B.Sc-II (Hons), Paper-III B (Inorganic chemistry)
Group-B, Unit-2 Comparative/General chemistry of Group-3 elements (Sc, Y & La).

[By Dr. Birendra Kumar, Maharaja College]

1. Position in Periodic table (PT):

Electronic Configuration: Scandium (Sc_{21}): $[Ar_{18}]3d^1 4s^2$
Yittrium (Y_{39}): $[Kr_{36}]4d^1 5s^2$
Lanthanum (La_{57}): $[Xe_{54}]5d^1 6s^2$

Outer electronic configuration of these elements is $(n-1)d^1 ns^2$. Valence electrons in them is 3 and last electron enters in d-orbital. Hence, Sc, Y & La occupy position in Group-3 under d-block in Modern periodic table, but different periods: 4, 5 & 6 respectively.

2. Oxidation States: Outer electronic configuration of Group-3 (Scandium group) elements is $(n-1)d^1 ns^2$. These elements always exist in the Oxidation state +3 and occur as M^{3+} ions. Removal of two s and one d electrons to make the trivalent ions (M^{3+}) gives a stable d^0 conf. Consequently, the ions (M^{3+}) and their compounds are stable. The sum of the first three ionization energies (IE_1, IE_2, IE_3) for Sc is little less than the sum for Al, and the properties of Sc are similar in some way to those of aluminium (Al).

3. Atomic/Ionic Size: Atomic (Covalent) and ionic radii of Group-3 elements increase regularly on descending in the group, due to increase of number of orbits.

	Sc	Y	La
Covalent radii (in Å):	1.44	1.62	1.69
Ionic (M^{3+}) radii (in Å):	0.70	0.90	1.06

4. Chemical reactivity/Properties: Group-3 elements (Sc, Y & La) are quite reactive and reactivity increases with the increase of atomic size (Sc<Y<La). Some of important chemical properties are:

(a) with O_2: They burn in oxygen giving oxides (M_2O_3), and turnish in air. Y forms a protective oxide coating in air, which makes it unreactive.

$$4M + 3O_2 \longrightarrow 2M_2O_3 \quad (M = Sc, Y \& La)$$

(b) with H_2O: They react slowly with cold water (H_2O) and more rapidly, on heating, liberating hydrogen gas and forming hydroxides/basic oxides.

$$2M + 6H_2O \xrightarrow{-3H_2} 2M(OH)_3 \longrightarrow MO(OH) \quad (\text{where } M = Sc, La \& Y.)$$
(Hydroxide) (Basic Oxide)

$Sc(OH)_3$ appears, not to exist as a definite compound, but $ScO.(OH)$ is well established, and is amphoteric like $Al(OH)_3$. Basic properties of the oxides & hydroxides increase on descending the group (Sc → Y → La).

(c) with hydrogen (H_2): All the elements react with hydrogen on heating to 300°C, forming $MH_{<3}$ type non-stoichiometric hydrides. The exact composition depends on the temperature and pressure of the H_2 gas. $M + H_2 \longrightarrow MH_n$ [where M = Sc, Y & La, n<3]

The hydrides (MH_n) react with water to form hydroxides liberating hydrogen gas. They are ionic/saltlike hydrides (H^-).

(d) with Carbon: Scandium forms, a carbide (ScC_2) when its oxide is heated with C.

$$Sc_2O_3 + C \xrightarrow[(1000°C)]{\Delta} ScC_2 \xrightarrow{+H_2O} ScO.(OH) + C_2H_2\uparrow$$
(Acetylene)

The carbide reacts with water liberating acetylene (C_2H_2).

5. Formation of Oxides: On heating or burning, Group-3 metals (Sc, Y & La) in air (O_2), metal Oxides (M_2O_3) formed. $4M + 3O_2 \xrightarrow{Burnt} 2M_2O_3$ (where M = Sc, Y & La)

They are also formed by heating metal hydroxides, carbonates etc.
e.g. $2Y(OH)_3 \xrightarrow{\Delta} Y_2O_3 + 3H_2O$; $Y_2(CO_3)_3 \xrightarrow{\Delta} Y_2O_3 + CO_2\uparrow$

Oxides of these metals are either amphoteric or weak bases. The basic properties of the oxides increase from Sc to La. Oxides form salts with acids.
$M_2O_3 + 6HCl \longrightarrow 2MCl_3 + 3H_2O$; $M_2O_3 + 3H_2SO_4 \longrightarrow M_2(SO_4)_3 + 3H_2O$

6. Formation of Halides: Group-3 (Scandium group) metals react with the halogens (X_2) forming trihalides (MX_3). The fluorides are insoluble, and the others are deliquescent and very soluble like $CaCl_2$. The anhydrous chlorides are prepared from their oxides.
e.g. $Sc_2O_3 + 6NH_4Cl \xrightarrow{300^\circ C} ScCl_3 + 6NH_3 + 3H_2O$.

$ScCl_3$ differs from $AlCl_3$, since $ScCl_3$ is monomeric while $AlCl_3$ is dimeric. $ScCl_3$ shows no Friedel-Crafts catalytic properties.

If chlorides are prepared in solution, they crystallize as hydrated salts. These hydrated halides decompose on heating, Sc giving the oxide (M_2O_3) rather than the anhydrous halides and the others giving oxyhalides (MOCl)

$ScCl_3 \cdot H_2O \xrightarrow{\Delta} Sc_2O_3 + HCl$; $YCl_3 \cdot H_2O \xrightarrow{\Delta} YOCl + HCl$;
$LaCl_3 \cdot H_2O \xrightarrow{\Delta} LaOCl + HCl$

The fluoride salts are generally insoluble in water.

7. Formation of Complex Compounds: Despite of high charge/oxidation state +3, the Group-3 metal ions (M^{3+}) do not have a strong tendency to form complexes, because of their fairly large size. Sc^{3+} is the smallest ion and forms complexes more readily than the other metal ions (Y^{3+} & La^{3+}). Some of the examples of Sc^{3+} complexes are $[Sc(OH)_6]^{3-}$, $[ScF_6]^{3-}$ etc. $[ScF_6]^{3-}$ formed by dissolving ScF_3 in HF or NH_4F.

$ScF_3 + 3NH_4^+F^- \longrightarrow [ScF_6]^{3-} + 3NH_4^+$

These complexes are octahedral in shape.

In addition, Complexes are formed with strong complexing agents, such as oxalic acid, citric acid, acetylacetone (acac) and EDTA (Ethylenediammine tetra acetic acid). The complexes of the large metals often have a coordination number greater than 6, for example, a coordination number of 8 in $[La(acac)_3(H_2O)_2]$ and C.No. 10 in $[LaEDTA(H_2O)_4] \cdot 3H_2O$. In latter compound, EDTA forms four bonds from oxygen atoms and two from nitrogen atoms, and the oxygen atoms in the four water molecules all form bonds to La.

—— o ——