B. Sc. Part-I (Sub.), Paper-I, Group-B (Inorganic Chemistry)
Unit: 2 Chemistry of Elements: Tin (Sn)
(By Dr. Birendra Kumar, Maharaja College)

⟹ Position of Tin (Sn) in Periodic table (PT):

Electronic configuration of Sn_{50}: $[Kr_{36}]4d^{10}5s^25p^2$, No. of valence electrons = 4
No. of orbits = 5, Period-5, Since last electron enters in p-subshell/p-bital, so block is p. For p-block, Group = ns+np+10 = 2+2+10 = 14. Thus, tin (Sn) is placed in group-14 under p-block in the modern PT along with Carbon (C), Silicon (Si), Germanium (Ge), Lead (Pb) & Flerovium (Fl). Position of tin in group-14 is justified on the basis of following similarity and gradation properties:

(i) They show similar outer electronic configuration ns^2np^2 (n=2 to 7).
(ii) They show common oxidation state: +4
(iii) They form oxides of type MO_2 with air or oxygen. $M+O_2 \xrightarrow{\Delta} MO_2$ (M = C, Si, Ge--)
(iv) They form tetrachloride (MCl_4) with chlorine (Cl_2). Their stability decrease from C to Pb.
(v) Electronegativity decrease from C to Pb and metallic property increase from C to Pb

⟹ Ores of Tin: Tin does not occur free state, but found in combined states in nature. Its important or chief ores are:

1. Oxide form/ore: Cassiterite or Tin stone (SnO_2), Contains 78% Sn.
2. Sulphide form/ore: Tin pyrites ($SnS_2.Cu_2S.FeS$), Contains 35% Sn.

⟹ Extraction of Tin: Tin metal is mainly extracted from tin stone ore. It involves following steps:

Step-1 Concentration of Ore: The tin stone ore contains 6-10% SnO_2. The rest is worthless gangue (sand & earthy matter), tungstates of Fe & Mo, FeS_2 etc. The powdered ore is made free from the impurities by following methods:

(a) Gravity Separation method: The powdered ore is washed in a stream of water when the lighter sand and earthy matter floats away while the heavier ore particles settle to the bottom.

(b) Electromagnetic Separation process: The magnetic impurities of Wolframite ($FeWO_4$) are removed by this method. The washed ore is dropped on a brass/leather belt moving over electromagnetic rollers. The wolframite particles being attracted by the magnet fall in separate heap near the magnetic rolles.

Step-2 Roasting: The Concentrated ore is roasted in a large rotating furnace which is slowly heated in the begining in a free supply of air to oxidise S to SO_2 and As to As_2O_3, which volatilize off. $S+O_2 \xrightarrow{\Delta} SO_2\uparrow$; $4As+3O_2 \xrightarrow{\Delta} 2As_2O_3\uparrow$ (Arsenious Oxide)

Step-3 Smelting: The roasted ore is mixed with anthracite coke in the ratio of 1:4, and the mixture is subjected to heat in a reverberatory furnace when tin oxide is reduced to the metallic tin. A small amount of lime is also added as flux. The molten Sn (tin) metal is tapped out of the furnace.

$$SnO_2 + 2C \xrightarrow{\Delta} Sn + 2CO\uparrow$$
(Tinstone) — Tin (molten, impure)

Step-4 Refining: Tin thus obtained is crude and contains Fe, Cu, S, As, W as chief impurities. Crude tin is purified in the following successive methods:

(a) **Liquation:** The crude tin is first heated on the sloping hearth of reverberatory furnace when the easily fusible tin melts at 232°C and flows away, leaving behind the impurities such as Cu, Fe, W etc.

(b) **Poling:** The molten tin is stirred by poles of green wood whereby the impurities of Cu, Fe etc. are oxidised and rise to the surface as scum, and removed. Tin, thus obtained is 99% pure.

(c) **Electrolytic refining:** Blocks of impure tin are suspended from the anode of an electrolytic bath containing a solution of tin sulphate ($SnSO_4$) with a little of glue and phenol sulphonic acid in dilute H_2SO_4, the cathode is a sheet of pure tin (thin). When electric current is passed, tin dissolves from anode slowly and deposited at the cathode.

$SnSO_4 \longrightarrow Sn^{2+} + SO_4^{2-}$; At anode: $Sn + SO_4^{2-} \longrightarrow SnSO_4 + 2e$ (Impure)

At Cathode: $Sn^{2+} + 2e \longrightarrow Sn$ (Pure).

⟹ **Important reactions of tin (Sn):** 1. Tin is a white, shinning, soft metal (M.Pt 232°C) (pure/impure)

2. **Reaction with air/O_2:** Tin does not react with dry air (O_2) at ordinary temp, but tarnishes (impure tin) in moist air. On heating it in air, SnO_2 (tin dioxide) is formed. $Sn + O_2 \xrightarrow{\Delta} SnO_2$

3. **Reaction with water:** It does not react with water at any temp, but red hot tin decomposes steam with the evolution of H_2. $Sn + 2H_2O \longrightarrow SnO_2 + 2H_2\uparrow$

4. **Reaction with non-metals:** On heating tin with Cl_2 gas or Sulphur vapour, stannic chloride ($SnCl_4$) or stannic sulphide (SnS_2) formed.

$Sn + 2Cl_2 \xrightarrow{\Delta} SnCl_4$; $Sn + 2S \xrightarrow{\Delta} SnS_2$.

5. **Reactions with acids:** (i) It reacts with dilute HCl & H_2SO_4 to form stannous salts.

$Sn + 2HCl \longrightarrow SnCl_2 + H_2\uparrow$; $Sn + H_2SO_4 \longrightarrow SnSO_4 + H_2\uparrow$.

(ii) It reacts with Concentrated H_2SO_4 to form stannic sulphate & SO_2 gas evolved.

$Sn + 4H_2SO_4 \xrightarrow{\Delta} Sn(SO_4)_2 + 2SO_2 + 4H_2O$

(iii) It reacts with dilute HNO_3 to form stannous nitrate & ammonium nitrate.

$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$

It reacts with conc. HNO_3 to form stannic acid and nitrogen dioxide (NO_2) evolved.

$Sn + 4HNO_3 \xrightarrow{\Delta} H_2SnO_3 + 4NO_2\uparrow + H_2O$.

6. **Reaction with alkali:** It reacts with caustic alkali (NaOH or KOH) to form stannate salt and H_2 gas evolved. $Sn + 2NaOH + H_2O \longrightarrow Na_2SnO_3 + 2H_2\uparrow$ (Sodium stannate)

7. **Reaction with $HgCl_2$:** When tin is heated with mercuric chloride ($HgCl_2$), stannous chloride is formed. $HgCl_2 + Sn \xrightarrow{\Delta} SnCl_2 + Hg\downarrow$.

⟹ **Uses/Applications of Tin:** Main applications/uses of tin are –

(i) It is used in preventing corrosion of iron sheets/tin plating.

(ii) Tin-foils are used as wrapper (iii) In making alloys; Solder (Pb+Sn), Bronze (Cu+Sn) etc.