Main Group Chemistry
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Lecture – 43
Chemistry of Group 15 Elements

Welcome to MSB lecture series on the chemistry of main group elements, in my previous lecture I was discussing about the oxyacids of group 15 elements with focus on nitrogen oxyacids and let me continue from where I had stopped before I proceed on to oxyacids, let me talk about another important reagent that is sodium nitrite; this is used in the preparation of diazonium compounds so; that means, sodium nitrate is an important reagent in the preparation of diazonium salts which finds lot of application in organic synthesis, and in this process what happens HNO2 is prepared in C2. So, let me write down that equation.

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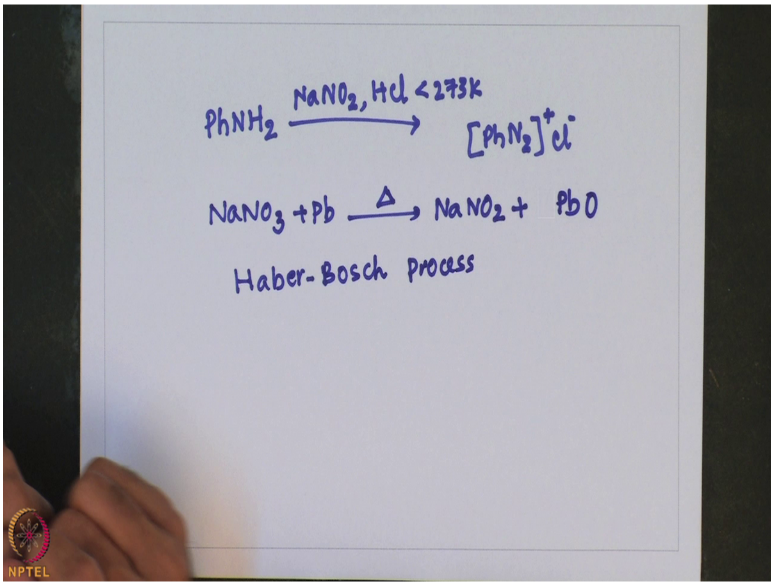

$$PhNH_2 \xrightarrow{NaNO_2,\ Hcl\ <273K} [PhN_2]^+Cl^-$$

$$NaNO_3 + Pb \xrightarrow{\Delta} NaNO_2 + PbO$$

Haber-Bosch process

For example aniline when it is treated with sodium nitrite with Hcl at less than 273 kelvin it forms minus. So, this is where the utility of sodium nitrite comes into the picture. So, alkali metal the nitrates when heated alone for example, sodium nitrate with led when it is heated it forms sodium nitrite through the formation of lead oxide. The product of the reduction of HNO2 nitrous acid depends on the reducing agent for example, NO is formed with iodide or iron 2 plus N2O is produced with tin 2 plus and

NH2 OH results from reduction by SO2 and ammonia is formed when zinc you used in alkaline solution.

Now, let us come back to nitric acid HNO3 and of course, it is an important industrial chemical that is manufactured on a large scale in the Haber Bosch process of course, Haber’s process is associated with the manufacturing of ammonia starting from N2 and H2.

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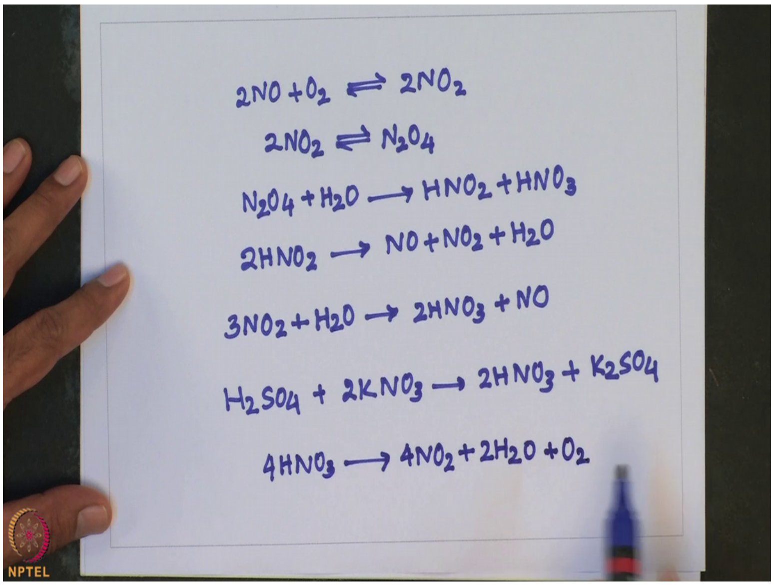

$$2NO + O_2 \rightleftharpoons 2NO_2$$

$$2NO_2 \rightleftharpoons N_2O_4$$

$$N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$$

$$2HNO_2 \longrightarrow NO + NO_2 + H_2O$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

$$H_2SO_4 + 2KNO_3 \longrightarrow 2HNO_3 + K_2SO_4$$

$$4HNO_3 \longrightarrow 4NO_2 + 2H_2O + O_2$$

So, let me give the sequence of reactions that are involved in the preparation of nitric acid HNO3. So, NO is first oxidized to NO 2 and of course, 2 if the NO 2 is in is in equilibrium with it is a dimer N2O4. So, N2O4 on treatment with water gives H NO 3 and HNO2.

So this HNO2 is used in the preparation of NO 2. So, treatment of NO 2 with water gives nitric acid and just recall that I had mentioned NO 2 as an anhydrous of nitric acid. So, I had mentioned that NO 2 is an anhydride of nitric acid. So, pure nitric acid can also be made in the laboratory by adding H2SO4 to potassium nitrate and distilling the product under vacuum. So, here H2SO4 in it is treated with potassium nitrate it forms. So, thus nitric acid obtained can be distilled under vacuum to get pure nitric acid. So, nitric acid is a colorless liquid must be stored below 273 kelvin to prevent slight decomposition which gives the acid a yellow color.

Of course yellow color is due to the formation of NO 2 on storing above 2 seventy three kelvin HNO 3 gives out NO 2 that imports yellow color to the acid nitric acid is quite reactive for example, tin arsenic and a few d block metals are converted to their oxides when treated with nitric acid, but others form nitrates let me show you some important reactions of nitric acid with various metals only magnesium manganese and zinc liberate H 2 when they are treated with dilute nitric acid in case of copper we get both NO as well as NO 2 depending upon the nature of the nitric acid For example when copper is treated with dilute nitric acid that leads to the formation of NO.

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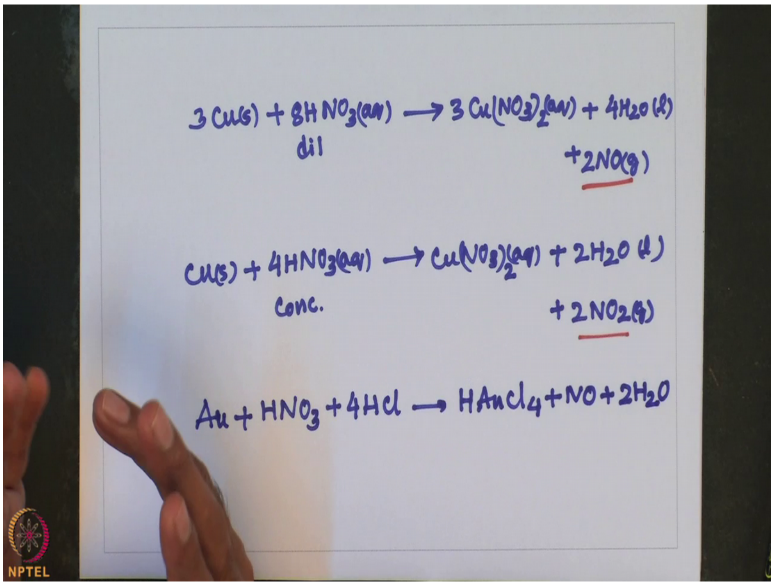

$$3\,Cu(s) + \underset{\text{dil}}{8HNO_3(aq)} \rightarrow 3\,Cu(NO_3)_2(aq) + 4H_2O(l) + \underline{2NO(g)}$$

$$Cu(s) + \underset{\text{Conc.}}{4HNO_3(aq)} \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + \underline{2NO_2(g)}$$

$$Au + HNO_3 + 4HCl \rightarrow HAuCl_4 + NO + 2H_2O$$

Whereas the treatment of copper with concentrated nitric acid leads to the formation of NO 2 let me write these 2 equations.

So you should remember here copper on treatment with dilute nitric acid gives NO whereas, copper when its treated with concentrated nitric acid it gives NO 2 of course, in both the cases formation of copper nitrate is observed, only difference is between the formation of NO and NO 2 .Aqua regia contains free chlorine and o n c l and attacks gold and platinum with the formation of respective chloro complexes. So, to make any coordination compounds are organometallic compounds, gold metal is first dissolved in aqua regia to form this eric acid HAucl4 and then for the reagents are added to make the specific compounds containing gold.

Now, let us look into the oxides of phosphorus. Oxides of phosphorus include P4O6 that is phosphorus trioxide and P4O10 phosphorus pentoxide both of which are cage compounds having tetrahedron symmetry tetrahedral geometry, phosphorous three oxide P4O6 is obtained by burning white phosphorus in restricted supply of oxygen, its a colorless volatile solid having melting 0.297 and boiling 0.447 kelvin each phosphorus atom in P4O6 carries a lone pair of electrons and thus P4 can be considered as a Lewis base attacks with one or 2 equivalents of BH3 have been reported. So, in case of phosphorus trioxide the PO bond distance let me write the structure for you.

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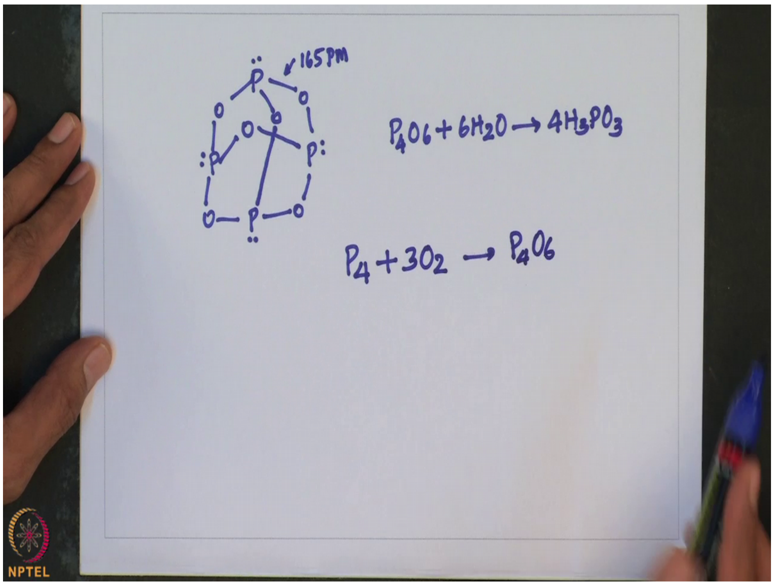

$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$

$P_4 + 3O_2 \rightarrow P_4O_6$

So, this is phosphorous trioxide. So, here this lone pairs of still intact as a result this can a perform as Lewis base and the PO distance is 165 picometer and P O P bond angles are anywhere between 128 to 98 this oxide is soluble in diethyl ether or benzene, but reacts with cold water so; that means, this is P4O6 when its reacts with water it forms H3 PO 3 the solid state structure confirms that dimension from P2O3 2 P4O6 occurs through PO bond cleavage in structure and reformation of PO bonds between the monomeric units and of course, free P a total has not to date been isolated, one can also prepare P2O6 by reacting P4 with restricted amount of oxygen.

Reaction of P4O6 with one equivalent of dimethyl sulfide adduct of BH 3 followed by slow crystallization from toluene solution leads to an adduct of the dimer of P4O6 that is P8O12.

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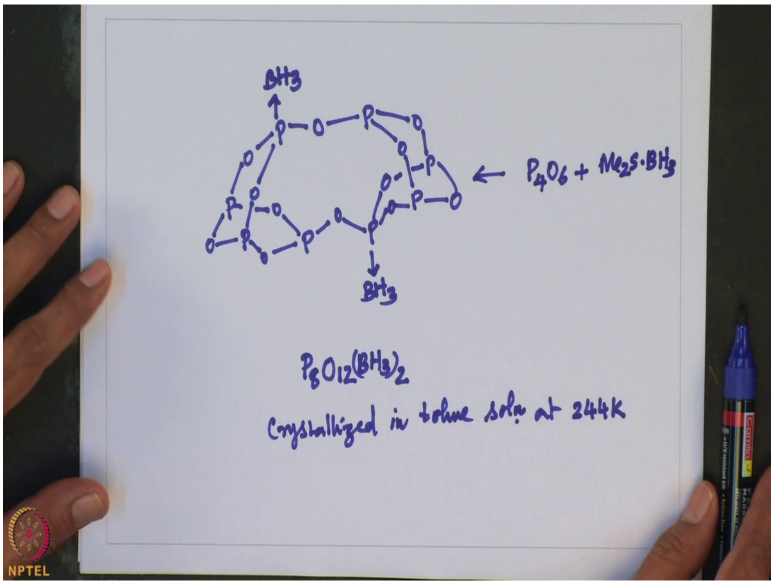

$P_4O_6 + Me_2S \cdot BH_3$

$P_8O_{12}(BH_3)_2$

Crystallized in tolune soln at 244K

Let me write the structure for you, you can see here we have one 2 3 4 5. So, this is one of the PO bond is broken and now we have another such unit comes here. So, now, this phosphorous known pair is known at to BH3. So, this is P8O12 BH3 twice oh. So, this was crystallized in toluene solution at 244 K. So, and of course, this was made by treating P4O6 with BH3 adduct of dimethyl sulphide, you may be a having some doubt that why only 2 of them are coordinated of course, although this has four phosphorus with each one lone pair these compounds are highly hydroscopic and highly reactive as a result reaction of this one and isolation is very difficult and that is for the same reason because of its high reactivity the free form of P8O12 in its pure form is not isolated.

However this compound has been crystallized and structure has been determined use a single crystal x ray analysis; nevertheless this type of compounds are highly reactive and using them as Lewis bases to interact with transfer metals is very very difficult task, but the most important oxide of phosphorus is P4O10 that is phosphorus pentoxide it can be made directly from P4 and using excess of oxygen or we can also call oxidation of P4O6 also gives P4O410 P4 plus 5O2 gives P4O10 ok.

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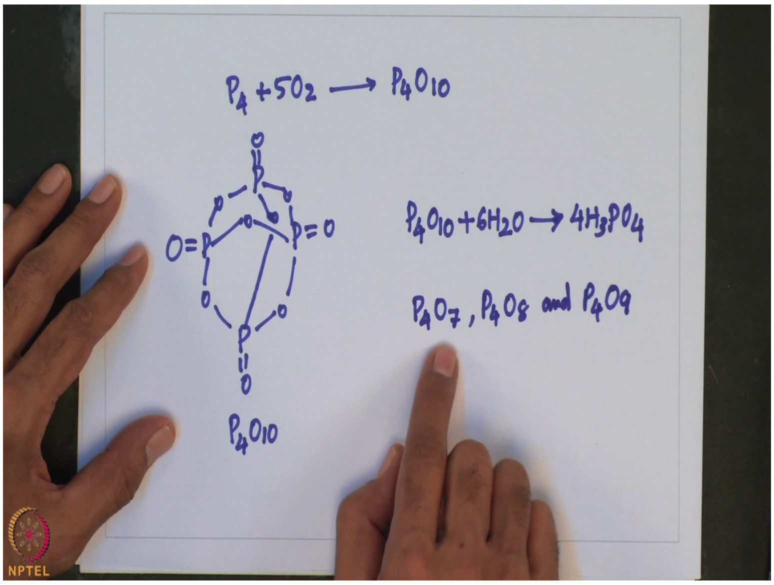

$P_4 + 5O_2 \longrightarrow P_4O_{10}$

$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$

P_4O_7, P_4O_8 and P_4O_9

P_4O_{10}

And in the vapor phase phosphorus pentoxide contains P4O10, molecules with structure having this kind of again this is very similar to P4O6 accept were the fact that phosphorous do not have lone pair and each phosphorus has a terminal double bonded oxygen.

So, this one is P4O10; of course, P4O10 is highly hydroscopic it can readily (Refer Time: 18:36) hydrolysis to from phosphoric acid there are three other oxides of phosphorus, they are essentially P4O7, P4O8 and P4O9 of course, these three structures are related to P4O10 as well as P4O6 for example, if you take P4O6 and start oxidizing one phosphorus at a time we can start getting this one for example, in case of P4O7 overall the phosphorus atom is oxidized from P4O6, and if oxidized 2 of them into P4 8 if you oxidize three leaving the lone pair or one phosphorus intact that is P4O10.

That means writing the structures is not at all difficult, you can see those structures I have shown here this is P4O6.

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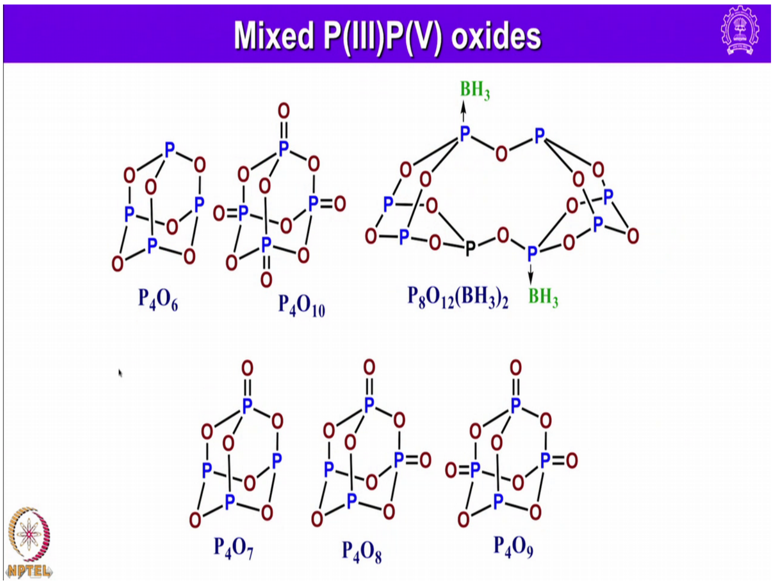

Mixed P(III)P(V) oxides

And this is P4O10 and of course, here the adduct of dimeric P4O6 that is P8O12, and here you can see P4O6 when it is oxidized one of the phosphorus atom is oxidized to P 5 it gives P4O7 similarly 2 of them on oxidation gives P4O8, and all the three are oxidize living only one in travelling state becomes P4O9. So, in contrast to the high stability of phosphorus five oxide, arsenic antimony and bismuth more readily form oxides with oxidation number plus three specifically AS2 O3 Sb2 O3 and Bi2 O3.

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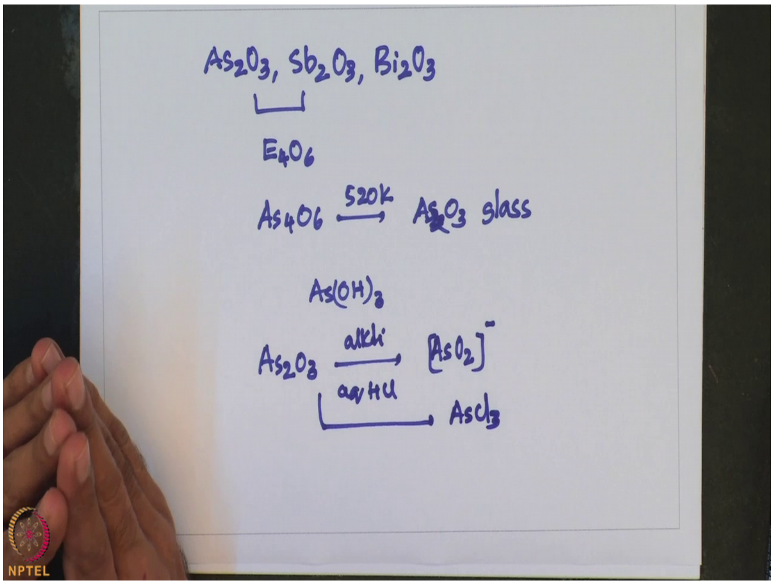

As_2O_3, Sb_2O_3, Bi_2O_3

E_4O_6

$As_4O_6 \xrightarrow{520K} As_2O_3$ glass

$As(OH)_3$

$As_2O_3 \xrightarrow[aq\ HCl]{alkali} [AsO_2]^-$

$\longrightarrow AsCl_3$

In the gas phase arsenic and antimony oxides have the molecular formula E4O6 and of course, E is arsenic or antimony condensation of As4O6 vapor above 520 kelvin leads to the formation of As2 O3 glass; that means, if you take As4O6 above 520 kelvin it leads the formation of As2 O3 glass. So, dissolution of As2 O3 in water gives a very weakly acidic solution and it is probably that the species present as AsOH thrice.

Although this has never been isolated crystallization of aqueous solution yields As2 O 3. So, if you take the aqueous solution of As2 O3 that yields As2 O3 crystals. So, arsenic 3 oxide dissolves in aqueous alkali to give salts containing As O2 minus ion. So, arsenic three oxide that is As2 O3 dissolves in alkali to give As O2 ions whereas, in aqueous Hcl it gives a H c l 3 the properties of Sb2 O3 in water and aqueous alkali or Hcl is very similar to arsenic oxide; that means, antimony a behaves in a similar fashion.

Bismuth three oxides occur naturally as bismite and is formed when bismuth combines with oxygen on heating and As2O5 has a lattice structure consisting of AsOs I linked octahedral AsO6 and tetrahedral AsO4 units.

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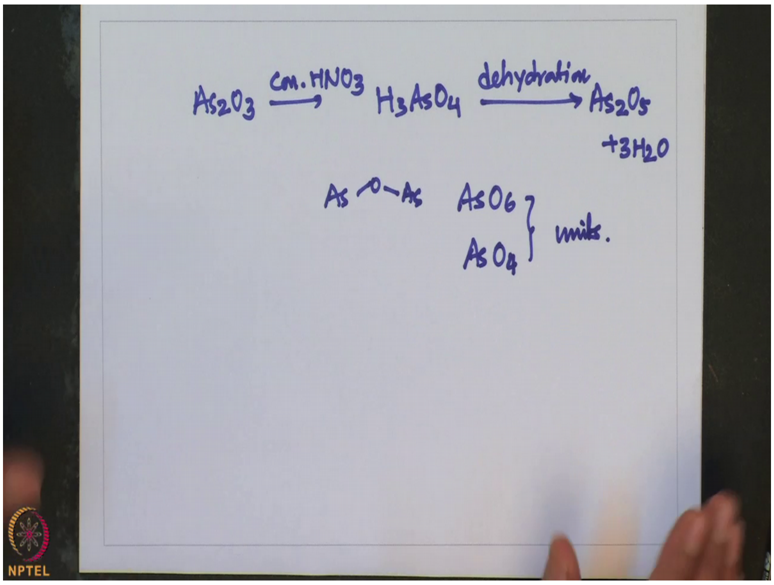

So, if you take As2O3 and treat this one with concentrated nitric acid, it forms H3AsO4 similar to phosphoric acid and this one on dehydration gives an oxide analogous of P2O5 that is phosphorus pentoxide, this is arsenic pentoxide. So, arsenic pentoxide has. So, AsOs linked octahedral AsO6 and tetrahedral AsO4 units.

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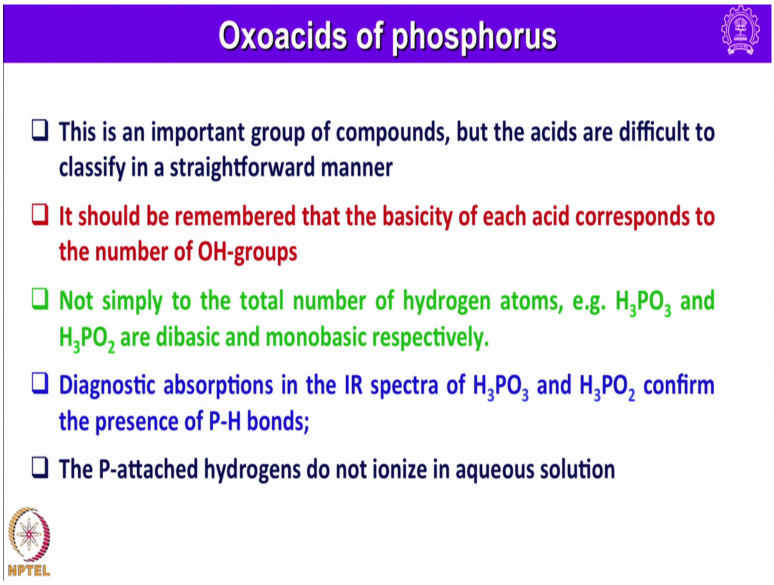

Oxoacids of phosphorus

❑ This is an important group of compounds, but the acids are difficult to classify in a straightforward manner

❑ It should be remembered that the basicity of each acid corresponds to the number of OH-groups

❑ Not simply to the total number of hydrogen atoms, e.g. H_3PO_3 and H_3PO_2 are dibasic and monobasic respectively.

❑ Diagnostic absorptions in the IR spectra of H_3PO_3 and H_3PO_2 confirm the presence of P-H bonds;

❑ The P-attached hydrogens do not ionize in aqueous solution

Now, let us look into the oxyacids of phosphorus, and this is an important group of compounds, but the acids are difficult to classify in a very straight forward manner you should be remember that basicity of each acid corresponds to the number of OH groups not simply to the total number of hydrogen atoms, but how many OH groups are there will decide whether it is a dibasic monobasic or tribasic diagnostic absorptions in the IR spectrum of H3PO3 as well as that of H3PO2 confirm the presence of PH bond of course, one can also look into the phosphorous enema to see whether PH bond exists in that case we will see a characteristic one j PH coupling, and phosphorus attached to hydrogens do not ionizing aqueous solution, one should remember when phosphorus is attached to hydrogen that do not ionize in aqueous solution let me talk about phosphinic acid before I conclude this lecture.

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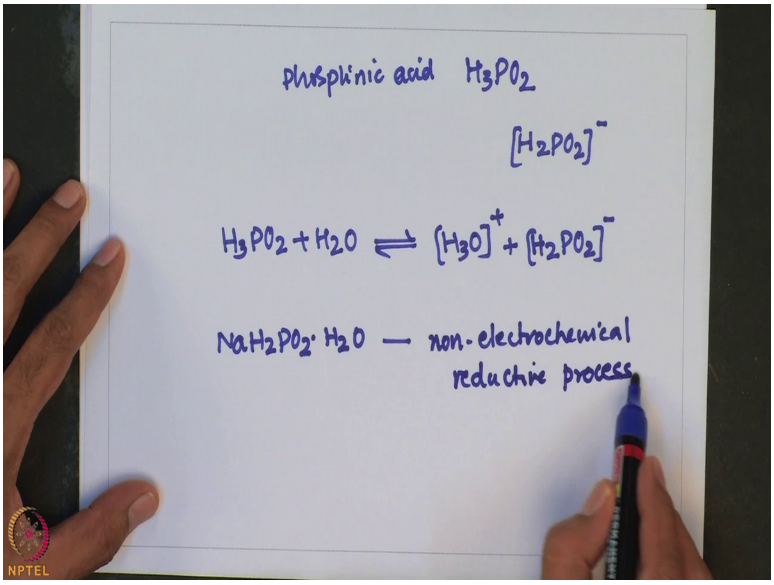

Phosphinic acid H_3PO_2

$[H_2PO_2]^-$

$H_3PO_2 + H_2O \rightleftharpoons [H_3O]^+ + [H_2PO_2]^-$

$NaH_2PO_2 \cdot H_2O$ — non-electrochemical reductive process

Phosphinic acid is H3PO2. So, they are the reaction of white phosphorus with aqueous alkali produces phosphate ion that is H2PO2 minus by using barium hydroxide as alkali precipitating Ba2plus ions as BaSO4 and evaporating the aqueous solution with deliquescent crystals of H3PO2 can be obtained so; that means, by using barium hydroxide as an alkali and precipitating Ba2 plus ions as BaSO4 and evaporating the aqueous solution white deliquescent crystals of H3PO2 can be obtained in aqueous solution phosphinic acid is fairly strong monobasic acid.

So, phosphinic acid and it is salts are reducing agents NaH2 PO2 is used industrially in a non electrochemical reductive process. So, this is finds application in non-electrochemical reductive process. So, when phosphinic acid is heated it undergoes disproportionation and gives PH3 and H3 PO3.

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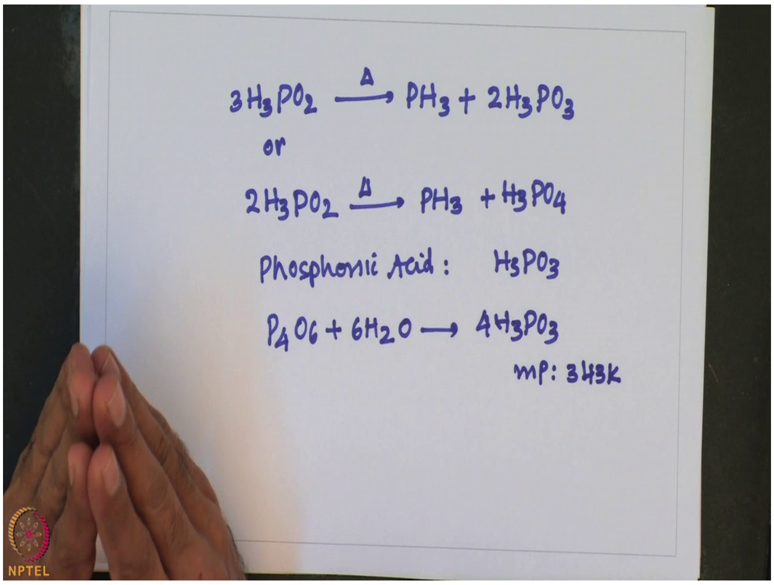

$3H_3PO_2 \xrightarrow{\Delta} PH_3 + 2H_3PO_3$

or

$2H_3PO_2 \xrightarrow{\Delta} PH_3 + H_3PO_4$

Phosphonic Acid : H_3PO_3

$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$

mp: 343K

For example on heating phosphinic acid forms PH3 and H3 PO3 or one can also write this equation in a different way so; that means, essentially one can get either H 3 PO three or H3PO4 along with PH3 when phosphinic acid is heated.

Now, let us look into phosphonic acid, this is H3PO3 of course, one can prepare phosphonic acid by treating P4O6 with water or on subjected to hydrolysis, P2O6 gives H3PO3 phosphonic acid and pure phosphonic acid is colourless to send crystals having melting point 343 kelvin, in the solid state the molecules of the acid are linked by hydrogen bonds to form a three dimensional network. So, let me discuss some more aspects of phosphorus acids in my next lecture until then have a pleasant reading of group 15 chemistry.

Thank you very much.