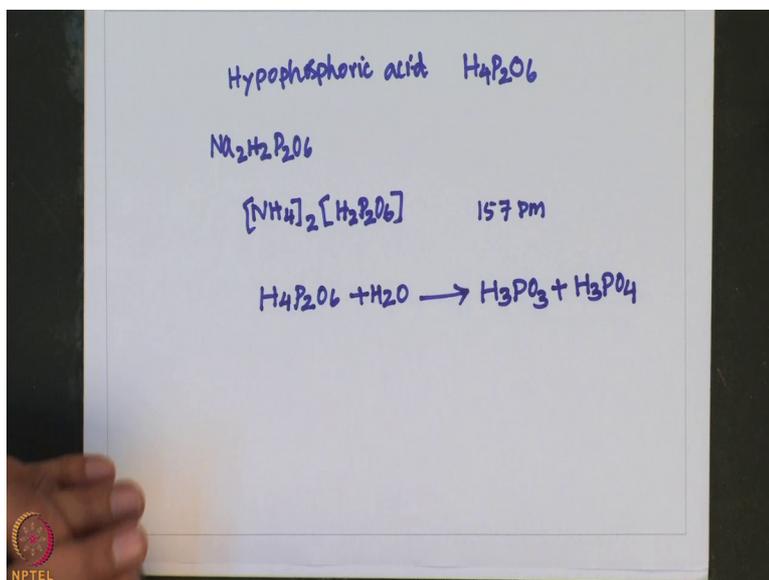


**Main Group Chemistry**  
**Prof. M. S. Balakrishna**  
**Department of Chemistry**  
**Indian Institute of Technology, Bombay**

**Lecture – 44**  
**Chemistry of Group 15 Elements**

Welcome to MSP lecture series on the chemistry of main group elements. In my previous lecture I had discussion about oxoacids of phosphorus and I gave information about phosphinic acid and phosphonic acid, let me introduce 2 more phosphorous acids that is hypo phosphoric acid and ultimately orthophosphoric acid.

(Refer Slide Time: 00:53)

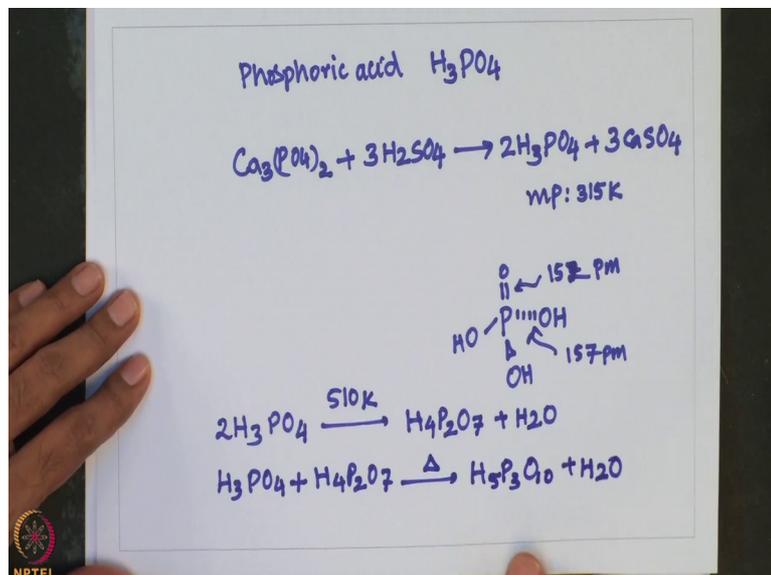


Let us look into hypophosphoric acid first. Hypophosphoric acid has formula  $H_4P_2O_6$ , the reaction between red phosphorus and NaOCl or NaClO<sub>2</sub> yields  $Na_2H_2P_2O_6$  ok.

Dehydration using  $P_4O_{10}$  gives  $H_4P_2O_6$ ; that means, dehydration using if you take this one and if you perform dehydration using  $P_4O_{10}$  that gives  $H_4P_2O_6$  and the first indication of a P P bonded dimer came from the observation, the acid was diamagnetic and x ray diffraction data for the salt was found to have this composition so; that means, all terminal P O bonds are of equal length, that is 157 picometer and in hydrolysis it gives 2 types of acids.

Now, let us look into phosphoric acid and one can prepare phosphoric acid by treating calcium phosphate with sulphuric acid.

(Refer Slide Time: 03:17)

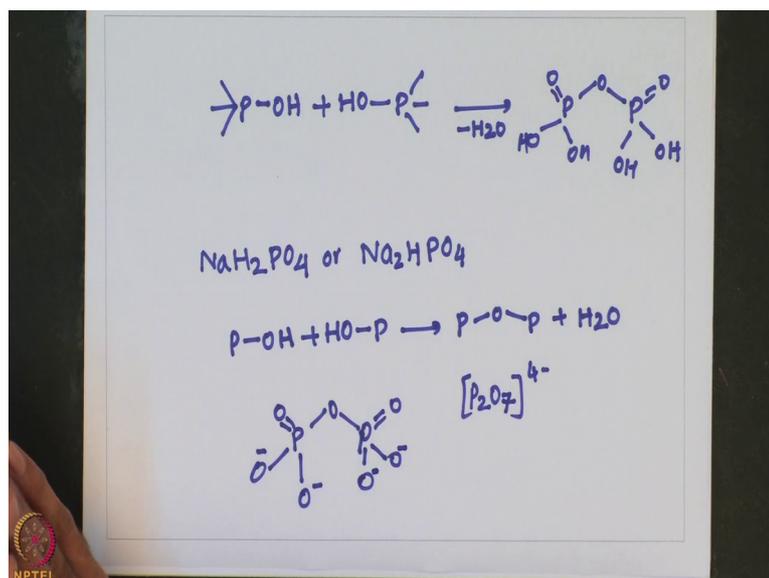


So, one can prepare by treating calcium phosphate with sulphuric acid. So, pure acids forms deliquescent colorless crystals with melting point 315 kelvin is white crystalline solid, it has a molecular structure with P H P O H and P O bond distance of 157 and 152. So, let me write the structure for you.

so (Refer Time: 04:32) O here this P O bond distance see 152 and this is 157 P O bond 157 picometer this is 152 picometer. In dilute aqueous solution acid molecules are hydrogen bonded to water molecules rather into each other so; that means, essentially in aqueous solution we do not come across intramolecular hydrogen bonding, instead we come across hydrogen bonding with water molecules. Phosphoric acid is a very stable and has no oxidizing properties except at very high temperature, aqueous phosphoric acid is a tribasic acid due to the presence of 3 O H groups.

When phosphoric acid is heated to 510 kelvin it is dehydrated to diphosphoric acid that is  $H_4P_2O_7$ . So, when phosphoric acid is heated to 510 kelvin it forms  $H_4P_2O_7$  plus  $H_2O$  and further heating its triphosphoric acid of course, this reaction can be represented in a simple way for example, ok.

(Refer Slide Time: 06:38)



So, one can write something like this and another one and essentially here condensation takes place through the elimination of water molecule.

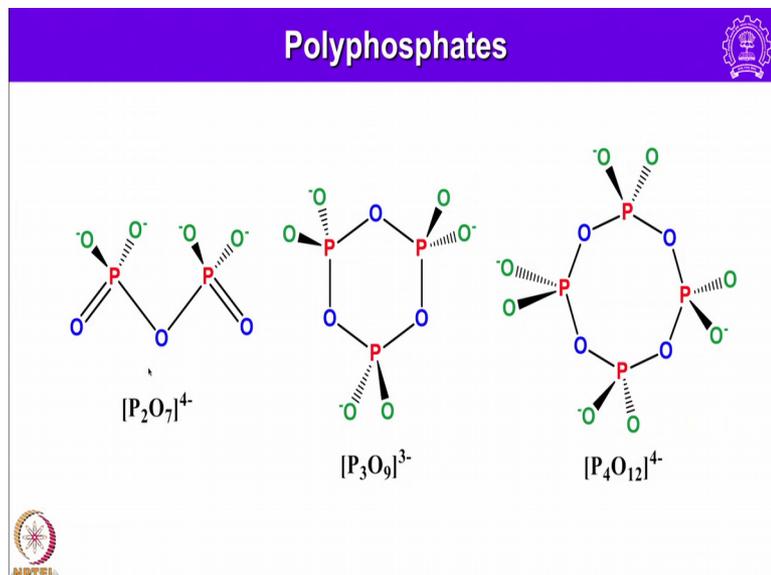
Of course, here one can write like complete structure here it can be. So, this how one can start writing having P O P linkages poly phosphates or poly phosphoric acid. So, now, with this let us begin discussion on poly phosphates, if acid phosphates such as  $\text{NaH}_2\text{PO}_4$  or  $\text{Na}_2\text{HPO}_4$ . So, containing essentially P O H groups are heated condensation reaction occurs to form P O P linkage via elimination of water to form polyphosphates. So, in a very simple way one can represent these reactions in this fashion to form P O P linkages through the elimination of a equivalent of water, for the condensation of 2 P O H bonds.

So, when disodium hydrogen phosphate is heated the pyrophosphate is formed. So, pyrophosphate is essentially  $\text{P}_2\text{O}_7^{4-}$ , minus if you are curious to know the structure of this one it is very simple to write. So, if you count P 2 1 2 3 4 5 6 7 and 1 2 3 4; 4 negative each (Refer Time: 09:11). So, this is pyrophosphate. So, if you have one P O P linkage they are called pyrophosphate if sodium hydrogen phosphate is heated, since each phosphorus has 2 P O H groups then cyclic phosphate can also be formed.

So, if we involve the condensation of 2 O H groups per phosphoric acid that can leads to the cyclic or linear polyphosphate and here in case of cyclic phosphates, we can have up

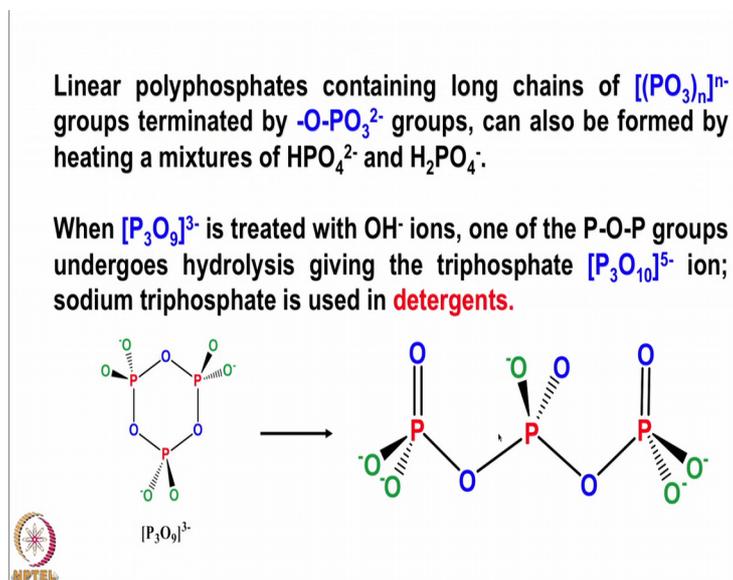
to 10 phosphorus atom; that means, cyclic phosphates having 10 phosphorus atoms in a cyclic system are known.

(Refer Slide Time: 09:51)



We can see here this is pyrophosphate and of course, here if you involve in the condensation of 2 O H groups per phosphorus phosphoric acid you can get either trimeric or you can get tetrameric up to having 10 phosphorus atom in the cyclic system are known, they are essentially called poly phosphates and linear polyphosphates containing long chains of  $PO_3$   $n$  minus 1, 1 consider here.

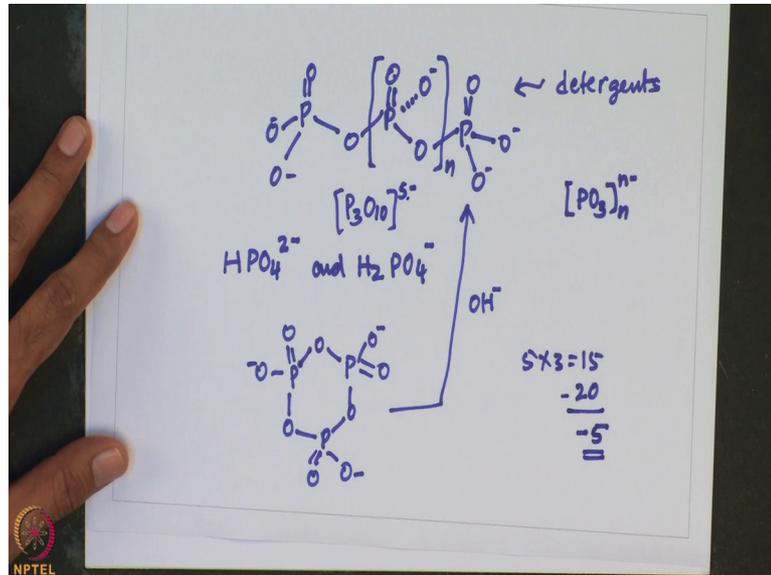
(Refer Slide Time: 10:25)



If you consider here as a monomer this is  $\text{P O}_3^-$  having 1 minus (Refer Time: 10:33).

So, one can conveniently show the monomeric unit in this one.

(Refer Slide Time: 10:42)

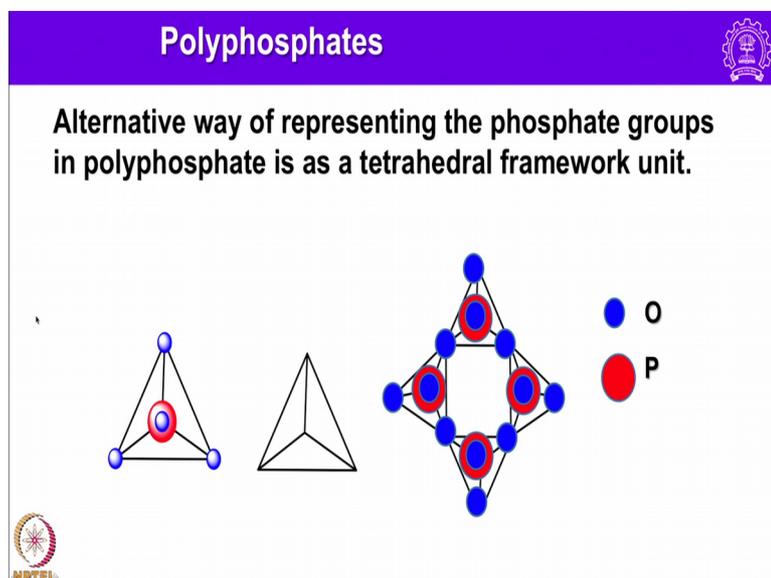


Something like this. So, in this one what one should consider is, this one is a monomeric unit and if you consider this as a monomeric unit we can write comfortably  $\text{P O}_3^-$  and  $n$  minus. So,  $n$  is 1 this also 1. So, this how and of course, here by adding  $\text{P O}_3^{2-}$  minus groups we can terminate heating a mixture of  $\text{HPO}_4^{2-}$  minus and  $\text{H}_2\text{PO}_4^-$  minus. So, we can control the chain length and of course, here now if I want to add I can keep on adding  $\text{HPO}_4^{2-}$  minus and then if I want to terminate you add another one having only one O H group. So, that it links and the chain growth is terminated.

So, when  $\text{P}_3\text{O}_{10}^{5-}$  is treated with  $\text{OH}^-$  ions one of the  $\text{P O P}$  group undergoes hydrolysis giving the triphosphate. So, it continues and of course, this triphosphate is used in detergents is very important in detergents this is used. Of course for example, if I take a cyclic one here, this essentially use this one is a nuclide this one with  $\text{OH}^-$  one can conveniently get this. So, this is essentially  $\text{P}_3\text{O}_{10}^{5-}$  you can count the charge now 1 2 3 4 5 5 minus 1 can write even if you do not know the charge here once we know the composition, we know that in this compounds the access state of phosphorous is 5. So, that we should be able to write here ok.

For example this one P is accounts for P 3 is 5 into 3 equals 15 and this is 10 into 2 20 and then that deficit is 5. So, you can have 5 minus here.

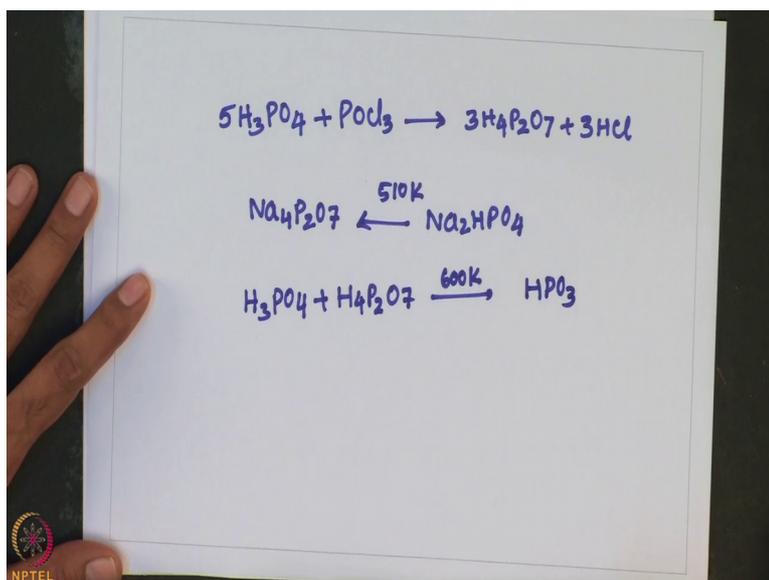
(Refer Slide Time: 14:36)



So, you can find out this charge on it very easily. So, polyphosphates one can explain a very similar way a 2 poly silicates. So, we have here  $\text{PO}_4^{3-}$  tetrahedral, there we had  $\text{SiO}_4^{4-}$  tetrahedra because there all are terminal bonds whereas, here one of the P O bond is P double bond O it does not have any charge. So, it is  $\text{PO}_4^{3-}$  is similar to  $\text{SiO}_4^{4-}$  and this how the tetrameric structure can be represented in this fashion here.

The simplest condensed phosphoric acid  $\text{H}_4\text{P}_2\text{O}_7$  is a solid at 298 kelvin.

(Refer Slide Time: 15:22)



And can be obtained from reaction of  $\text{POCl}_3$  with  $\text{H}_3\text{PO}_4$  if you treat phosphoric acid with  $\text{POCl}_3$  at least the formation of  $\text{H}_4\text{P}_2\text{O}_7$ , and it is much more stronger than phosphoric acid the sodium salt  $\text{Na}_4\text{P}_2\text{O}_7$  can be obtained by heating  $\text{Na}_2\text{HPO}_4$  at 510 kelvin of course, here  $\text{Na}_4$  essentially you replace all O H with O N a you will get the sodium salt the acid refers to as metaphosphoric acid with an empirical formula  $\text{HPO}_3$  here it is actually a sticky mixture of polymeric acids obtained by heating  $\text{H}_3\text{PO}_4$  and  $\text{H}_4\text{P}_2\text{O}_7$  at 600 degree 600 kelvin.

So; that means, if a mixture of  $\text{H}_3\text{PO}_4$  and  $\text{H}_4\text{P}_2\text{O}_7$  is heated to 600 kelvin, it gives metaphosphoric acid having composition  $\text{HPO}_3$  ok.

(Refer Slide Time: 17:08)

Oxoacids of phosphorus		
Formula	Name	Structure
$H_3PO_2$	Phosphinic acid (hypophosphorous acid)	
$H_3PO_3$	Phosphonic acid (phosphorous acid)	
$H_3PO_4$	Phosphoric acid (orthophosphoric acid)	

You can see sum of the all oxoacid structures I have shown here, this is phosphinic acid you can see here its monobasic acid because we have one O H group and of course, 2 P H groups and then phosphonic acid we have 2 O H groups. So, say dibasic acid and phosphoric acid has 3OH groups it is tribasic acid ok.

(Refer Slide Time: 17:29)

Oxoacids of phosphorus		
$H_4P_2O_6$	Hypophosphoric acid	
$H_4P_2O_7$	Diphosphoric acid (pyrophosphoric acid)	
$H_5P_3O_{10}$	Triphosphoric acid	

Similarly, hypophosphoric acid if you see here it has 4 of them. So, its say tetra basic acid and similarly diphosphoric acid  $H_4P_2O_7$  we have 1 2 3 4 its also tetrabasic acid and similarly  $H_5P_3O_{10}$  triphosphoric acid we have 1 2 3 4 5. So, this is penta basic acid.

(Refer Slide Time: 17:55)

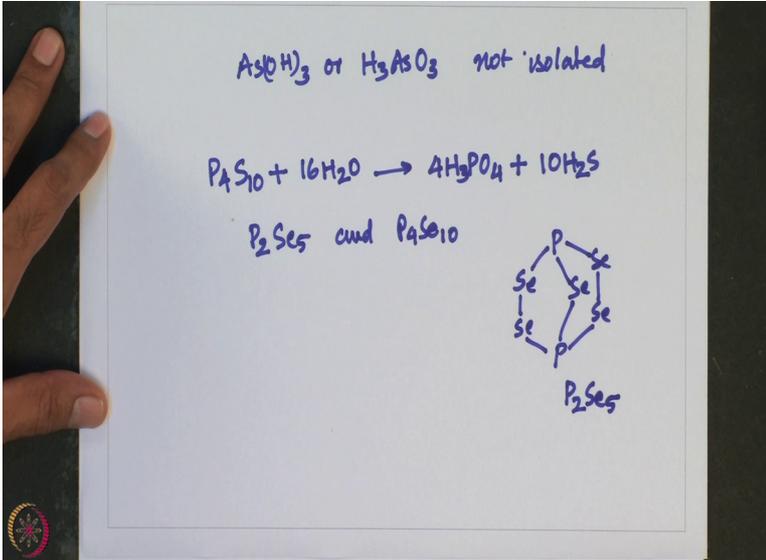
**Oxoacids of arsenic, antimony and bismuth**

- ❑ Arsenous acid ( $\text{As}(\text{OH})_3$  or  $\text{H}_3\text{AsO}_3$ ) has not been isolated
- ❑ Aqueous solutions of  $\text{As}_2\text{O}_3$  probably contain  $\text{H}_3\text{AsO}_3$
- ❑ Arsenic acid,  $\text{H}_3\text{AsO}_4$ , is obtained by dissolving  $\text{As}_2\text{O}_5$  in water or by oxidation of  $\text{As}_2\text{O}_3$  using nitric acid.  
$$\text{As}_2\text{O}_3 \xrightarrow{\text{conc HNO}_3} \text{H}_3\text{AsO}_4$$
- ❑ Oxoacids of Sb(III) are not stable, and few antimonite salts are well characterized
- ❑ No oxoacids of Bi are known, although some bismuthate salts are well characterized
- ❑ Sodium bismuthate is an insoluble, orange solid, obtained by fusing  $\text{Bi}_2\text{O}_3$  with  $\text{NaOH}$  in air or with  $\text{Na}_2\text{O}_2$



Ok. So, now, let us look into oxoacids of arsenic antimony and bismuth, arsenous acid that is  $\text{AsOH}$  thrice or  $\text{H}_3\text{AsO}_3$  has not been isolated so far.

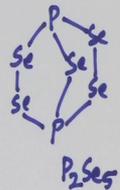
(Refer Slide Time: 18:14)



$\text{As}(\text{OH})_3$  or  $\text{H}_3\text{AsO}_3$  not isolated

$\text{P}_4\text{S}_{10} + 16\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4 + 10\text{H}_2\text{S}$

$\text{P}_2\text{Se}_5$  and  $\text{P}_4\text{Se}_{10}$



So that means  $\text{AsOH}$  thrice or  $\text{H}_3\text{AsO}_3$  is not isolated. So, aqueous solution of  $\text{As}_2\text{O}_3$  probably contained  $\text{H}_3\text{AsO}_3$  and arsenic acid similar to phosphoric acid, thus  $\text{H}_3\text{AsO}_4$  is obtained by dissolving  $\text{As}_2\text{O}_5$  in water or by oxidation of  $\text{As}_2\text{O}_3$  using concentrated nitric acid. So, you can see here  $\text{As}_2\text{O}_3$  on treatment with concentrated nitric acid gives

H<sub>3</sub>AsO<sub>4</sub> oxoacids of antimony or not stable and few antimonite salts are well characterized.

So, no oxoacids of bismuth are known although some bismuthate salts are well characterized. So, sodium bismuthate is an insoluble orange solid obtained by fusing Bi<sub>2</sub>O<sub>3</sub> with sodium hydroxide in air or with sodium peroxide.

(Refer Slide Time: 19:30)

**Sulfides and selenides of phosphorus** 

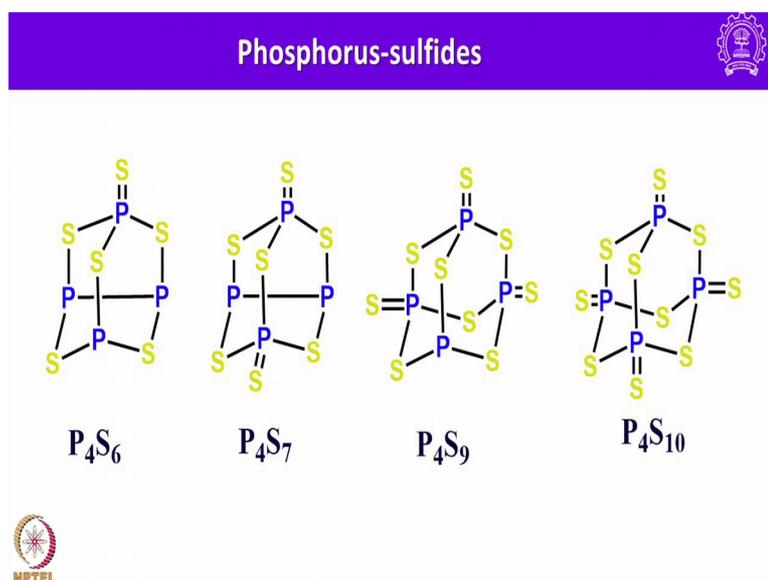
- Although the structures of the sulfides appear to be closely related to those of the oxides but there are some notable differences.
- P<sub>4</sub>O<sub>6</sub> and P<sub>4</sub>S<sub>6</sub> are not isostructural
- The bond distances within the cages of all the sulfides indicate single P-P and P-S bonds
- The terminal P-S bonds are shorter than those in the cage
- The reaction of red phosphorus with sulfur above 450 K yields P<sub>4</sub>S<sub>3</sub> and P<sub>4</sub>S<sub>7</sub>
- Above 570 K, white phosphorus combines with sulfur to give P<sub>4</sub>S<sub>10</sub> which is the most useful of the phosphorus sulphides.



Now, let us look into the sulfides and selenides of phosphorus although the structures of this sulfides appears to be closely related to those of oxides, but there is remarkable difference is there for example, P<sub>4</sub>O<sub>6</sub> and P<sub>4</sub>S<sub>6</sub> are not isostructural, you are already familiar with the structure of P<sub>4</sub>O<sub>6</sub> in a couple of minutes I will be showing the structure of P<sub>4</sub>S<sub>6</sub>, you can see the differences in the structure; that means, although they appear similar they are not isostructural.

The bond distances within the cages of all the sulfides indicate single P P and P S bonds the terminal P S bonds are always shorter because of having P S double bond. The reaction of red phosphorus with sulfur above 450 kelvin yields this phosphorous sulfide such as P<sub>4</sub>S<sub>3</sub> and P<sub>4</sub>S<sub>7</sub> above 570 kelvin white phosphorus combines with sulfur to give P<sub>4</sub>S<sub>10</sub> similar to phosphorus thi pentoxide which is the most useful of the phosphorous sulfides ok.

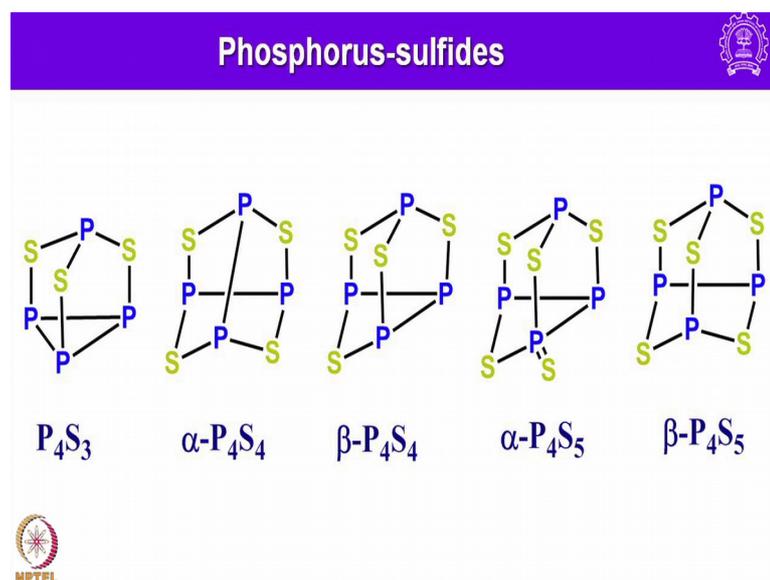
(Refer Slide Time: 20:39)



So, these are the structures you can see here and of course, in in case of  $P_4O_6$  this P P bond is not there in place of P P bond we had a P O P bond. So, in case of  $P_4S_6$  what we have is we have a P P bond intact and then the sulfur is oxidizing one of this one as a result what happens we have 3 trivalent phosphorous and one pentavalent phosphorus; and similarly  $P_4S_7$  still P P bond is intact and only in case of  $P_4S_9$  that P P bond is changed to P S P bond and then here we have 3 phosphorus are in pentavalent state and one phosphorous in trivalent state.

In case of  $P_4S_{10}$  you can see it is very similar to  $P_4O_{10}$ .

(Refer Slide Time: 21:26)



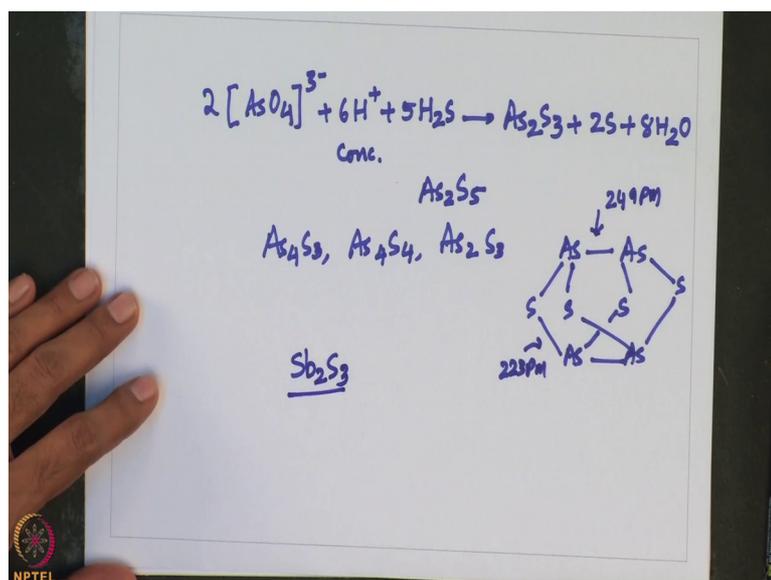
And you can see here  $P_4S_3$  you we have 3 P S P bonds and  $P_4S_4$  of course, another P P bond is broken, and in case of  $P_4S_4$  we also have a different one beta  $P_4S_4$  and in case of this one we have one P P bond intact and one of the phosphorus season pentavalent state P 4 S 5, and similarly we can also have a P 4 S 5 of different structure where except one P P bond all P P bonds are broken with P S P bond. So, this is where this structural similarities between phosphorus oxides and phosphorus sulfides can be looked into and phosphorous sulfides ignite easily and  $P_4S_3$  is used in strike anywhere matches and essentially it is combined with KCl O<sub>3</sub> and the compounds in frame when subjected to friction whatever we have in matchbox it has a combination of  $P_4S_3$  plus K c l O<sub>3</sub> and all striking it catches fire.

So,  $P_4S_3$  is stable to water. So, other phosphorous sulfides are slowly hydrolyzed. So, what would happen when we treat phosphorus pentasulfide with water can be seen from this equation. So, reactions of phosphorus pentasulfide is very similar to the reaction of phosphorus pentoxide with water. So, instead of 10 equivalents of water what we are getting is 10 equivalence of hydrogen sulfide. And similar to phosphorous sulfides phosphorus selenides are also known for example, P<sub>2</sub>Se<sub>5</sub> and P<sub>4</sub>Se<sub>10</sub> are known and P<sub>2</sub>Se<sub>5</sub> structure can be written in this fashion.

Of course this kind of properties tends from the fact that chalcogens are known for undergoing catenation that is a reason we see here having SeSe bonds and does the

composition is P<sub>2</sub>Se<sub>5</sub> and of course, these compounds can be made by direct combination of white phosphorus with selenium under appropriate reaction conditions. In fact, arsenic and antimony sulfide ores are the major sources of group 15 elements, in the laboratory As<sub>2</sub>S<sub>3</sub> and As<sub>2</sub>S<sub>5</sub> are usually precipitated from aqueous solutions of arsenides or arsenides reaction proceeds when H<sub>2</sub>S is passed slowly through the solution at 298 kelvin.

(Refer Slide Time: 25:15)



Of course, here you concentrated as (Refer Time: 25:45). If the temperature is lower to 273 kelvin and the rate of flow of H<sub>2</sub> is increased one can get As<sub>2</sub>S<sub>5</sub> same reaction if it is carried out at a lower temperature with a high flow rate of H<sub>2</sub>S, one can get As<sub>2</sub>S<sub>5</sub> instead of As<sub>2</sub>S<sub>3</sub> and the sulfides of arsenic such as As<sub>4</sub>S<sub>3</sub>, As<sub>4</sub>S<sub>4</sub> and As<sub>2</sub>S<sub>3</sub> occur naturally let me show you the structure of As<sub>2</sub>S<sub>4</sub>. So, you should while writing structure is should make sure that all arsenic atoms are trivalent and whereas, sulfur or (Refer Time: 27:02) are divalent and this distance is 249 picometer and this is 223 picometer ok.

The bond distance is in alpha As<sub>4</sub>S<sub>4</sub> are consistent with As<sub>2</sub>S<sub>6</sub> and a s e a single bonds. So, in this view of the cage allows a comparison of S<sub>4</sub>n<sub>4</sub> of course, S<sub>4</sub>n<sub>4</sub> compounds are very similar in structure to As<sub>4</sub>S<sub>4</sub>. The only well characterized binary sulfide of antimony is the naturally occurring or stibnite that is Sb<sub>2</sub>S<sub>3</sub>, let me stop here and in my next lecture I will be discussing on another important type of compounds of phosphorus

and nitrogens that is called phosphazenes, until then have a very pleasant reading of group 15 chemistry.

Thank you very much.