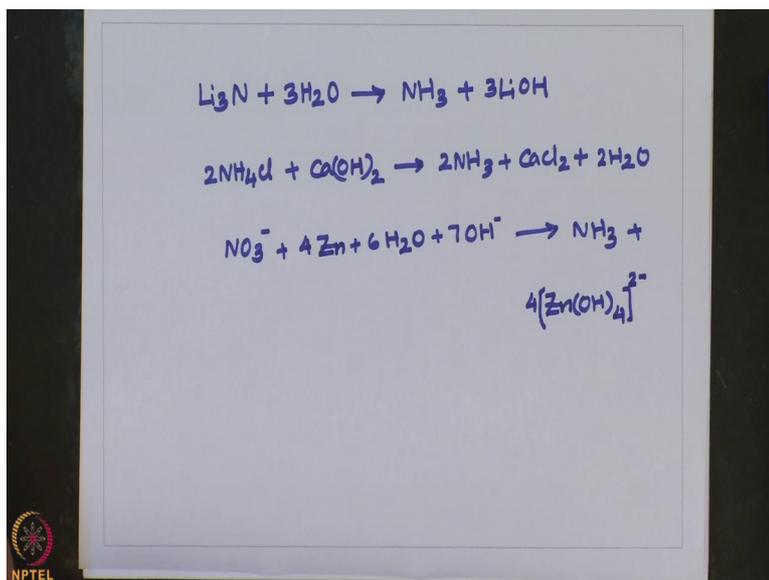


**Main Group Chemistry**  
**Prof. M. S. Balakrishna**  
**Department of Chemistry**  
**Indian Institute of Technology, Bombay**

**Lecture – 41**  
**Chemistry of Group 15 Elements**

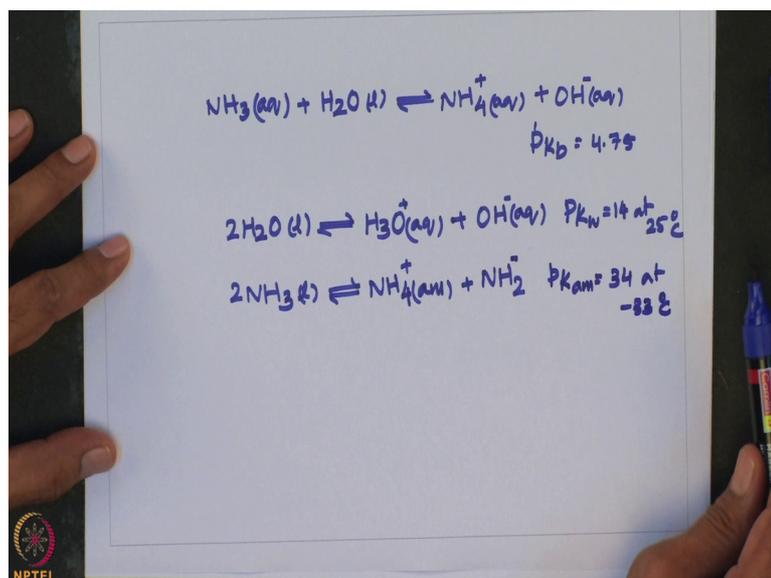
Welcome to MSB lecture series on the chemistry of main group elements, in my previous lecture, I gave introduction to hydrides of group 15 elements. So, let me continue from where I had stopped; let me give that preparation of hydrides of group 15 elements of course, the important hydride being ammonia, ammonia is prepared by Haber's process and ammonia finds lot of applications. Ammonia is obtained by the action of water on the nitrides of lithium or magnesium or by heating ammonium salts with base or by reducing a nitrite in alkaline solution with zinc or aluminum.

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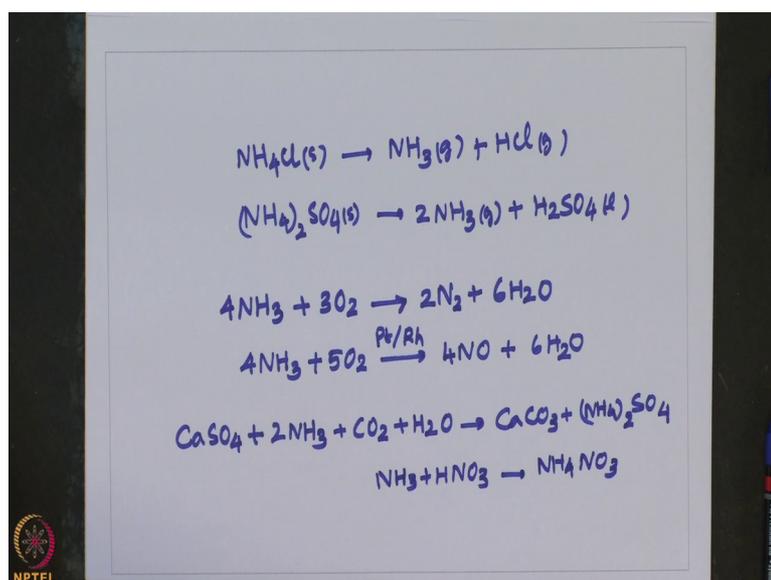
Let me write down few of this reaction methods; so by heating ammonium chloride or by reducing nitrite or nitrate in alkaline solution. So, reaction in liquid ammonia closely resemble those in aqueous solution. So, the other hydrides of group 15 elements are essentially as I mentioned earlier, phosphene arsine stibin.

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So, ammonia is water soluble weak base that can be seen from this reaction. So, for this one if we consider  $pK_b$  that is about 4.75, and if you consider and these two reaction that I am going to write, that will show you the difference in the behavior of ammonia. So,  $N$  is ammonia. So, these two equations have written here indicate, their similarities between water and ammonia. Ammonium salts decompose readily on heating and for salts such as the halides carbonates sulfates ammonia is evolved; let me show a couple of examples ammonium chloride it gives ammonia and HCl.

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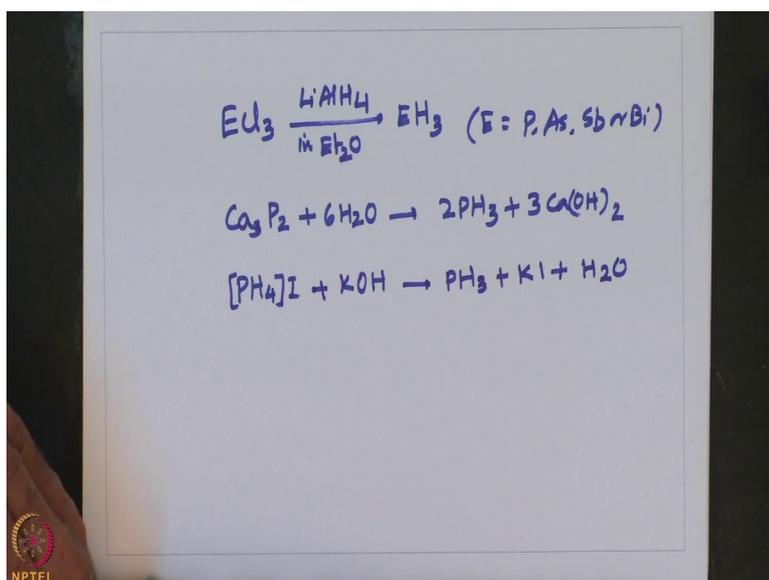


Similarly, if you take ammonium sulfate, it gives  $\text{H}_2\text{SO}_4$ . So, ammonia is a colorless gas with a pungent odor. Oxidation products of ammonia depend on the conditions that are used. For example, ammonia when it reacts with oxygen  $\text{N}_2$  is liberated.

And when the reaction is performed using a catalyst of platinum or rhodium  $\text{NO}$  is formed. So, both ammonium sulfate and nitrate are important fertilizers. So, they can be prepared using the following method, starting from calcium sulfate. Of course,  $\text{NH}_3$  combines with  $\text{HNO}_3$  to form  $\text{NH}_4\text{NO}_3$ .

So, ammonium sulfate and ammonium hydrogen phosphate are also used as fertilizers because phosphate is essentially a plant nutrient. Ammonium perchlorate is used as the oxidizing agent in solid fuel rocket propellants. Trihydrides of heavier elements are best made by treating lithium aluminum hydride with their corresponding metal trichlorides.

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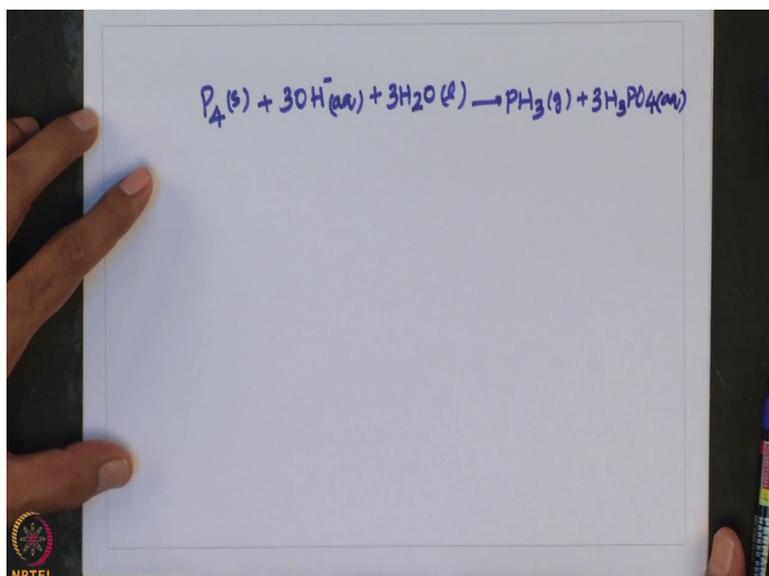
For example, a general equation involving the preparation of these trihydrides is  $\text{ECl}_3 + \text{LiAlH}_4$  in ether, preferably in an ether. So, here E is essentially phosphorus, arsenic, antimony, or bismuth. And also, in the case of phosphine, calcium phosphate can also be hydrolyzed. For example,  $\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O}$  gives  $2\text{PH}_3$  and  $3\text{Ca}(\text{OH})_2$ .

Or one can take similar to phosphonium ion and treat that one with an alkali for example,  $\text{PH}_4^+$  on treatment with  $\text{KOH}$  gives  $\text{PH}_3$  and  $\text{H}_2\text{O}$  and of course, phosphene is an extremely toxic colorless gas, which is much less soluble in water than is  $\text{NH}_3$  and unlike liquid ammonia liquid phosphene, arsine and stibine do not associate through hydrogen bonding they are much more stable alkyl and aryl analogues are useful soft ligands.

For example phosphene if you replace one hydrogen with an alkyl or aryl group it is called primary phosphine, if you replace two hydrogen atoms we get  $\text{R}_2\text{PH}$  it's called secondary phosphine and if you replace all hydrogen atoms we get  $\text{R}_3\text{P}$  they are called tertiary phosphines and tertiary phosphines are extensively used in coordination chemistry and organometallic chemistry to stabilize transition metals in a variety of oxidation states, and besides their application as soft ligands both phosphene and arsine are used in the semiconductor industry to dope silicon or to prepare, other semiconductor compounds such as gallium arsenide.

The commercial synthesis of  $\text{PH}_3$  uses the disproportionation of white phosphorus in basic solution  $\text{P}_4\text{S}$ .

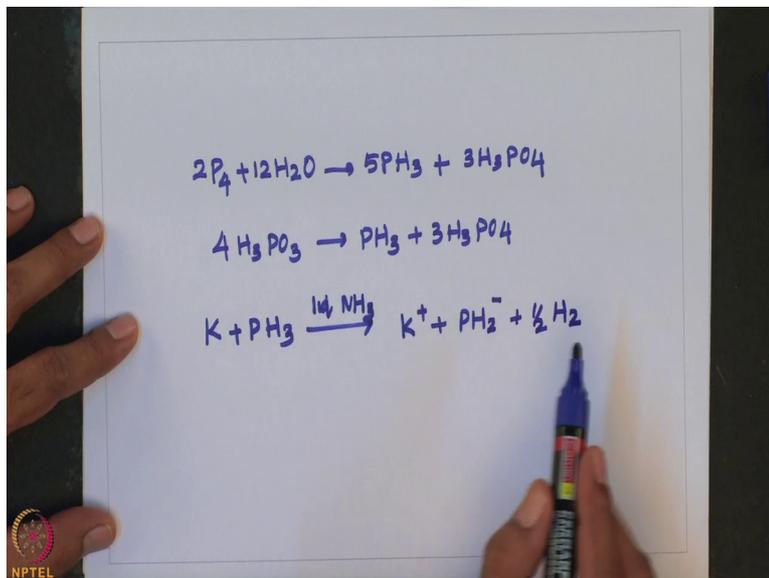
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Basic solution as I had mentioned. So, this is the commercial method of preparation of phosphene, and treatment of white phosphorus with water can also lead to the formation of phosphene, to have ultra pure  $\text{PH}_3$  one has to go for thermal disproportionation of

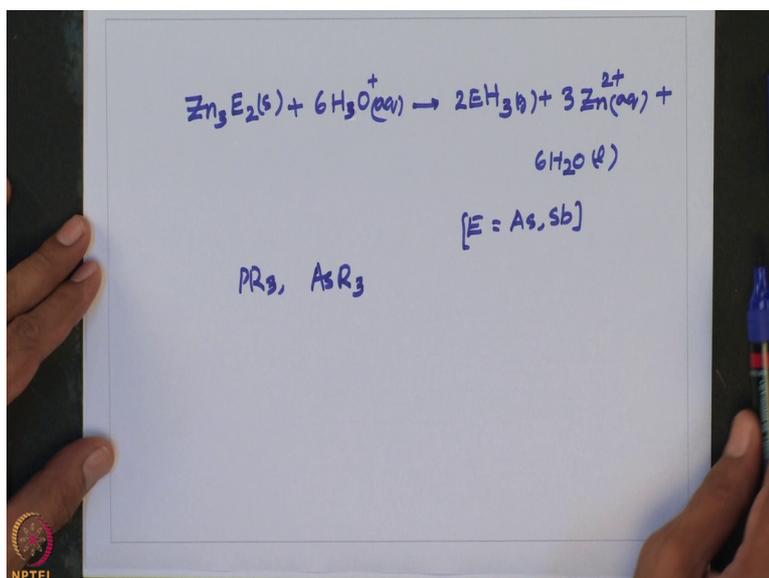
phosphorus acid for example,  $\text{H}_3\text{PO}_3$  gives  $\text{PH}_3$  plus  $3\text{H}_3\text{PO}_4$ . So, this is the method preferred for preparation of ultra pure phosphine and of course, aqueous solution of a  $\text{PH}_3$  is neutral.

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But in liquid ammonia  $\text{PH}_3$  acts as an acid for example,  $\text{K}$  plus  $\text{PH}_3$  in liquid ammonia gives  $\text{K}$  plus  $\text{PH}_2^-$  plus  $\frac{1}{2}\text{H}_2$  and of course, arsine and stibine may be prepared by the proteolysis of compounds that contain an electro positive metal in combination with arsenic or antimony.

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So, here E is arsenic or antimony.

As I said much more stable ergonomic derivatives such as tertiary phosphines and tertiary arsines can be conveniently prepared by treating phosphene with the corresponding metal reagents or one can take phosphene and convert that in to sodium salts and that can be used with appropriate aryl or alkyl halides.

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Thermal stability of hydrides		
□ Thermal stabilities decrease down the group. Enthalpies of formation parallel the E-H bond energies for these compounds.		
	$\Delta_f H^\circ$ (kJ mol <sup>-1</sup> )	E-H bond energy (kJ mol <sup>-1</sup> )
NH <sub>3</sub>	-46.2	+391
PH <sub>3</sub>	+9.3	+322
AsH <sub>3</sub>	+172.2	+247
SbH <sub>3</sub>	+142.8	+255
<b>Orbital mismatch</b>		

So, let us look into the thermal stability of hydrides you can see here for NH<sub>3</sub> delta h is minus 46.2 kilo joules and here if you look into N 2 H bond energy that is plus 391 kilo joules per mol and as we go down the group the bond energy decreases that also resulted in these values. In fact, SbH<sub>3</sub> as a positive 142.8 and here the bond energy is 255 kilo joules per mol.

So, that indicates essentially heavier group 15 hydrides are unstable and here it is essentially because of the orbital mismatch, the sp<sup>3</sup> or p<sup>3</sup> orbitals involved from heavier elements essentially overlapping with 1 s 1 very small one. So, in this case what happens because of orbital mismatch, the bonds are not very strong and that can be seen from these thermodynamic entities given here?

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**Ask a Question**

**All the Group 15 hydrides are pyramidal, but the bond angle decreases down the group:**

**NH<sub>3</sub>, 107.8°    PH<sub>3</sub>, 93.6°    AsH<sub>3</sub>, 91.8°    SbH<sub>3</sub>, 91.3°**

**Explain**



So, let us have a simple question all the group 15 hydrides are pyramidal, but the bond angles decrease down the group. For example, you can see here NH<sub>3</sub> has 107.8 and whereas PH<sub>3</sub> is 93.6, arsine it is 91.8 in case of antimony hydride it is 91.3; that means, apart from ammonia in the rest of the phosphenes angles are very close to 90 degree one can explain this one essentially one can explain by looking into the electro negativity of nitrogen and hydrogen.

For example in case of and well here the difference in the angles can be explained by two methods one is simply looking into the electro negativity difference between n and h, p and h arsenic and hydride and antimony and hydride of course, electro negativities steadily decreasing, and in case of n it is nitrogen having a negative charge as a result what happens the NH electrons are essentially staying very close to n and increasing that angle here.

And in case of phosphene phosphorus is little less electro negative compared to hydrogen as a result more electron density will be residing on hydrogen and same thing is true in case of arsenic as well as antimony di hydrides, and one can also explain by simply looking into the p character in this bond formation, it appears like when we look into 3 p orbitals p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub>; they are essentially orthogonal to each other. If they are not associated with s prior to the hybridization then we will be having pure p<sup>3</sup> hybridization in that case the bonds are essentially whatever the relationship is there between p<sub>x</sub>, p<sub>y</sub>,

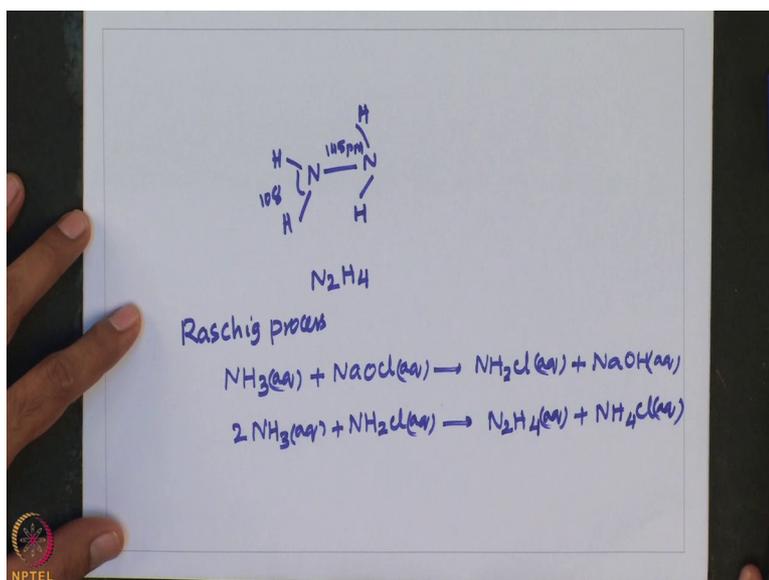
p z with an angle of 90 is retained that could be seen here. So, that clearly indicates in PH<sub>3</sub>, AsH<sub>3</sub> and SbH<sub>3</sub> if it is undergone sp<sup>3</sup> hybridization.

The p character is maximum and s character is very minimum, so, that can also one can also evoke Bent's rule also to explain these things and of course.

In case of arsenic contain antimony the lone pair has maximum s character and are or it will simply s electrons are not touched and only their p<sup>3</sup> p orbitals are undergoing hybridization to form 3 p hybrid orbitals, and they combine with 3 hydrogen atoms to form. So, we can explain by several ways of course, I have given lot of information about these things, when I was discussing valence bond theory bringing hydration concept.

You can go back to the structure and bonding concept and you can look into it. Hydrogen is N<sub>2</sub>H<sub>4</sub> its essentially a fuming colorless liquid with an odor like that of ammonia and hydrogen is weaker base than ammonia, and forms two series of salts, it has a liquid rain similar to that of water around 2 to 4 114 degree centigrade indicating the presence of hydrogen bonding, in the liquid phase hydrogen adopts a gauche confirmation around N-N bond so; that means, one can write the structure in this fashion.

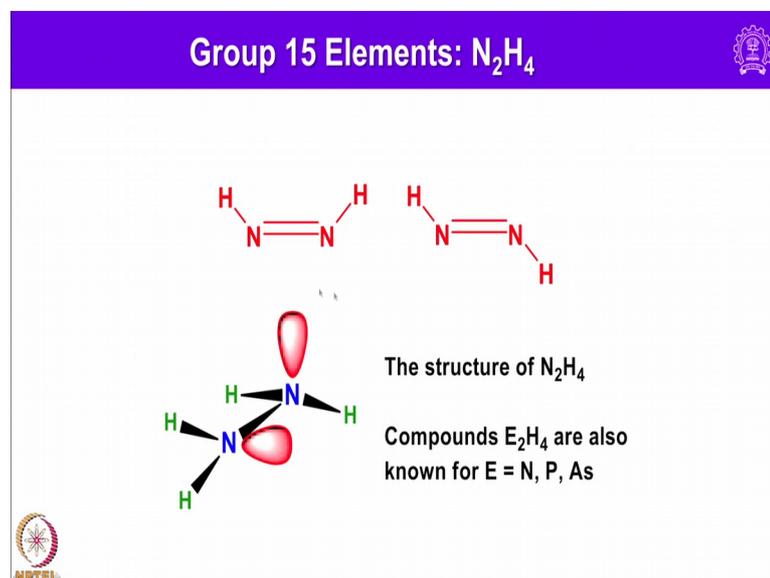
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So, here if you look in the angle this is 108 and the distance between NN is 145 picometer. So, this is N<sub>2</sub>H<sub>4</sub> ok.

And essentially it has this kind of gauche structures to minimize the lone pair lone pair interactions.

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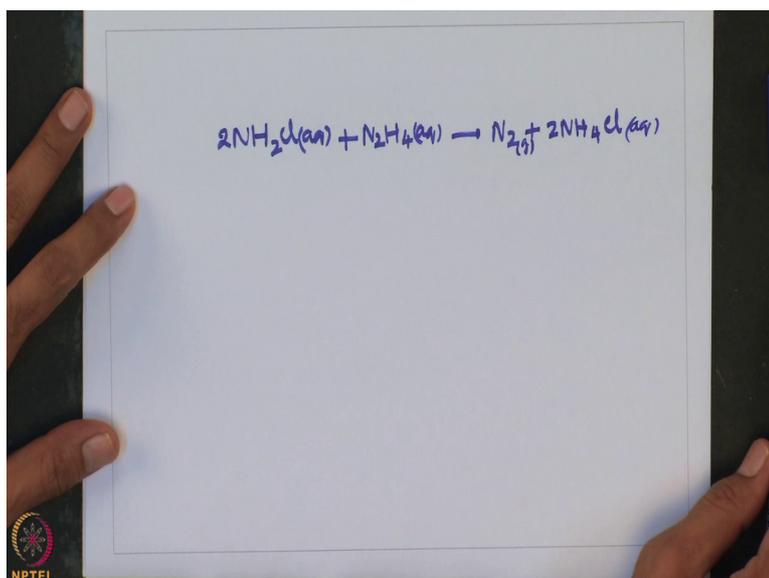


You can see here I have shown a two different type of structure for hydrogen here and of course, similar to  $N_2H_4$  arsenic and antimononic compounds are also known having  $E_2H_4$  composition and hydrogen is manufactured by the Raschig process. So, in which ammonia and sodium hypochlorite react in dilute aqueous solution.

For example  $NH_3 + NaOCl$  react to give  $NH_2Cl$  this  $NH_2Cl$  undergoes dimerization in this fashion in presence of ammonia. So, here  $NH_2Cl$  reacts further with ammonia to form  $N_2H_4$  through the formation of ammonium chloride of course, here we are using two equivalents of ammonia to extract 1  $HCl$  in the form of ammonium chloride.

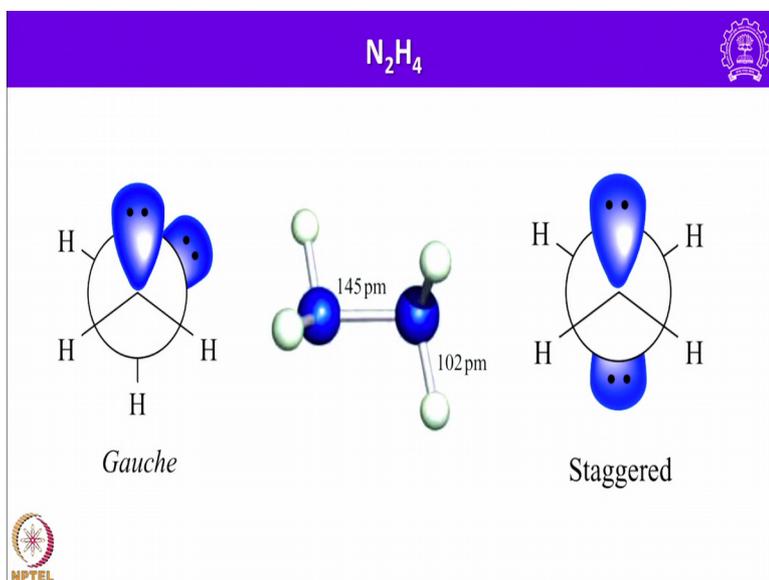
So, there is a competing side reaction that is essentially catalyzed by de metal ions.

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For example if  $\text{NH}_2\text{Cl}$  is treated with  $\text{N}_2\text{H}_4$  it forms  $\text{N}_2$  gas and in this case is gelatin added to the reaction mixture to trap the de metal ion to form a complex with them you can see here.

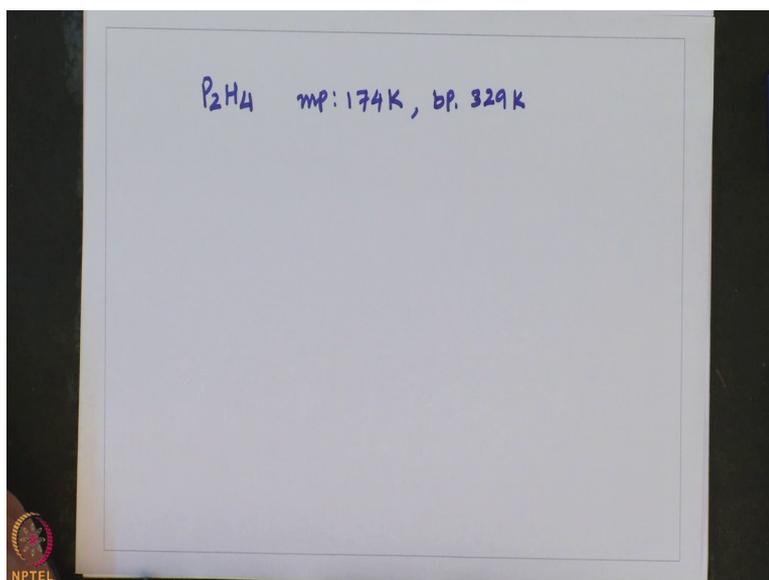
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I have shown more structures of  $\text{N}_2\text{H}_4$  here and this is how the gauche structure looks like and you can see here the N to H bond distance is 102 picometer and N-N distance is 145 picometer and this is the staggered structure of  $\text{N}_2\text{H}_4$ .

So, diphosphide I had mentioned  $\text{P}_2\text{H}_4$  is a colorless liquid melting point is 174 kelvin.

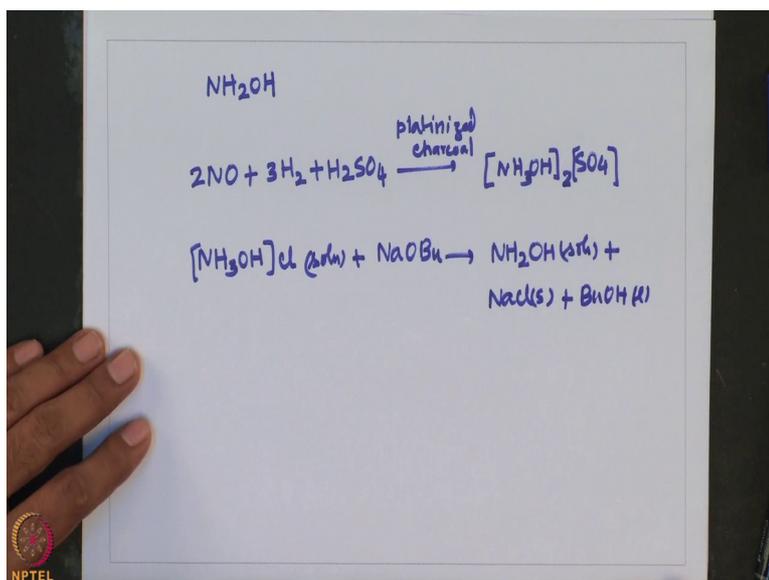
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So, melting point is 174 kelvin and boiling point is 39 kelvin. So, and these highly toxic and spontaneously inflammable.

The gauche confirmation is also adopted by  $P_2H_4$  in the gas phase, in the solid state  $P_2H_4$  has a staggered confirmation the eclipsed confirmation is not observed because which would maximize, the lone pair lone pair repulsion as a result these compounds have gauche or staggered confirmation, di diphosphine one is found as a minor product in several reactions in which  $PH_3$  is prepared. It can be separated from  $PH_3$  by condensation in a freezing mixture and it do not exhibit basic properties and hydroxyl amine is a colorless hygroscopic solid, with a low melting point of 32 degree centigrade.

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And there are several routes to synthesize hydroxyl amine that is  $\text{NH}_2\text{OH}$ , which is usually handled as a salt sulfate preferably in aqueous solution. So, NO on treatment with hydrogen gas in presence of sulphuric acid of course, here platinumized charcoal used as a catalyst is used as a catalyst to form sulfate salt ok.

So, anhydrous hydroxyl amine can be preferred by adding sodium butoxide to a solution of hydroxyl amine hydrochloride for example,  $\text{NH}_2\text{OH}\cdot\text{HCl}$  will react with the sodium butoxide, it forms  $\text{NH}_2\text{OH}$  plus  $\text{NaCl}$  plus butanone. So, let me stop here and continue more discussion on nitrogen hydrides or ammonia and hydrogen and other related compounds in my next lecture until then have a present reading of group 15 chemistry.

Thank you very much.