

Important questions of periodicity (CHEM-406)

- **Discuss p π -p π bonding in the heavier congeners of group 14A.**

In the heavier congeners of group 14A, particularly in silicon (Si), germanium (Ge), tin (Sn), and lead (Pb), p π -p π bonds play a crucial role in bonding. A p π -p π bond forms when the p orbitals of adjacent atoms overlap sideways, creating a bond that involves the sharing of electrons above and below the bonding axis. These bonds are characteristic of double and triple bonds in molecules where π -bonds are involved.

Silicon (Si)

Silicon primarily forms covalent bonds in its compounds. In addition to the usual σ bonds formed by the direct overlap of atomic orbitals, silicon can also form p π -p π bonds. These bonds involve the sideways overlap of the p orbitals of adjacent silicon atoms, allowing for the sharing of electrons in a π bond configuration. This enables the formation of double bonds, especially in molecules where silicon atoms are bonded to each other. The compounds containing silicon-silicon double bonds (Si=Si) called disilenes, akin to carbon-carbon alkenes. Despite similarities to alkenes, silicon's larger size and lower electronegativity introduce differences. An example of a disilene molecule is R $_2$ Si=SiR $_2$, where R represents bulky substituents.

Germanium (Ge)

Germanium exhibits similar bonding behavior to silicon due to its position in the same group of the periodic table. Like silicon, germanium forms covalent bonds and can participate in p π -p π bonding. The sideways overlap of the p orbitals of adjacent germanium atoms allows for the formation of double bonds, contributing to the structural diversity of germanium compounds. Germanium displays p π -p π bonding in compounds like digermenes (Ge=Ge), akin to carbon alkenes. Digermenes, germanium atoms form double bonds through a σ bond and a π bond, exemplified by Mes $_2$ Ge=GeMes $_2$, are rare and stabilized by bulky substituents to prevent polymerization. Despite similarities with disilenes, differences arise due to germanium's larger size and lower electronegativity. While less common than in silicon.

Tin (Sn)

As we move down the group to tin, the involvement of d-orbitals becomes more significant due to the larger atomic size. Tin compounds can form both σ and p π -p π bonds, with the latter becoming increasingly important. The participation of d-orbitals allows for the formation of additional π bonds, enabling tin to exceed the octet rule in some compounds. This can lead to hypervalency, where tin forms more than the usual number of bonds, contributing to the bonding complexity observed in tin compounds. Tin exhibits p π -p π bonding in certain organotin compounds like distannenes, akin to carbon alkenes. In distannenes, tin atoms form double bonds (Sn=Sn) through a σ bond and a π bond, as seen in R $_2$ Sn=SnR $_2$. These compounds are rare and stabilized by bulky substituents to prevent polymerization. Despite similarities with disilenes and digermenes, differences arise due to tin's larger size and lower electronegativity.

Lead (Pb)

Similar to tin, lead compounds exhibit a complex bonding behavior influenced by the larger atomic size and the significant contribution of d-orbitals. Lead forms both σ and $p\pi-p\pi$ bonds, with the involvement of d-orbitals enabling the formation of multiple bonds. The larger atomic size of lead allows for greater flexibility in bonding arrangements, contributing to the structural diversity and complexity of lead compounds. Lead exhibits $p\pi-p\pi$ bonding in certain organolead compounds like diplumbenes, akin to carbon alkenes. In diplumbenes, lead atoms form double bonds ($Pb=Pb$) through a σ bond and a π bond, exemplified by $R-Pb=Pb-R$. These compounds are rare and less stable compared to silicon and germanium analogs. Diplumbenes are highly reactive and sensitive to environmental factors, requiring specific synthetic conditions and stabilizing groups for synthesis.

In summary, the bonding in the heavier congeners of group 4A elements is characterized by the interplay of σ and $p\pi-p\pi$ bonds, with the involvement of d-orbitals becoming more pronounced as we move down the group. These elements exhibit diverse bonding patterns, influenced by factors such as atomic size, orbital hybridization, and electron configuration.

• Discuss the periodic anomalies of post-transition metals?

The periodic anomalies of post-transition metals is following:

- **Atomic Radii:** Post-transition metals typically exhibit a decrease in atomic radii across a period. However, anomalies occur due to factors such as electron configuration and shielding effects. Elements with partially filled d orbitals may have larger than expected atomic radii due to poor shielding of outer electrons by inner d electrons.
- **Ionization Energies:** The ionization energies of s electrons in post-transition metals are lower than expected. This anomaly is influenced by electronic configuration. In some cases, electrons in the s orbitals are easier to remove than predicted due to the presence of partially filled d orbitals, which offer less effective shielding from the nucleus.
- **Electronegativity:** Electronegativity measures an atom's ability to attract electrons in a chemical bond. Post-transition metals typically have lower electronegativity than expected. This anomaly can be attributed to the presence of partially filled d orbitals, which reduce the effective nuclear charge experienced by outer electrons, thus decreasing their ability to attract electrons.
- **Reactivity:** Post-transition metals are generally less reactive than expected due to the stability conferred by fully filled or partially filled d subshells. This anomaly arises from the reluctance of post-transition metals to lose or gain electrons, leading to lower reactivity compared to other metals.
- **Formation of Compounds:** Post-transition metals can form compounds with unexpected oxidation states. This anomaly is influenced by complex electronic configurations and the

ability of post-transition metals to exhibit variable oxidation states due to the availability of d orbitals for bonding.

- **Magnetic Properties:** Post-transition metals can exhibit unusual magnetic properties. This anomaly arises from the presence of unpaired electrons in d orbitals, which can give rise to paramagnetism or other magnetic phenomena depending on the arrangement of electrons and the coordination geometry of the metal center.
- **Catenation:** Catenation refers to the ability of atoms to form chains through covalent bonding. Some post-transition metals, particularly those with partially filled d orbitals, exhibit catenation. This anomaly arises from the ability of d orbitals to participate in bonding, allowing the formation of stable chains or clusters of metal atoms.
- **Multiple Bonding:** Post-transition metals can form multiple bonds with other elements, similar to the behavior observed in certain carbon compounds. This anomaly occurs due to the ability of post-transition metals, particularly those with vacant or partially filled d orbitals, to share multiple pairs of electrons with other atoms, resulting in the formation of double or triple bonds.

- **What is s-inert pair effect?**

2.9 Inert Pair Effect

There are two types of oxidation states of lower elements in group III-A, IV-A and V-A. Some oxidation states shown by the elements of these groups are given below.

Group III A	$(ns^2p^1) \rightarrow B = +3;$	Al = +3;	Ga = +3, +1;	In = +3, +1;	Tl = +3, +1
Group IV A	$(ns^2p^2) \rightarrow C = +4;$	Si = +4;	Ge = +4, +2;	Sn = +4, +2;	Pb = +4, +2
Group V A	$(ns^2p^3) \rightarrow N = +3;$	P = +5, +3;	As = +5, +3;	Sb = +5, +3;	Bi = +5, +3

Cause of Inert Pair Effect:

Let us consider valence shell electronic configuration of the atoms of the elements of group IVA. It is ns^2np^2 . Two np electrons are farther away from the nucleus and can easily be removed or be excited to the higher orbitals than the latter ns^2 electron in case of atoms of hi-

gher at No. in these groups. The two ns^2 electrons are thought to be inert. It means that ns^2 electrons remain paired and donot take part in bonding. This is especially true in the heaviest element namely lead ($_{82}\text{Pb}$). The above discussion shows that lead forms Pb^{2+} is more easily formed than Pb^{4+} .

Variation of Inert Pair Effect:

Inert pair effect increases as we move down the group. This means that as we move down the group, ns^2 electron pair present in the cations having lower oxidation states becomes more and more inert and hence tends to remain paired.

Relative Stability of +1 and +3 Oxidation States of group III-A

Since inert pair effect is absent in B and Al. Both these elements lose or share all their three ns^2p^1 electrons. Thus B and Al show consistently +3 oxidation state. Since inert pair effect in Ga^{\ominus} and In^{\ominus} ions both is not effective to any great extent. $4s^2$ electron pair in Ga^{\ominus} ion and $5s^2$ electron pair in In^{\ominus} ion, is not stable ($Ga^{\ominus} > Ga^{\oplus}$, $In^{\ominus} > In^{\oplus}$). In other words we can say that **Ga and In are more stable in their group oxidation states (+3). Being less stable, Ga (+1) and In (+1) compounds are readily oxidised to more stable Ga (+3) and In (+3) compounds and in this conversion they reduce other substances. So remember that ^{31}Ga and ^{49}In in their lower oxidation states i.e., act as reducing agents.**

It means that $6s^2$ electron pair of Ti^{\ominus} ion ($Ti^{\ominus} = 6s^2 6p^0$) is very stable or inert and hence is not lost easily to convert Ti^{\ominus} to Ti^{+1} . Thus Ti^{\ominus} ion is more stable than Ti^{+1} ion. Being less stable, $Ti(+3)$ compounds are readily reduced to $Ti(+1)$ compounds and in this conversion they oxidise some other substance. **Consequently $Ti(+3)$ compounds act as oxidising agents while $Ti(+1)$ compounds act as reducing agents.**

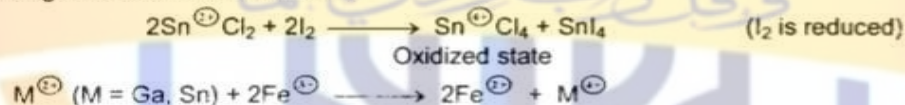
The inert pair effect increases from Ga to Tl, the stability of Ga^{\oplus} , In^{\oplus} and Tl^{\oplus} also increases as: $\text{Ga}^{\oplus} < \text{In}^{\oplus} < \text{Tl}^{\oplus}$ while that of Ga^{\ominus} , In^{\ominus} and Tl^{\ominus} decreases in the same direction ($\text{Ga}^{\ominus} > \text{In}^{\ominus} > \text{Tl}^{\ominus}$).

Relative Stability of +2 and +4 Oxidation States of Group IVA

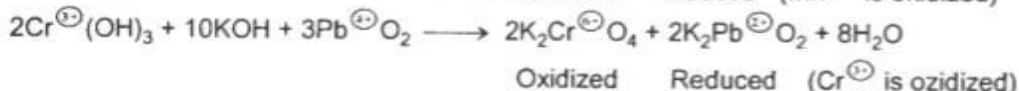
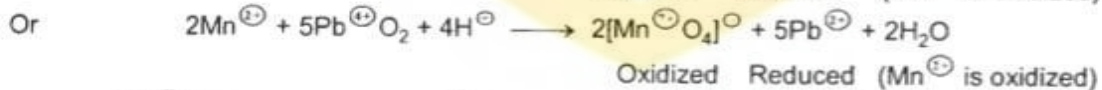
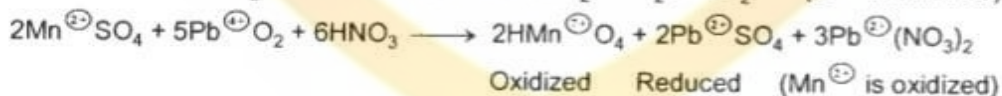
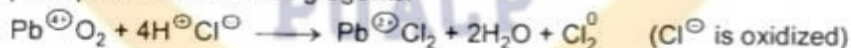
Carbon and silicon both show consistently +4 oxidation states. The heavier elements i.e., ${}_{32}\text{Ge}$, ${}_{50}\text{Sn}$ and ${}_{82}\text{Pb}$ show +2 as well as +4 oxidation states. On the same lines of arguments, the following conclusions can be drawn in connection with the relative stability of various oxidation states.

- (ii) Ge^{4+} and Sn^{4+} both are more stable than Ge^{2+} and Sn^{2+} respectively or you can say that $\text{Ge}^{2+} < \text{Ge}^{4+}$ and $\text{Sn}^{2+} < \text{Sn}^{4+}$.

Ge (+2) and Sn (+2) compounds are good reducing agents as is evident from the following reducing properties shown by Ge (+2) and Sn (+2) compounds. Some ionic reactions are given to convince ourselves.



- (iii) Pb^{+2} compounds are more stable than Pb^{+4} compounds ($\text{Pb}^{2+} > \text{Pb}^{4+}$) and hence Pb^{+4} compounds are oxidising agents.



The increasing order of +2 state is supported by the fact that only a few compounds of Ge^{2+} are known while Pb^{2+} forms many compounds. Similarly the decreasing order of +4 state is evident from the fact that very few compounds of Pb^{4+} have been obtained and they are unstable.

Relative Stability of +3 and +5 Oxidation States of Group VA

The valence-shell configuration of the atoms of elements in V-A group is ns^2p^3 . +3 state is caused when only three np electrons are involved in chemical bonding. +5 state is obtained when all the three np and both ns electrons are involved. On the basis of inert pair effect it can be shown that the stability of +3 oxidation state increases and that of +5 decreases as we move down the group from N to Bi. The last element Bi prefers to show +3 oxidation state and shows reluctance to exhibit +5 oxidation state.