Main Group Chemistry

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Lecture – 40
Chemistry of Group 15 Elements

Welcome to MSB lecture series on main group elements. In my previous lecture I was discussing about group 15 elements. While discussing I did mention that white phosphorus having 4 phosphorus atoms with each one having a pair of electrons can perform as a ligand. And of course, many metal complexes of white phosphine as such are known a couple of examples I displayed in my previous lecture. And of course, I would be giving you more information about the utility of phosphines or phosphorus compounds are ligands, before I conclude the chemistry of group 15 elements.

So, let me continue on phosphorus compounds. And phosphorus can also have ring chain or cage structure anionic phosphorus rings chains or clusters are also known.

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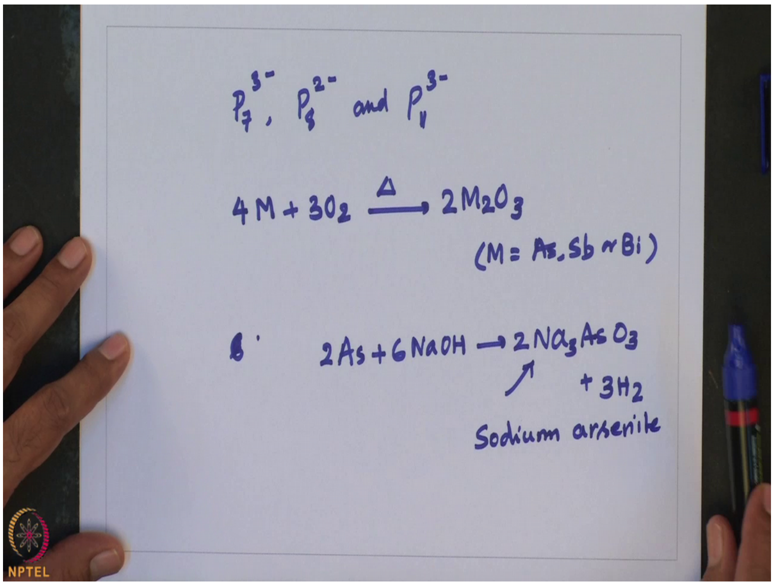

P_7^{3-}, P_8^{2-} and P_{11}^{3-}

$$4M + 3O_2 \xrightarrow{\Delta} 2M_2O_3$$

(M = As, Sb or Bi)

$$2As + 6NaOH \rightarrow 2Na_3AsO_3 + 3H_2$$

Sodium arsenite

For example, P 7 3 minus P 8 2 minus and P 11 3 minus are some of the examples of anionic phosphorus cages rings or chains. I will show you the structure of some of these in my next slide.

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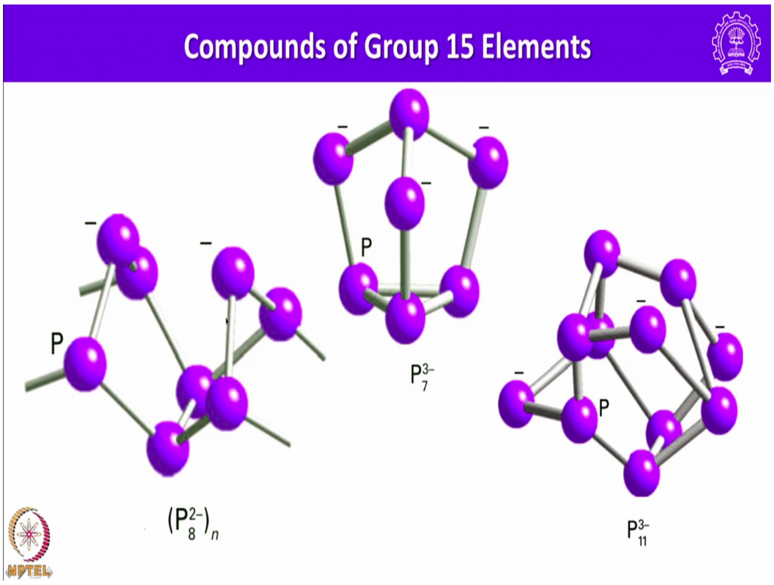

Compounds of Group 15 Elements

You can see here P 8 2 minus has this structure here. And also, you can see where the negative charge is residing this is P 7 3 minus of course, basically what happens, wherever the charge is there essentially this phosphorus atoms are 2 coordinated.

And P 11 3 minus has a cage structure like this. And arsenic antimony and bismuth occur predominantly as sulphides, these 3 elements essentially form layer structures very similar to that of black phosphorus, and arsenic vapour contains As 4 molecules very similar to P 4. And the unstable yellow form of solid arsenic probably also contains arsenic 4 units. At very low temperatures, antimony vapours contained molecular S b f 4 units. At room temperature and pressure, arsenic antimony and bismuth are essentially grey solids with lattice structures resembling that of black phosphorus. And arsenic antimony and bismuth burn in air and combine with halogen. For example, and here M equals arsenic antimony or bismuth. None of these elements reacts with aqueous alkali. But arsenic is attacked by fused sodium hydroxide to form sodium arsenite. So, this is essentially called sodium arsenite.

Let us look into the compounds of group 15 elements. The group 15 elements form binary compounds on direct interaction with many elements.

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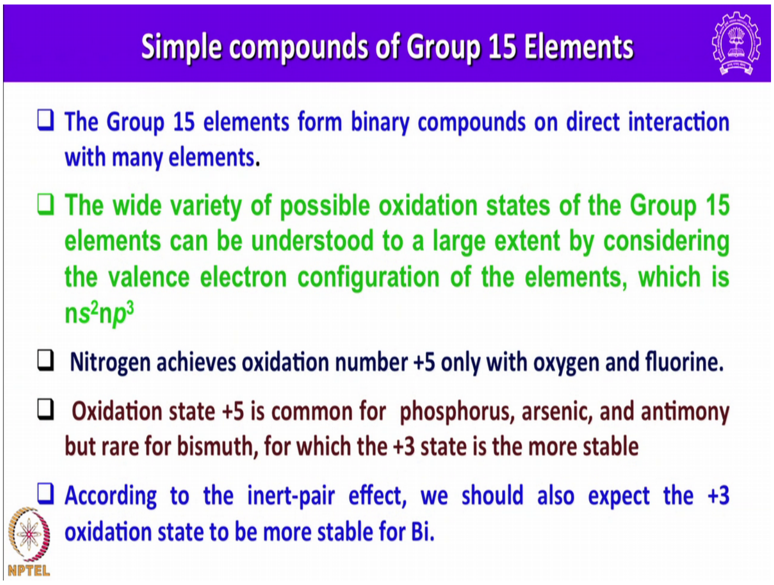

Simple compounds of Group 15 Elements

☐ The Group 15 elements form binary compounds on direct interaction with many elements.

☐ The wide variety of possible oxidation states of the Group 15 elements can be understood to a large extent by considering the valence electron configuration of the elements, which is ns^2np^3

☐ Nitrogen achieves oxidation number +5 only with oxygen and fluorine.

☐ Oxidation state +5 is common for phosphorus, arsenic, and antimony but rare for bismuth, for which the +3 state is the more stable

☐ According to the inert-pair effect, we should also expect the +3 oxidation state to be more stable for Bi.

And the wide variety of possible oxide states of group 15 elements can be understood, simply by looking into their electronic configuration, which is essentially N s 2 N P 3 one can anticipate besides having plus 3 and plus 5 state other oxide states also; however, compounds having a other than plus 2 and plus 3 are very scarce nitrogen achieves oxide state plus 5. Only with more electronegative elements such as oxygen and fluorine. Of course, when we look into the electronegativity of all elements in the periodic table, nitrogen is the 4th most electronegative element. So, in order to make nitrogen compound exist in higher positive oxide state. Only they have to be combined with either oxygen fluorine or to an extent by chlorine.

Oxide state plus 5 is common for phosphorus arsenic and antimony. But rare for bismuth, and most of the base compounds have plus 3 as the most stable oxide state. And of course, here inert pair effects dominates the chemistry of bismuth. As a result, plus 3 state is more stable for bismuth compounds.

Since nitrogen is the 4th most electronegative element. It can also form compounds with negative oxide state. For example, N 3 minus ion nitrate and ammonia in which N is also in minus 3 state are known. And nitrogen achieves positive oxide states only in compounds with more electronegative elements such as oxygen. And fluorine as I mentioned nitrogen does achieve the group oxide state plus 5 nitrogen forms simple binary compounds with other elements. They are classified as nitrates or azides. Nitrates are classified as celine covalent or interstitial depending upon the other combining elements. The nitrates of metal can be prepared by direct interaction of the element with nitrogen or ammonia, or by thermal decomposition of an amide. I will give you some methods of preparation of various nitrates.

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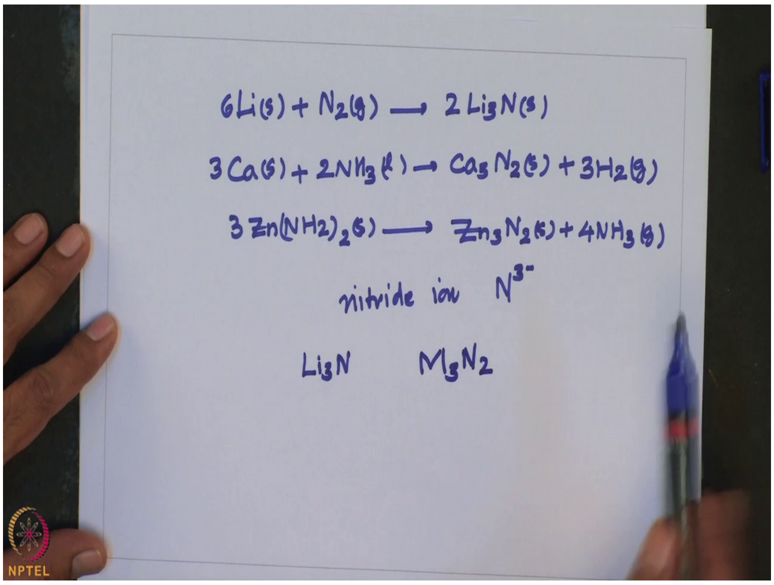

$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$

$3Ca(s) + 2NH_3(l) \rightarrow Ca_3N_2(s) + 3H_2(g)$

$3Zn(NH_2)_2(s) \longrightarrow Zn_3N_2(s) + 4NH_3(g)$

nitride ion N^{3-}

Li_3N M_3N_2

So, this are the few methods of preparation of nitrates. So, essentially celine nitrates contains nitrate ion. This is nitrate ion having 3 negative charges. And saline nitrates occur for lithium among the group one elements and also for group 2 elements. It has composition M 3 N 2. Whereas, in case of group one essentially only lithium forms. Others cannot form stable azides because of the larger size. You can see Li 3 N for group one. Whereas, in case of group 2 elements. It is the general nature.

So, in covalent nitrates due to the presence of a covalent bond possess a wide range of properties depending on the element to which nitrogen is bonded. Some examples of covalent nitrates are essentially boron nitrate.

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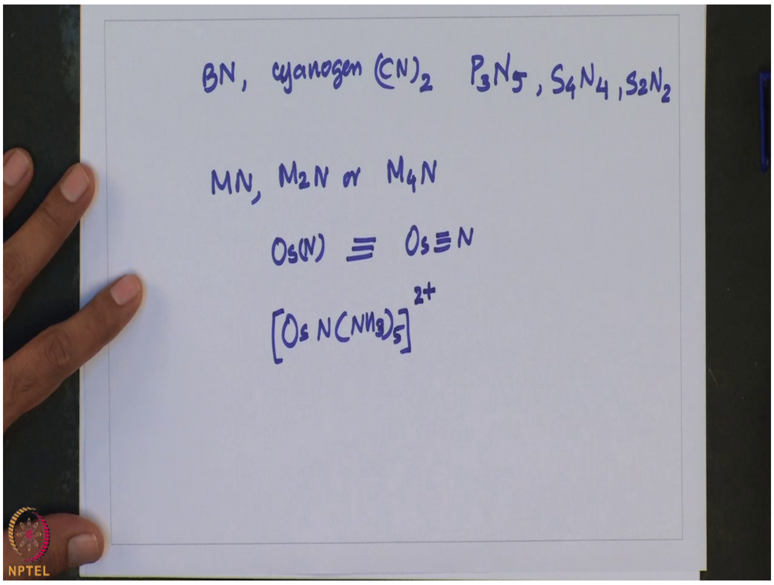

BN, cyanogen $(CN)_2$ P_3N_5, S_4N_4, S_2N_2

MN, M_2N or M_4N

$Os(N) \equiv Os\equiv N$

$[OsN(NH_3)_5]^{2+}$

So, born nitrate has composition 1 is to 1 and cyanogen and also phosphorus nitride. And tetra sulphur nitride. Now so, disulphur di nitride, so the largest category of nitrates consists of interstitial nitrates of the d block elements with formula M N or M 2 N or M 4 N that depends on the oxide state of the metal. Essentially d block element where the N occupies some or all the octahedral sides with in the cubic or hexagonal close packed lattice of metal atoms. And transed metal nitrates are hard and inert in nature. So, they are essentially used as refractory materials, and find applications as crucibles high temperature reaction vessels and thermocouple sheets. Nitrate ions is often found as a ligand in transed metal complexes as well. I am going to show a one or 2 examples of metal complexes having nitrate as a ligand.

As one of the ligand it is high negative charge small size and ability to serve as a good pi donor. As well as sigma donor means, that it can stabilize metals in higher oxide state. Very similar to oxygen, the short coordinate bond between the ion and metal atom is often represented as M N. An example is the complex of this type. One can write like this or one can also like something like this. So, one example is; I will show you the structure of this compound here. You can see the structure of pentamine osmium nitrate complex.

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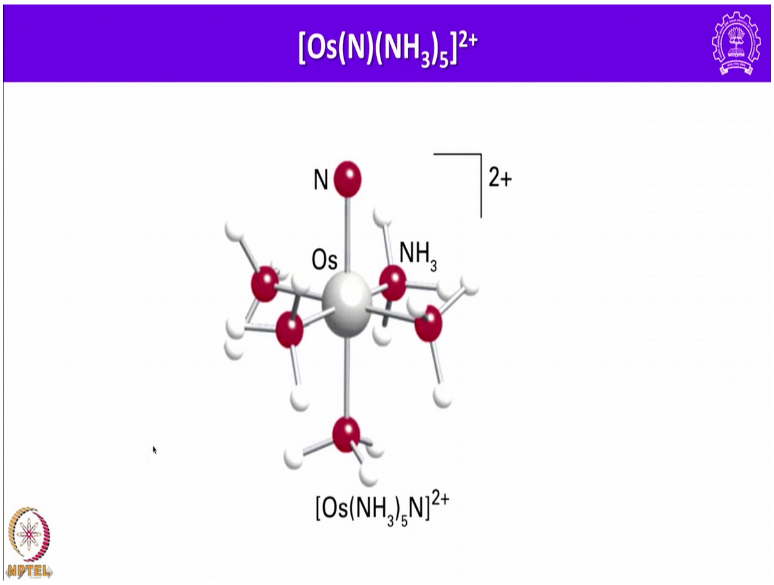

$[Os(N)(NH_3)_5]^{2+}$

It has an octahedral geometry where one of the actual position is occupied by N. And essentially, we have osmium to N triple bond here.

Another important class of nitrogen compounds are essential azides. Azides are toxic and unstable. And they are used as detonators in explosives.

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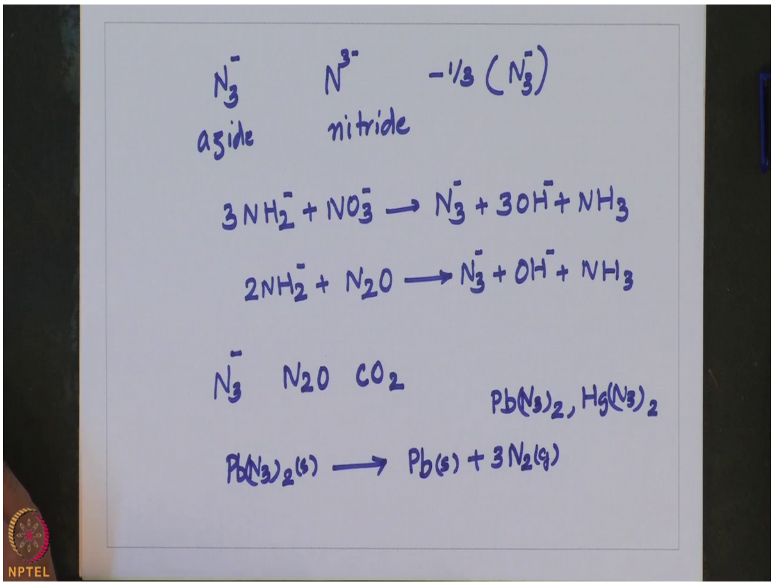

N_3^- N^{3-} $-1/3$ (N_3^-)

azide nitride

$$3NH_2^- + NO_3^- \rightarrow N_3^- + 3OH^- + NH_3$$

$$2NH_2^- + N_2O \rightarrow N_3^- + OH^- + NH_3$$

N_3^- N_2O CO_2

$Pb(N_3)_2$, $Hg(N_3)_2$

$$Pb(N_3)_{2(s)} \rightarrow Pb_{(s)} + 3N_{2(g)}$$

So, one should not confuse between azide and nitrate; so the N 3 single negative charge whereas, in case of nitrate we have one nitrogen with 3 negative charges. So, this is azide and this is nitride. So, azides in which nitrogen is present as N 3 minus, may be synthesized by the oxidation of sodium amide with either N O 3 minus ion or N 2 O at elevated temperature. For example, N H 2 minus reacts with N O 3 minus to give N 3 minus. Or one can also start from N 2 O. In N 3 minus the average oxidation number of N is minus 1 by 3. The ion is N 3 minus ion.

So, this is for I am telling N 3 minus ion. So, here each one is 3 minus only one here 3 nitrogen's are there the oxidation number can be considered as minus 1 by 3 for each nitrogen. This azide ion is isoelectronic with N 2 O as well as C O 2. And of course, azide is also a very good ligand towards transed metal ions. And heavy metal complexes are salt such as P b N 3 twice or H g N 3 twice are shock sensitive detonators. And decompose to produce the metal and nitrogen. Ionic azides such as N an 3 sodium azide are thermodynamically unstable, but kinetically inert. They can be handled at room temperature. They can also be used as source of azide for various other preparation such as organic azide and inorganic azides.

Sodium azide is toxic. And is used as a chemical preservative and in pest control. And when alkali metal azides are heated at denominated by impact they explode liberating, nitrogen depending upon the quantity of metal azide involved in it. This reaction is used in the inflation of airbags in cars in which the heating of the azide is by electrical means. Of course, I elaborated more about airbag, and the utility of sodium azide in it for inflation. Besides azide nitrogen compounds containing polynitrogen cations are also known for example, N 5 plus is synthesized from species containing N 3 minus and N 2 F plus ions.

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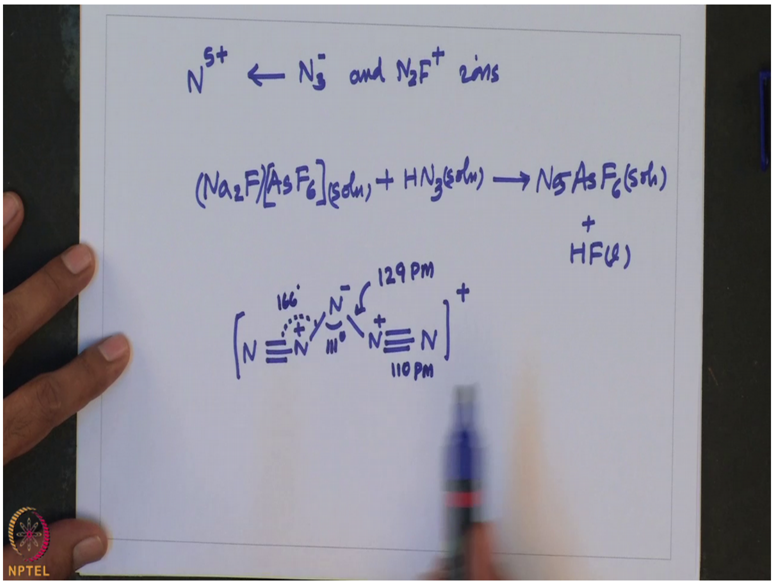

$N^{5+} \leftarrow N_3^-$ and N_2F^+ ions

$(N_2F)[AsF_6]_{(soln)} + HN_{3(soln)} \longrightarrow N_5AsF_{6(soln)} + HF(l)$

For example, if you consider N a 2 F As F 6 in solution when it is treated with H N 3. It forms and H F formation will be there. You may be surprised to know the structure of N 5 plus, this how it looks like. So, overall charge will be plus. So, overall charge will be plus here and here this angle is 111 degree and this distance is 129 picometre. And this is 110 picometre. And whereas, this angle is 166 degree.

And similar to nitrogen. Phosphorus forms compounds with almost all elements in the periodic table. Phosphides maybe metal rich or phosphorous rich depending upon the composition. And that is based on the oxide state of the metal or the other element with which phosphorus is combined. The phosphides of other elements can be prepared by heating the appropriate element with red phosphorus inert atmosphere.

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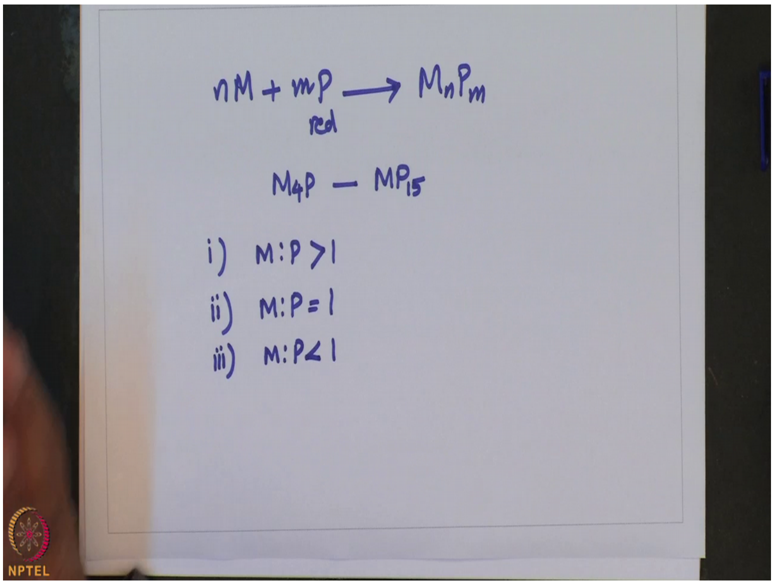

$$nM + mP \xrightarrow{} M_nP_m$$

red

M_4P — MP_{15}

i) $M:P > 1$

ii) $M:P = 1$

iii) $M:P < 1$

For example, here phosphorus we are considering is red phosphorus. So, there are many varieties of phosphides with formulas ranging from M 4 P to M P 15. They include a metal rich phosphides in which metal to phosphorus ratio is greater than 1. And monophosphides so, one is with metal to phosphorus ratio greater than 1. And another class is metal to phosphorus ratio equals 1. And another set of compounds metal to phosphorus ratio greater than 1.

They are essentially phosphorus rich horse phosphides. And here they are metal rich phosphides the structures have a trigonal prismatic arrangement of 6 7 8 9 metal ions around a phosphorus atom monophosphides essentially adopt a variety of structures depending on the relative size of other atoms. For example, aluminium phosphide adopts, the zinc blend structure tin phosphide adopts rock salts structure. And vanadium phosphide adopts the nickel arsenide structure. And phosphorus rich phosphides have lower melting points. And are less stable than metal rich phosphides and also mono phosphides. I will show you some of this phosphides in this slide.

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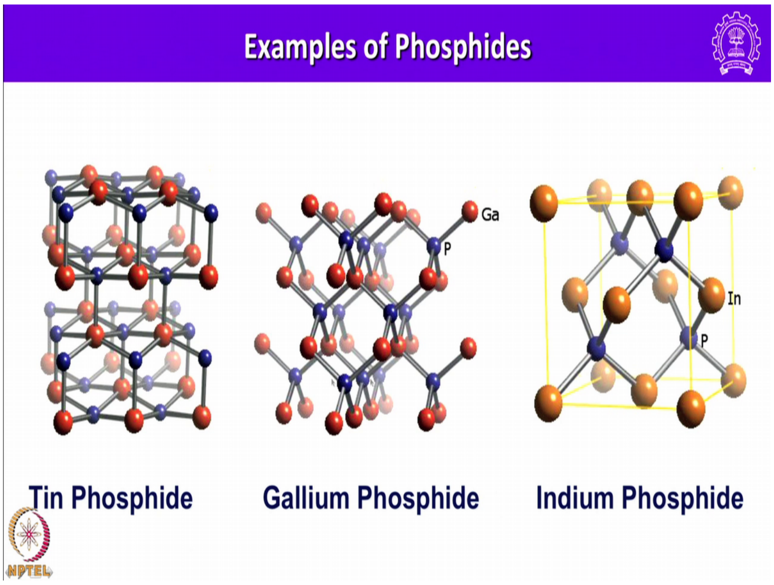

Examples of Phosphides

Tin Phosphide Gallium Phosphide Indium Phosphide

This is a tin phosphide, you can see here the ratio is 1 is to 1. And here we have gallium phosphide, and you can see the red ones are gallium and grey ones are phosphorus. And this is indium phosphide. So, other hydrides of group 15 are essentially phosphenes, formally phosphane or essentially it is a the hydrides of group 15, we have ammonia and of course, with phosphorus that is they are called phosphenes or phosphanes having the formula P H 3.

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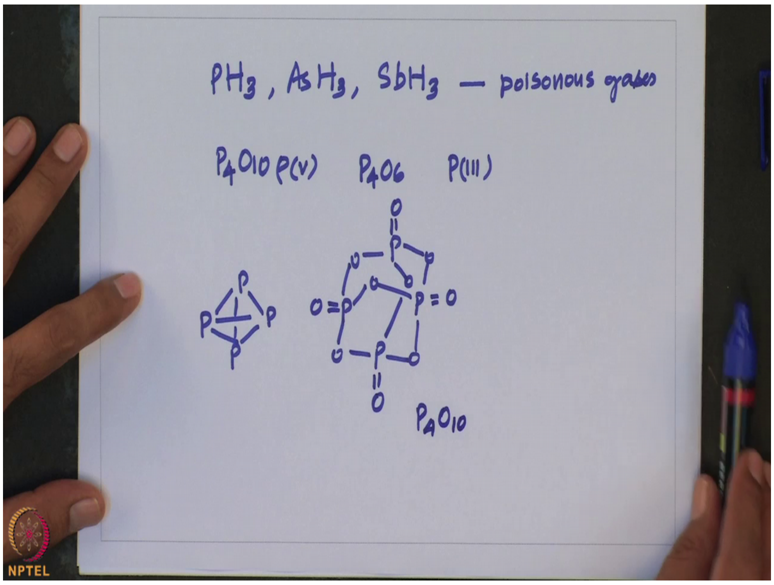

PH_3, AsH_3, SbH_3 — poisonous gases

P_4O_{10} P(V) P_4O_6 P(III)

P_4O_{10}

And similarly, we have arsine As H 3 and stibine S b H 3. All are poisonous gases. The difficulty of oxidising bismuth 3 to bismuth 5 by chlorine or bromine is an example of the inert pair effect. Essentially if you take any of the trivalent bismuth compound if we try to make an attempt to oxidize using chlorine or bromine. It is not easy because of the inert pair effect. The complete combustion of phosphorus yields phosphorus pentoxide; that is, P 4 O 10. Combustion in a limited supply of oxygen results in the formation of phosphorus trioxide or P 4 O 6, O 6 here phosphorous is in plus 3 state and here phosphorous is in plus 5 state. And essentially; that means, combustion of white phosphorus in a limited supply of oxygen needs P 4 O 6 phosphorous trioxide. Whereas the complete combustion needs phosphorus pentoxide. So, this how P 4 O 6 looks here.

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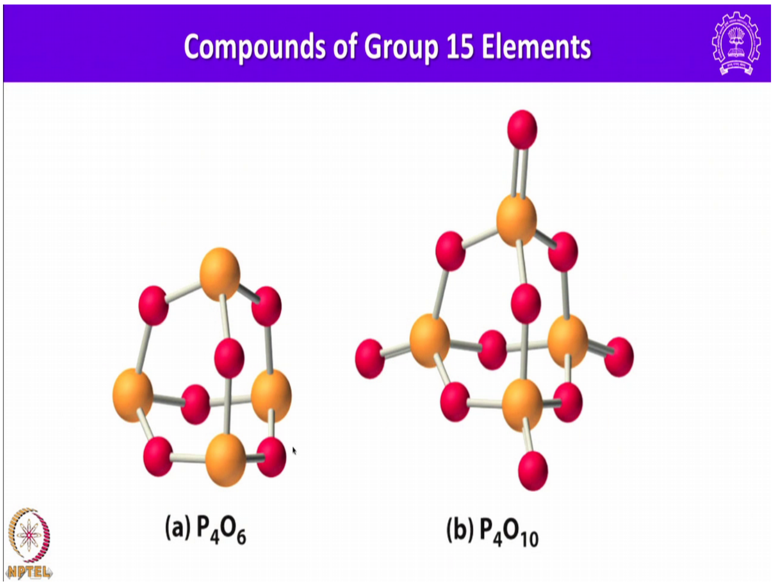

Compounds of Group 15 Elements

(a) P_4O_6 (b) P_4O_{10}

And it is very easy to write the structure of P 4 O 6 or P 4 O 10 starting from P 4. For example, we all know that this how the structure of white phosphorus. So, one can simply like this here. And then connect them with O. So, this is P 4 O 6 partially oxidized one you can see all phosphorus atoms are in trivalent state. And if excess of oxygen is there this essentially forms P 4 O 10. So, all phosphorus are going to plus 5 oxide state this is P 4 O 10.

So, indium and gallium arsenides and antimonides are essentially semiconductors. The compounds formed between metals and arsenic antimony and bismuth can be prepared by direct reaction of the elements.

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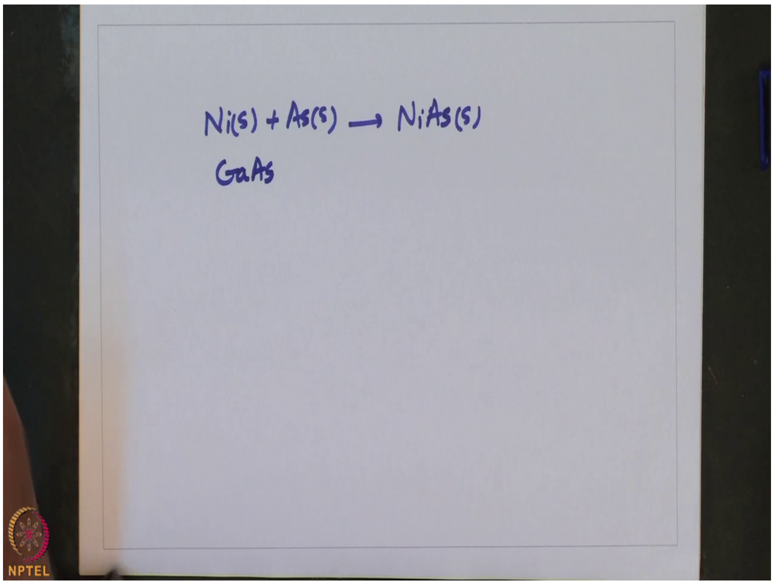

$Ni_{(s)} + As_{(s)} \longrightarrow NiAs_{(s)}$

GaAs

For example, nickel when it is treated with arsenic. It gives nickel arsenide. Gallium arsenide is the more important and is used to make devices such as integrated circuits light emitting diodes and laser diodes. Gallium arsenide, it is band gap is similar to that of silicon and larger than those of other group 13 and 15 semiconductor. As a result, gallium arsenide finds application and it is most sought after compared to others. Gallium arsenide integrated circuits are commonly used in mobile phones; satellite communications and some radar systems.

So now let me begin the discussion on hydrides of group 15 elements. All the group 15 elements from binary compounds with hydrogen are toxic having the composition like E H 3.

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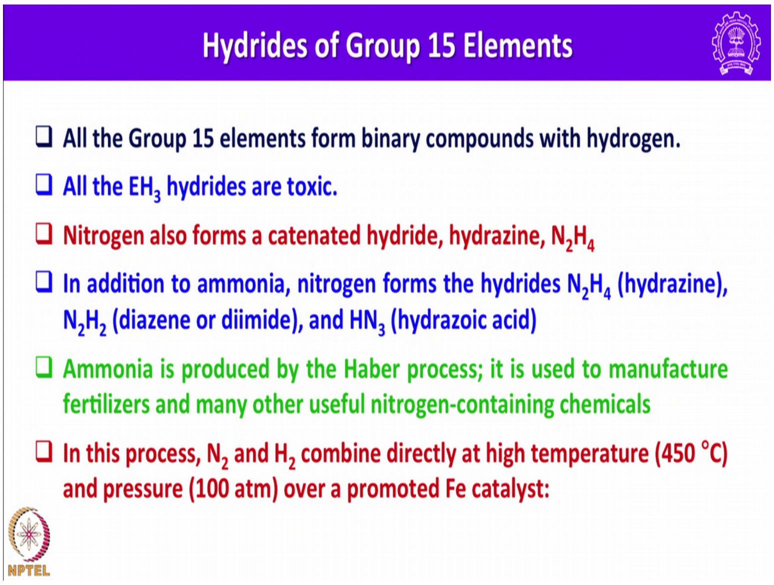

Hydrides of Group 15 Elements

- ☐ All the Group 15 elements form binary compounds with hydrogen.
- ☐ All the EH_3 hydrides are toxic.
- ☐ Nitrogen also forms a catenated hydride, hydrazine, N_2H_4
- ☐ In addition to ammonia, nitrogen forms the hydrides N_2H_4 (hydrazine), N_2H_2 (diazene or diimide), and HN_3 (hydrazoic acid)
- ☐ Ammonia is produced by the Haber process; it is used to manufacture fertilizers and many other useful nitrogen-containing chemicals
- ☐ In this process, N_2 and H_2 combine directly at high temperature (450 °C) and pressure (100 atm) over a promoted Fe catalyst:

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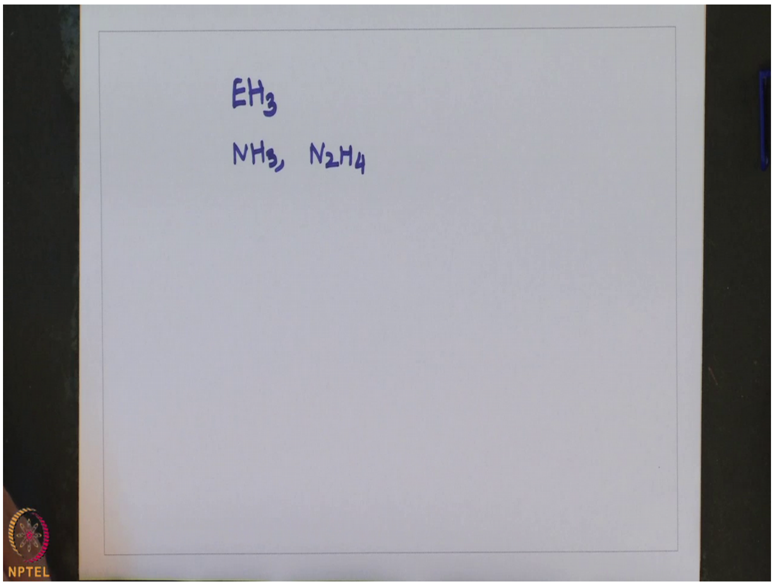

EH_3

NH_3, N_2H_4

Nitrogen also forms a catenated hydride besides N H 3 N 2 H 4. That is called hydrozide hydrazine. You can see there in addition to ammonia nitrogen forms the hydrides N 2 H 4 or diazene N 2 h 2. And of course, H N 3 it is called hydrazoic acid. There should not be any confusion between ammonia N H 3 and hydrazoic acid H N 3.

Ammonia is produced by a habers process. It is used to manufacture fertilizers. And many other useful nitrogen containing chemicals. So, in this process nitrogen and hydrogen combined directly at high temperature of 450 degree centigrade and high pressure of 100 atmosphere over a promoted iron catalyst to form ammonia.

So, let me stop here, and continue the discussion on hydrides of group 15 elements in my next lecture. Until then have a pleasant reading of inorganic chemistry.

Thank you.