Group 14 : Tin Chemistry

AP

$\text{Sn} : 1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}5s^{2}5p^{2}$

A. G. Massey, *Main Group Chemistry*, 2nd ed., John Wiley, New York, pp. 213 – 264.

- Symbol Sn from Latin *stannum*
- One of the longest known elements
- Tin has more stable isotopes (10) than any other element.
- 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

The Group 14 Elements

Element	Electronic Configuration	1st Ionization Energy (kJmol^{-1})	2nd Ionization Energy (kJmol^{-1})	Covalent Radius (Å)
${}^{12.011}_{6}\mathrm{C}$	$1s^2\ 2s^2\ 2p^2$	1086	2352	0.77
${}^{28.0855}_{14}\mathrm{Si}$	$[\mathrm{Ne}]\ 3s^2\ 3p^2$	786.1	1576	1.17
${}^{72.61}_{32}\mathrm{Ge}$	$[\mathrm{Ar}]\ 3d^{10}\ 4s^2\ 4p^2$	761.5	1537	1.22
${}^{118.710}_{50}\mathrm{Sn}$	$[\mathrm{Kr}]\ 4d^{10}\ 5s^2\ 5p^2$	708.5 ↓	1412 ↓	1.41
${}^{207.2}_{82}\mathrm{Pb}$	$[\mathrm{Xe}]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$	715.5 ↑	1450 ↑	1.54

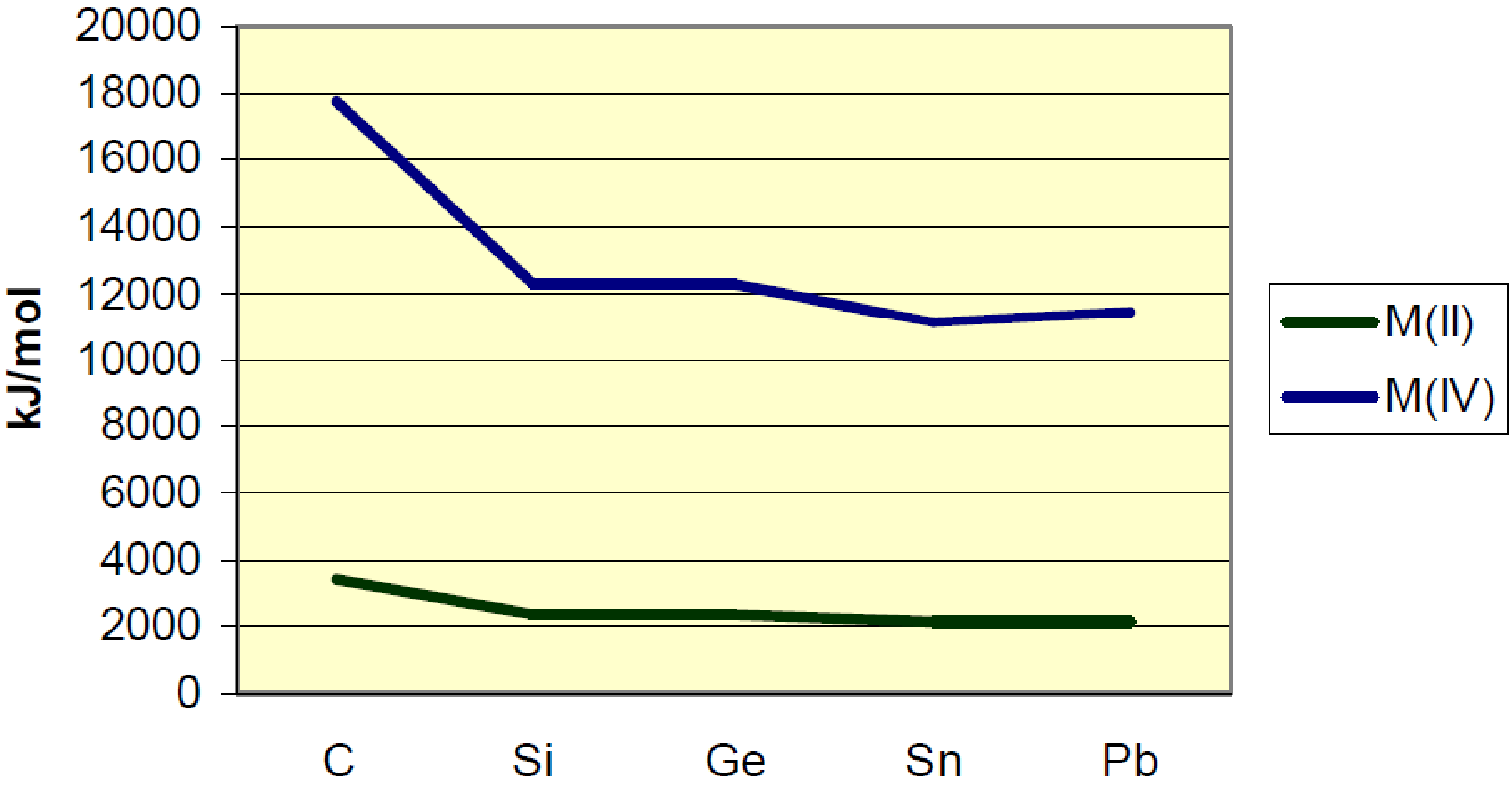
- All Group 14 elements have the valence configuration ns^2np^2.
- Stable carbon and silicon compounds are observed in the +4 state.
- Going down the group the +2 state becomes more stable.

Group 14 Ionization Energies

- The ionization energies for Group 14 elements are irregular due to inner *d* orbitals (Ge, Sn, Pb), inner *f* orbitals (Pb) and relativistic effects (Pb).
- The exceedingly ***high energies required to form M^{4+} ions*** *(next slide)*, coupled to the fact that such ions would be small and highly polarizing, means that the existence of M^{4+} cations is highly unlikely.
- ***Group 14 compounds are predominantly molecular*** with only SnO_2 , PbO_2 and the Sn,Pb fluorides thought to have significant ionic character.

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

Group 14 Ionization Energies

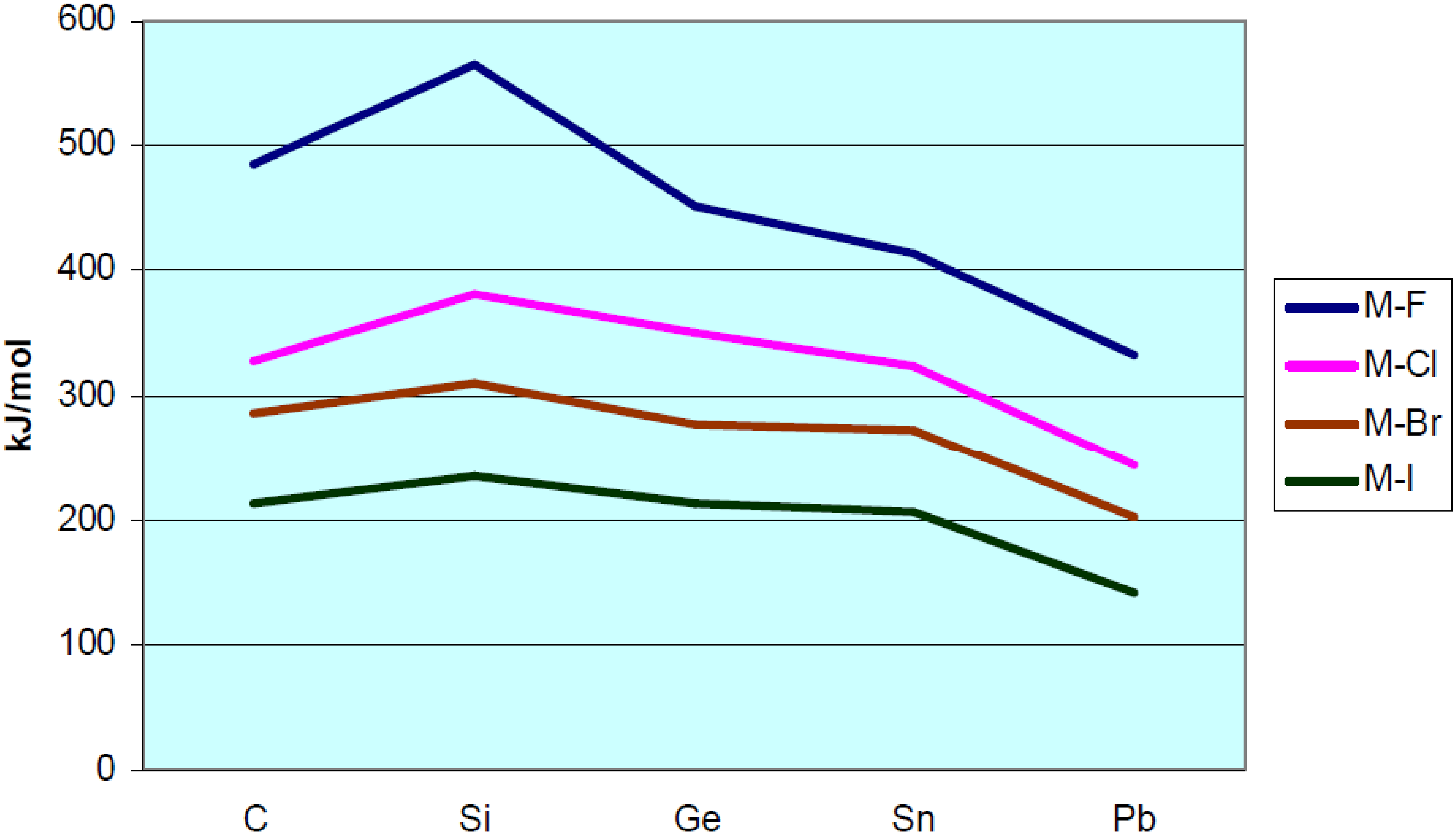


- Ionization energy drops dramatically after C, declining slowly through the rest of the group with Pb breaking this trend due to decreased shielding and enhanced relativistic effects.

Inert Pair Effect

- ***The increasing stability of the lower state (+2) as we descend the Group*** has been called the “inert pair effect” for the tendency of the n*s*^{2} configuration to be retained *(most prominent for Sn and Pb).*
- This has nothing to do with inherent “inertness” of the n*s*^{2} configuration, but rather ***simply a consequence of thermodynamics*.**
- Although energy “cost” of forming M(IV) is high for the lighter elements, the “pay-back” of bond formation is high, too.
- 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.
- A similar "inert pair" effect is found in groups 13 and 15.

Group 14 MX_4 Bond Enthalpies



Tetravalency of the Group 14 Elements

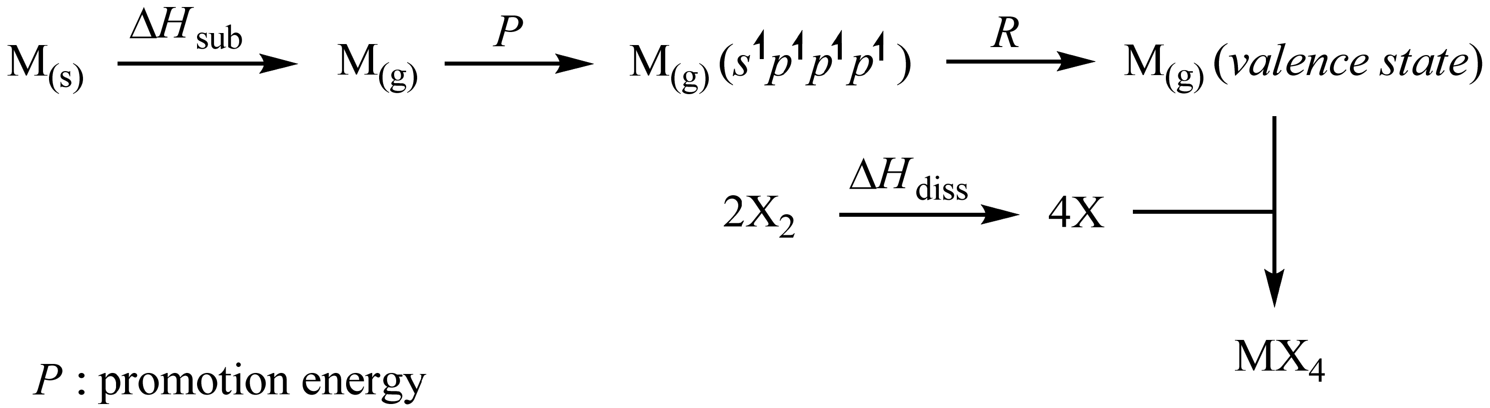
- From their outer electron configuration of ns^2np^2 , one might expect the Group 14 elements to form covalent compounds on which they bond only to two other atoms using their half-filled *p*-orbitals.

- However, this is contrary to observation because, in the vast majority of their compounds, **the Group 14 elements (especially carbon) are tetrahedrally surrounded by four other groups.**

- This occurs because it is relatively easy for an n*s* electron to be promoted to the unfilled n*p* orbital.

- For C the 2*s* → 2*p* promotion energy is 405.8 kJ mol^{-1} , with the n*s* → n*p* promotion energy decreasing slightly as we descend the Group.

- Although the n*s* → n*p* promotion certainly leaves the element with four unpaired electrons, the electron have all their spins parallel. To obtain the element in its *valence 'reacting'* state work must be done to randomize the electron spins.*
- Therefore to form MX_4 *(X = halide)* from the Group 14 element M and X_2 the following energy steps must be considered:



$$\begin{tikzcd}
M_{(s)} \arrow[r, "\Delta H_{\mathrm{sub}}"] & M_{(g)} \arrow[r, "P"] & M_{(g)}\,(s^{\upharpoonleft}p^{\upharpoonleft}p^{\upharpoonleft}p^{\upharpoonleft}) \arrow[r, "R"] & M_{(g)}\,(\textit{valence state}) \arrow[dd] \\
& 2X_2 \arrow[r, "\Delta H_{\mathrm{diss}}"] & 4X \arrow[r, dash] & {} \\
& & & MX_4
\end{tikzcd}$$

P : promotion energy

R : electron spin randomization energy

$$\boxed{\textbf{Total energy input} = \Delta H_{\mathbf{sub}} + \boldsymbol{P} + \boldsymbol{R} + 2\Delta H_{\mathbf{diss}}}$$

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*The hypothetical process of hybridization from $s\ p_{x,y,z}$ → four sp^3 orbitals is a mathematical step and requires no energy input.

$$\boxed{\textbf{Total energy input} = \boldsymbol{\Delta H}_{\textbf{sub}} + \boldsymbol{P} + \boldsymbol{R} + \boldsymbol{2\Delta H}_{\textbf{diss}}}$$

- This ***energy has to be regained by the formation of four strong M-X bonds***.
- However, the production of MX_2 requires fewer energy-consuming steps:

$$\begin{tikzcd}
M_{(s)} \arrow[r, "\Delta H_{\mathrm{sub}}"] & M_{(g)} \arrow[r, "R'"] & M_{(g)}\ (\textit{valence state}) \arrow[dd] \\
X_2 \arrow[r, "\Delta H_{\mathrm{diss}}"] & 2X \arrow[r, dash] & {} \\
 & & MX_2
\end{tikzcd}$$

$$\boxed{\textbf{Total energy input} = \boldsymbol{\Delta H}_{\textbf{sub}} + \boldsymbol{R'} + \boldsymbol{\Delta H}_{\textbf{diss}}}$$

- But only two M-X bonds are formed to compensate for the required energy input.

- ***Which of process leads to the more thermodynamically stable molecule?***

- MX_4 is favored for at least C, Si, Ge and Sn. For example, the enthalpy of formation at 25 °C for CH_2 and CH_4 is +343 kJ mol^{-1} and -74.9 kJ mol^{-1} , respectively.

- Thus, although the utilization of the ns^2 electrons requires a higher initial input of energy, this is more than offset by the formation of two extra stabilizing M-X bonds.

- However, the ***M-X covalent bond strength decreases as we descend the group***, with the result that not all Pb-X bonds are capable of supplying the energy required to stabilize the Pb(IV) state with respect to Pb(II).

- PbF_4 , $PbCl_4$ and $PbBr_4$ readily decompose upon heating, e.g.

$$PbCl_4 + \Delta \rightarrow PbCl_2 + Cl_2$$

- PbI_4 is too unstable to exist at room temperature!!

- Although C–X bonds are strong, carbon tetraiodide CI_4 has significant steric crowding and decomposes on heating or exposure to UV light forming 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 ***Group 14 compounds are very volatile, suggesting covalent bonding with weak van der Waals forces between molecules***.

[For organotin compounds SnR_n and SnH_n *($n = 2,4$)* this can render them with a high toxicity]

SnX_4 Halides

- 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.
- SnX_4 compounds hydrolyze to give hydrated SnO_2 and HX.

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

- Similar reaction occurs with alcohols.

- 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.

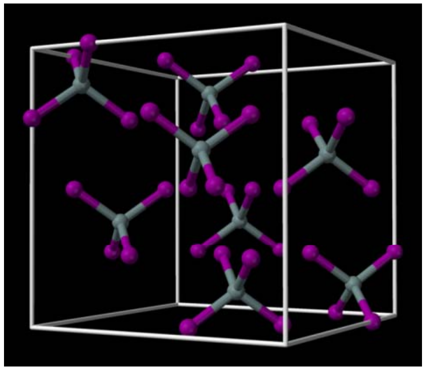
$$Sn + 2I_2 \rightarrow SnI_4$$

$$Sn + I_2 \rightarrow SnI_2$$

- 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. ≈ 330 °C

SnI_4 m.p. = 143-144 °C



- ***Elemental iodine*** is harmful if swallowed, inhaled, or absorbed through the skin.
- It readily sublimes (vaporizes from the solid state) at atmospheric pressure, especially if warmed.
- It is a lachrymating agent (makes your eyes tear up).

- ***Methylene chloride*** (b.p. = 40 °C), the solvent in this preparation, is also harmful if swallowed, inhaled, or absorbed through the skin.
- Exposure may cause nausea, dizziness, and headache. It is a narcotic at high concentration and a possible carcinogen. Exposure should be minimized.