Main Group Chemistry
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Lecture – 14
Chemistry of Hydrogen

I will come you again to the lecture series on main group chemistry, in my last lecture I was discussing about the chemistry of hydrogen and when I just concluded I give the method of preparation of hydrogen using the several methods and now let me discuss the method of preparation of deuterium or a deuterium compounds such as water D 2 O that is also called heavy water.

So, industrial production of deuterium is from ordinary water; that means, as I mentioned the ocean consists of 99.9 percent of water that is H 2 O and 0.02 percentage of D 2 O and this is the major source of D 2 O and separating out the heavy water from ocean water is carried out by two methods; that is called, girdler sulfide process and distillation and few other methods are also have been employed.

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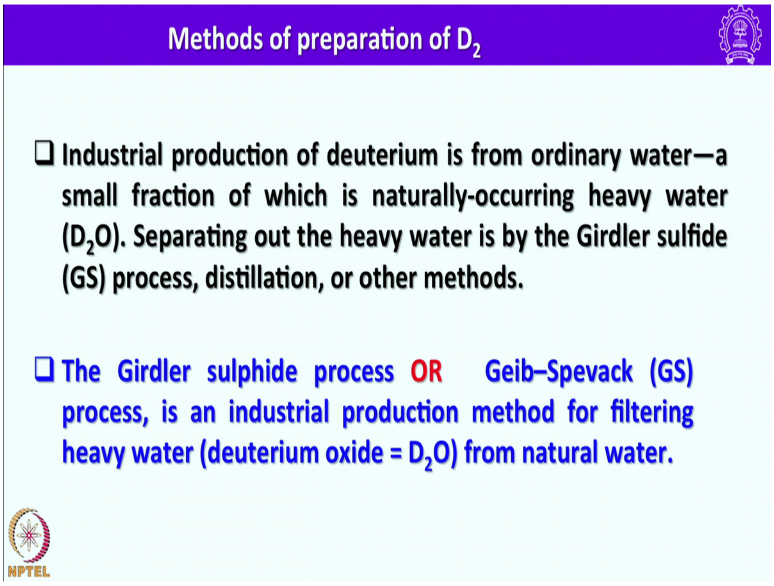

Methods of preparation of D_2

- ❑ Industrial production of deuterium is from ordinary water—a small fraction of which is naturally-occurring heavy water (D_2O). Separating out the heavy water is by the Girdler sulfide (GS) process, distillation, or other methods.
- ❑ The Girdler sulphide process OR Geib–Spevack (GS) process, is an industrial production method for filtering heavy water (deuterium oxide = D_2O) from natural water.

So, the girdler sulfide process or Geib Spevack process is an industrial production method for filtering heavy water from natural water and of course, several compounds of course, the major source of deuterium compounds is essentially D 2 O, using D 2 O several other compounds have been made.

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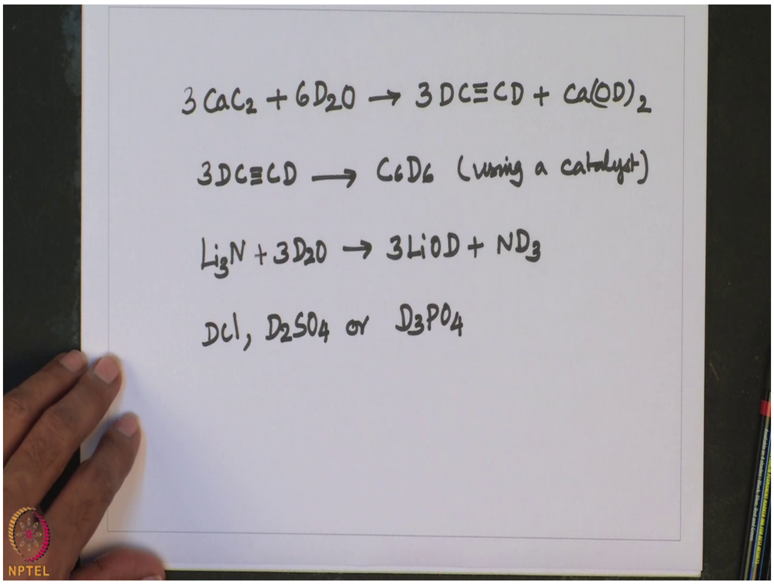

$3CaC_2 + 6D_2O \rightarrow 3DC\equiv CD + Ca(OD)_2$

$3DC\equiv CD \longrightarrow C_6D_6$ (using a catalyst)

$Li_3N + 3D_2O \rightarrow 3LiOD + ND_3$

DCl, D_2SO_4 or D_3PO_4

For example; let us consider, the reaction between calcium carbide and when it is treated with D 2 O it forms deuterated acetylene plus calcium deuteroxide, similarly once after preparing acetylene one can do 2 plus 2 plus 2 cycloaddition using an appropriate method to generate deuterated benzene for example; 3 equivalents of deuterated acetylene can generate C 6, D 6 that is; deuterated benzene, of course here we are using the catalyst. And lithium nitrate is also very reactive and it undergoes readily hydrolysis to form lithium hydroxide and ammonium, so that method is also used here.

Lithium nitrate on treatment with D 2 O readily forms lithium deuteroxide plus N D three; that means, if you want to make deuterated ammonia for some experiments one can conveniently prepared by treating lithium nitrate with D 2 O and one can also make several other compounds such as; D C L, D 2 S O 4 or D 3 P O 4 using appropriate reaction conditions and appropriate starting compounds along with D 2 O as the major source of deuterium.

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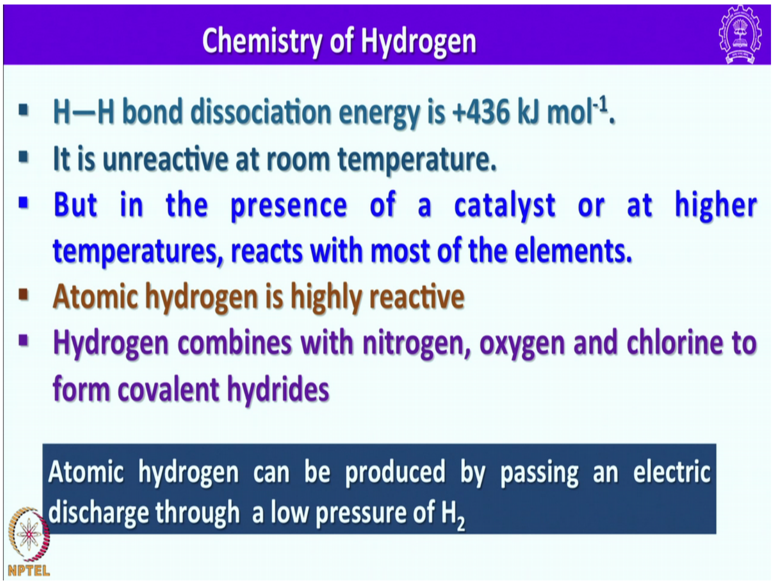

Chemistry of Hydrogen

- H—H bond dissociation energy is +436 kJ mol^{-1}.
- It is unreactive at room temperature.
- But in the presence of a catalyst or at higher temperatures, reacts with most of the elements.
- Atomic hydrogen is highly reactive
- Hydrogen combines with nitrogen, oxygen and chlorine to form covalent hydrides

Atomic hydrogen can be produced by passing an electric discharge through a low pressure of H_2

So, let us look into the chemistry of hydrogen with this information let us look into the chemistry of hydrogen. And hydrogen exist in the form of a dimeric species we all known and here H-H bond dissociation energy is plus 436 kilo joules per mole, it is unreactive at room temperature, but in the presence of a catalyst or higher temperature it reacts with most of the elements in the period table in fact at higher temperature it reacts violently with oxygen to form H 2 O and atomic hydrogen is highly reactive and hydrogen is capable of combining with nitrogen oxygen and chlorine to form covalent hydrides. And atomic hydrogen can be produced by passing an electric discharge through a low pressure of hydrogen; that means, one can cause an electric discharge through a low pressure of hydrogen molecule to generate atomic hydrogen.

Atomic hydrogen is very reactive and when it combines with other elements it usually forms three type of chemical compounds; that means, we know the fact that it can lose an electron to form H plus or it can gain an electron to form H minus or it can share the electron with other element to form a covalent bond so that means, for example; when you remove that electron ionize that electronic it forms H plus which has no chemically existence; that means, it cannot exist in it is freeform similar to several other cat ions, but it is always solvated due to it is extremely high charge density.

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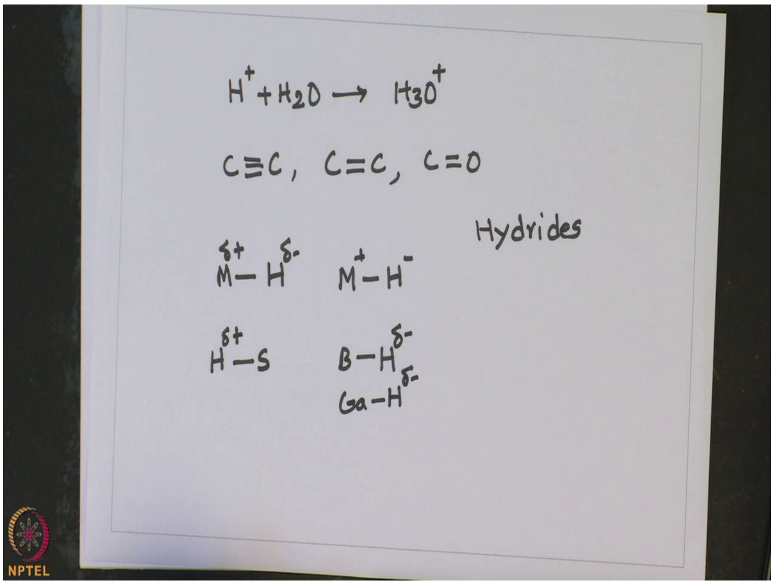

$H^+ + H_2O \rightarrow H_3O^+$

$C\equiv C$, $C=C$, $C=O$

Hydrides

$\overset{\delta+}{M}-\overset{\delta-}{H}$ $\overset{+}{M}-\overset{-}{H}$

$\overset{\delta+}{H}-S$ $B-\overset{\delta-}{H}$

$Ga-\overset{\delta-}{H}$

For example; the moment H plus is generated it readily combines with water, if it is a aqueous medium to form H 3 O plus. So, it can also share an electron with any other elements to form a covalent bond and it can gain an electron to form the hydride H ion H minus species and attain 1 S 2 electronic configuration, which is essentially isoelectronic with immediate noble gas helium, so this are the three important type of compounds; it can form H plus, it can form H minus or it can share an electron to forming a covalent bond.

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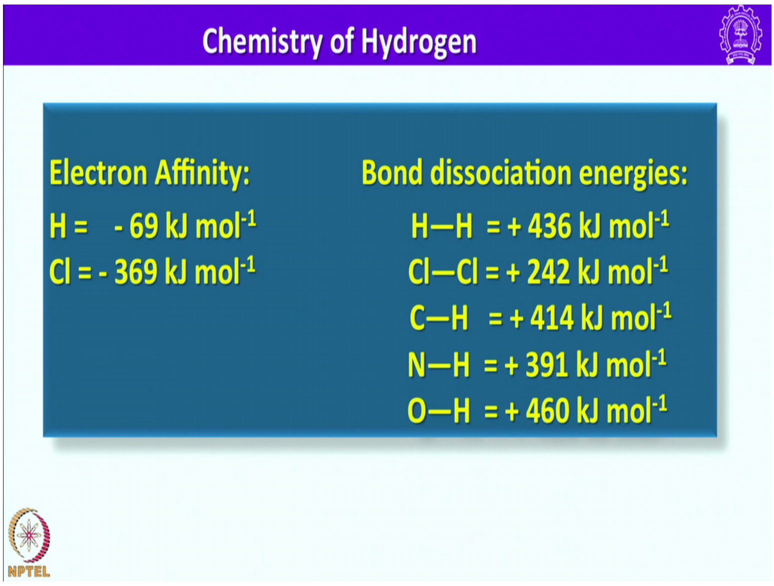

Chemistry of Hydrogen

Electron Affinity:

H = - 69 kJ mol^{-1}

Cl = - 369 kJ mol^{-1}

Bond dissociation energies:

H—H = + 436 kJ mol^{-1}

Cl—Cl = + 242 kJ mol^{-1}

C—H = + 414 kJ mol^{-1}

N—H = + 391 kJ mol^{-1}

O—H = + 460 kJ mol^{-1}

Let us look into the electron affinity; for hydrogen it is minus 69 kilo joules per mole and whereas, in case of chlorine; it is minus 369 kilo joules per mole and let us look into the bond dissociation energy of several other compounds; H-H I mentioned it is 436 kilo joules per mole, in case of chlorine it is 242 kilo joules per mole and in case of C H bond it is 414 kilo joules per mole and N H bond dissociation energy is 391 kilo joules per mole whereas, O H bond dissociation energy is 460 kilo joules per mole so; that means, elemental hydrogen is a very good reducing agent.

It can reduce many metal oxides to metals and in all such cases H 2 O is essentially the byproduct and also hydrogenate many unsaturated organic compounds containing; C double bond, C triple bond or C double bond O to the corresponding saturated analogues; that means, essentially it can reduce either C triple bond C or C double bond C or C O to the corresponding saturated compounds and compounds produced on combining element hydrogen with an element are essentially called hydrides; that means, whether H minus H plus or it is for me a covalent bonds such compounds are essentially called as hydrides ok

So, let us look into these different type of hydrides; that means, we have now three different type of hydrides one is ionic hydrides, another one is covalent hydride and one the last is metallic hydrides; that means, metals with the electro negativity less than 1.2 form ionic hydrides in this case essentially delta plus delta minus will be there or you can also call his plus and H minus; that means, with metals having electro negativity less than 1.2 means they have to be alkali metals and alkaline earth metals, so alkali metals and alkaline earth metals when they combine with hydrogen form ionic hydrides and hydrogen behaves very similar to halogens in these compounds as both are one electrons are at a time and next inert gas configuration.

And elements with electro negativity in the range of 1.5 form covalent hydrides and covalent bond get polarized from delta plus to delta minus depending on the electro negativity of values; that means, when it forms a covalent bond we come across two different types of covalent bonds; one is polar covalent bond, one is nonpolar covalent bond, when the electro negativity difference is marginal it is nonpolar covalent bond, when the electro negativity difference is remarkable then depending upon the electro negativity of the combining atom.

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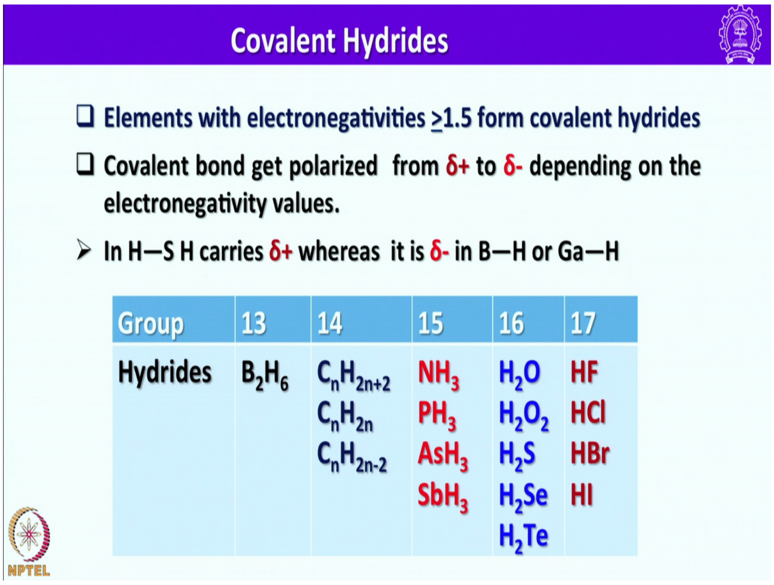

Covalent Hydrides

☐ Elements with electronegativities ≥1.5 form covalent hydrides

☐ Covalent bond get polarized from δ+ to δ- depending on the electronegativity values.

➢ In H—S H carries δ+ whereas it is δ- in B—H or Ga—H

Group	13	14	15	16	17
Hydrides	B_2H_6	C_nH_{2n+2} C_nH_{2n} C_nH_{2n-2}	NH_3 PH_3 AsH_3 SbH_3	H_2O H_2O_2 H_2S H_2Se H_2Te	HF HCl HBr HI

So, hydrogen can carry either plus charge or minus charge for example; if you look into the H S bond. In H S bond; H carries, delta plus charge because sulphur is more electronegative and where is in case of B H hydrogen is more electronegative as a result H carries minus charge and similarly in case of gallium hydride also has carries negative charge. So, this how one can classify the covalent hydrides into polar covalent and nonpolar covalent hydrides ok.

So, I have listed here some hydrides of P block elements, that is; group 13, 14, 15, 16 and 17 and in case of group 13 the simplest hydride one can think of is B H 3, but it utterly undergoes dime ration to form B 2 H 6. So, simplest one is B 2 H 6 and in case of group 14 especially with carbon we have 3 different type of hydrides having this formula shown their; C n H 2 n plus 2 and C n H 2 n and C n H 2 n minus 2, so aliphatic alkenes and alkynes and similarly with group 15 almost all elements form trivalent try coordinated hydrides for example; N H 3 ammonia, P H 3 phosphine and stabbing.

In case of group 16 elements they form; H 2 O, H 2 O to hydrogen peroxide, H 2 H hydrogen sulphide, hydrogen selenite and hydrogen telluride. And with group 17 elements it forms; hydrogen fluoride, hydrogen chloride, hydrogen bromide and hydrogen iodide and of course, here one can see in the polarity of the bond by looking into the electro negativity of the heteroatom that is making bond with hydrogen.

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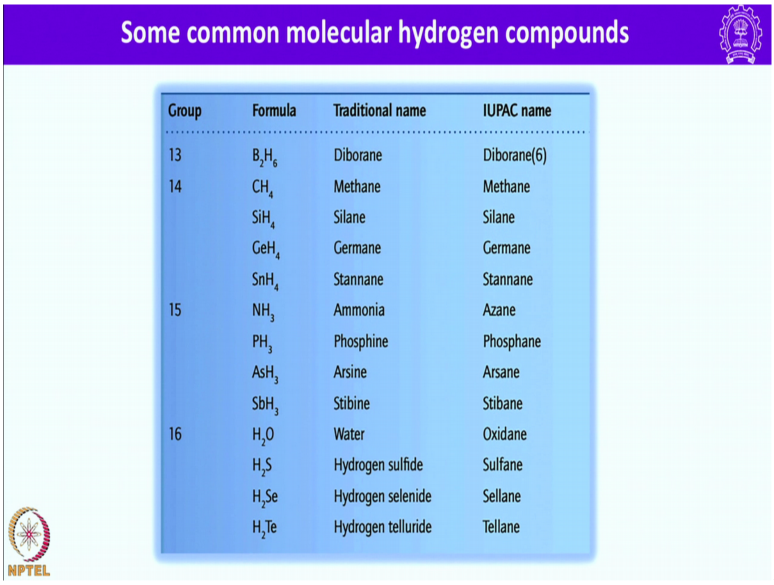

Some common molecular hydrogen compounds

Group	Formula	Traditional name	IUPAC name
13	B_2H_6	Diborane	Diborane(6)
14	CH_4	Methane	Methane
	SiH_4	Silane	Silane
	GeH_4	Germane	Germane
	SnH_4	Stannane	Stannane
15	NH_3	Ammonia	Azane
	PH_3	Phosphine	Phosphane
	AsH_3	Arsine	Arsane
	SbH_3	Stibine	Stibane
16	H_2O	Water	Oxidane
	H_2S	Hydrogen sulfide	Sulfane
	H_2Se	Hydrogen selenide	Sellane
	H_2Te	Hydrogen telluride	Tellane

And here I have listed some common molecular hydrogen compounds and their traditional names; so H 2 H 6 is called diborane and C H 4 is methane and S I H 4 is silane and similarly germanium hydride is germane and tin hydride is stannane and of course, I am N H 3 we have the name ammonia and P H 3 is called phosphine, A S H 3 is arsane, S P H 3 is stibane and H 2 O is water and of course, water is not the right name for H 2 O, it should be called as oxidane and H 2 S is hydrogen sulphide in the same line if you want to call it is appropriate to call it as a sulfane and in case of hydrogen selenide it should be called as sellane and tellane, but; however, those names are not common let us go with their traditional names and suggested by text books.

So, water still it should be called as; water, hydrogen sulfide, hydrogen selenide, hydrogen telluride. And let us look into the synthetic methodologies we come across for making hydrogen hydrides different kind of hydrides; one is the direct combination of an element with hydrogen, so the second method involves the reduction of halide or an oxide.

So; that means, we have several methods to generate these hydrides or hydrogen compounds one method is the direct combination, the second method is reduction of a halide or oxide, hydrolysis of compounds such as; metal phosphide, carbide, silicide and boride, hydrolysis of metal phosphide will give you phosphine, carbide will give you hydrocarbon, silicide will give you sellane and boride will give you borine.

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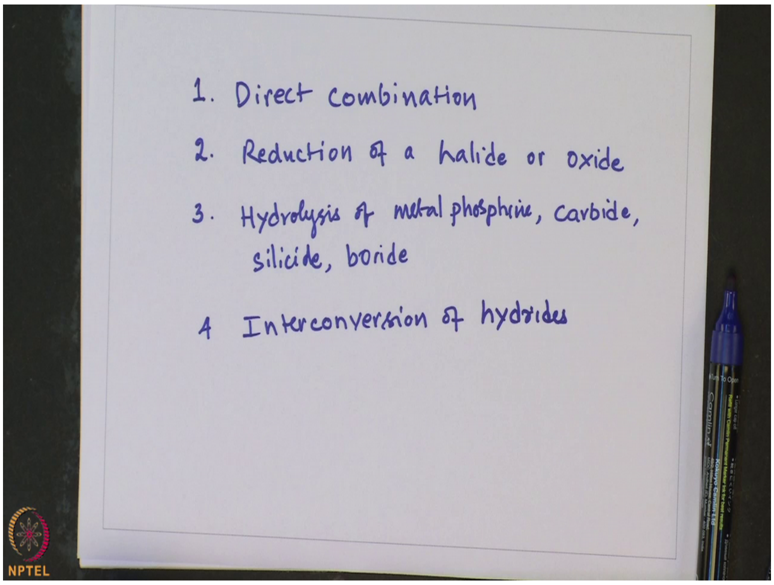

1. Direct combination
2. Reduction of a halide or oxide
3. Hydrolysis of metal phosphide, carbide, silicide, boride
4 Interconversion of hydrides

So, another method is the inter conversion of hydrides. Of course, one can use several methods the important method used is; subjecting the hydrides to electrical discharge, that is very frequently used in the case of boron hydrides to prepare higher boron hydrides. So, let me give in each case at least one example direct combination ah.

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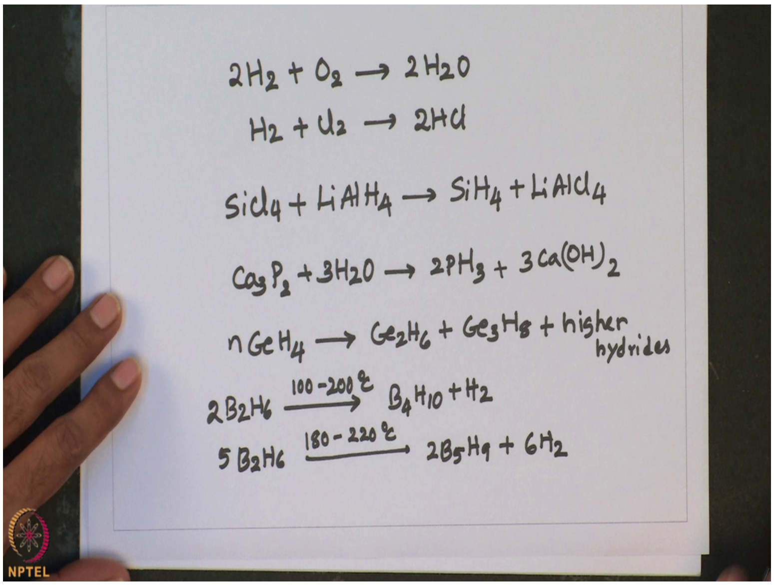

$2H_2 + O_2 \rightarrow 2H_2O$

$H_2 + Cl_2 \rightarrow 2HCl$

$SiCl_4 + LiAlH_4 \rightarrow SiH_4 + LiAlCl_4$

$Ca_3P_2 + 3H_2O \rightarrow 2PH_3 + 3Ca(OH)_2$

$nGeH_4 \rightarrow Ge_2H_6 + Ge_3H_8 +$ higher hydrides

$2B_2H_6 \xrightarrow{100-200\,^\circ C} B_4H_{10} + H_2$

$5B_2H_6 \xrightarrow{180-220\,^\circ C} 2B_5H_9 + 6H_2$

Is i can show you here in case of direct combination; example is take H 2 and combine with O 2 to give 2 H 2 O or take H 2 combine with C l 2 to give 2 H C l. And then reduction of a halide or an oxide I mentioned, let us take S i C l 4 tetrachlorosilane treat this one with lithium aluminum hydride it gives silane plus L i A l C l 4 of course, one should remember these reactions has to be carried out in non aqueous medium. And hydrolysis of metal phosphide I will give one example; let us consider calcium phosphide, treat this one with water is used to P H 3 that is phosphine and three equivalents of calcium hydroxide ok.

So, as I mentioned one can use inter conversion method in which, the hydrides are subjected to electrical discharge for example; let us take, germanium hydride such as; G e H 4, this can give you G e 2 h 6 plus G e 3 h 8 very similar to ethane and propane and plus higher hydrides, but these higher analogous of germanium are not stable, similarly D 2 H 6 on heating 100 to 200 degree centigrade it gives; B 4, H 10 plus H 2 for example we take two equivalents and similarly instead of heating 100 to 200 degree, if you heat it it 20 degree centigrade it gives B 5, H 9 plus 6 H 2 S.

So, this are some more methods of preparation of various hydrides and let us look into the properties of these hydrides covalent hydrides of P block elements are reducing agents so; that means, all P block hydrides are essentially covalent in nature and their all reducing agents some of them spontaneously burn in air, while many other hydrides require a spark to initiate or trigger the reaction.

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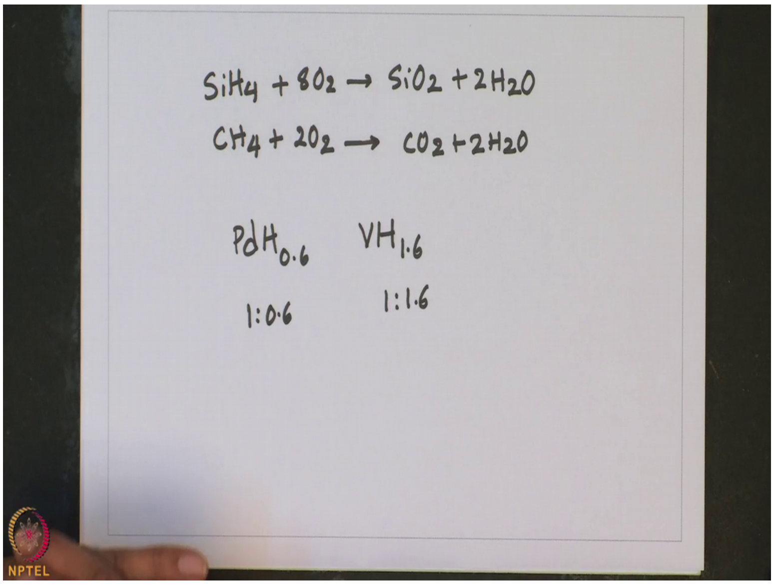

$SiH_4 + 8O_2 \rightarrow SiO_2 + 2H_2O$

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$PdH_{0.6}$ $VH_{1.6}$

1:0·6 1:1·6

For example; and let us look into S i H 4, it readily reacts with oxygen to form silicon oxide or silica, whereas C H 4 does not readily react but with the spark it readily react with oxygen to form C O 2 plus H 2 O, we look into the properties of covalent hydrides and ionic hydrides. Let us look into metallic hydrides elements such as; transition metals and also lanthanides and to an extent actinides, observe variable amount of hydrogen to form non stoichiometric metal hydrides which retain most of the properties of the metals examples; hardness, conductivity and luster.

However they become little brittle in nature, so in these hydrogen occupy interstitial tetrahedral sides in a closed packed metal lattice, lanthanides can also take up hydrogen in octahedral sides giving ionic M H 3 phases for example; we have non stoichiometric compounds, example I will right here P d H with 0 6 nonstoichiometric and in case of vanadium hydride we have a ratio of 1 is to 1.6 and here we have 1 is to 0.6 and here we have 1 is to 1.6, in these compounds essentially they not really combining with metal, but they occupy in interstitial sites they can be the tetrahedral or octahedral depending upon the metal with which it is combining.

And let us look into the compounds containing H plus iron removal of loan electron atom gives H plus ion; that means, once the loan electron present in 1 S orbital it is ionized, it generates H plus and conversion of H 2 into gas phase that is H plus please requires a large amount of energy it is not very easy.

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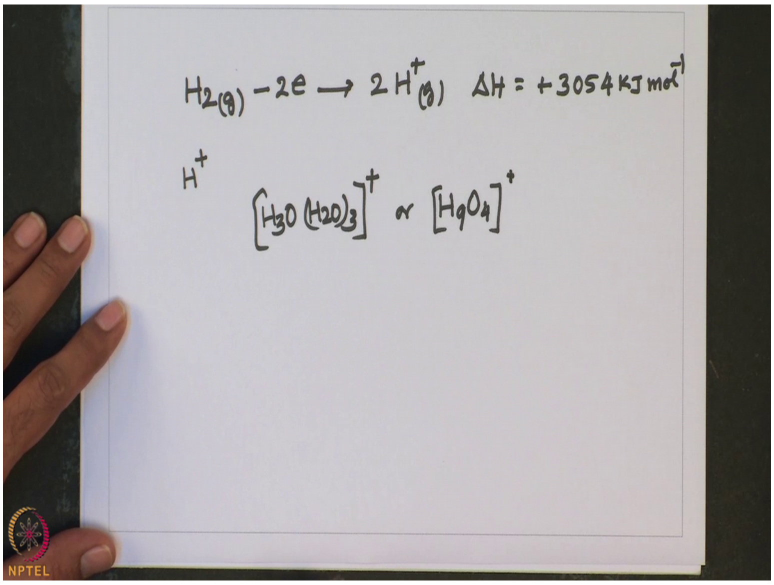

$H_{2(g)} - 2e \rightarrow 2H^{+}_{(g)}$ $\Delta H = +3054\ \mathrm{kJ\ mol^{-1}}$

H^{+} $[H_3O(H_2O)_3]^{+}$ or $[H_9O_4]^{+}$

So, let us look into this equation here. Essentially you have to ionize from H 2 to electrons to generate 2 H plus gaseous species the enthalpy of this reaction is very high that is equal to 3054 kilo joules per mole. So, H plus generated in aqueous solution is always solvated by water to form (Refer Time: 22:10) that is H 3 plus ion also called hydronium ion, due to the delta plus on each hydrogen they interact with oxygen atoms or water molecules to get solvated to have a composition for example; these do not have an independent existence.

This H plus does not have an independent existence as a result what happens the moment it is generated in aqueous medium it readily combines with H 2 O to form H 3 O called hydronium or oxonium ion, due to the positive charge it is carrying what it does is? It interacts with the oxygen atoms of water molecules in it is close vicinity and gets solvated and it will assume several composition one such composition is; H 3 O, H 2 O, 3 plus or it can also be written as; H 9, O 4 plus H 9, O 4 plus so let us look into it, we will have H 3 O plus is there and here hydrogen atoms carries delta plus charge.

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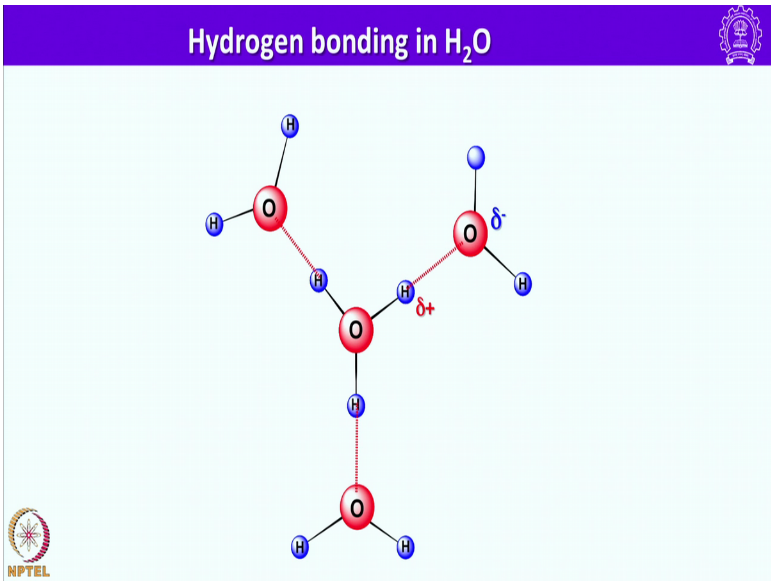
Hydrogen bonding in H_2O



So, as a result it will start interacting with neighboring H 2 O molecule with O directed towards H. Similar one more; because here, because again due to the polarization delta oxygen carries delta minus charge and they orient in this fashion in all the three direction; that means, three such water molecules will orient and they establish a interaction and this interaction is called hydrogen bonding interaction.

And these hydrogen bonding interactions are very strong, when the O H O angles are linear or close to 180 degrees you can see here, this delta plus is there and O with delta minus will be oriented and similarly here and similarly here this accounts for the H 3 O, H 2 O, 3 times having a composition of H 9 O 4 plus ok.

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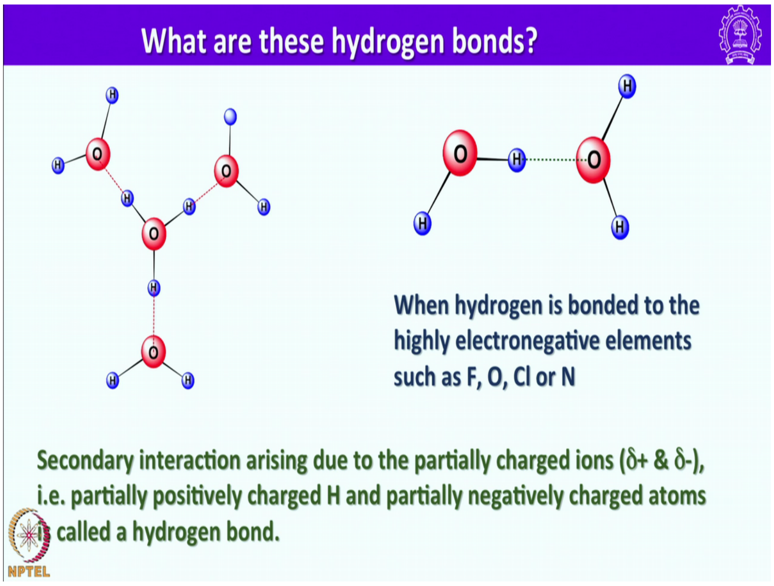

What are these hydrogen bonds?

When hydrogen is bonded to the highly electronegative elements such as F, O, Cl or N

Secondary interaction arising due to the partially charged ions (δ+ & δ-), i.e. partially positively charged H and partially negatively charged atoms called a hydrogen bond.

So, what are these hydrogen bonds there? We can see here this H 2 O is there and another H 2 O orients in this fashion to establish a bond in here and this is called O H O this is called hydrogen bonding interaction and as I mentioned this hydrogen bonding interaction is very strong when this angle at H is 180 degree or linear. So, when that happens? When hydrogen is bonded to be highly electronegative elements such as; fluorine, oxygen, chlorine or nitrogen, there exist a secondary interaction due to the positivity charged ions exist in the mixture that means delta plus and delta minus. So, partially positively charged H and partially negatively charged the electro negative atoms start interaction to establish hydrogen bonding, this hydrogen bonding is very strong when we have fluorine and oxygen and to an extending case of chlorine and nitrogen.

So, remaining elements do not have any inclination to establish hydrogen bonding and even if there is any hydrogen bonding is there with sulphur and hydrogen, they are very weak and they can be ignored for all practical purposes. The most strong hydrogen bonding we come across, when hydrogen is in the vicinity of fluorine, oxygen, chlorine or nitrogen.

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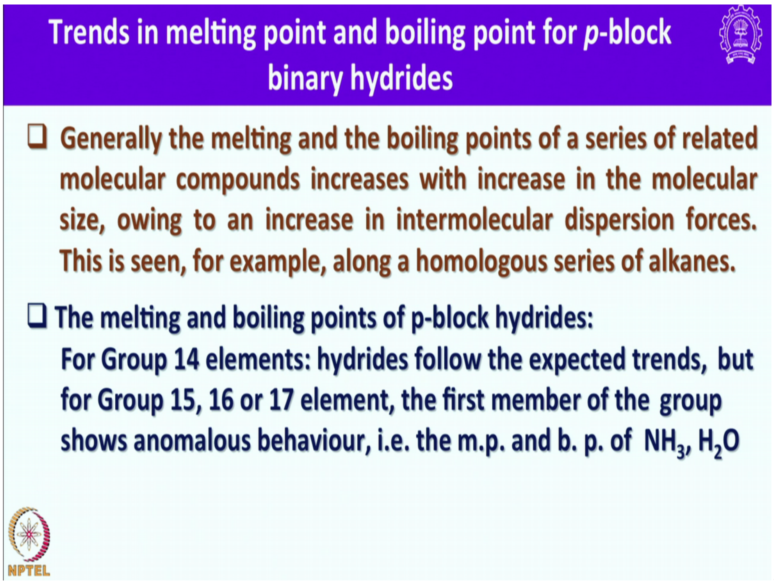

Trends in melting point and boiling point for *p*-block binary hydrides

- ☐ Generally the melting and the boiling points of a series of related molecular compounds increases with increase in the molecular size, owing to an increase in intermolecular dispersion forces. This is seen, for example, along a homologous series of alkanes.
- ☐ The melting and boiling points of p-block hydrides:
  For Group 14 elements: hydrides follow the expected trends, but for Group 15, 16 or 17 element, the first member of the group shows anomalous behaviour, i.e. the m.p. and b. p. of NH_3, H_2O

Let us look into the trends in melting point and boiling point for P block binary hydrides. So, generally the melting and the boiling points of a series of related molecular compounds increases with increase in the molecular size, going to an increase in intermolecular dispersion forces this is seen for example; along a homologous series of alkanes. For example; you take methane, ethane, propane and butane and pentane, both methane and ethane are gases and propane and butane are also gases, but pentane is a liquid low boiling liquid and also the boiling point increases, so here intermolecular dispersion dispersive forces increases with the increasing the size, because more such sites are available for interaction as a result the melting and boiling point increases ok.

The melting and boiling point of P block hydrides can be compared; the for group 14 elements: hydrides follow the expected trends what I had discussed, but in case of group 15, 16 and 17 elements, the first member of the group has a different melting and boiling point compared to higher congenious in those respective groups and this anomalous behavior can be explained again using hydrogen bonding interactions.

For example in case of group 15: we have ammonia and phosphine ammonia shows remarkable high melting and boiling point, similarly oxygen in case of water shows remarkable high melting and boiling point, so these properties can be correlated with their ability to form very strong hydrogen bonding interactions and H F also shows you know extensive hydrogen bonding interactions so; that means, especially why? A first members of the groups of 15, 16 and 17 show anomaly their melting and boiling points can be correlated with their hydrogen bonding abilities. So, let me discuss the hydrogen bonding concept in my next lecture. So, until then have a pleasant reading of organic chemistry.

Thank you very much.