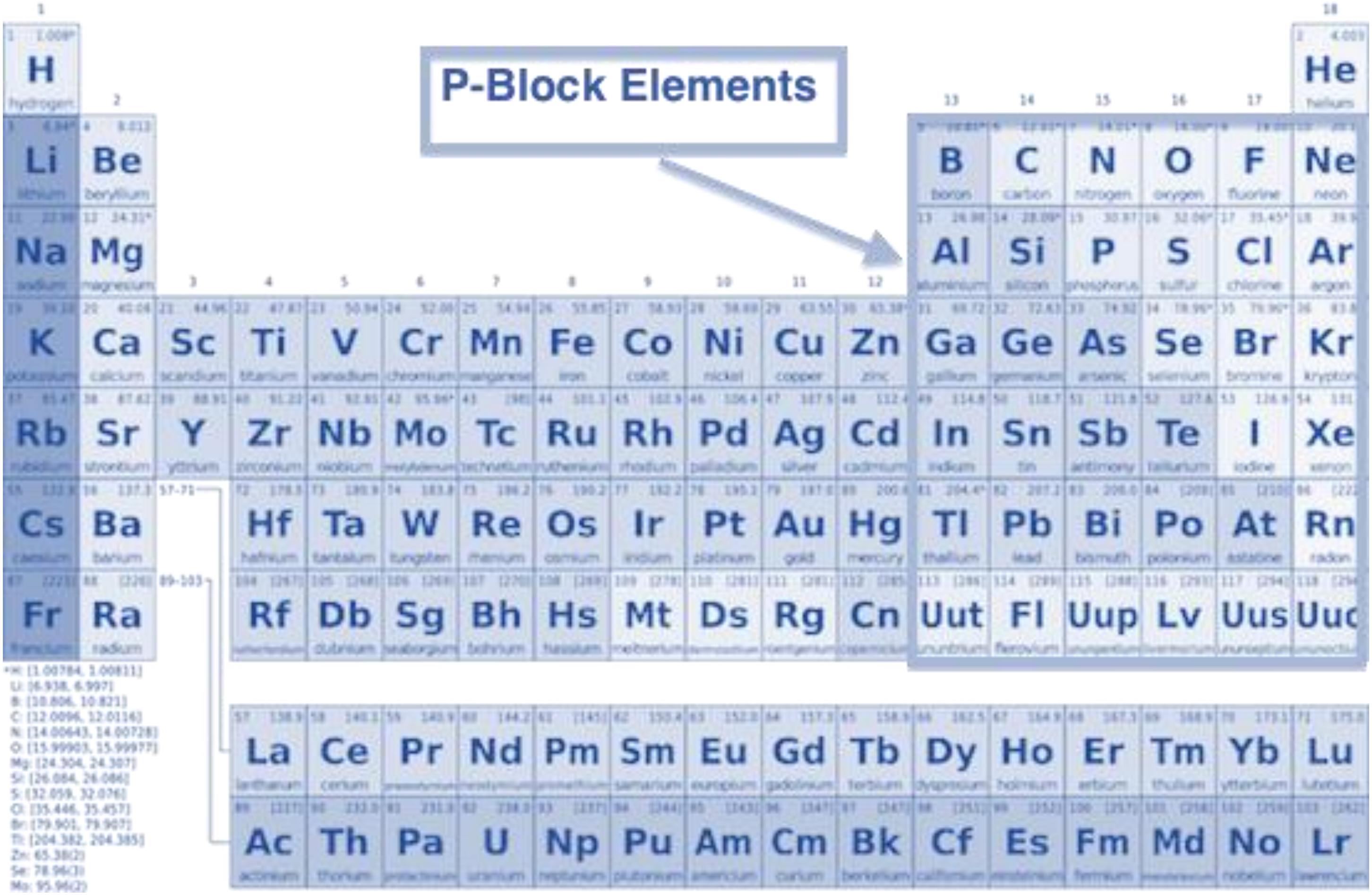
Uses of Slaked lime [$Ca(OH)_2$]

- Slaked lime is used as a building material in form of mortar. It is prepared by mixing 3 – 4 times its weight of sand and by gradual addition of water. Its sets into a hard mass by loss of H_2O and gradual absorption of CO_2 from air.
- In manufacture of bleaching powder by passing Cl_2 gas.
- In making glass and in the purification of sugar and coal gas.
- It is used in softening of hard water.

Uses of lime stone ($CaCO_3$)

- It is used as building material in form of marble.
- In manufacture of quick lime.
- It is used as a raw material for the manufacture of Na_2Co_3 in solvay – ammonia process.
- Commercial limestone contains iron oxide, alumina, magnesia, silica & sulphur with a CaO content of 22 – 56% MgO content upto 21%. It is used as such as a fertilizer.

Revision Notes on p-Block Elements:



Boron Family (Group 13 Elements)

- **Members:** B, Al, Ga, In & Tl
- **Melting Point**: Decreases from B to Ga and then increases up to Tl.
- **Ionization Energies:** 1st <<< 2nd < 3rd
- **Metallic Character:** Increases from B to Tl. B is non-metal

Boron

Preparation of Boron:

- From Boric Acid: $B_2O_3(s) + 3Mg(s) \rightarrow 2B(s) + 3MgO(s)$
- From Boron Trichloride
  - (at 1270 k): $2BCl_3 + 3H_2(g) \rightarrow 2B(s) + 6HCl(g)$
  - (at 900 ^{0}C): $2BCl_3(g) + 3Zn(s) \rightarrow 2B(s) + 3ZnCl_2(s)$
- By electrolysis of fused mixture of boric anhydride (B_2O_3) and magnesium oxide (MgO) & Magnesium fluoride at 1100 ^{0}C
  - $2MgO- \rightarrow 2Mg + O_2(g)$
  - $B_2O_3 + 3Mg \rightarrow 2B + 3MgO$

- By thermal decomposition of Boron hydrides & halides:
  $B_2H_6\,(g) + \Delta \rightarrow 2B(s) + 3H_2\,(g)$

Compounds of Boron:

Orthoboric acid (H_3BO_3)

Preparation of Orthoboric acid

- **From borax** : $Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$
- **From colemanite** : $Ca_2B_6O_{11} + 2SO_2 + 11H_2O \rightarrow 2Ca(HSO_3)_2 + 6H_3BO_3$

Properties of Orthoboric acid

- **Action of Heat**:

$$4H_3BO_3 \xrightarrow[-4H_2O]{373\,k} 4HBO_2 \xrightarrow[-H_2O]{413\,k} H_2B_4O_7 \xrightarrow[-H_2O]{\text{Read heat}} 2B_2O_3$$

Metaboric acid Tetraboric acid Boron trioxide

- **Weak monobasic acidic behavior:**
  $B(OH)_3 \leftrightarrow H_3BO_3 \leftrightarrow H^+ + H_2O +$
  Thus on titration with NaOH, it gives sodium metaborate salt
  $H_3BO_3 + NaOH \leftrightarrow NaBO_2 + 2H_2O$

- **Reaction with Metaloxide:**

$$B(OH)_3 + MO \xrightarrow{\text{Fusion}} M - \text{borates}$$

Where M stands for a bivalent metal

- **Reaction with Ammonium boro fluoride:**

$$B(OH)_3 \xrightarrow[\text{Fusion}]{NH_4HF_2} NH_4BF_4 \xrightarrow[\text{heat}]{B_2O_3} BF_3$$

Ammonium boro fluoride

Borax (sodium tetraborate) $Na_2B_4O_7.\ 10H_2O$

Preparation from Boric Acid

$4H_3BO_3 + Na_2CO_3 \dashrightarrow Na_2B_4O_7 + 6H_2O + CO_2$

Properties of Borax

- **Basic Nature**:-
  Aqueous solution of borax is alkaline in nature due to its hydrolysis
  $Na_2B_4O_7 + 3H_2O \rightarrow NaBO_2 + 3H_3BO_3$
  $NaBO_2 + 2H_2O \rightarrow NaOH + H_3BO_3$

- **Action of heat:**

$$Na_2B_4O_7.10H_2O \xrightarrow[-10H_2O]{heat} Na_2B_4O_7 \xrightarrow{740^{\circ}C} 2NaBO_2 + B_2O_3$$

Diborabe(B_2H_6)

<u>Preparation of Diborane:</u>

Reduction of Boron Trifluoride:

$BF_3 + 3LiAlH_4 \rightarrow 2B_2H_6 + 3\ LiAl\ F_4$

From $NaBH_4$:

$2NaBH_4 + H_2SO_4 \rightarrow B_2H_6 + 2H_2 + Na_2SO_4$

$2NaBH_4 + H_3PO_4 \rightarrow B_2H_6 + 2H_2 + NaH_2PO_4$

Properties of Diborane:

- **Reaction with water**: $B_2H_6 + H_2O \text{-->} 2H_3BO_3 + 6H_2$
- **Combustion:** $B_2H_6 + 2O_2$ --? $B_2O_3 + 3H_2O$ $\Delta H = -2615$ kJ/mol

Compounds of Aluminium:

Aluminium Oxide or Alumina (Al_2O_3)

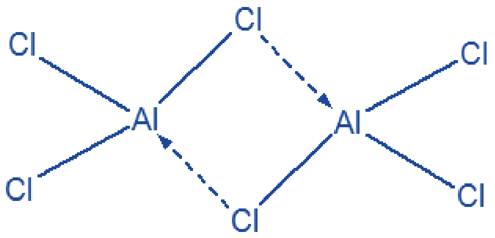
$2Al(OH)_3 + Heat \rightarrow Al_2O_3 + 2H_2O$

$2Al(SO_4)_3 + Heat \rightarrow Al_2O_3 + 2SO_3$

$(NH_4)_2Al_2(SO_4)_3 \cdot 24H_2O \text{-->} 2NH_3 + Al_2O_3 + 4SO_3 + 25\ H_2O$

Aluminum Chloride $AlCl_3$:

Structure of Aluminium Chloride:



<u>Properties of Aluminium Chloride</u>

- White, hygroscopic solid
- Sublimes at 183 ^{0}C
- Forms addition compounds with NH_3, PH_3, $COCl_2$ etc**.**
- Hydrolysis: $AlCl_3 + 3H_2O \text{-->} Al(OH)_3 + 3HCl + 3H_2O$
- Action of Heat: $\mathbf{2}AlCl_3\ .6H_2O \text{-->} 2Al(OH)_3$ à $Al_2O_3 + 6HCl + 3H_2O$

Carbon Family (Group 14 Elements):

- **Members:** C, Si, Ge, Sn, & Pb
- **Ionization Energies:** Decreases from C to Sn and then increases up to Pb.
- **Metallic Character:** C and Si are non metals, Ge is metalloid and Sn and Pb are metals
- **Catenation:** C and Si show a tendency to combine with its own atoms to form long chain polymers

Compounds of Carbon:

Carbon Monoxide

Preparation of Carbon Monoxide

- By heating carbon in limited supply of oxygen: $C + 1/2O_2$ --> CO.
- By heating oxides of heavy metals e.g. iron, zinc etc with carbon.
  - $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$
  - $ZnO + C \rightarrow Zn + CO$
- By passing steam over hot coke: $C + H_2O \rightarrow CO + H_2$ (water gas)
- By passing air over hot coke: $2C + O_2 + 4N_2 \rightarrow 2CO + 4N_2$ (Producer gas)

?Properties of Carbon Monoxide:

- A powerful reducing agent : $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
  $CuO + CO \rightarrow Cu + CO_2$
- Burns in air to give heat and carbon dioxide: $CO + 1/2O_2 \rightarrow CO_2$ + heat.

Tests For Carbon Monoxide:

- Burns with blue flame
- Turns the filter paper soaked in platinum or palladium chloride to *pink or green*.

Carbon di-oxide

Preparation of Carbon di-oxide

- By action of acids on carbonates: $CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O + CO_2$
- By combustion of carbon: $C + O_2 \rightarrow CO_2$

Properties of Carbon di-oxide

- It turns lime water milky $Ca(OH)_2 + CO_2 \rightarrow CaCO_3{}^{-} + H_2O$,
- Milkiness disappears when CO_2 is passed in excess
  $CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$
- Solid carbon dioxide or *dry ice* is obtained by cooling CO2 under pressure. It passes from the soild state straight to gaseous state without liquefying (hence dry ice).

Carbides:

- **Salt like Carbides :** These are the ionic salts containing either C_2^{2-} (acetylide ion) or C^{4-} (methanide ion)e.g. CaC_2, Al_4C_3, Be_2C.
- **Covalent Carbides :** These are the carbides of non-metals such as silicon and boron. In such carbides, the atoms of two elements are bonded to each other through covalent bonds. SiC also known as *Carborundum*.
- **Interstitial Carbides :** They are formed by transition elements and consist of metallic lattices with carbon atoms in the interstices. e.g. tungsten carbide WC, vanadium carbide VC.

Compounds of Silicon:

Sodium Silicate (Na_2SiO_3):

?Prepared by fusing soda ash with pure sand at high temperature:

$Na_2CO_3 + SiO_3 \rightarrow Na_2SiO_3 + CO_2$

Silicones:

Silicon polymers containing Si – O – Si linkages formed by the hydrolysis of alkyl or aryl substituted chlorosilanes and their subsequent polymerisation.

Silicates:

Salts of silicic acid, H_4SiO_4 comprised of SiO_4^{4-} units having tetrahedral structure formed as result of sp^3hybridization.

Nitrogen Family (Group 15 Elements)

- **Members:** N, P, As, Sb & Bi
- **Atomic Radii:** Increases down the group. Only a small increases from As to Bi.
- **Oxidation state:** +3, +4 & +5.Stability of +3 oxidation state increases down the group.
- **Ionization energy:** Increases from N to Bi.

Nitrogen

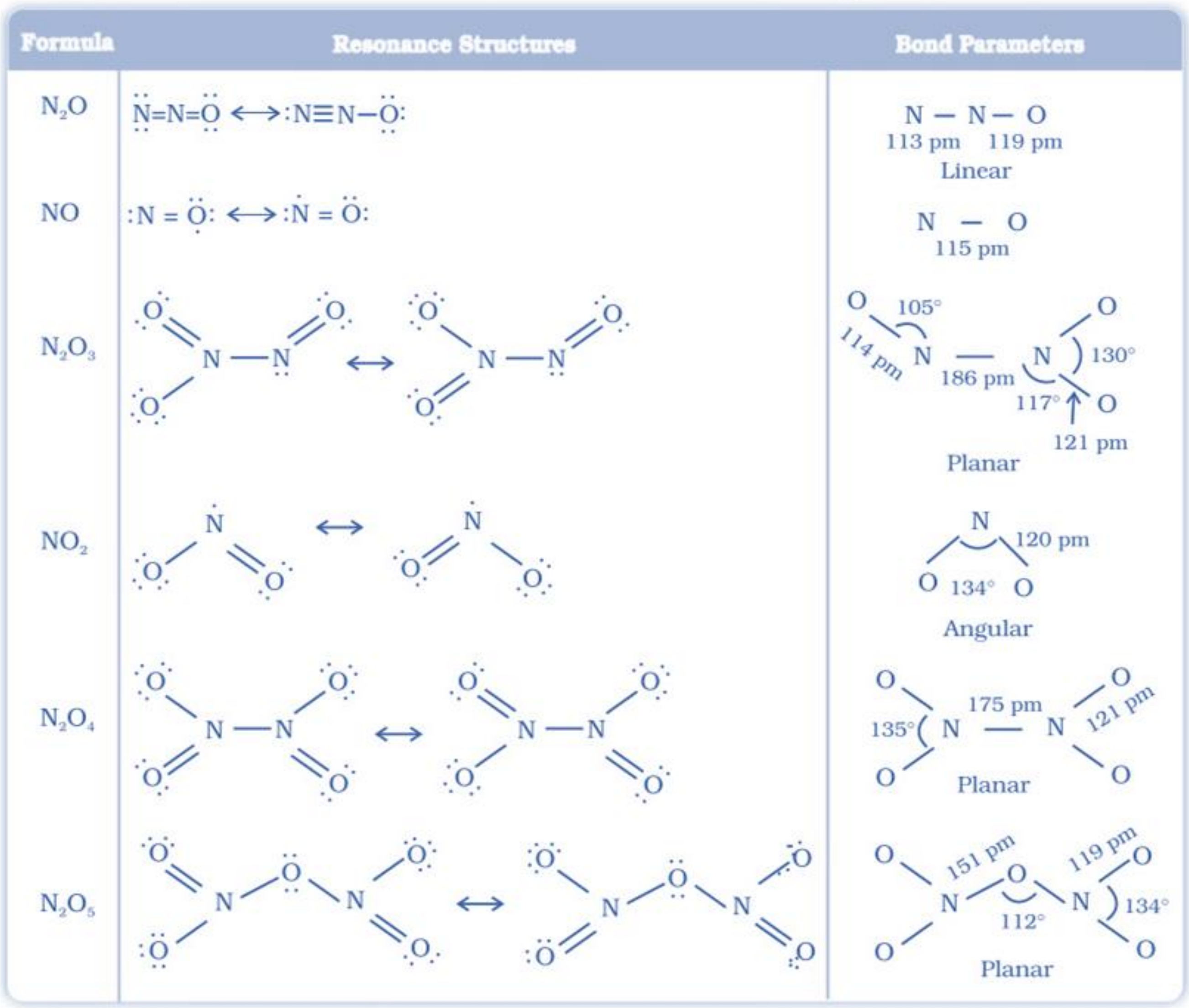
Preparation of Nitrogen:

- $3CuO + 2NH_3 + \text{Heat} \dashrightarrow N_2 + Cu + 3H_2O$
- $CaOCl_2 + 2NH_3 + \text{Heat} \dashrightarrow CaCl_2 + 3H_2O + N_2$
- $NH_4NO_2 + \text{Heat} \dashrightarrow 3H_2O + N_2 + Cr_2O_3$

Properties of Dinitrogen:

- Formation of Nitrides (with Li, Mg, Ca & Al): $Ca + N_2 + \text{Heat} \rightarrow Ca_3N_2$
- Oxidation: $N_2 + O_2 \rightarrow 2NO$
- Reaction with carbide (at 1273 K): $CaC_2 + N_2 \rightarrow CaCN_2 + C$

Oxides of Nitrogen



Oxy -Acids of Nitrogen :

Oxy Acids	Name of oxy – acid
1. $H_2N_2O_2$	Hyponitrous acid
2. H_2 NO_2	Hydronitrous acid
3. HNO_2	Nitrous acid
4. HNO_3	Nitric acid
5. HNO_4	Per nitric acid

Ammonia (NH_3):

Preparation of Ammonia:

- By heating an ammonium salt with a strong alkali ;$NH_4Cl + NaOH$ --> $NH_3 + NaCl + H_2O$
- By the hydrolysis of magnesium nitride: $Mg_3N_2 + 6H_2O$ --> $3Mg(OH)_2 + 2NH_3$.
- Haber's process : $N_2(g) + 3H_2(g)$ --> $2NH_3(g)$.

Properties of Ammonia:

- **Basic nature** : Its aq. solution is basic in nature and turns red litmus blue. $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$

- **Reaction with halogens :**
    - $8NH_3 + 3Cl_2$ --> $6NH_4Cl + N_2$
    - NH3 + $3Cl_2$ (in excess) $\rightarrow NCl_3 + 3HCl$
    - 8NH3 + $3Br_2 \rightarrow$ 6NH4Br + N_2
    - $NH_3 + 3Br_2$ (in excess) $\rightarrow NBr_3 + 3HBr$
    - $2NH_3 + 3I_2 \rightarrow NH_3.NI_3 + 3HI$
    - $8NH_3.NI_3 \rightarrow 6NH_4I + 9I_2 + 6N_2$

- **Complex formation :**
    - $Ag^+ + NH_3 \rightarrow [Ag(NH_3)_2]^+$
    - $Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$
    - $Cd^{2+} + 4NH_3 \rightarrow [Cd(NH_3)_4]^{2+}$

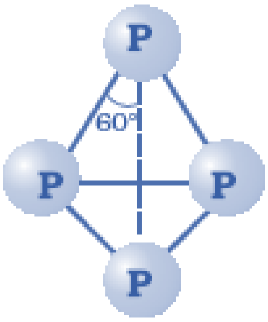
Precipitation of heavy metal ions from the aq. solution of their salts :

- $FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl$
  Brown ppt.
- $AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4Cl$
  White ppt.
- $CrCl_3 + 3NH_4OH \rightarrow Cr(OH)_3 + 3NH_4Cl$
  Green ppt.

Phosphorus:

Allotropy of Phosphorus:

a) White phosphorus:



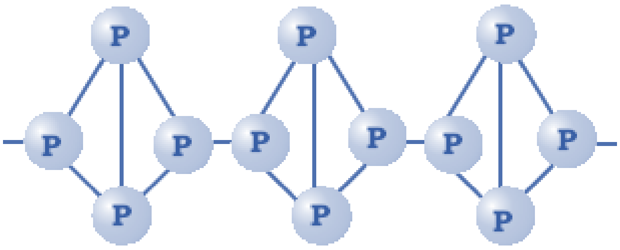
- Translucent white waxy solid
- Extremely reactive
- Poisonous and insoluble in water

b) Red Phosphorus:

- Formed by heating white phosphorus in absence of air.
- Does not burn spontaneously at room temperature.

c) Black Phosphorus: Formed by further heating of red phosphorus.

Compounds of Phosphorus:



a) Phosphine, PH_3:

Preparation of Phosphine

- $Ca_3P_2 + 6H_2O \rightarrow 2 PH_3 + 3 Ca(OH)_2$
- $4H_3PO_3$ +Heat → PH_3+ 3 H_3PO_4
- $PH_4I + KOH \rightarrow PH_3 + KI + H_2O$
- $P_4 + 3KOH + 3H_2O \rightarrow PH_3 + 3KH_3PO_2$

Properties of Phosphine:

- Formation of Phosphonic Iodide: $PH_3 + HI$ à PH_4I
- Combustion: $PH_3 + 2O_2$ à H_3PO_4

b) Phosphorous Halides:

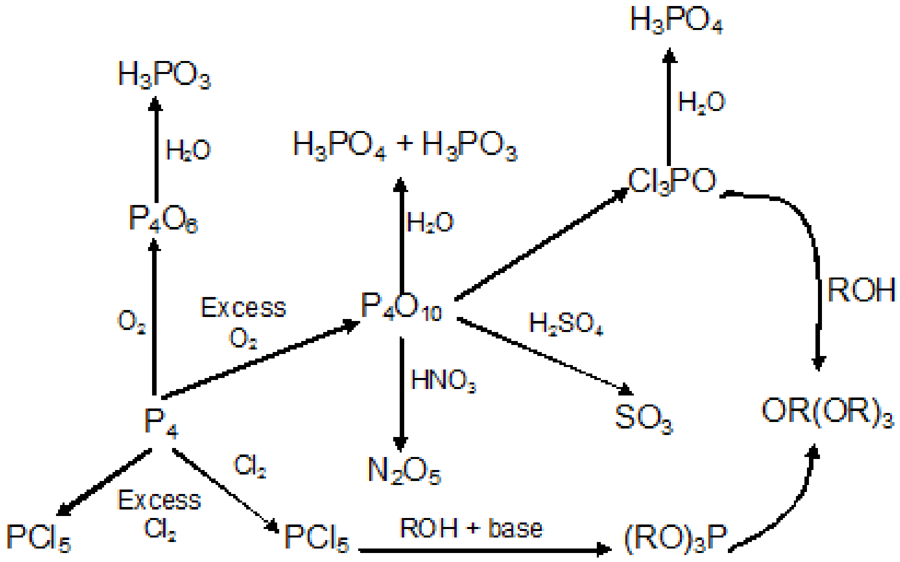
Preparation:

- $P_4 + 6Cl_2 \rightarrow 4PCl_3$
- $P_4 + 10Cl_2 \rightarrow 4PCl_5$
- $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$
- $P_4 + 10SOCl_2 \rightarrow 4PCl_5 + 10SO_2$

Properties:

- $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$
- $PCl_5 + 4H_2O \rightarrow POCl_3$ à $H_3PO_4 + 5HCl$
- $PCl_3 + 3CH_3COOH \rightarrow 3 CH_3COCl + H_3PO_3$
- $PCl_5 + CH_3COOH \rightarrow CH_3COCl + POCl_3 + HCl$
- $2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$
- $2Sn + PCl_5 \rightarrow SnCl_4 + 2PCl_3$
- PCl_5 + Heat → $PCl_3 + Cl_2$

?C) Oxides of Phosphorus:



d) Oxy – Acids of Phosphorus:

Oxo acid	Name
H_3PO_2	Hypophosphorus acid
H_3PO_3	Phosphorus acid
$H_4P_2O_6$	Hypophosphoric acid
H_3PO_4	Orthophosphoric acid
$H_4P_2O_7$	Pyrophosphoric acid
HPO_3	Metaphosphoric acid

Oxygen Family (Group 16 Elements) :

Sr. No.	Property	Oxygen	Sulfur	Selenium	Tellurium	Polonium
1.	Configuration	$[He]2s^2 2p^4$	$[Ne]3s^2 3p^4$	$[Ar]4s^2 4p^4$	$[Kr]5s^2 5p^4$	$[Xe]6s^2 6p^4$
2.	Common oxidation state	-2	-2, +4, +6	+4, +6	+4, +6	
3.	Atomic radius (pm)	66	104	116	143	167
4.	First ionization energy (KJ/mol)	1314	1000	941	869	812
5.	Electronegativity	3.5	2.5	2.4	2.1	2.0

Chemical Properties of Group 16:

Formation of volatile Hydrides:

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$$

$$Na_2Se + 2HCl \longrightarrow 2NaCl + H_2Se$$

Formation of Halides:

$$\frac{1}{8}S_8(s) + 3F_2(g) \longrightarrow SF_6(g)$$

$$\frac{1}{4}S_8(\ell) + Cl_2(g) \longrightarrow S_2Cl_2(\ell)$$

$$Te(s) + 2Cl_2(g) \longrightarrow TeCl_4(s)$$

$$Te(s) + 2I_2(g) \longrightarrow TeI_4(s)$$

Formation of Oxide:

a) All elements (except Se) forms monoxide.

b) All elements form dioxide with formula MO_2, SO_2 is a gas, SeO_2 is volatile solid. While TeO_2 and PoO_2 are non – volatile crystalline solids.

c) **Ozone:** It is unstable and easily decomposes into oxygen. It acts as a strong oxidising agent due to the case with which it can liberate nascent oxygen.

Oxyacids:

Sulphur	Selenium	Tellurium
Sulphurous acid H_2SO_3. **Sulphuric acid H_2SO_4** **Peroxomonosulphuric acid H_2SO_5(Caro's acid)** **Peroxodisulphuric acid** **$H_2S_2O_8$ (Marshell's acid)** **Thio sulphuric acid $H_2S_2O_3$** **Dithiconic acid $H_2S_2O_6$** **Pyrosulphuric acid $H_2S_2O_7$**	Selenious acid H_2SeO_3 Selnenic acid H_2SeO_4	Tellurous acid H_2TeO_3. Telluric acid H_2TeO_4.

Allotropes of Sulphur :

Rhombic sulphur:

- It has bright yellow colour.
- It is insoluble in water and carbon disulphide. Its density is 2.07 gm cm^{-3} and exists as S_8 molecules. The 8 sulphur atoms in S_8 molecule forms a puckered ring.

Monoclinic Sulphur :

- Stable only above 369 K. It is dull yellow coloured solid, also called *b - sulphur*. It is soluble in CS_2 but insoluble in H_2O.
- It slowly changes into rhombic sulphur. It also exist as S_8 molecules which have puckered ring structure. It however, differs from the rhombic sulphur in the symmetry of the crystals

Plastic Sulphur:

- It is obtained by pouring molten sulphur to cold water.
- It is amorphous form of sulphur.
- It is insoluble in water as well as CS_2.

Sulphuric Acid:

- Due to strong affinity for water, H_2SO_4 acts as a powerful dehydrating agent.
- Concentrated H_2SO_4 reacts with sugar, wood, paper etc to form black mass of carbon. This phenomenon is called charring.
- It is moderately strong oxidizing agent.

$$C + 2H_2SO_4 \longrightarrow 2H_2O + 2SO_2 + CO_2$$

$$\frac{1}{8}S_8 + 2H_2SO_4 \longrightarrow 2H_2O + 3SO_2$$

$$P_4 + 10H_2SO_4 \longrightarrow 4H_3PO_4 + 10SO_2 + 4H_2O$$

$$2HBr + H_2SO_4 \longrightarrow 2H_2O + SO_2 + Br_2$$

$$H_2S + H_2SO_4 \longrightarrow 2H_2O + S + SO_2$$

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$Pb + 2H_2SO_4 \longrightarrow PbSO_4 + SO_2 + 2H_2O$$

- Decomposes carbonates, bicarbonates, sulphides, sulphites, thiosulphates and nitrites at room temperatures.

$$H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + H_2O + CO_2 \uparrow$$

$$H_2SO_4 + 2NaHCO_3 \longrightarrow Na_2SO_4 + 2H_2O + 2CO_2 \uparrow$$

$$H_2SO_4 + Na_2S \longrightarrow Na_2SO_4 + H_2S \uparrow$$

- Salts like chlorides, fluorides, nitrates, acetates, oxalates are decomposed by hot conc. H_2SO_4 liberating their corresponding acids.

$$H_2SO_4 + CaCl_2 \longrightarrow CaSO_4 + 2HCl \uparrow$$

$$H_2SO_4 + CaF_2 \longrightarrow CaSO_4 + 2HF$$

? $$H_2SO_4 + 2KNO_3 \longrightarrow K_2SO_4 + 2HNO_3$$

Halogen Family (Group 17 Elements)

Inter halogen compounds:

Type XX'_1 (n = 1) (with linear shape)	Type XX'_3 (n = 3) (with T-shape)	XX'_5 (n = 5) (with square pyramidal shape)	XX'_7 (n = 7) with pentagonal bipyramidal shape)
ClF	ClF_3	ClF_5	
BrF BrCl	BrF_3	BrF_5	
ICl, IBr, IF	ICl_3, IF_3	IF_5	IF_7

Hydrogen Halides:

Properties of Hydrogen Halides:

- All the three acids are reducing agents HCl is not attacked by H_2SO_4.
  - $2HBr + H_2SO_4 \rightarrow 2H_2O + SO_2 + Br_2$
  - $2HI + H_2SO_4 \rightarrow 2H_2O + SO_2 + I_2$
- All the three react with $KMnO_4$ and $K_2Cr_2O_7$
  - $2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl2 + 8H_2O + 5Cl_2$
  - $K_2Cr_2O_7 + 14HBr \rightarrow 2KBr + 2CrBr_3 + 7H_2O + 3Br_2$
- Other reactions are similar.
  - Dipole moment : HI < HBr < HCl < HF
  - Bond length: HF < HCl < HBr < HI
  - Bond strength: HI < HBr < HCl < HF
  - Thermal stability: HI < HBr < HCl < HF
  - Acid strength: HF < HCl < HBr < BI
  - Reducing power: HF < HCl < HBr < HI

Pseudohalide ions and pseudohalogens:

Ions which consist of two or more atoms of which at least one is nitrogen and have properties similar to those of halide ions are called pseudohalide ions. Some of these pseudohalide ions can be oxidised to form covalent dimers comparable to halogens (X_2). Such covalent dimers of pseudohalide ions are called pseudohalogens.

The best known psuedohalide ion is CN^{-}\

Pseudohalide ions	**Name**
CN^{-}	Cyanide ion
OCN^{-}	Cyanate ion
SCN^{-}	Thiocyante ion
$SeCN^{-}$	Selenocyanate ion
NCN^{2-}	Cyanamide ion
N_3^{-}	Azide ion
OMC^{-}	Fulminate ion

Pseudohalogen

- $(CN)_2$ cyanogen
- $(SCM)_2$ thiocyanogen

Some important stable compound of Xenon

- XeO_3 Pyramidal
- XeO_4 Tetrahedral
- $XeOF_4$ Square pyramidal
- XeO_2F_2 Distorted octahedral

First rare gas compound discovered was $Xe^{+}(PtF_6)^{-}$ by Bartlett.

Oxyacids of Chlorine

Formula	Name	Corresponding Salt
$HOCl$	Hypochlorous acid	Hypochlorites
$HClO_2$	Chlorous acid	Chlorites
$HClO_3$	Chloric acid	Chlorates
$HClO_4$	Perchloric acid	Perchlorates

Acidic Character: Acidic character of the same halogen increases with the increase in oxidation number of the halogen: $HClO_4 > HClO_3 > HClO_2 > HOCl$

Preparation

HOCl :

- $Ca(OCl)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2HOCl$

$HClO_2$:

- $BaO_2 + 2ClO_2 \rightarrow Ba(ClO_2)_2$ (liquid) $+ O_2$
- $Ba(ClO_2)_2 + H_2SO_4$(dil.) $\rightarrow BaSO_4{}^{-} + 2HClO_2$

$HClO_3$:

- $6Ba(OH)_2 + 6Cl_2 \rightarrow 5BaCl_2 + Ba(ClO_3)_2 + 6H_2O$
- $Ba(ClO_3)_2 + H_2SO_4$(dil.) $\rightarrow BaSO_4{}^{-} + 2HClO_3$

$HClO_4$:

- $KClO_4 + H_2SO_4 \rightarrow KHSO_4 + HClO_4$
- $3HClO_3 \rightarrow HClO_4 + 2ClO_2 + H_2O$

The Noble Gases (Group 18 Elements):

The noble gases are inert in nature. They do not participate in the reactions easily because they have

- stable electronic configuration i.e. complete octet.
- high ionization energies.
- low electron affinity.

Compounds of Xenon

$$Xe + F_2 \xrightarrow[673K]{\text{Nickel tube}} XeF_2$$
$$(1:2)$$

$$Xe + 2F_2 \xrightarrow[5-6\text{ atm}]{\text{Nickel tube, }673K} XeF_4$$
$$(1:5)$$

$$Xe + 3F_2 \xrightarrow[50-60\text{ atm}]{\text{Nickel tube, }575\text{ K}} XeF_6$$
$$(1:20)$$

Molecule	Total electron pairs (BP + LP)	Hybridisation	Shape
XeF_2	5s	Sp^3d	Linear
XeF_4	6	Sp^3d^2	Square planar
XeF_6	7	sp^3d^3	Distorted octahedral

Uses of Nobles gas

The noble gases are used in following ways:

(A) Helium

- It is used to fill airships and observation balloons.
- In the oxygen mixture of deep sea divers.
- In treatment of asthma.
- Used in inflating aeroplane tyres.
- Used to provide inert atmosphere in melting and welding of easily oxidizable metals.

(B) Neon

- It is used for filling discharge tubes, which have different characteristic colours and are used in advertising purposes.
- Also used in beacon lights for safety of air navigators as the light possesses fog and stram perpetrating power.

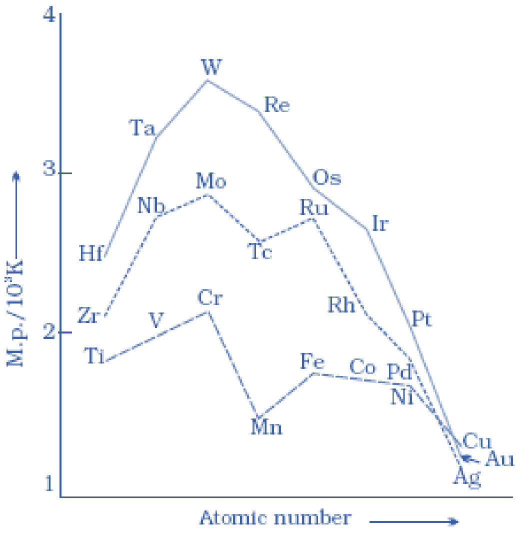
(C) Argon

Along with nitrogen it is used in gas – filled electric lamps because argon is more inert than nitrogen.

Revision Notes on Transition Elements:

Physicochemical Properties

a. Melting and Boiling Points:

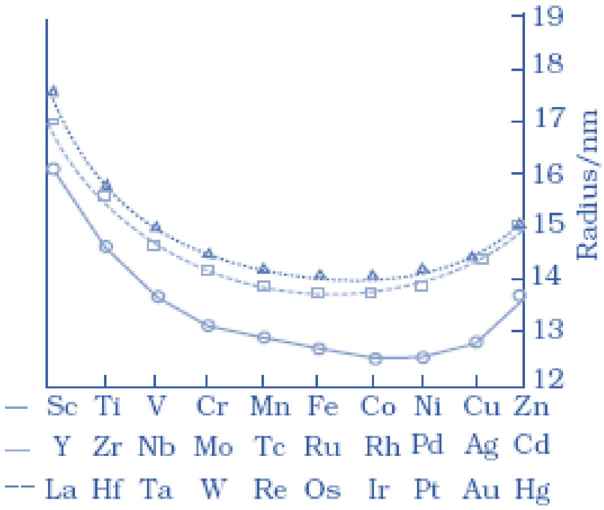


Melting and boiling points show no definite trends in the three transition series.

The metals having the highest melting and boiling points are towards the middle of each transition series.

b. Atomic (Covalent) and Ionic Radii:

Atomic and ionic radii values decrease generally, on moving from left to right in the period.



The atomic radii for the elements from Cr to Cu are very close to one another.

Radii of 5d series elements are virtually the same as those of corresponding members of 4d series due to lanthanoid contraction.

c. Ionisation Potentials:

- **First Ionization Potentials:** I_1 values for the first four 3d block elements (Sc, Ti, V and Cr) differ only slightly from one another. The value of I_I for Zn is considerably higher. This is due to the extra-stability of $3d^{10}$ level which is completely filled in Zn-atom.
- **Second ionisation potentials:** The value of I_{II} for Cr and Cu are higher than those of their neighbours. This is due to the fact that the electronic configurations of Cr^+ and Cu^+ ions have extra stable $3d^5$ and $3d^{10}$levels.There is a sudden fall in the values of ionisation potentials in going from II B (Zn-group elements) to IIIA sub-group.

d. Oxidation States:

- The higher oxidation state of 4d and 5d series elements are generally more stable than those of the elements of 3d series,
- In short it may be said that in going down a sub-group the stability of the higher oxidation states increases while that of lower oxidation states decreases.
- Transition elements cannot form ionic compounds in higher oxidation states because the loss of more than three electrons is prevented by the higher attractive force exerted (on the electrons) by the nucleus

e. Colour: Transition elements with partially filled d orbitals form coloured compounds.

f. **Complex Formation:** Transition elements show tendency to form complex compounds due to. Small size and high effective nuclear charge.

- Availability of low lying vacant d–orbitals which can accept lone pair of electrons donated by a ligand.

g. **Catalytic properties:**

Transition metals and their compounds are known to act as good catalyst due to

1. variable oxidation state, they form unstable intermediate compounds and provide a new path with lower activation energy for the reaction (Intermediate compound formation theory)
2. In some cases the finely divided metals or their compounds provide a large surface area for adsorption and the adsorbed reactants react faster due to the closer contact(Adsorption theory)

h. **Magnetic Properties:**

Magnetic moment is which is related to the number of unpaired electrons as follows

$$\mu = \sqrt{n(n+2)}\ \text{B.M.}$$

n = number of unpaired electrons

B.M. = Bohr Magneton, unit of magnetic moment

More the magnetic moment more is the paramagnetic behavior

i. **Formation of Alloys:**

As the transition elements have similar atomic sizes hence in the crystal lattice, one metal can be readily replaced by another metal giving solid solution and smooth alloys. The alloys so formed are hard and have often high melting point.

j. **Interstitial Compounds:**

Transition metals form no. of interstitial compounds, in which they take up atoms of small size e.g. H, C and N in the vacant spaces in the their lattices. The presence of these atoms results in decrease in malleability and ductility of the metals but increases their tensile strength.

Potassium Dichromate ($K_2Cr_2O_7$)

a. Preparation

It is prepared from the ore called chromate or ferrochrome or chrome iron, $FeO.Cr_2O_3$.

Steps: 1, Preparation of sodium chromate

$4FeO.Cr_2O_3 + O_2 \rightarrow Fe_2O_3 + 4Cr_2O_3$

$4Na_2CO_3 + 2Cr_2O_3 + 3O_2 \rightarrow 4Na_2CrO_4 + 4CO_2$

Step: 2, Conversion of sodium chromate into sodium dichromate.

$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

Step: 3, Conversion of sodium dichromate into potassium dichromate.

$Na_2Cr2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

b. Properties

1. Action of heat: When heated, it decomposed to its chromate

$4K_2Cr_2O_7 + \Delta \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$

2. Action of alkalis

$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O$

$2K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$

3. Action of conc. H_2SO_4 solution

(a) In cold conditions

$K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2CrO_3 + 2KHSO_4 + H_2O$

(b) In hot conditions

$2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2K_2SO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2$

4. Oxidising propertiesIt is a powerful oxidising agent.

In the presence of dil. H_2SO_4 it furnishes 3 atoms of available oxygen.

$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

Some of the oxidizing properties of $K_2Cr_2O_7$ are

It liberates I_2 from KI

$K_2Cr_2O_7 + 7H_2SO_4 + 6Kl \rightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$

It oxidises ferrous salts to ferric salts

$K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 2H_2O$

It oxidises S^{-2} to S

$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$

It oxidises nitrites to nitrates

$K_2Cr_2O_7 + 4H_2SO_4 + 3NaNO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3NaNO_3 + 4H_2O$

It oxidises SO_2 to SO_4^{2-}

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3H_2O$

It oxidises ethyl alcohol to acetaldehyde and acetic acid.

5. Chromyl chloride test

When heated with conc. HCl or with a chloride in the presence of sulphuric acid, reddish brown vapours of chromyl chloride are obtained.

$K_2Cr_2O_7 + 4KCl + 6H_2SO_4 \rightarrow 2CrO_2Cl_2 + 6KHSO_4 + 3H_2O$

Thus reaction is used in the detection of chloride ions in qualitative analysis.

c. Uses

In volumetric analysis for the estimation of Fe^{2+} and I^-.

In chrome tanning in leather industry.

In photography and in hardening gelatin film.

Potassium Permanganate

a. Preparation:

It is prepared from the mineral pyrolusite, MnO_2.

Step:1, Conversion of MnO_2 into potassium manganate.

$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

Step:2, Oxidation of potassium manganate into permanganate

Chemical oxidation

K_2MnO_4 is oxidised to $KMnO_4$ by bubbling CO_2 or Cl_2 or ozone into the former.

$3K_2MnO_4 + 2CO_2 \rightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$

Electrolytic oxidation

$2K_2MnO_2 + H_2O + O \rightarrow 2K_2MnO_4 + 2KOH$

b. Properties

$KMnO_4$ exists as deep purple prisms. It is moderately soluble in water at room temperature and its solubility in water increases with temperature.

(i) Action of heat

When heated it decomposes to K_2MnO_4.

$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

(ii) Action of conc. H_2SO_4

With cold conc. H_2SO_4 it gives Mn_2O_7 which on warming decomposes to MnO_2.

$2MnO_2 + 2H_2SO_4 \rightarrow Mn_2O_7 + 2KHSO_4 + 2H_2O$

$2Mn_2O_7 + \Delta \rightarrow 4MnO_2 + 3O_2$

With hot Conc. H_2SO_4 O_2 is evolved

$4KMnO_4 + 6H_2SO_4 \rightarrow 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_{21}$

(iii) Oxidising properties

$KMnO_4$ is a powerful oxidizing agent. The actual oxidizing action depends upon themedium i.e. acidic, basic or neutral.

(a) In neutral solution, it acts as moderate oxidizing agent.

$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3O$

Some oxidizing properties of $KMnO_4$ in neutral medium are

$2KMnO_4 + 3Na_2S_2O_3 + H_2O \rightarrow 3K_2SO_4 + 8MnO_2 + 3Na_2SO_4 + 2KOH$
$2KMnO_4 + 4H_2S \rightarrow 2MnS + S + K_2SO_4 + 4H_2O$

(b) In strong alkaline solution, it is converted into

$2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + O$

Some reaction in alkaline medium are

$2KMnO_4 + H_2O + KI \rightarrow 2MnO_2 + 2KOH + KIO_3$

(c) In acidic medium, Mn^{+7} is converted into Mn^{+2}

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$

Some other reactions are

(i) $2KMnO_4 + 3H_2SO_4 + 5H_2S \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5S$

(ii) $2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

(iii) $2KMnO_4 + 3H_2SO_4 + 5KNO_2 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5KNO_3$

(iv) $2KMnO_4 + 3H_2SO_4 + 5C_2H_2O_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

(v) $2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$

(vi) $2KMnO_4 + 3H_2SO_4 + 10KI \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$

c. Uses

(i) Used in volumetric analysis for estimation of ferrous salts, oxalates, iodides & H_2O_2.

(ii) Used as oxidizing agent in the laboratory as well as in industry.

Inner Transition Elements

The f-block elements are known as inner transition elements because they involve the filling for inner sub-shells (4f or 5f)

a. Lanthanides:

It consists of elements that follows lanthanum and involve the filling of 4 subshell

Electronic Configuration : [Xe] $4f^{n+1}$ $5d^{\circ}$ $6s^2$ or [Xe] $4f^n$ $5d^1$ $6s^2$

Oxidation State: +3, +2 and +4.

Colouration: Many of the lanthanides ions are coloured in solid state as well as in solutions. The colour is due to the f-f transition since they have partly filled f-orbitals.

Lanthanide Contraction: The steady decrease in the size of lanthanide ions (M^{3+}) with the increase in atomic no. is called lanthanide contraction.

Causes: As we move down the group from left to right in a lanthanide series, the atomic no. increases and for every proton in the nucleus the extra electron goes to 4f orbital. The 4f orbital is too diffused to shield the nucleus effectively, thus there is a gradual increase in the effective nuclear charge experienced by the outer electrons. Consequently , the attraction of the nucleus for the electrons in the outermost shell increases with the increase of atomic number, thus size decreases.

Consequence of Lanthanide Contraction:

Separation of Lanthanides: Due to the similar sizes of the lanthanides, it is difficult to separate them but due to lanthanide contraction their properties slightly vary (such as ability to form complexes). The variation in the properties is utilized to separate them.

Basic Strength of Hydroxide: Due to the lanthanide contraction, size of M^{3+} ions decreases and there is increase in covalent character in M–OH and hence basic character decreases.

Similarity of second and third transition series: The atomic radii of second row transition elements are almost similar to those of the third row transition elements because the increase in size on moving down the group from second to third transition elements is cancelled by the decrease in size due to the lanthanide contraction.

b. Actinides:

It consists of elements that follow Actinium and involve the filling of 5f subshell.

These are radioactive substances.

$7s^2$ is stable configuration for actinides.

Show +3,+4,+5,+6 & +7 oxidation state.