

# Periodicity

## "Introduction:"

Periodicity is usually concerned with the trends that run all over periodic table. Increases the atomic number in given period will increase the Polarization energy, electron affinity and electronegativity due to the decrease in size.

But this chapter is mainly associated with the participation of d-orbital in bonding by the p-block elements.

### 1-<sup>v</sup> FIRST AND SECOND ROW ANOMALIES

In many ways the first ten elements differ considerably from remaining 99. Hydrogen is a classic example it belongs neither alkali metals nor halogens although it has some properties common with both the elements of 2nd

12

How also differ from their heavier analogues. Lithium is anomalous among alkali metals and resembles magnesium more than its congeners and in return Group IIA the Beryllium is more closely to the aluminium than to other alkaline earths.

2)

### "The diagonal Relation"

3)

It was mentioned previously that a strong resemblance obtains between Li & Mg, Be & Al and other diagonal elements. It is considered that this could be related to size-charge phenomena.

- Lithium and Magnesium

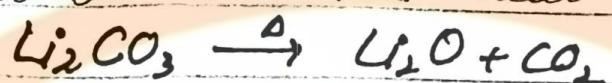
2015

- 1) Unlike Na, K, Rb or Cs but like Mg lithium reacts directly with the nitrogen to form nitride



In chemistry a diagonal relationship is said to exist between certain pairs of diagonally adjacent elements in the second and third periods of the periodic table.

2) The carbonates of both lithium and magnesium are unstable and can decompose to form oxides. But the carbonates of other alkali metals are stable towards heat.



3) Like Mg, Li decomposes water slowly to liberate  $\text{H}_2$  whereas other alkali metals reacts vigorously:



## Beryllium and Aluminium

2017

1- The oxidation emf's values of beryllium and aluminium is similar almost

$$E^\circ_{\text{Be}} = 1.85$$

$$E^\circ_{\text{Al}} = 1.66$$

2- The reaction with acid is also thermodynamically favoured in both it is rather slow especially if surface is protected by oxide

- 3) The similarity of ionic potentials for ions is remarkable.

$$\text{Be}^{+2} = 48 \quad \text{Al}^{+3} = 56$$

and results in similar polarizing power and acidity of cations.

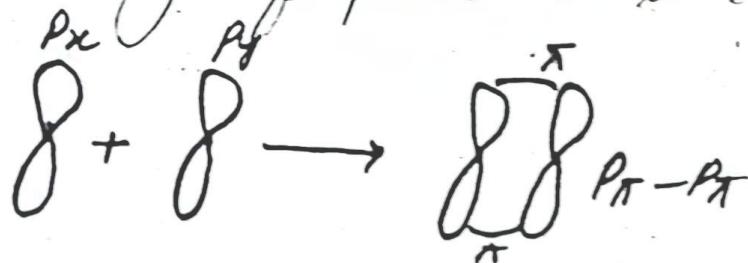
- 4) The carbonates of both elements are unstable

## USE OF P-ORBITAL IN $\pi$ -BONDING

2014, 2015  
2016, 2017

✓ 2-

$\pi$ -bond is formed by the side to side overlapping of dumble shaped orbitals. Hence p-orbital may be involved in both sigma and pi bonding. But here we will discuss only about pi-bonding. The pi bonding of p-orbital is:

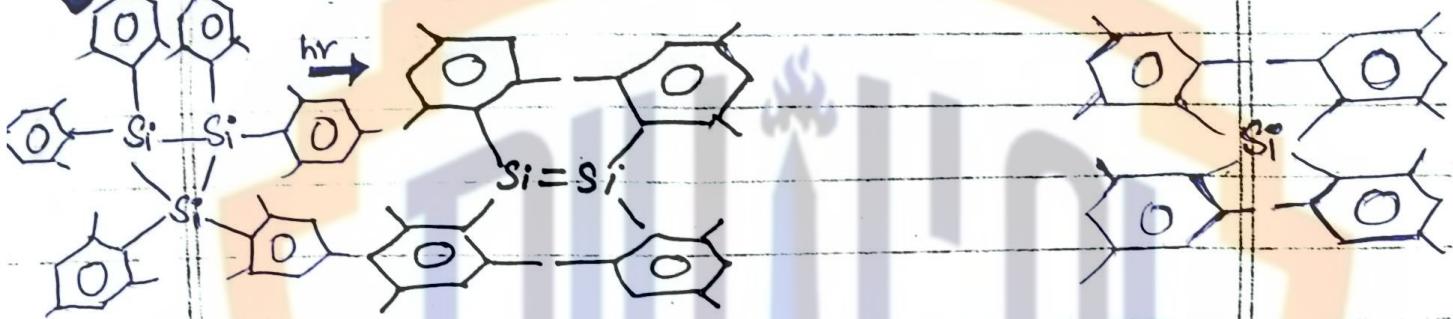


Here, we will discuss about the  $\pi$ -bonding in non-metals.

## Explanation:

The first

stable  $C=Si$  and  $Si=Si$  were synthesized about a decade ago. One synthesizes also involved the rearrangements of cyclotrisilane.



The pi-bonding present in first elements is quite different from their heavier congeners. But at the same time, this bonding may be analogous to one another. The examples are as follows:

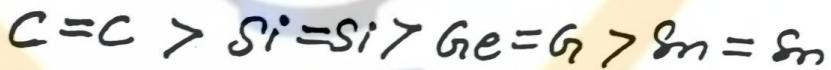
PUACP

- C-Si similarities & contrast
- N-P similarities & contrast

These examples makes us cleare the relation of p-orbital in pi-bonding in first elements with their heavier congeners.

## Pi-bonding in Carbon and their members

The contrast between the strength of  $2p_x - 2p_x$  bond and their higher  $n$ -congeners is also responsible for the stability of groups i.e. alkenes, aldehydes, ketones etc. A source of greater stability of  $\pi$ -bonds between the smaller atoms could be better overlap of  $2p$ -orbital. As the size increase so, overlapping is usually poorer. Now the order of stability of  $\pi$ -bonding in C-group is

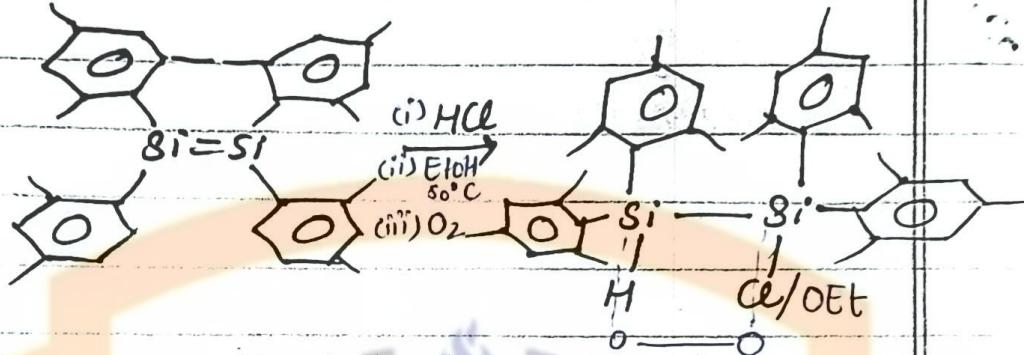


### Similarities

Similarities b/w the  $\pi$ -bonding of carbon group are as follows:

- 2) It is possible to add reagents across the  $Si=Si$  double bond

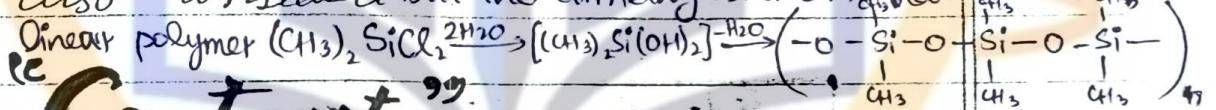
in some way analogous to  $C=C$   
in alkenes.



2) Carbon dioxide is a gaseous monomer but silicon dioxide is a infinite <sup>single bonded</sup> polymer.



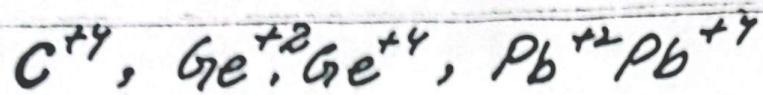
3) <sup>relative to ketones</sup>  
Gem-disols are unstable and the analogous silicon compounds are also unstable but the dimethyl silicon <sup>that</sup> forms is a



### Contrast

The difference b/w the pi-bonding of carbon and their heavier congeners are as follows:

1) Carbon is generally tetravalent except as carbene. But it is possible to prepare divalent Germanium, lead compounds



If bulky substituents are present the compounds  $R_2Ge$ ;  $R_2Sn$  and  $R_2Pb$  exist as dimagnetic monomers in solution; although there is a tendency to form dimer in solid. But this is not possible in carbon.

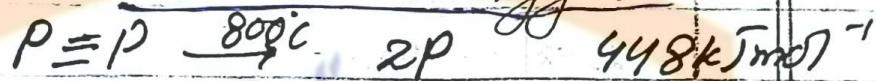
The calculated bond orders of  $Ge-Ge = 1.61$  and  $Sn-Sn = 1.46$  which shows that bonding is more stronger in  $Ge$  due to smaller size than  $Sn-Sn$ .

### Pi Bonding in Nitrogen & their members

The stable form of nitrogen at room temperature is  $N_2$ , which has an extra-ordinary strong triple bond  
 $N \equiv N = 946 \text{ kJ mol}^{-1}$

But in contrast white phosphorus consist of  $P_4$  molecules.

and thermodynamically stable form is black phosphorus which is a polymer. At temperature above  $800^{\circ}\text{C}$  dissociation of  $\text{P}_4$  molecule does takes place because it has less bond energy.



In heavier elements of nitrogen group, several single bond is more effective than multiple bonds."

One of the first challenges facing chemist attempting to prepare the phosphorus analogous to nitrogen compounds was phosphabenzene.



The  $\text{p}_{\pi}$ -bond of heavier member of nitrogen group is weak due to the lesser overlap of  $\text{p}$ -orbital. So, it forms

or

the poorer  $\pi$ -bond as compared to nitrogen atom.



### Summary of $P\pi - P\pi$ bonding in heavier non-metals

The occurrence of double and triple bond for Si and P was equally rare among other non-metals leading to following conclusions :

"Only  $C=C$ ,  $C \equiv N$ ,  $C \equiv O$ ,  $N \equiv N$  etc were stable multiple bonds"

None of the multiple bonds between heavier non-metals is as strong as those between  $2p$  elements. Some typical estimates of the strength of the  $\pi$  bond are

$$C=C = 272$$

$$Si=Si = 105 \quad Si=Ge = 105$$

$$Ge=Ge = 105$$

$$C=Si = 189$$

$$C=Ge = 130$$

$$C=Sn = 79$$

✓ 3- **The use of d-orbitals by non-metals:**

2011, 2013

2014

The d-orbital of non-metals is usually considered to be the part of bonding either in sigma bond. It is only possible when the elements are present in their ~~higher~~ <sup>higher</sup> oxidation state. But still there are certain theoretical and experimental evidences in favour and against the participation of d-orbital. Let us discuss step by step.

**Theoretical evidences against d-orbital participation in non-metals**

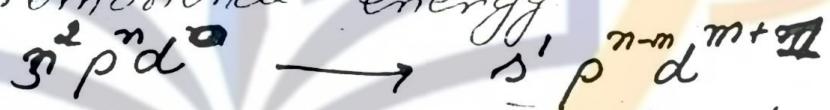
Several workers have been objected to the inclusion of d-orbital in bonding in non-metals.

The theoretical arguments against the participation of d-orbital in non-metals is bases of two factors:

- Large promotional energy
- Poor overlapping

### 1- LARGE PROMOTIONAL ENERGY

One of the basic objection on the participation of d-orbital in non-metals is the large promotional energy.



As d-orbital has larger energy as compared to s and p-orbital So, large amount of promotional energy is required for the excitation of electrons from p to d-orbital this is one of the main factor against participation of d-orbital in bonding.

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## POOR OVERLAPPING

The second factor which doesn't favour the utilization of d-orbital is the poorer overlapping, that they make with the orbitals of neighbouring atoms.

**Example:** The 3d-orbital of sulphur atom is completely shielded by the lower lying electrons and hence they are extremely diffuse. Due to the large diffused structure of d-orbital it causes poor overlapping and weak bonding.

Theoretical argues  
in favour of d-orbital participation

Several workers have been pointed out that large promotional energies and diffuse character of d-orbital describe

the properties of an isolated sulphur or phosphorus atom.

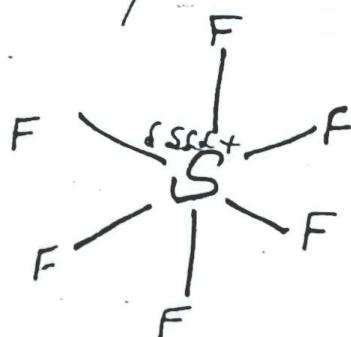
But we need to know the properties of sulphur atom in a molecules  $SF_6$ ,  $PF_5$

These molecules involved the participation of d-orbital which is favoured by two factors.

- Large partial charges.
- Large effective nuclear charge.

## 1- LARGE PARTIAL CHARGE

As in  $SF_6$  molecules Sulphur is attached with large electronegative substituents that cause to develop the large partial positive charge on Sulphur atom.



Large partial charges leads to more compact orbitals that results in effective overlapping"

Example: d-orbital in sulphur

SF<sub>6</sub> is contracted to a extent that cause the strong overlapping of orbitals with neighbouring atoms.

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## LARGE EFFECTIVE NUCLEAR CHARGE:

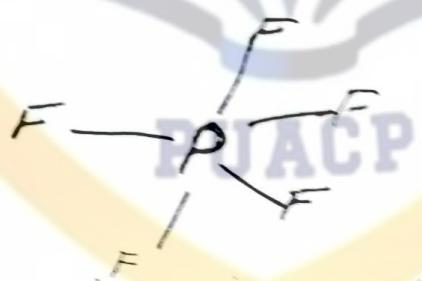
Increasing the effective nuclear charge of atom makes the energy levels approach more closely to the nucleus

Increasing effective nuclear charge results in larger inductive effect that cause to lower the promotional energy of d-orbital "

Hence, increasing the inductive effect result in lowering of the d-orbital more than the corresponding s and p orbitals. This results in better overlapping of d-orbitals.

### Example:

If we will take the example of  $\text{PF}_5$ , the atomic number of phosphorus is 15. So, it's this large effective atomic number that cause the shrinking of d-orbital result in better overlapping.



### Conclusion

It is concluded from the above theoretical argument,

that elements present in their lower oxidation state doesn't involve the participation of d-orbital but when they present in higher oxidation state then d-orbital involved in bonding of non-metals

Higher oxidation state on non-metals results in the participation of d-orbital"

Experimental Evidence for d-orbital Contraction and participation

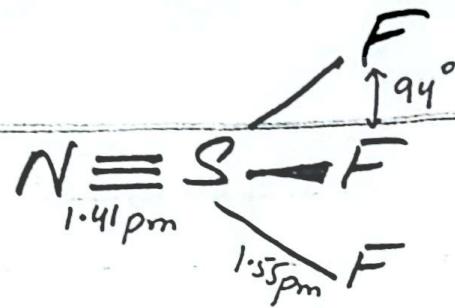
2014

2015

2016

2017

It is clear from the theoretical arguments that in non-metal the only condition for the participation of d-orbital is their higher oxidation state. One of the examples of the most remarkable molecules is thiacyl trifluoride  $NSF_3$



### Properties of $NSF_3$ :

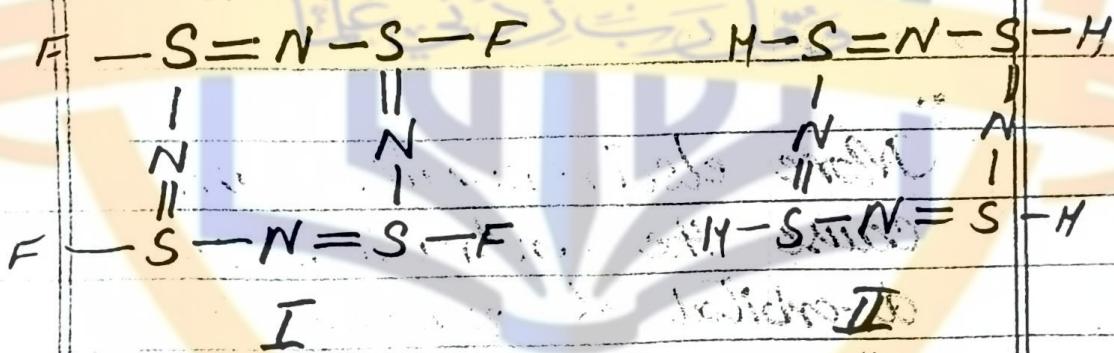
- ⇒ This compound is very stable and it does not react with  $NH_3$  at room temperature.
- ⇒ It reacts with HCl on heating and with Na metal below temperature 400°C.
- ⇒ The contraction of d-orbital of sulphur atom due to the inductive effect of fluorine atom permits the effective overlapping and  $\pi$ -bond formation with N atom.
- ⇒ The relative bond lengths of  $S-N$ ,  $S=N$ ,  $S\equiv N$  bonds are thus  $1.00 : 0.88 : 0.81$

This molecule just represent the participation of d-orbital

in bonding. But the ~~stability~~ of bond formed by d-orbital is not explained by this molecule. Let us takes few examples:

### d-orbital in Sulphur Compounds

If we took an example of  $S_4N_4F_4$  and that of  $N_2S_4H_4$



In structure I the ~~less~~ substituent is fluorine atom but in II the substituent is Hydrogen atom. The most stable bond formation is takes place in structure I.

Structure I show effective d-orbital participation than structure II

### Reason:

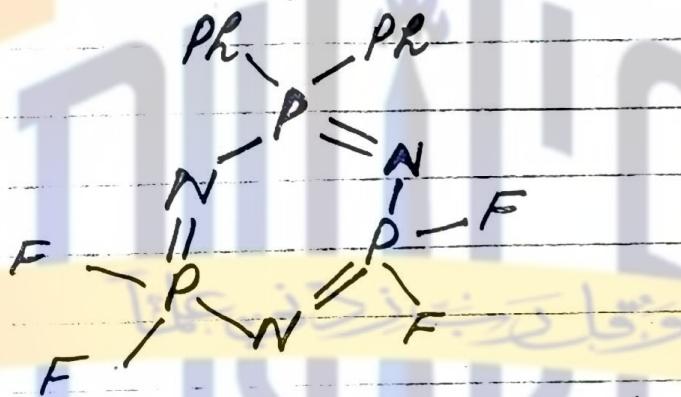
As both molecules contains the doubly bonded system which is shown by the alternation of  $S-N$  with  $S=N$  in ring. As fluorine atom is more electronegative So, due to inductive effect it cause the contraction of d-orbital of sulphur atom that results in more efficient overlapping of sulphur atom than with p-orbital of nitrogen atom.

"More electronegative atom cause the contraction of d-orbital of non-metals that results in efficient overlapping"

As hydrogen is electropositive atom So, it cause the expansion of d-orbital of Sulphur atom So, due to expansion it cause the weakness of  $\pi$ -bond formed with nitrogen atom.

## d-orbital in the Phosphorus compound

Now let us take an example of phosphazene for phosphorus compounds:



(1,1 diphenyl-3,3,5,5 tetrafluoro-triphosphazene)

Unsymmetrical substitution is involved in this molecule. This may allow the normally planar ring to bend. The three nitrogen atoms and fluoro-substituted phosphorus atoms are co-planar but phenyl-substituted phosphorus atom lies 20.5 pm above the plane.

We know that this ring

bent out of the plane the reason for this is as follows

"Reason"

The explanation offered is that more electrophilic phenyl group cause an expansion of phosphorus d-orbital that results in less efficient overlap with p-orbital of nitrogen atom and a weakening of  $\pi$ -system at that point. This allows the ring to deform and  $\text{Ph}_2\text{P}$  group bend out of the plane.

## Conclusion

The question of d-orbital participation in non-metals is still an open controversy. In case of sigma-bonded, the question is not too much of importance. But in case of  $\pi$ -bonding, the question for poor

overlapping and large promotional energy is not solved for participation of d-orbitals by non-metals.

#### ✓ 4- Evidence for $\delta\pi-\pi$ bonding 2016 A.S.

In the case of  $\delta\pi-\pi$  bonding, we can infer the presence of  $\sigma$ -bond when we find two atoms at a distance considerably shorter than the sum of their vander wall's radii. But the detection of  $\pi$ -bond depend upon the bond.

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- Shortening & strengthening of a bond.
- Stabilization of charge distribution.

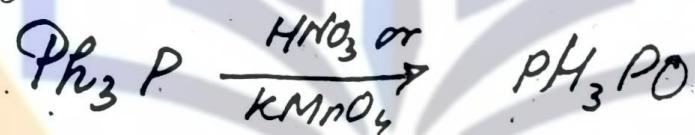
**Example:**  $\text{N}_2$ ,  $\text{NO}_2$ ,  $\text{N}_3^-$

The apparent existence

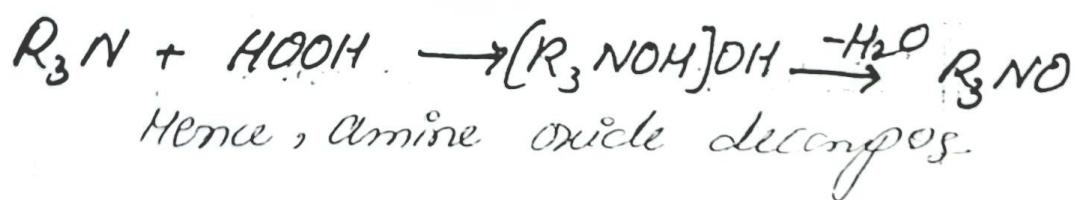
of  $\pi$ -bonding is in phosphine oxide. Most tertiary phosphines are unstable relative to oxidation to phosphine oxide:



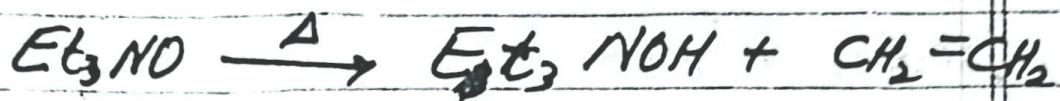
This reaction take place so readily that aliphatic phosphines must be protected from atmospheric oxygen. The triaryl phosphines are more stable but still oxidized readily:



But in contrast: aliphatic amine don't have to be protected from atmosphere <sup>oxygen</sup> although they can be oxidised.



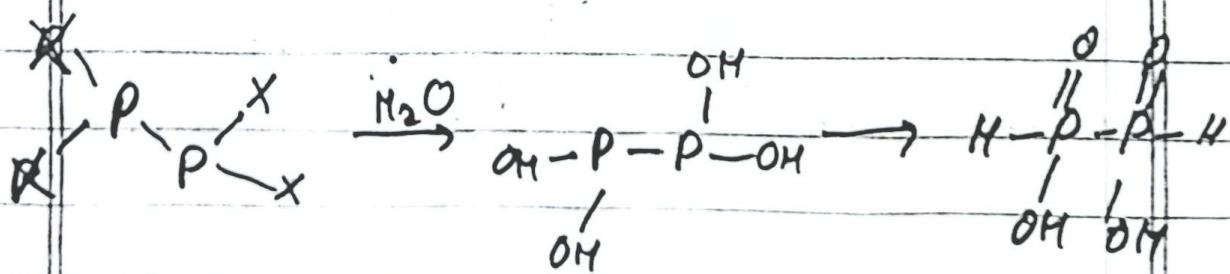
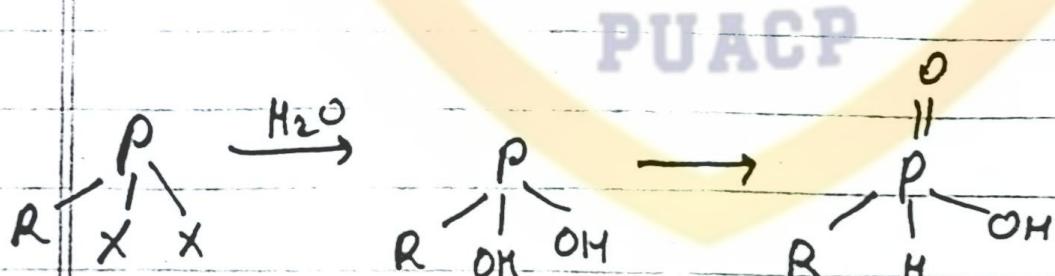
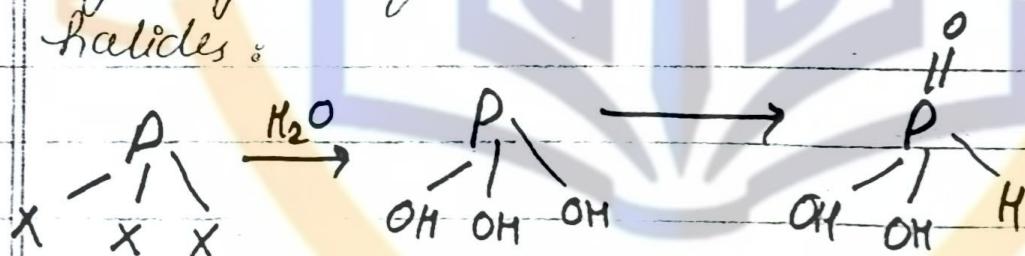
on heating:



This reaction is completely unknown for phosphine oxide which are thermally stable.

### P $\rightarrow$ O or P=O linkages

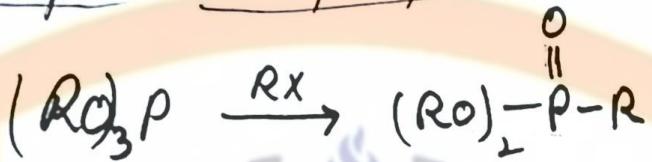
Phosphorus acids exist in four co-ordinate structures even though they are prepared by the hydrolysis of three-co-ordinate halides.



## Arbuzov Reaction:

2 The reaction of a trialkyl phosphite with an alkyl halide to produce an alkyl phosphonate

The tendency to form  $P=O$  is responsible for the Arbuzov reaction.  
The typical reaction for the re-arrangement of Trialkylphosphite to phosphonate:



The phosphine oxides can have contribution from  $d\pi-p\pi$  bonding between phosphorus oxygen atom.

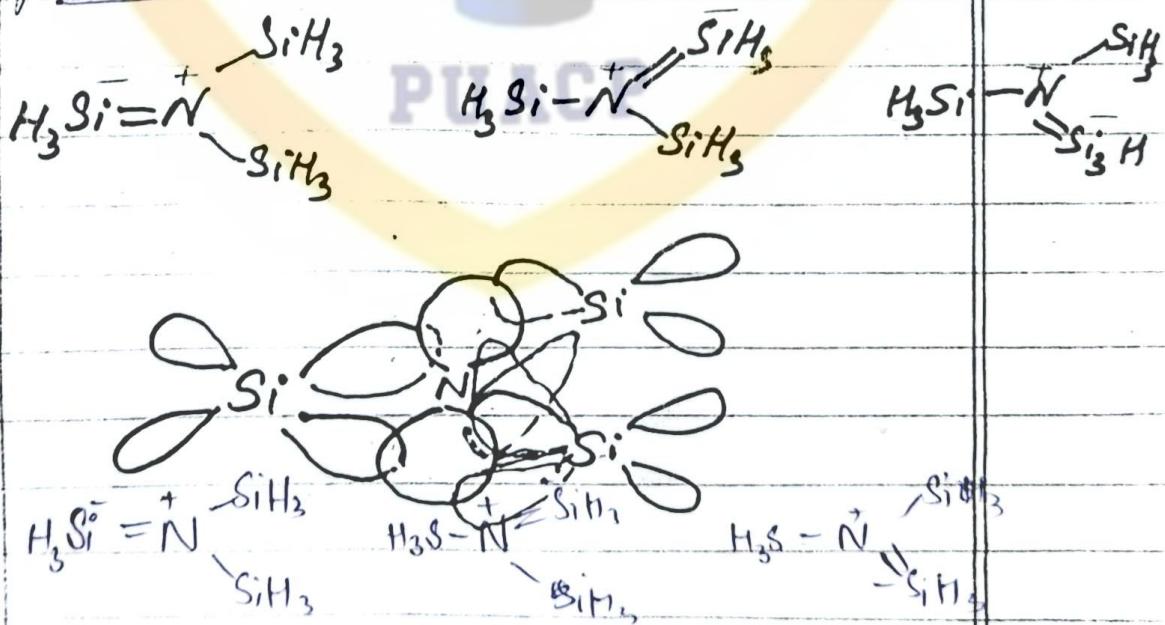


The correlation between electronegative substituent and strength of  $P=O$  provides support for  $\pi$ -bond but not for alternative dative  $\sigma$  bond.  $\sigma$  bond might be expected destabilized as electron density is removed from phosphorus requiring it to withdraw electrons from  $P \rightarrow O$  bond, weakening it. In contrast if oxygen atom can back bond to phosphorus through  $d-p\pi$  bond the induced charge

on phosphorus can be diminished and  $P=O$  bond strengthened.

### Evidences from bond Angles

The trimethyl amine molecule has a pyramidal structure much like that of  $NH_3$ . In contrast, triisilylamine molecule is planar. Although, steric effects of larger silyl groups might be expected to open up the bond angles. It seems hardly possible that they could force the lone pair out of fourth tetrahedral orbital and make the molecule perfectly planar.



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## Periodic Anomalies of non-metals and Post-transition metals

It is supposed that the properties of various families of periodic table change smoothly from less metallic at the top of family to more metallic at bottom of family. We know that the alkali metals are present on left and halogens and noble gas on right, this fact is true. But the ionization potential varies in a monotonous way. This is not true for certain central parts of the periodical table.

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- Reluctance of fourth row non-metals to exhibit maximum valence :

There is a definite tendency for non-metals of

fourth row - As, Se and Br to be  
unstable in their maximum  
oxidation state

### Example:

Synthesis of arsenic pentachloride is highly unstable. Although, both  $\text{PCl}_5$  and  $\text{SbCl}_5$  are stable. The only stable arsenic pentahalide is  $\text{AsF}_5$ .

In Group VIIA the same phenomena is encountered.  $\text{SeO}_3$  is thermodynamically unstable relative to  $\text{SO}_3$  and  $\text{TeO}_3$ . The enthalpies of formation of  $\text{SF}_6$ ,  $\text{SeF}_6$  and  $\text{TeF}_6$  are  $-1210$ ,  $-1117$  and  $-1320 \text{ kJ mol}^{-1}$  respectively. This indicates comparable bond energies for  $\text{S-F}$  and  $\text{Te-F}$  bond which are more stable than  $\text{Se-F}$ . The bond energies are :-

$$\text{S-F} = 317 \text{ kJ mol}^{-1}$$

$$\text{Se-F} = 285 \text{ kJ mol}^{-1}$$

$$\text{Te-F} = 330 \text{ kJ mol}^{-1}$$

## Anomalies of Group III A and Group IV A

o An explanation

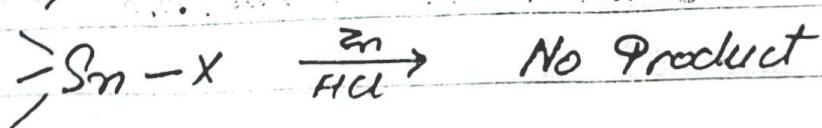
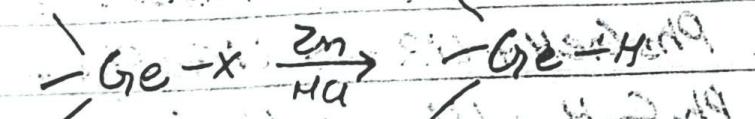
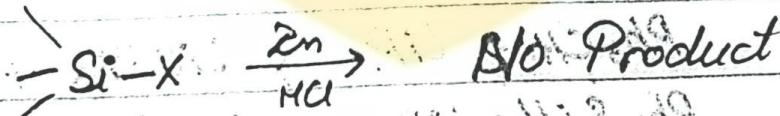
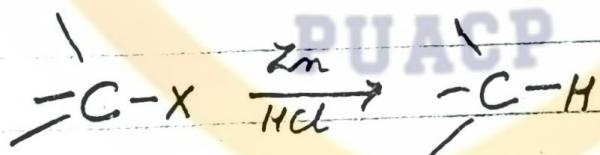
of the reluctance of As, Se and Br to exhibit maximum oxidation state a related phenomena will be explored. This involves a tendency of germanium to resemble carbon more than Si.

Some examples are:

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Reduction of halides  
with Zn and HCl

Germanium resembles  
carbon and Tin resembles  
silicon



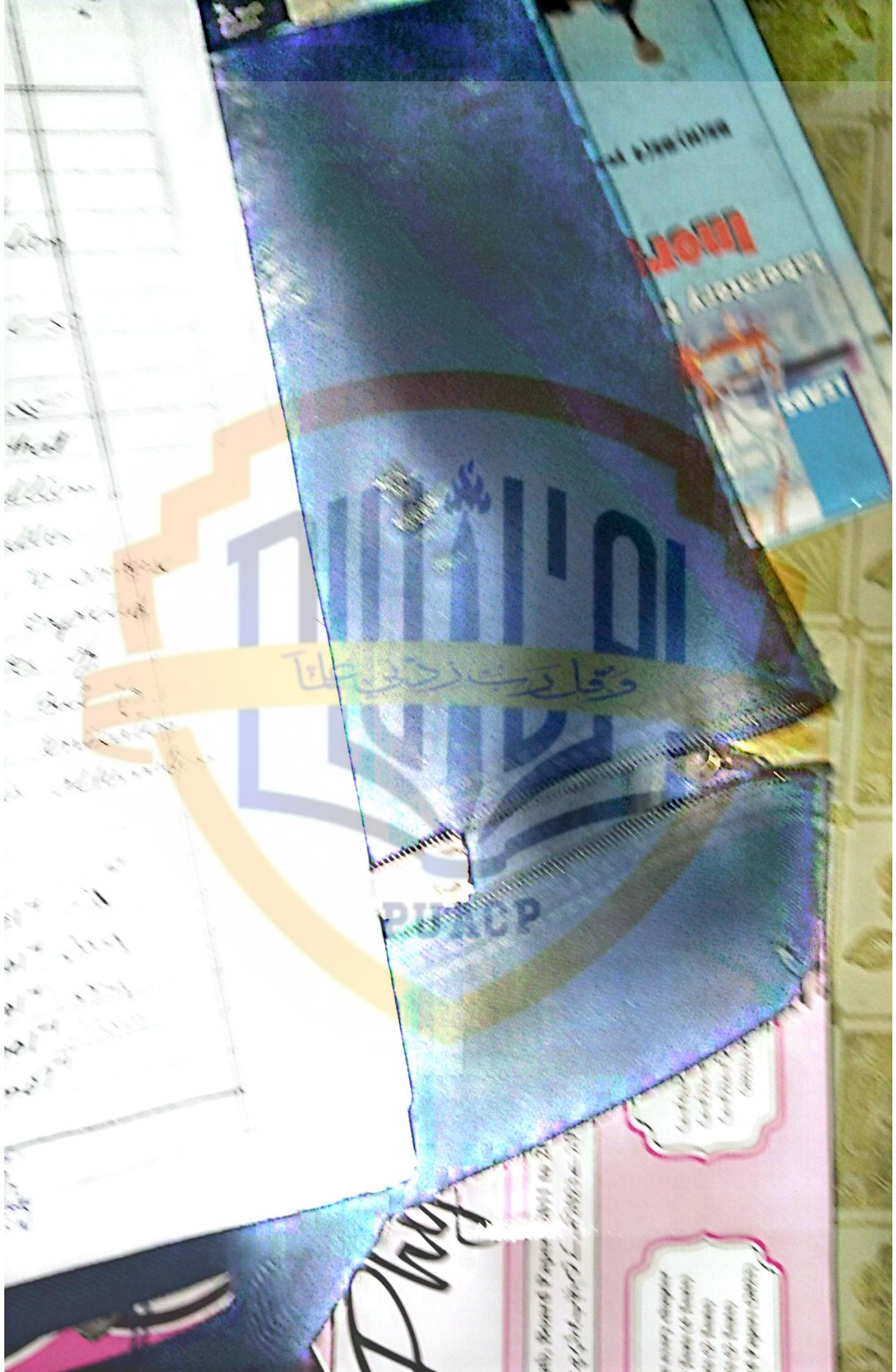
## Hydrolysis of Tetrahydrides

Silane hydrolyzes in the presence of catalytic amounts of hydroxide. In contrast, methane, germane and stannane don't hydrolyze ~~as~~ even in the presence of large amounts of hydroxide ion.

## Reaction of organo- lithium with $(Ph_3)_nMH$

Triphenylmethane and Triethyl triphenylgermane differ in their reaction with organo-lithium compounds from Triphenylsilane and Triphenylstannane.





6-

## Inert Pair Effect

Among the heaviest post-transition metals there is a definite reluctance to exhibit the higher possible oxidation state.

**Example:**

In group IV A, tin has a stable +2 oxidation state in addition to +4 and for lead the +2 oxidation state is far more important. Other examples are  $Tl^+$  and  $Bi^{+3}$ . These oxidation states corresponds to the loss of  $np$  electrons and retention of  $ns$  electron as "Inert Pair".

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"The s-orbital electron pair that don't take part in bonding is called inert pair effect"

## Exceptions:

It is shown that there is no exceptional stability of s-electrons in the heavier elements. The 6s electrons are stabilized to extent of  $300 \text{ kJmol}^{-1}$  relative to 5s electrons. This can't be only source of inert pair. But the 4s electrons don't show inert pair effect.

Relative instability of higher oxidation states for heavier elements stand for the weakening of bonds.

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