

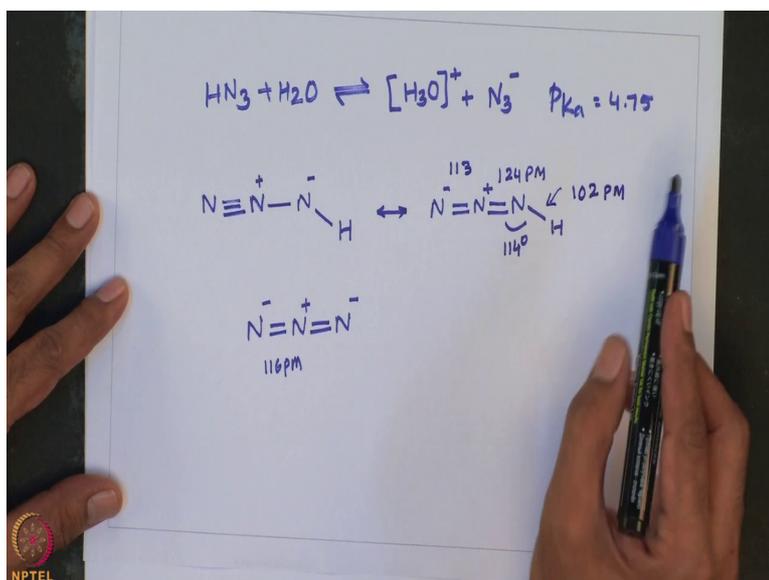
**Main Group Chemistry**  
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**Lecture – 42**  
**Chemistry of Group 15 Elements**

Welcome to MSB lecture series on the chemistry of main group elements. This is 42nd lecture in the series. So, I when I stopped I was discussing about hydrides of group fifteen elements. So, let me continue from where I had stopped. Let us look into hydrogen azide and azide salts.

I had given introduction about azides and nitrites in previous lecture. Sodium azide is an important starting compound this is  $\text{NaN}_3$ . So, this can be obtained from the molten sodium amide reacting with sodamide with sodium nitrite. Further treatment of sodium azide with  $\text{H}_2\text{SO}_4$  yields hydrogen azide or hydrazoic acid  $\text{HN}_3$ . Hydrogen azide or hydrazoic acid is a colourless liquid melting 0.193 Kelvin and boiling point is 309 Kelvin it is a dangerously explosive material and it is also a highly poisonous aqueous solution of hydrazoic acid essentially a weak acid.

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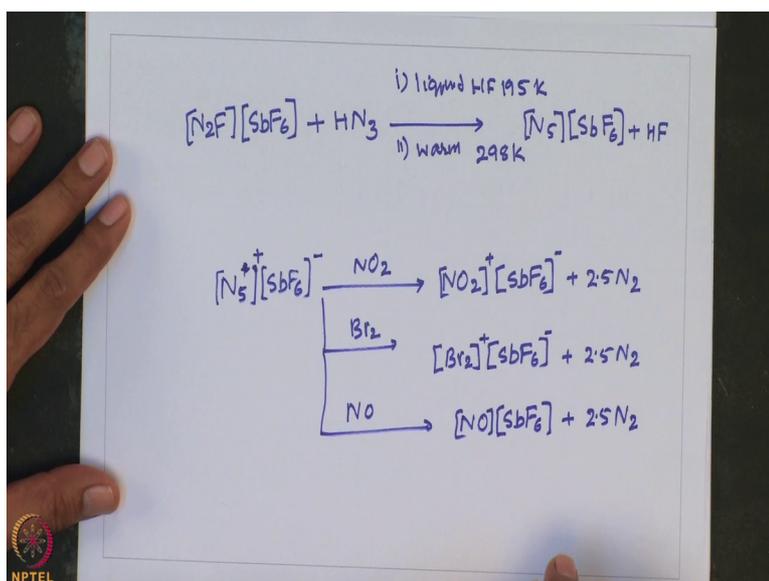
So, here  $\text{p}K_a$  for this one is 4.75 and of course, azide ion is isoelectronic with carbon dioxide. And let us look in to hydrazoic acid structure. So, linear azide  $\text{N}_3^-$  can be found by deprotonation of hydrazoic acid and is symmetrical with the 2 identical n n

bond with a distance of 116 pico meter of course, azide ion is also called as pseudo halogen because of its similarities to halides

So, here it is 116 picometer both are essentially same in case of hydrazoic acid this is 124, where this one is 113, and this angle is 114 degree. And this is distance N H distance bond distance is 102 picometer. I did mention about pentazole ion reaction of HN<sub>3</sub> with this hexafluorophosphate ion with in hydrofluoric acid at 195 Kelvin leads the formation of this pentazole.

For example, here one can use arsenic or antimony hexafluoride. So, I am using here antimony hexafluoride. It involves 2 steps, treating with liquid HF at 195 Kelvin and then warming to 298 Kelvin, it gives pentazole cation HF.

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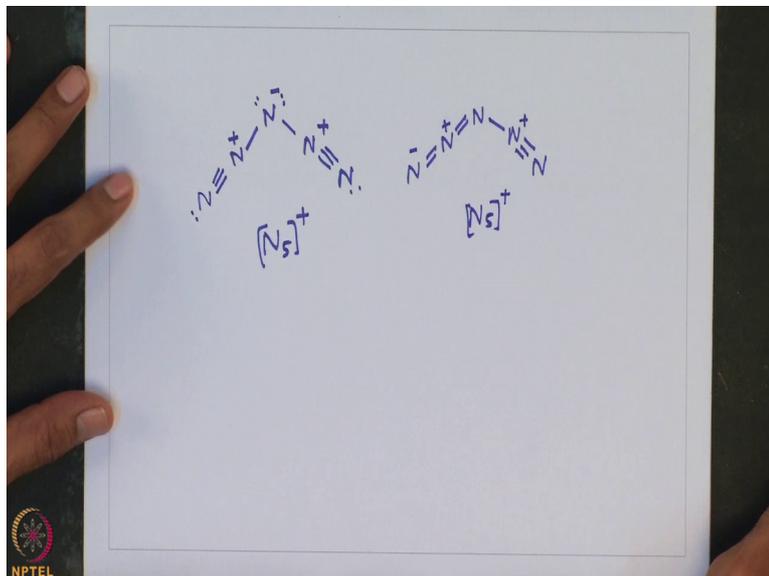


And of course, if you take solid pentazole cation it oxidizes NO, NO<sub>2</sub> and Br<sub>2</sub>, but not Cl<sub>2</sub> or O<sub>2</sub>. So, let us look into a few of these reactions here.

If you treat this one with NO<sub>2</sub> it gives nitrogen, when it is treated with bromine same reaction is repeated here it forms 2.5 equivalents of nitrogen. Of course here counter cation is Br<sub>2</sub> plus. Similarly on treatment with NO, this has some of the reactions of pentazole ion. If you are curious to know the structure of pentazole ion I had showed you in my one of my previous lectures let write again of course, one can write several resonance structures I am not going to write all the resonance structures for this one.

Let me write simply the structure you can make an attempt to write all possible resonance structures for this N 5 plus cation.

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So, if you see here these lone pairs are intact here and of course, here positive charge is there here positive charge is there, so here negative charge of course, here we have 2 lone pairs. So, now overall net charge will be for this one N 5 plus. So, of course, you can start writing several other resonance structures.

Let me write one more. Once after writing like this you can see cation and anionic once this is neutral and this is and this is here. So, again you can clearly see N 5 plus. So, you can write 4 more resonance structures you can make attempt to write in a similar fashion.

Now, let us look into the oxides of group 15 elements. As in group 14 the first element of group 15 stands apart informing oxides in which p pi p pi bonding predominates; that means, in case of nitrogen p pi and its oxygen compounds p pi p pi bonding is very very important.

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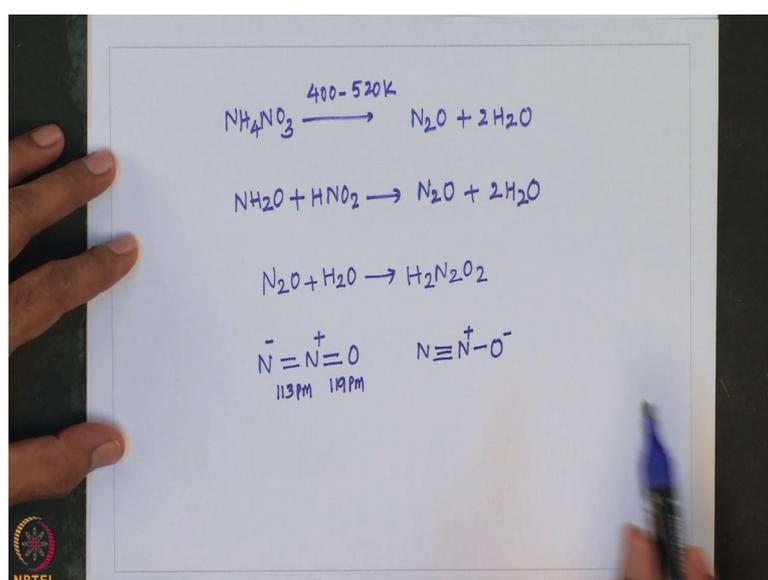
### Oxides of group 15 Elements

- As in group 14, the first element of group 15 stands apart in forming oxides in which (p-p) $\pi$ -bonding is important.
- Nitrogen oxides: NO<sub>3</sub> which is an unstable radical; NO<sub>2</sub> exists in equilibrium with N<sub>2</sub>O<sub>4</sub>.
- Reactions of nitrogen-oxygen compounds that liberate or consume N<sub>2</sub> are generally very slow at normal temperatures and pH = 7



Let us consider some of these nitrogen oxides one at a time. So, NO<sub>3</sub> which is an unstable radical NO<sub>2</sub> exists in equilibrium with N<sub>2</sub>O<sub>4</sub> its dimer. Reactions of nitrogen oxygen compounds that liberate or consume nitrogen are generally very slow at normal temperature and at a pH of 7. Now let us consider dinitrogen monoxide N<sub>2</sub>O it is also called nitrous oxide.

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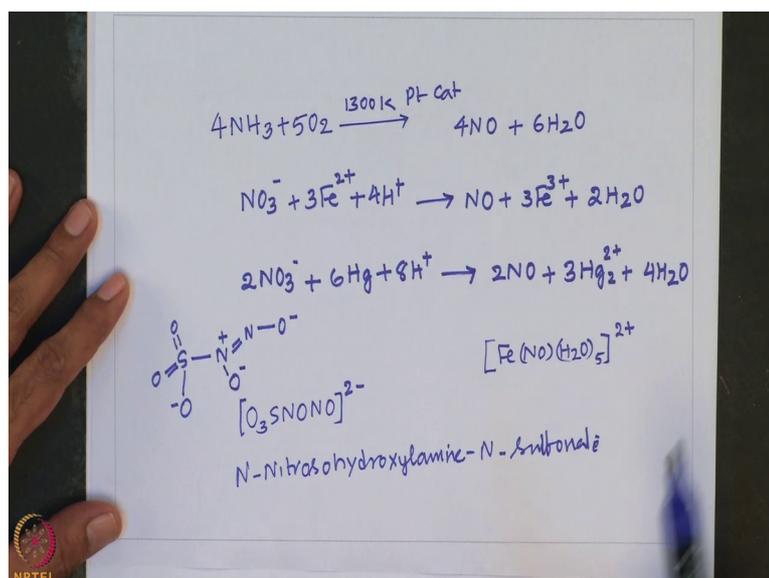
So, one can prepare by decomposing ammonium nitrate, when ammonium nitrate is heated to 400 to 520 Kelvin N<sub>2</sub>O is formed, similarly NH<sub>2</sub>OH when its combined

with  $\text{HNO}_2$  it leads to the formation of  $\text{N}_2\text{O}$ . Dinitrogen monoxide that is  $\text{N}_2\text{O}$  as a faint sweet odor it dissolves in water to give a neutral solution and if you are curious to know the structure of  $\text{N}_2\text{O}$  this is how once can write and of course, here it is 113 pico meter and it is little longer once can also write this structure.

We come cross one important application of nitrous oxide that is as a general anesthetic it is also known as laughing gas, but its major use is in the preparation of whipped cream and it is used commercially to prepare sodium azide. Let us look into nitrogen monoxide that is  $\text{NO}$ . Nitrogen monoxide is made industrially from ammonia and on a laboratory scale by reducing nitric acid in the presence of sulphuric acid.

Let me write down all these reactions for you.

(Refer Slide Time: 11:58)



So, when ammonia is treated with oxygen at 1300 Kelvin using platinum catalyst. So,  $\text{NO}$  is formed,  $\text{NO}$  can also be formed in this fashion or. And of course, if you just look into this reaction this is the reaction basis for brown ring test for  $\text{NO}_3^-$  after the addition of an equal volume of aqueous ferrous sulphate to the test solution cold concentrated sulphuric acid is added slowly to form a separate lower layer.

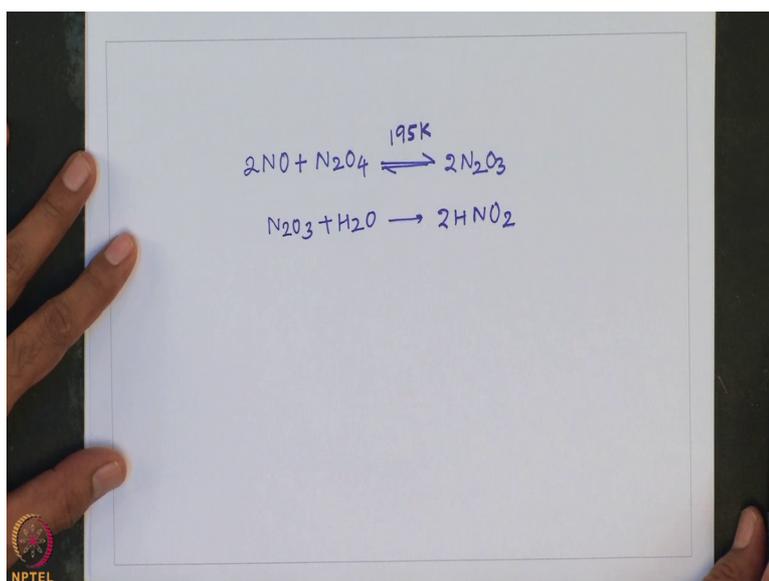
If  $\text{NO}_3^-$  is present  $\text{NO}$  is liberated and a brown ring forms between the 2 layers the brown color is essentially due to the formation of iron complex penta aqua nitrosyl complex of iron. So, that is responsible compound is essentially penta aqua nitrosyl

complex. So, of course, NO is a plus. So, essential iron is in plus 3 state because of NO is giving one electron it appears like it is in plus 3 plus 2 state actually iron is in plus 3 state.

So, one of the oldest known reactions of NO is in the formation of N nitroso hydroxylamine N sulfonate and that is known since 1800 it is a very interesting one, that compound is  $\text{O}_3\text{SNONO}_2$  minus this is called N nitroso hydroxylamine N sulphonate. The structure of this one is interesting let me write the structure of this compound. So, this is nothing, but N nitroso hydroxylamine N sulphonate.

Let us look into dinitrogen trioxide  $\text{N}_2\text{O}_3$ .  $\text{N}_2\text{O}_3$  can be prepared conveniently by treating NO with  $\text{N}_2\text{O}_4$ .

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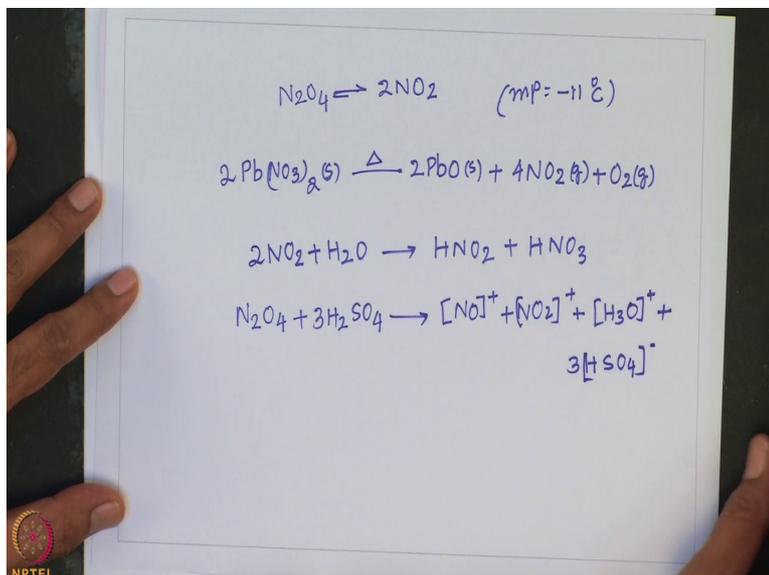


Dinitrogen trioxide is obtained as a dark blue liquid in reaction of NO and  $\text{N}_2\text{O}_4$  at low temperature; that means, temperature should be around 195 Kelvin. It should be remember we had to do it at very low temperature.

If temperature is raised it would dissociate back to give NO and  $\text{N}_2\text{O}_4$ , dinitrogen trioxide is water soluble and is the acid anhydro of  $\text{HNO}_2$  that is nitrous acid. So, if you remove the water it gives anhydrous dinitrogen trioxide, but on addition of water it gives back nitrous acid. So, dinitrogen tetra oxide is essential a dimer of nitrogen dioxide NO

2 and this one is always in equilibrium with dimeric structure that is  $\text{N}_2\text{O}_4$  is always in equilibrium with  $2\text{NO}_2$ .

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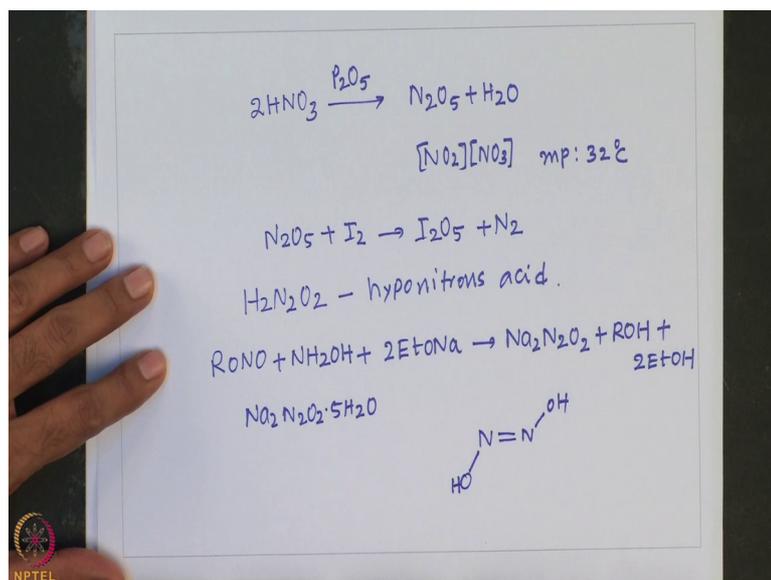


They are solid is colorless and is diamagnetic consistent with the presence of only  $\text{N}_2\text{O}_4$  species. Of course melting point is minus 11 degree centigrade. And dissociation of this dimer gives brown  $\text{NO}_2$  radicals solid  $\text{N}_2\text{O}_4$  melts to give yellow liquid the color arising from the presence of a little bit of  $\text{NO}_2$  in it. Of course, laboratory scale preparation of  $\text{NO}_2$  involves decomposition of lead nitrate.

If the brown gaseous  $\text{NO}_2$  is cooled to 273 Kelvin  $\text{N}_2\text{O}_4$  condenses as a yellow liquid. Dinitrogen tetroxide is a powerful oxidizing agent which attacks many metals including mercury at as low as 298 Kelvin and the reaction of  $\text{NO}_2$  or  $\text{N}_2\text{O}_4$  with water gives a one is to one mixture of nitrous and nitric acids. So, one is to one mixture of nitrous and nitric acids. In concentrated sulphuric acid  $\text{N}_2\text{O}_4$  yields the nitrosin and nytryl cations.

Now, let us look into the last one in the series dinitrogen pent oxide. Again dinitrogen pent oxide can be prepared by treating nitric acid with  $\text{P}_2\text{O}_5$ ; that means, it is a essentially an anhydride of  $\text{HNO}_3$ , nitric acid on treatment with  $\text{P}_2\text{O}_5$  gives  $\text{N}_2\text{O}_5$  plus  $\text{H}_2\text{O}$ .

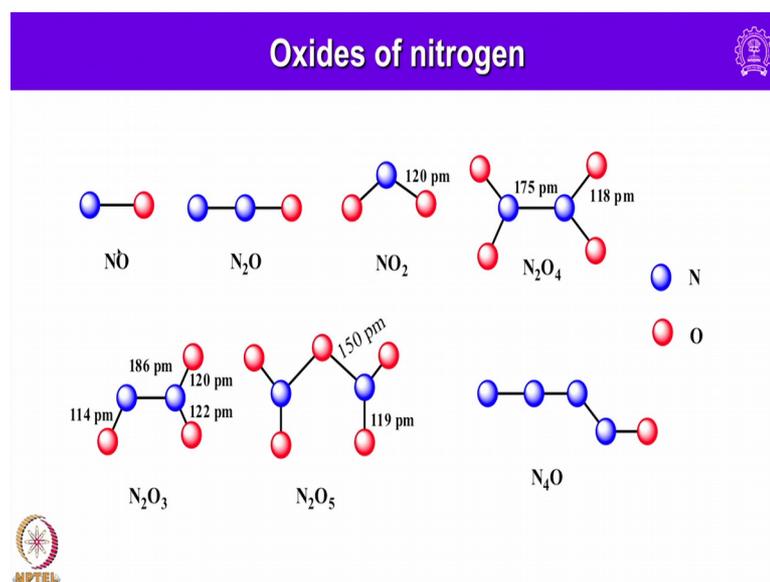
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So,  $\text{N}_2\text{O}_5$  is a colorless ionic solid. Ionic solid means it is a combination of  $\text{NO}_2$  and  $\text{NO}_3$  and melting point is 32 degree centigrade. This is highly unstable it forms colourless deliquescent crystals, but slowly decomposes about 273 Kelvin to give  $\text{N}_2\text{O}_4$  and  $\text{O}_2$ . So, dinitrogen pentoxide reacts violently with water yielding  $\text{HNO}_3$  and also it is a very powerful oxidizing agent. For example,  $\text{N}_2\text{O}_5$  when it is treated with the iodine it forms  $\text{I}_2\text{O}_5$ . So, iodine goes to plus 5 oxygen state plus  $\text{N}_2$  is formed. It indicates it is a very powerful oxidizing agent.

You can see the structures of some of these oxides shown here.

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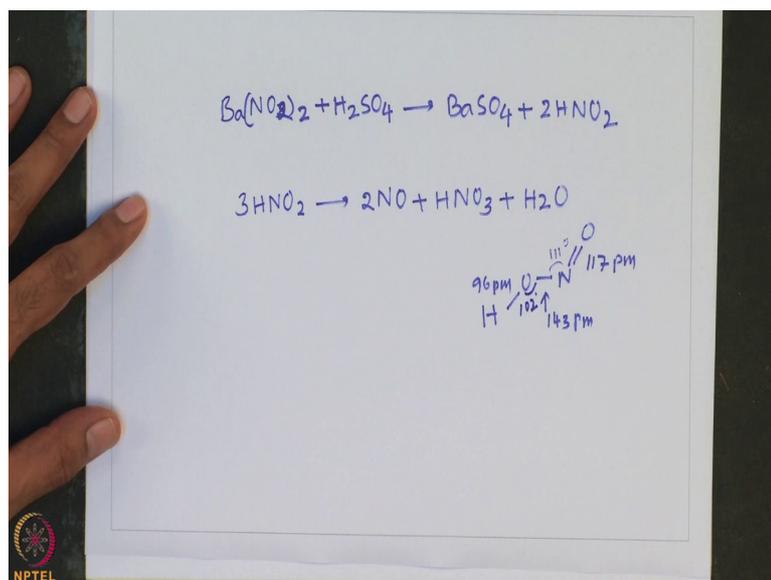


This is linear  $\text{N}_2\text{O}$  is linear whereas,  $\text{NO}_2$  has a bent structure,  $\text{N}_2\text{O}_4$  as this structure and  $\text{N}_2\text{O}_3$  this how it looks and this is  $\text{N}_2\text{O}_5$  and this is  $\text{N}_4\text{O}$ .

Let us look into the oxo acids of nitrogen. One important acid is  $\text{H}_2\text{N}_2\text{O}_2$  that is called hypo nitrous acid  $\text{H}_2\text{N}_2\text{O}_2$  is known as hypo nitrous acid. An aqueous solution of sodium hypo nitrate can be made from organic nitrates by this reaction that I am going to write here and free  $\text{H}_2\text{N}_2\text{O}_2$  hypo nitrous acid is a weak acid, but it is a potentially explosive. It decomposes spontaneously into  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$ . The trans configuration is kinetically the more stable and has been confirmed in the solid state structure of  $\text{Na}_2\text{N}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$  hydrated.

So, structure looks like this one. So, nitrous acid, nitrous acid is known only in solution and in vapor phase  $\text{HN O}_2$  it maybe again prepared in  $\text{C}_2$  by treating barium nitrate with sulphuric acid barium nitrate. So, it can be prepared by treating barium nitrate with sulphuric acid.

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So, whenever we need it has to be generated in C 2 and it should be used and it is a weak acid p k values 3.37, but is unstable with respect to disproportionation in solution. Let me write disproportionation reaction the destabilizes  $\text{HNO}_2$  and if you are curious to the structure this is how it looks like and this is 117 picometer and this is 143 picometer and OH bond distance is 96 picometer and this where as this angle is 111 where this angle is 102.

So, let me stop here and continue discussion on oxo acids of group 15 elements in my next lecture, until then have a very pleasant reading of group 15 chemistry.

Thank you very much.