Main Group Chemistry
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Lecture – 39
Chemistry of Group 15 Elements

Welcome to MSB lecture series on Main Group Chemistry, so this is 39th lecture in the series. In this lecture I will be discussing the Chemistry of Group 15 Elements. As you all know group 15 elements are essentially called as Pnictogens.

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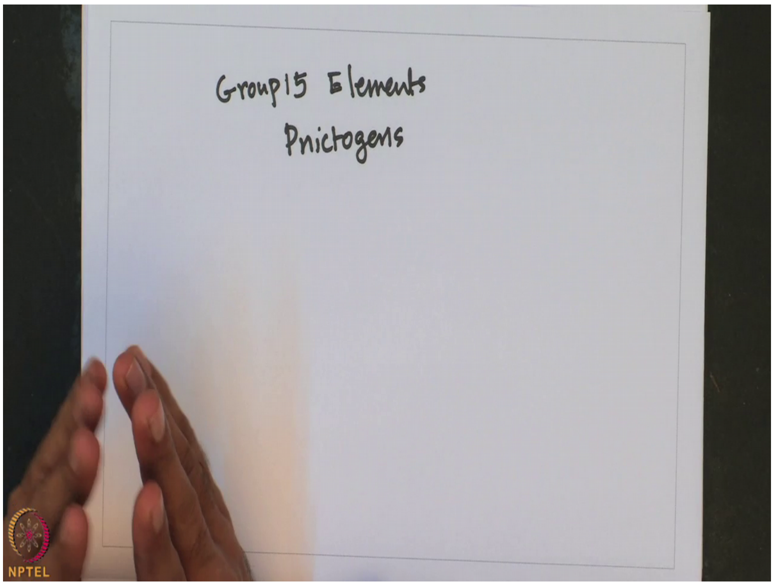
Group 15 Elements
Pnictogens

So, we have in group 15, the first element is nitrogen, next phosphorus, arsenic, antimony, and bismuth.

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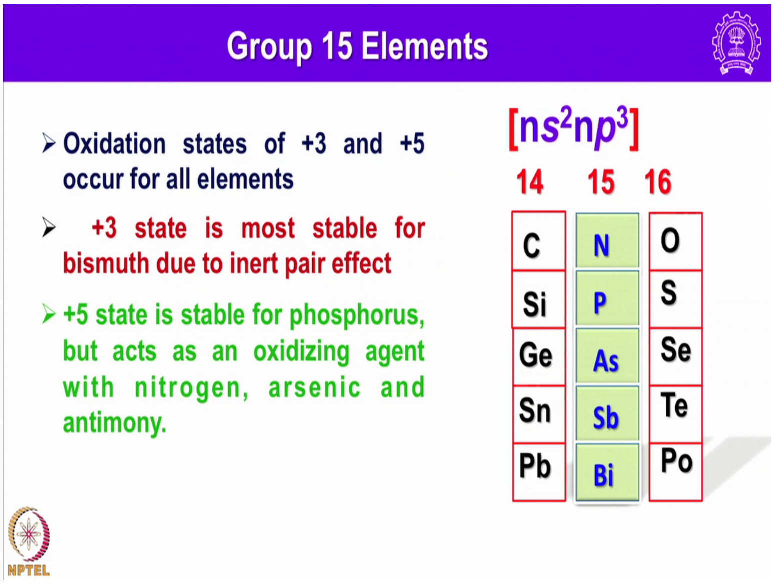

Group 15 Elements

- Oxidation states of +3 and +5 occur for all elements
- +3 state is most stable for bismuth due to inert pair effect
- +5 state is stable for phosphorus, but acts as an oxidizing agent with nitrogen, arsenic and antimony.

[ns^2np^3]

14	15	16
C	N	O
Si	P	S
Ge	As	Se
Sn	Sb	Te
Pb	Bi	Po

They have the electronic configuration of ns 2 np 3; that is they have 5 electrons in their valence shell. So, as a result group 15 element show oxidation states of plus 3 and plus 5; and of course plus 3 and plus 5 occur for all elements. Whereas, heavier elements especially bismuth shows plus 3 as the most stable oxide state due to inert pair effect. And plus 5 state is quite stable for phosphorus, but acts as an oxidising agent with nitrogen, arsenic, and antimony.

And let us look into the discoverers of group 15 elements.

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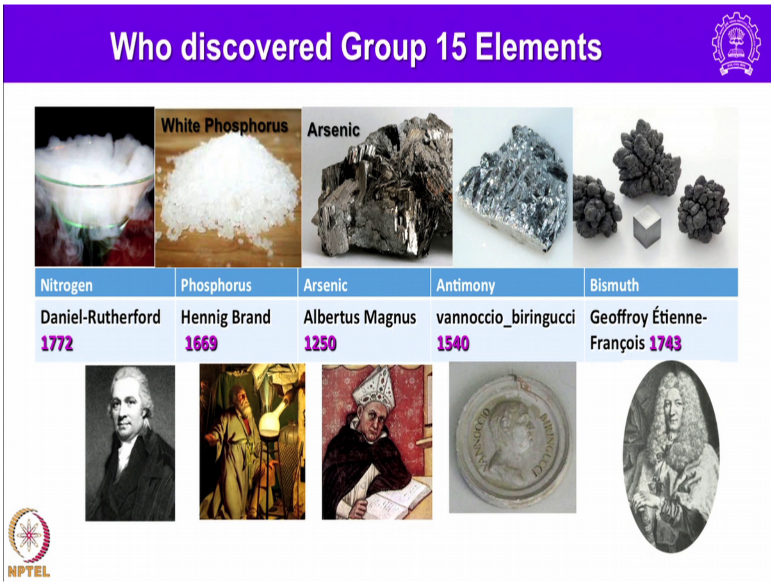

Who discovered Group 15 Elements

Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Daniel-Rutherford 1772	Hennig Brand 1669	Albertus Magnus 1250	vannoccio_biringucci 1540	Geoffroy Étienne-François 1743

Of course nitrogen was identified by Daniel Rutherford in 1772 and phosphorus was discovered in a very disgusting manner by Hennig Brand in 1669. Albert Magnus is responsible for the discovery of arsenic in 1250. And Vannoccio Biringucci is responsible for discovering antimony in 1540. And Geoffrey Etienne Francois discovered Bismuth in 1743; I have shown their pictures here along with how these elements look like in the elemental form. And of course here, nitrogen is a gas and when it is liquefied this how it looks like it is a operating. And this is white phosphorus, and this is arsenic, and this is antimony, and this is bismuth.

And there is very interesting story about the discovery of phosphorus. In fact, Hennig Brand in alchemist had an inclination to make elixir to convert any base metal into gold and also to live longer. So in that effort what he did was, he collected about 1100 litres of urine and he started distilling it. After distilling for several days he ended up with some waxy substance that was growing in during dark; waxy substance that.

So, since it was showing luminescence the phosphorus the name as originated because of its property; and of course, I can keep on talking about fascinating stories of phosphorus and its discovery. It is the 13 element to be discovered; and since 13 is a bad number and also due to the association of phosphorus in all toxic substances it was called as devil's element. Of course, I will discuss little bit more later at some point of time before I conclude the chemistry of group 15 elements. Let me move on to looking into the other aspects.

Naturally occurring nitrogen makes up for about 78 percent by volume of the earth's atmosphere.

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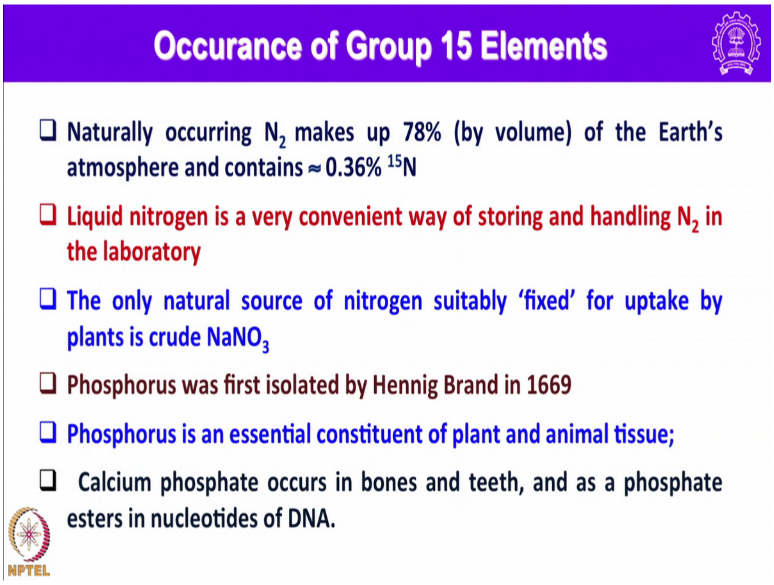

Occurance of Group 15 Elements

- ☐ Naturally occurring N_2 makes up 78% (by volume) of the Earth's atmosphere and contains ≈ 0.36% ^{15}N
- ☐ Liquid nitrogen is a very convenient way of storing and handling N_2 in the laboratory
- ☐ The only natural source of nitrogen suitably 'fixed' for uptake by plants is crude $NaNO_3$
- ☐ Phosphorus was first isolated by Hennig Brand in 1669
- ☐ Phosphorus is an essential constituent of plant and animal tissue;
- ☐ Calcium phosphate occurs in bones and teeth, and as a phosphate esters in nucleotides of DNA.

And contain very very small percentage of 15 [noise]; that is 0.36 percentage. And liquid nitrogen is a very convenient way of storing and handling nitrogen in the laboratory. Of course, we can also store it in cylinders. The only natural source of nitrogen's suitably fixed for uptake by plants is crude sodium nitrate. Phosphorus as I mentioned was isolated by Hennig Brand in 1669 from urine. And phosphorus is an essential constituent of plant and animal tissue. And calcium phosphate occurs in bones and teeth, and as a phosphate ester in nucleotides of DNA. And phosphorus occurs naturally in the form of appetites, calcium fluroapatite then important mineral.

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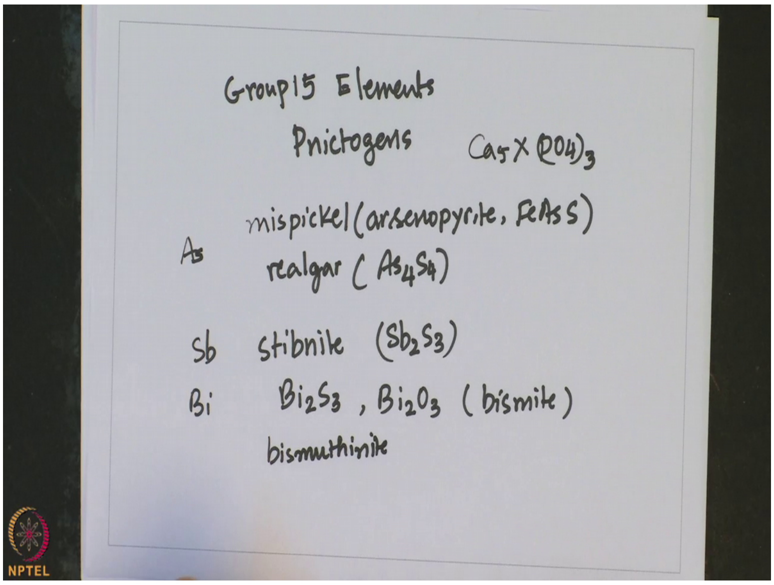

Group 15 Elements

Pnictogens $Ca_5X(PO_4)_3$

As mispickel (arsenopyrite, FeAsS)
realgar (As_4S_4)

Sb stibnite (Sb_2S_3)

Bi Bi_2S_3, Bi_2O_3 (bismite)
bismuthinite

For example the formula of that one is Ca 5 X PO4 3: this is fluroapatite. So, arsenic occurs in elemental form. Commercial sources of arsenic are essentially mispickel and realgar. This also called arsenopyrite because it has iron, so this is the composition of this mineral arsenopyrite also called as mispickel. And another is realgar. So, this two are the important minerals of arsenic.

Native antimony is rare and the only commercial ore is stibnite, and stibnite has the composition. This is for arsenic and for antimony the ore is stibnite, the composition of this one is essentially sulphur ore Sb 2 S 3. Bismuth occurs as the element and the ore bismuthinite Bi 2 S 3 and also bismite Bi 2 O 3 is called bismite, and this one is bismuthinite. So, these two are the ores of bismuth.

And you can just see the relative abundances of group 15 elements in the earth crust.

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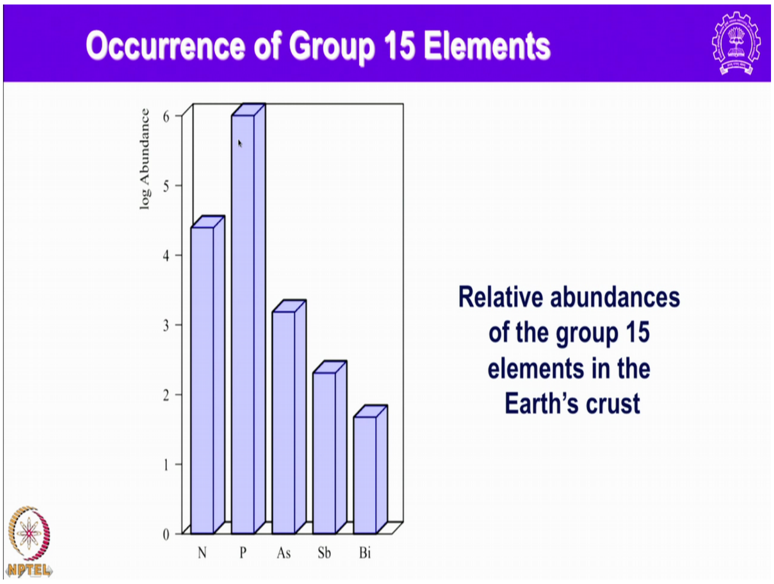

Occurrence of Group 15 Elements

Relative abundances of the group 15 elements in the Earth's crust

Of course, phosphorus is considerably larger compared to rest of the elements. So, let us look into the extraction of group 15 elements. One can obtain pure nitrogen in industrial scale by fraction distillation of liquid air. Often, the product contains small quantity of argon and oxygen. Small amounts of nitrogen can be prepared by thermal decomposition of sodium aside or ammonium nitrate.

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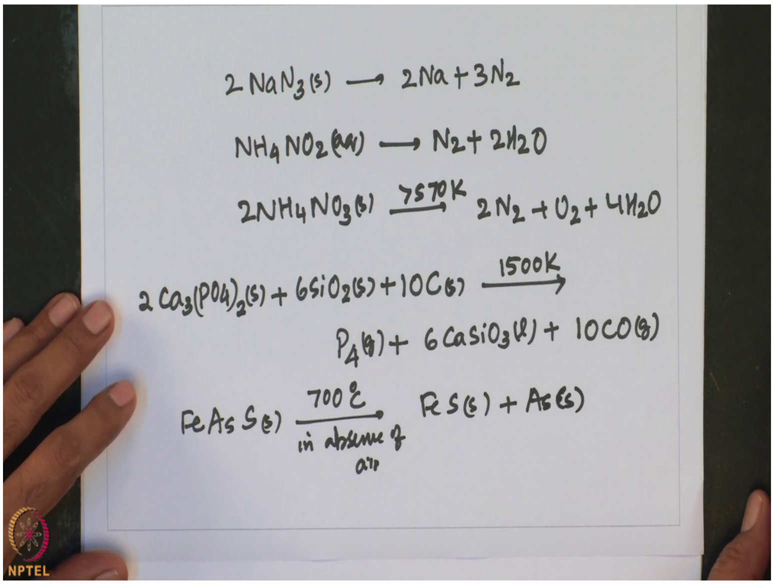

$$2NaN_3(s) \longrightarrow 2Na + 3N_2$$

$$NH_4NO_2(aq) \longrightarrow N_2 + 2H_2O$$

$$2NH_4NO_3(s) \xrightarrow{>570K} 2N_2 + O_2 + 4H_2O$$

$$2Ca_3(PO_4)_2(s) + 6SiO_2(s) + 10C(s) \xrightarrow{1500K} P_4(g) + 6CaSiO_3(l) + 10CO(g)$$

$$FeAsS(s) \xrightarrow[\text{in absence of air}]{700^\circ C} FeS(s) + As(s)$$

For example: simply if you heat sodium aside it gives nitrogen. You remember I had mentioned about this one this is used in car air bags. And similarly ammonium nitrate can also be; on heating gives nitrogen. Ammonium nitrate also solid on heating to 570 Kelvin it gives nitrogen.

So, elemental phosphorus is extracted from calcium phosphate; that is called phosphate rock. So, essentially Ca 3 PO 4 twice when it is heated with sand and coke in an electric furnace gives white phosphorus. For example I will write that reaction here. So, this is actually this is the general method of preparation of white prosperous in large scale. Phosphorus vaporizers and is condensed to the a solid which is stored under water to protect it from reaction with air, because it readily reacts with air to form phosphorus pentoxide. Most phosphorus produced in this way is burnt to form P 4 O 10; that is phosphorus pentoxide which is then hydrated to yield pure phosphoric acid; that means, P 4 O 10 is highly hygroscopic and it readily reacts with water to form phosphoric acid.

The principal source of arsenic is as I said, arsenic from mispickle it is a sulphide ore on heating this ore to 700 degree centigrade, in absence of air it forms iron sulphide plus arsenic, arsenic comes out. That means, heating this mispickle to 700 degree centigrade in absence of air leads to formation of Fe S plus arsenic, elemental arsenic is formed.

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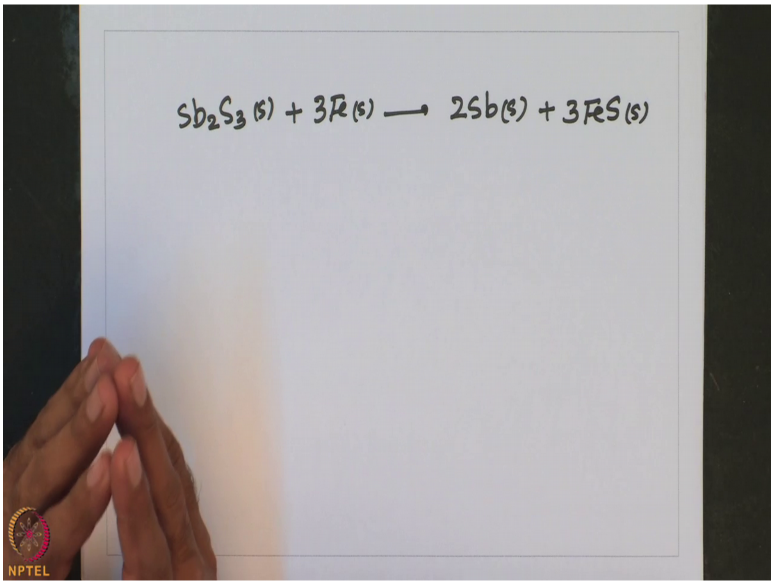

$Sb_2S_3(s) + 3Fe(s) \longrightarrow 2Sb(s) + 3FeS(s)$

So, antimony can be extracted from stibnite by treating with iron. For example: Sb 2 S 3. So, the extraction of bismuth from its sulphide or oxide ore involves the reduction with carbon; one can also use carbon as a reducing agent. But the metal is also obtained as a byproduct of lead, copper, tin, silver, and gold refining processes, because it also present in the trace amounts along with lead, copper, tin, silver, and gold.

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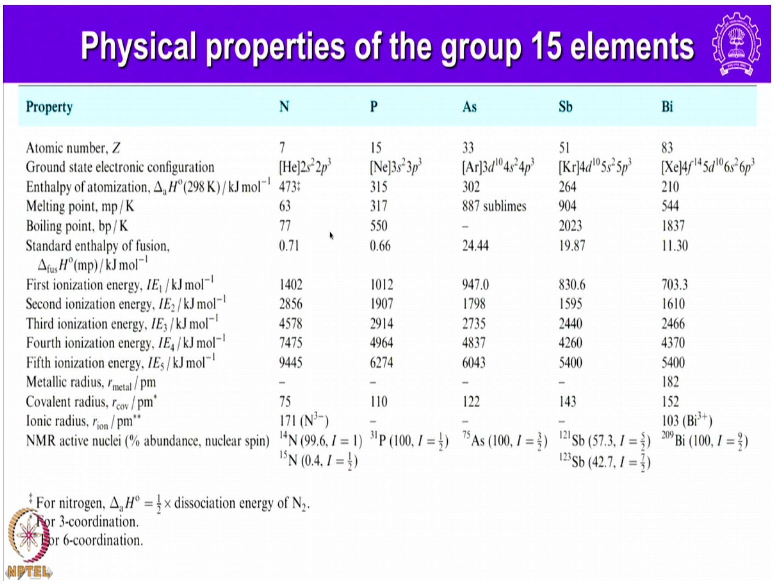

Physical properties of the group 15 elements

Property	N	P	As	Sb	Bi
Atomic number, Z	7	15	33	51	83
Ground state electronic configuration	$[He]2s^22p^3$	$[Ne]3s^23p^3$	$[Ar]3d^{10}4s^24p^3$	$[Kr]4d^{10}5s^25p^3$	$[Xe]4f^{14}5d^{10}6s^26p^3$
Enthalpy of atomization, $\Delta_aH^o(298\,K)\,/\,kJ\,mol^{-1}$	473‡	315	302	264	210
Melting point, mp / K	63	317	887 sublimes	904	544
Boiling point, bp / K	77	550	–	2023	1837
Standard enthalpy of fusion, $\Delta_{fus}H^o(mp)\,/\,kJ\,mol^{-1}$	0.71	0.66	24.44	19.87	11.30
First ionization energy, $IE_1\,/\,kJ\,mol^{-1}$	1402	1012	947.0	830.6	703.3
Second ionization energy, $IE_2\,/\,kJ\,mol^{-1}$	2856	1907	1798	1595	1610
Third ionization energy, $IE_3\,/\,kJ\,mol^{-1}$	4578	2914	2735	2440	2466
Fourth ionization energy, $IE_4\,/\,kJ\,mol^{-1}$	7475	4964	4837	4260	4370
Fifth ionization energy, $IE_5\,/\,kJ\,mol^{-1}$	9445	6274	6043	5400	5400
Metallic radius, $r_{metal}\,/\,pm$	–	–	–	–	182
Covalent radius, $r_{cov}\,/\,pm^*$	75	110	122	143	152
Ionic radius, $r_{ion}\,/\,pm^{**}$	171 (N^{3-})	–	–	–	103 (Bi^{3+})
NMR active nuclei (% abundance, nuclear spin)	^{14}N (99.6, $I = 1$) ^{15}N (0.4, $I = \frac{1}{2}$)	^{31}P (100, $I = \frac{1}{2}$)	^{75}As (100, $I = \frac{3}{2}$)	^{121}Sb (57.3, $I = \frac{5}{2}$) ^{123}Sb (42.7, $I = \frac{7}{2}$)	^{209}Bi (100, $I = \frac{9}{2}$)

‡ For nitrogen, $\Delta_aH^o = \frac{1}{2} \times$ dissociation energy of N_2.

* For 3-coordination.

For 6-coordination.

You can see some of the physical properties of the group 15 elements in this table. Of course, whatever the properties we come across it is quite agreement with the periodic trends we have observed for group 14 elements and that is true with respect to group 16 elements also; not much changes are there except for the fact that nitrogen is slightly different from phosphorus, arsenic, antimony, and bismuth. And, antimony and bismuth show little more different chemical properties compared to first three elements because of the dominance of inert pair effect.

And of course, when we look into the first second and third ionization energy that is decreasing down the group that is expected; ionization energy increase rather sharply of removal of the P electrons. And of course, after removal of the P electron and effective nuclear charge increases and the S electrons are held more firmly by the nucleus making it difficult to remove fourth and fifth. And hence increasing the ionization enthalpy for fourth and fifth electron; that means, fourth ionization enthalpy fifth ionization enthalpy increases rapidly.

It decreases only slightly between phosphorus and arsenic. Similar behaviour is observed in case of aluminium and gallium, and also between silicon and germanium. For removal of the S electron there is an increase between antimony and bismuth, just as between indium and thallium and between tin and lead. Arsenic with completely filled 3 d inner shell which is relatively poor shielding is rather more difficult to oxidise to the plus 5 state due to added inner pair effect.

So here, in case if we generate compounds in plus 5 state they are very powerful oxidizing agents. Minus 3 oxide state occurs in the hydrides, such as NH 3 and in anion such as phosphate especially sodium phosphate. In sodium phosphate phosphorus is in minus 3 state and in case of NH 3 nitrogen is in minus 3 oxygen state.

Dinitrogen is generally un reactive, it combines slowly with lithium at ambient temperature to form lithium nitrate. The reaction between calcium carbide and nitrogen is used industrially for manufacturing nitrogenous fertilizer calcium cyanamide. And at ambient temperature nitrogen is reduced to hydrazine; that is N 2 H 4 by venidium 2 and magnesium hydroxides. A large number of d block metal complexes containing coordinated N 2 are known. And of course, coordinated N 2 can also be activated and NN bond can be cleaved. N 2 is essentially isoelectronic with carbon monoxide. And the bonding in complexes containing the N 2 ligand can be described in the similar manner to that in metal carbonyl complexes. But however, nitrogen complexes are unstable compared to carbonyl complexes.

Because, N 2 dinitrogen is a very stable molecule both thermodynamically and kinetically other species comprised of nitrogen atoms are rare that is N 5 plus was isolated in 1999.

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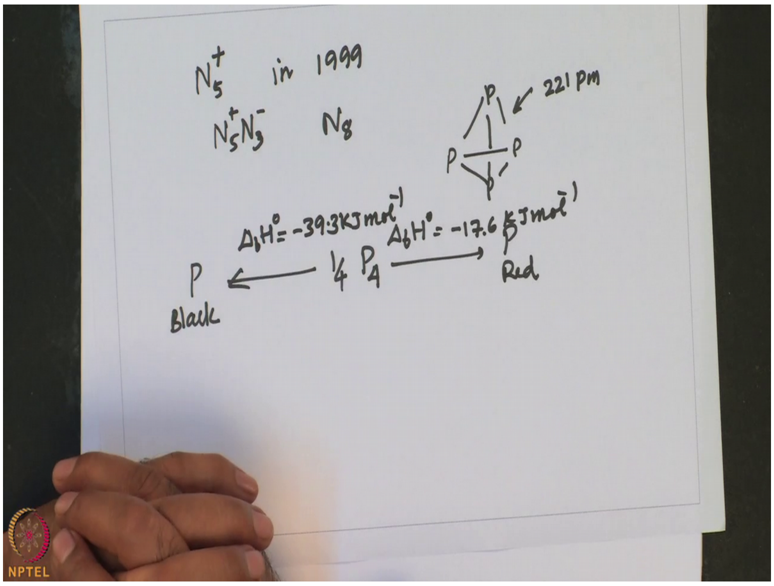

Was actually isolated in 1999; those who discovered this one in 1999 are of the opinion that high energy ionic allotropes of nitrogen having this composition N i 5 N 3 minus and N after plus can also be isolated. So, another nitrogen compound is essentially N 8 having a cubane like structure. Of course, these are all highly reactive and compounds they have now been isolated hypothetical molecules. You can see here N 2 is quite stable.

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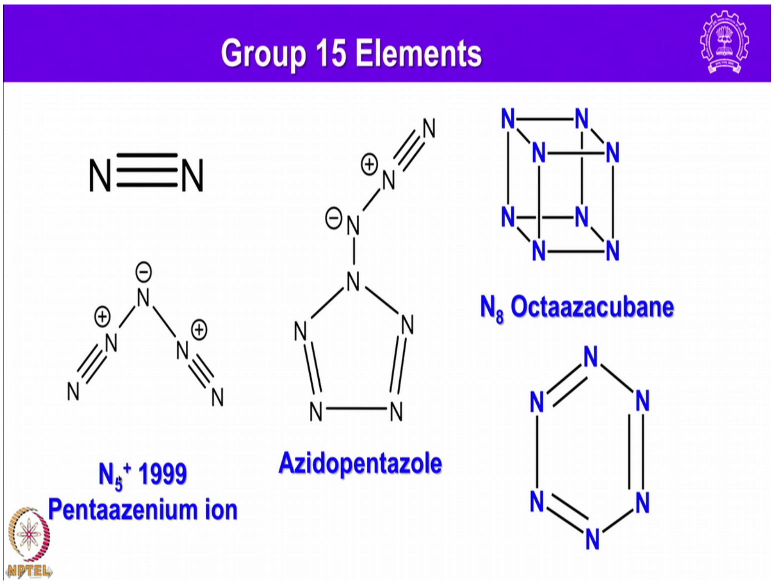

Group 15 Elements

N_5^+ 1999

Pentaazenium ion

Azidopentazole

N_8 Octaazacubane

And this one is pentaazenium ion N 5 plus was discovered in 1999. And also they are of the opinion that this compound can also be isolated. Having N 5 plus and N 3 minus, and of course, another one is N 8 octaazacubane and this one is similar to benzene; hexaza benzene. And these compounds if they may in case if they are made they are going to be highly reactive. And so far these compounds are not been isolated.

Let us ask our self say question, why N is dimeric and P is tetrameric. In fact, we come across such anomaly among P block elements: oxygen is dimeric, nitrogen is dimeric, phosphorous is tetrameric, and all halogens are dimeric. So here we should look into single double and triple bond strengths for these compounds. For example in case of nitrogen and phosphorus, let us look into the single bond double bond and triple bond strengths for NN and PP bonds. And if you just look into these things and do simple analysis we can understand why P 2 is unstable whereas P 4 is stable, and similarly why N 2 is stable and N 4 is unstable.

So, NN triple bond energy. So, before that I will give you some bond parameters. You can see here.

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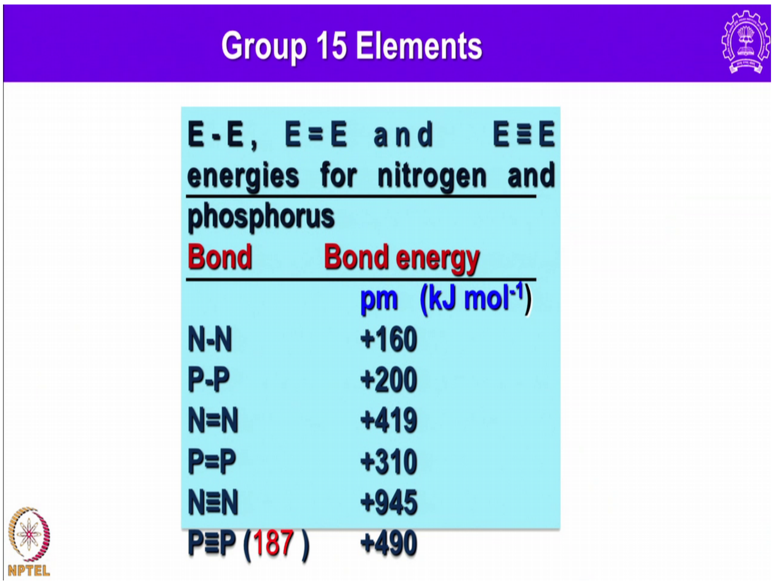

Group 15 Elements

E-E, E=E and E≡E energies for nitrogen and phosphorus

Bond	Bond energy
	pm (kJ mol^{-1})
N-N	+160
P-P	+200
N=N	+419
P=P	+310
N≡N	+945
P≡P (187)	+490

I have listed here bond energies for NN single bond, NN double bond, NN triple bond; as well as phosphorus single bond, double bond, and triple bond. And in this one you can see NN single bond energy is 160 kilojoules per mole, and whereas PP bond is quite stable compared to NN that is about 200 kilojoules per mole. Then, when you go to NN double bond its 490, it is more than twice the value for 2 NN single bonds; it should have been 320, but it is 490.

Whereas, in case of phosphorus for PP double bond it is about 310 kilojoules per mole; it should have been at least 400 kilojoules per mole. If we just some of that the values for to PP single bond that is 200 plus 200, but instead it is 310; that means, a phosphorus by making a double bond it loses an amount of energy equivalent to 90 kilojoules per mole.

And then let us look into NN triple bond. Energy is 945 kilojoules per mole. And at least it should have been about 480 kilojoules per mole if we just some of 3 NN single bonds, like one NN bond energy is 160 kilojoules per mole. So that means, instead of having 480 we have almost double the value of 945 kilojoules per mole, whereas in case of phosphorus it should have been at least 600 kilo joules per mole to have a PP triple bonds, whereas here what we have is about 490 kilo joules per mole. That means, phosphorous by making 3 single bonds it would have a total energy of 600 kilo joules per mole. On the other hand if it forms a PP triple bond to exist as a dimeric species it will have only about 490 kilo joules per moles.

So, from this point of view what happens? Phosphorous has less inclination to form a PP double bond, PP triple bond that is highly unstable. As a result it exists in the form of a white phosphorus having each phosphorous single PP bonds. And whereas, in case of N it is quite opposite by forming NN triple bond it gains much more than what it would have been if nitrogen's are connected by 3 single bonds, ok. So, that would have amounted to only about 480 kilo joules per mole.

So, this analysis explains why NN triple bond is stable and nitrogen occurs as a dimeric species. In the same way we can also do analysis in case of oxygen-oxygen and sulphur-sulphur. Let us look into this kind of aspects and also problems when we move on to the chemistry of group 16 elements.

So, phosphorus exhibits complicated allotropy. There are eleven forms of phosphorous allotropes have been known out of which at least 5 are crystalline. And crystalline white phosphorus contains tetrahedral P 4 moieties in which PP distance is 221 picometre. That means, essentially white phosphorus has; I will be showing you this in the next slide. So, this how it exist and this PP distances is 221 picometre, which is consistent with single bond covalent radius of about 110 picometre; white phosphorus is defined as the standard state of the element, but is actually metastable.

For example P block is obtained from white phosphorus and then it can also go to their red. So, here if you just look into the value, here it is about minus 17.6 kilo joules per mole, whereas here it is minus 39.3 kilojoules per mole. So, this clearly indicates that white phosphorus is essentially as the standard state of the element, but is actually a metastable state. On melting all allotropes give a liquid containing P 4 molecule and this are also present in the vapour above 1070 Kelvin or at higher pressure P 4 is in equilibrium with P 2. But so far P 2 is not isolated.

As I had mentioned phosphorus is the 13th element to be discovered, due to this reason and also its use in explosives, poisons, and nerve reagents it was called as devils element by German alchemist Hennig Brand who discovered it in 1669. And Robert Boyle was the first to use phosphorus to ignite sulphur tipped wooden splints and that actually we use it as matches. And this was shown by Robert Boyle in 1680. The principal source of phosphorus is phosphate rock; a complex calcium phosphate I had mentioned. And of course, if we heat it for a prolong duration white phosphorus in a sealed vessel that leads to the formation of red phosphorus. And red phosphorus is essentially a relatively inert form of phosphorus with a very poorly defined, but complex structure. However, the most stable allotrope is black phosphorus found by heating phosphorus at high pressure which has several structures out of which rhombohedral structure is quite known.

So, one can see this is how the white phosphorus structure looks like, it is tetrahedral.

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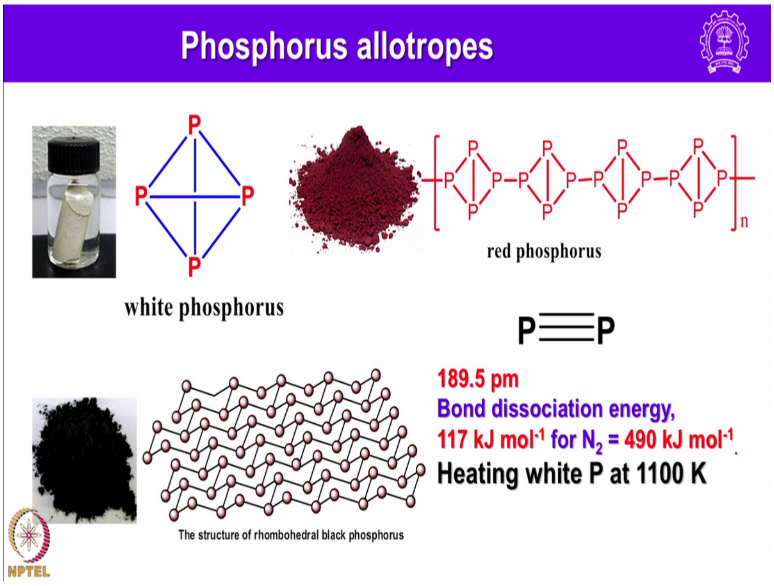

Phosphorus allotropes

white phosphorus

red phosphorus

$P \equiv P$

189.5 pm

Bond dissociation energy,

117 kJ mol^{-1} for N_2 = 490 kJ mol^{-1}

Heating white P at 1100 K

The structure of rhombohedral black phosphorus

And then basically what happens? If you break one of the PP bond of white phosphorus and connect with an adjacent one that leads to the red phosphorous. You can see here. And it has a one dimensional structure due to the breakage of one of the PP bond and formation of a link with the neighbouring white phosphorus. So, this is red phosphorus. And then this is the black phosphorus, here we have this kind of cyclohexyl type structure for phosphorus. And of course P 2, the PP distance is 189.5 picometre.

And just let us look into the bond dissociation energy of P triple bond. P this is only 117 kilojoules per mole. If you try to compare this one with nitrogen, nitrogen has a bond dissociation energy of 490 kilo joules per mole that indicates why N 2 is stable, whereas P 2 not. And of course, heating white phosphorus at 1100 Kelvin leads to the formation of transient species P 2.

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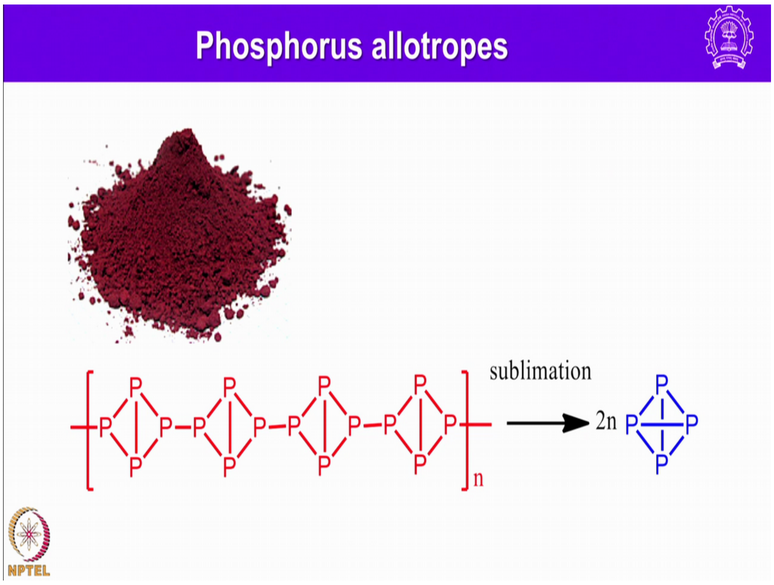

Phosphorus allotropes

And of course, red phosphorus on sublimation it gives white phosphorus back. Above 323 Kelvin white phosphorus inflames yielding phosphorus 5 oxide.

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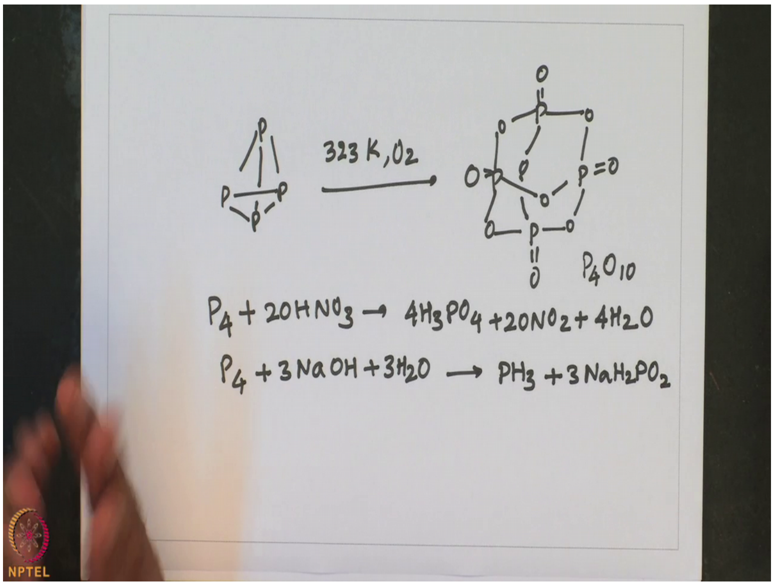

$$P_4 + 20HNO_3 \rightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

$$P_4 + 3NaOH + 3H_2O \rightarrow PH_3 + 3NaH_2PO_2$$

So, this is P 4 O 10. So, concentrated nitric acid oxidizes P 4 to phosphoric acid. And with hot aqueous sodium hydroxide one can form P H 3 phosphine from white phosphorus. For example: white phosphorous on treatment with concentrated nitric acid, similarly P 4 on treatment with sodium hydroxide gives phosphene.

Similar to nitrogen P 4 can also act as a ligand in d-block metal complexes. You can see here some of the complexes of white phosphorus I have shown here.

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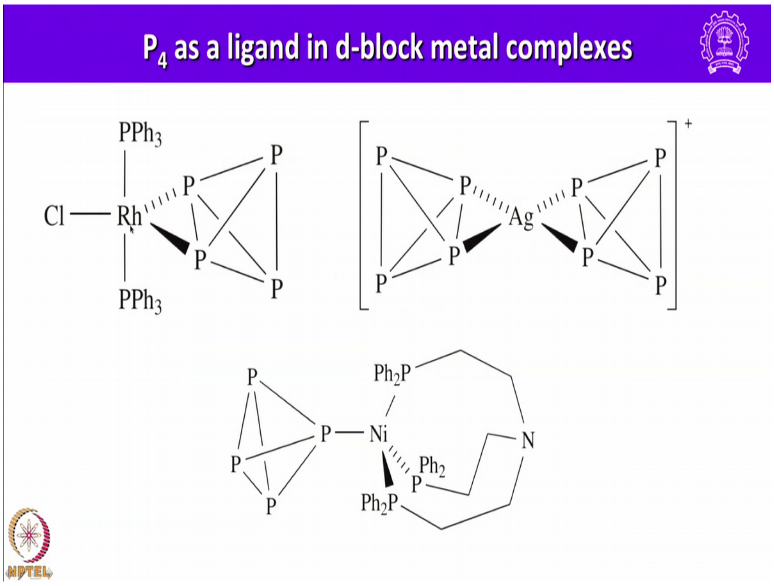

P_4 as a ligand in d-block metal complexes

With rhodium here 2 phosphorous are coordinated, whereas in this case with silver 2 phosphorus of white phosphorous are coordinated here. And of course, here all the bonds are intact still white phosphorus retains all the 3 bonds to each other and retains its tetrahedral geometry. But the lone pairs on 2 phosphorus atoms are involved in coordination, whereas in this case here one of the lone pairs of phosphorus is coordinated to nickel. The P atoms maybe arranged in the rings, chains or cages having composition something like this.

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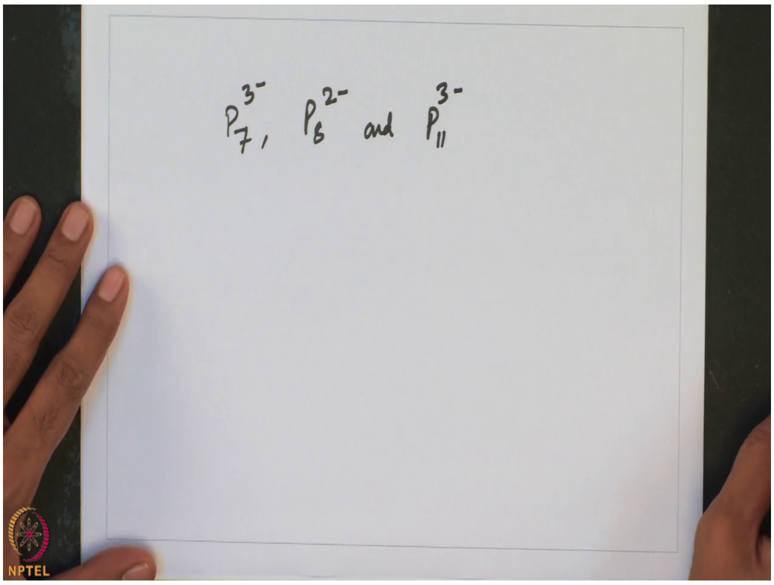

P_7^{3-}, P_8^{2-} and P_{11}^{3-}

For example: P 7 3 minus or P 8 2 minus and also P 11 3 minus.

So, I will be discussing more chemistry of group 15 elements in my next class. So, until then have a pleasant reading of the chemistry of group 15 elements.

Thank you very much.