Tin

- One of the longest known elements
- Symbol Sn from Latin *stannum*
- Bronze items from ca. 3500 B.C.E. contain 10-15% Sn alloyed with Cu.
- Cassiterite, mineral SnO_2, found in Britain, was an early source.
- Malaysia, Russia, and Bolivia are current principal sources.
- About 40% of tin used in plating to provide a non-toxic coating for sheet metal and “tin” cans.
- Important component of many alloys.

Solder	50% Sn, 50% Pb
Aluminum solder	86% Sn, 9% Zn, 5% Al
Pewter	85% Sn, 6.8% Cu, 6% Bi, 1.7% Sb
Bronze	80% Cu, 15% Sn, 5% Zn
Bell metal	78% Cu, 22% Sn
Babbitt	90% Sn, 7% Sb, 3% Cu

- Tin has more stable isotopes than any other element.

Tin Chemistry

- Tin is stable toward water and oxygen at 25 °C, but reacts with steam or when heated in oxygen to give SnO_2.

$$Sn(s) + 2H_2O(g) \rightarrow SnO_2(s) + 2H_2(g)$$
$$Sn(s) + O_2(g) \rightarrow SnO_2(s)$$

- Tin shows little reaction with dilute HCl or H_2SO_4, but with dilute HNO_3 it forms $Sn(NO_3)_2$ and NH_4NO_3.

- Hot conc. HCl gives $SnCl_2$ and H_2, and hot conc. H_2SO_4 gives $SnSO_4$ and SO_2.

- In hot KOH(*aq*), Sn dissolves to give $K_2[Sn(OH)_6]$ and H_2.

☛ Note that both +2 and +4 Sn compounds form, showing that both states have comparable stability.

☛ Which oxidation state forms depends upon the thermodynamics of ionization versus bond stability.

State Trends in Group 14

- All group 14 elements have the valence configuration ns^2np^2.

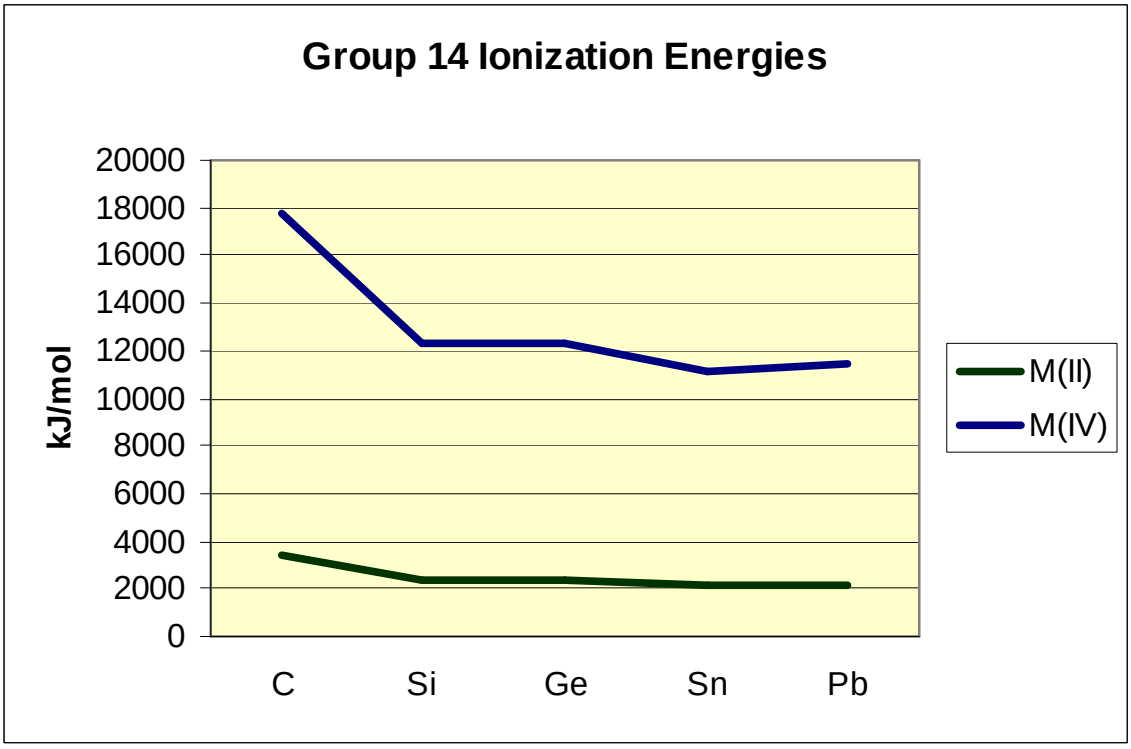
$$M(ns^2np^2) \rightarrow M^{2+}(ns^2np^0) \rightarrow M^{4+}(ns^0np^0)$$

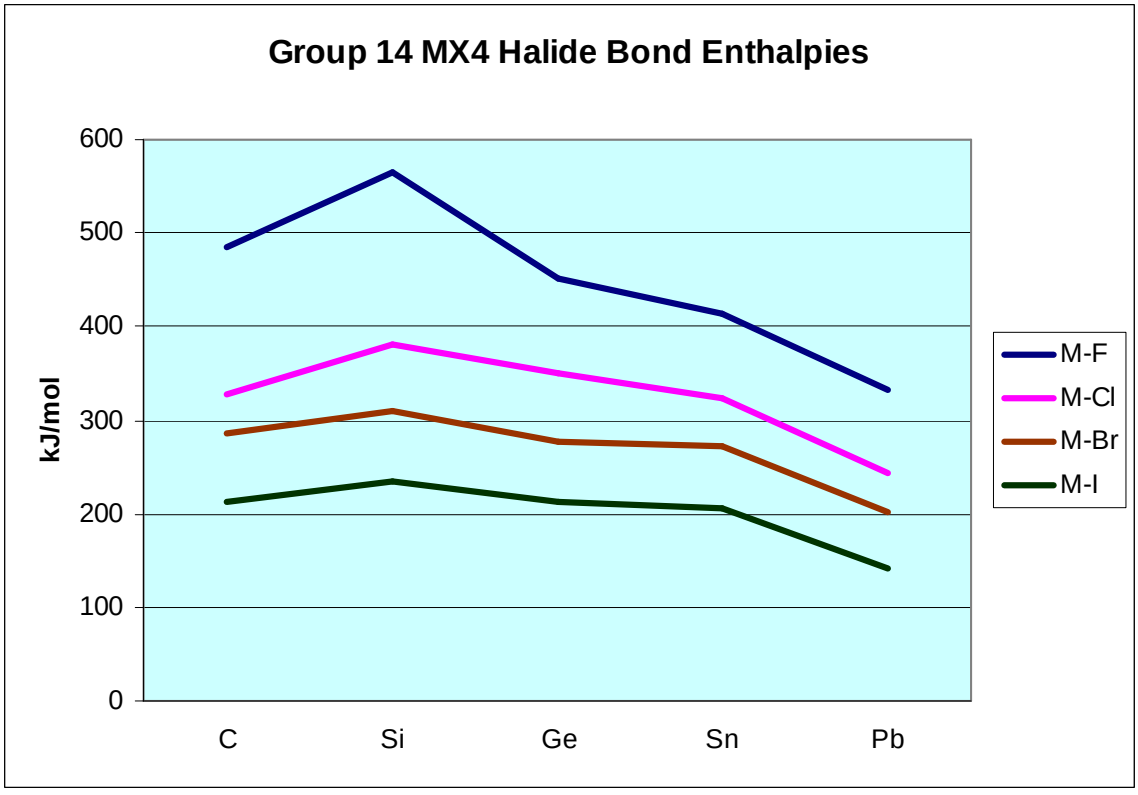
- Stable carbon and silicon compounds have the group 14 element in the +4 state.

☛ Going down the group, the +4 state becomes less stable and the +2 state becomes more stable.
  - The increasing stability of the lower state (+2) has been called the “inert pair effect” for the tendency of the ns^2 configuration to be retained.
  - This has nothing to do with inherent “inertness” of the ns^2 configuration, but rather thermodynamics.

- A similar "inert pair" effect is found in groups 13, 14, 15.

Ionization Energies and Bond Enthalpies





Explanation of Inert Pair Effect

- Although energy "cost" of forming M(IV) is high for the lighter elements, the "pay-back" of bond formation is high, too.

- Ionization energy drops dramatically after C, declining slowly through the rest of the group.

- Bond strengths peak at Si, slowly decline through Sn, and then drop off significantly at Pb.

- At Ge and Sn, both M(II) and M(IV) states are stable.

- At Pb, the bond strength is too low to compensate for the slightly higher ionization energy requirement of the Pb(IV) state in many cases. Hence, the +2 state is favored.

☞ In all these compounds, the oxidation state is merely a formalism, because all are molecular (not ionic) compounds.

Group 14 Tetrahalides

- All are known, except PbI_4, whose Pb-I bonds are too weak to support the higher oxidation state.

- Although C–X bonds are strong, CI_4 has significant steric crowding and decomposes on heating or in u.v. light to C_2I_4, whose I–C–I angle of 114.2° reduces the strain.

$$2CI_4 \rightarrow I_2C{=}CI_2 + 2I_2$$

- Except for SnF_4 and PbF_4, all are very volatile, suggesting covalent bonding with weak van der Waals forces between molecules.

- SnX_4 compounds can act as Lewis acids in the presence of excess halide ion.

$$SnX_4 + 2X^- \rightarrow SnX_6^{2-}$$

  - Lewis acid strength is in the order $SnF_4 > SnCl_4 > SnBr_4 > SnI_4$.
  - SnI_4 can also undergo redox with I^- to give SnI_2.

$$SnI_4 + I^- \rightarrow SnI_2 + I_3^-$$

    The resulting solution is brown in polar solvents.

- Except for CX_4, all hydrolyze in water to give various hydrated oxides, although it is possible to isolate a few hydrates of Sn(IV).

- SnX_4 compounds hydrolyze to give hydrated SnO_2 and HX.

$$SnX_4 + 2H_2O \rightarrow SnO_2 + 4HX$$

  - Similar reaction occurs with alcohols.

Synthesis of SnI_4

- Direct reaction of tin metal with iodine in methylene chloride yields SnI_4 as the principal product, with formation of SnI_2 as a side reaction.

$$Sn + 2I_2 \rightarrow SnI_4$$
$$Sn + I_2 \rightarrow SnI_2$$

- SnI_4 is a red-orange solid; SnI_2 is a yellow-red solid.
  - Color due to polarizability of I^-, probably involving charge transfer ($I \rightarrow Sn$).

- SnI_2 is polar, and SnI_4 is non-polar.
  - As a result, SnI_2 is slightly more soluble in CH_2Cl_2.

- SnI_2 is somewhat more ionic and has a higher m.p.

SnI_2 m.p. $\approx$ 330 ^oC SnI_4 m.p. = 143-144 ^oC