Main Group Chemistry

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Lecture – 15
Chemistry of Hydrogen, Hydrides and Hydrogen Bonding

Welcome to MSB lecture series on Main Group Chemistry. In my last lecture while discussing about the chemistry of hydrogen I did mentioned that the melting points and boiling points for p-block elements for some trend; however, in some groups those trends are violated let us look into those things.

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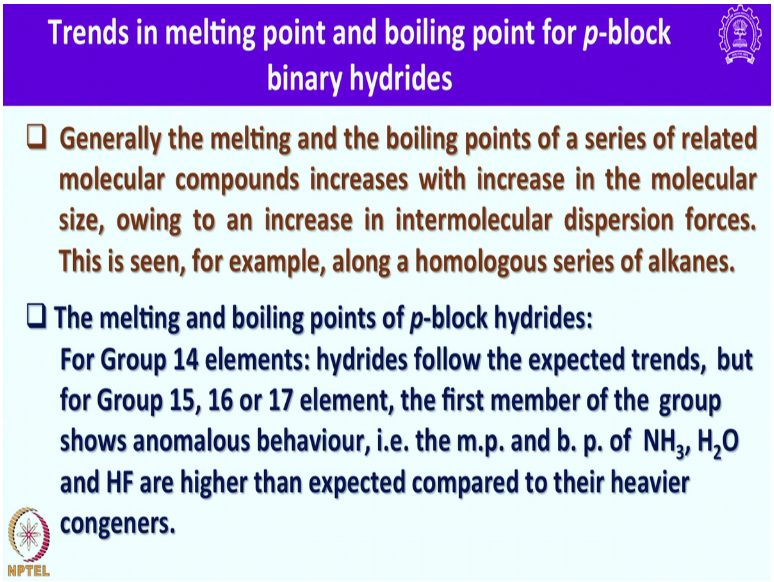

Trends in melting point and boiling point for *p*-block binary hydrides

❑ 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 and HF are higher than expected compared to their heavier congeners.

That means, when you look into some of this physical or chemical properties in a particular group generally the melting and the boiling points of a series of related molecular compounds increases, with increase in the molecular size going to an increased inter molecular dispersion forces.

This is seen for example, allowing a homologous series of alkalines that is in case of group 14 hydrides of carbon if we consider CH 4 methane, ethane, propane, butane and pentane and if you look into the melting point and boiling point they are steadily increasing and here as more and more CH 2 groups are added more and more groups are available for to have inter molecular dispersion forces will be generated. So, as more and more dispersive force centers are generated as a result what happens the association between these molecules increases and as a result they come close to each other resulting in melting and boiling point increase.

So that means, then what would happen to the melting and boiling points of p-block hydrides. So, trend is for group 14 elements hydrides follow the same trend as expected has I had mentioned earlier, but in case of group 15, 16 and 17, the first member of the group behaves in a different way compared to their higher congeners, that means, for example, in case of group 15 nitrogen hydride or ammonia or in case of group 16 water or in group 17 hydrogen fluoride they behave little different than the rest of the elements. That means, essentially these hydrides first member from 15 16 and 17 show remarkably high melting and boiling points compared to rest of the congeners.

So, why that happens? For example, if we take melting point and boiling point of ammonia and water and hydrogen fluoride they are remarkably high compared to rest of the hydrides in the respective group. Let us look into this what makes these compounds to show different properties.

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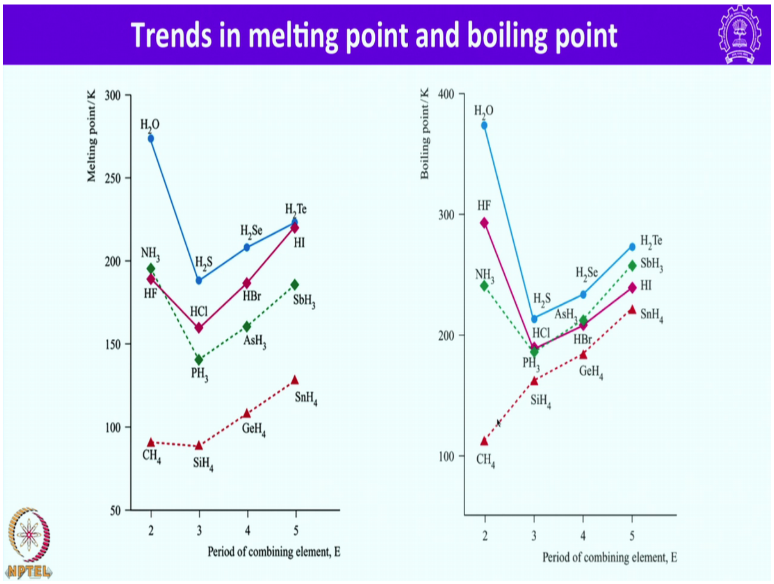

Trends in melting point and boiling point

Let us to analyze this, these trends. Let us look into the melting points of several hydrides of group 14 to group 17 I have listed here for example, CH 4 some methane silane germane and stannane is given here and similarly for group 15 ammonia phosphine arsine and stibine is there, and in case of group 16 water hydrogen sulphide, hydrogen selenide and hydrogen telluride are given and similarly for group 17 HF HCl HBr and HI are given.

You can see the trends, trends from the second elements follows the expected order; that means, steadily increasing their melting point with increasing the atomic number or atomic weight of the corresponding hydride or when you proceed down the group with for heavier elements this melting point is increasing. But you can abnormally is here water shows around 100 degree and where as ammonia shows different HF shows different if you extrapolate this one back word you expect them to have much lower than what it is seen here. So, these trends can be explained using hydrogen bonding concept.

And of course, same analogy one can make for boiling points also you can see here boiling points also to begin with we have highest boiling point for the first member like water, hydrogen fluoride, ammonia and whereas, in case of group 14 no such trends are observed. So, methane shows where exactly it suppose it to be according to the expected patron. So that means, it seems group 14 elements follows this trend whether we take alkane series or silane series or germane series whereas, this trends are not followed and the hydrides of first elements show remarkably high melting and boiling points.

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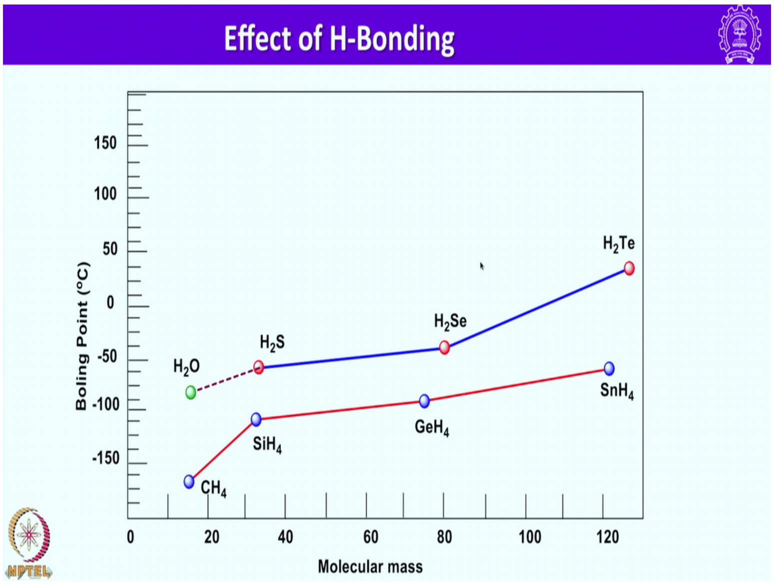

Effect of H-Bonding

So, for this one I have just chosen 2 sets of compounds here to verify their boiling point I have chosen group 14 hydrides such as methane ethane sorry methane, sellene, germane and stannane. And in case of group 16 water, hydrogen sulphide, hydrogen selenide and hydrogen telluride are considered. You can see in absence of any a normally water is expected to show a boiling point of minus 100, but that is not the case we all know that the boiling point of water is 100 degree centigrade; that means, it deviates. Why it is deviating, that can be explained again very effectively using hydrogen bonding concept.

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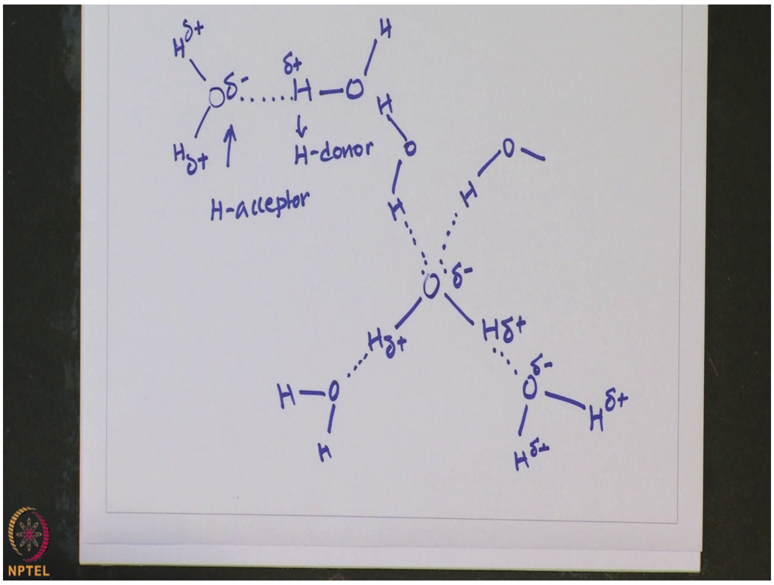

If you take a water molecule we have this polar covalent bonds polar covalent bonds and here we all know that because oxygen is being more electro negative it carries delta minus and both the hydrogen atoms carry delta plus, when it comes in contact with another water molecule it orients in this fashion and their establishes a interaction between H plus and this is hydrogen donor and this is hydrogen acceptor. This is hydrogen donor and this is oxygen is hydrogen acceptor because of these interactions this O and H 2 molecules come together; that means, a water molecule can show 4 such interactions. Let me show you all 4, one can keep writing like this so that means, each H 2 O molecule participates in 4 hydrogen bonding interactions and this is spread across the entire molecule are association something like this.

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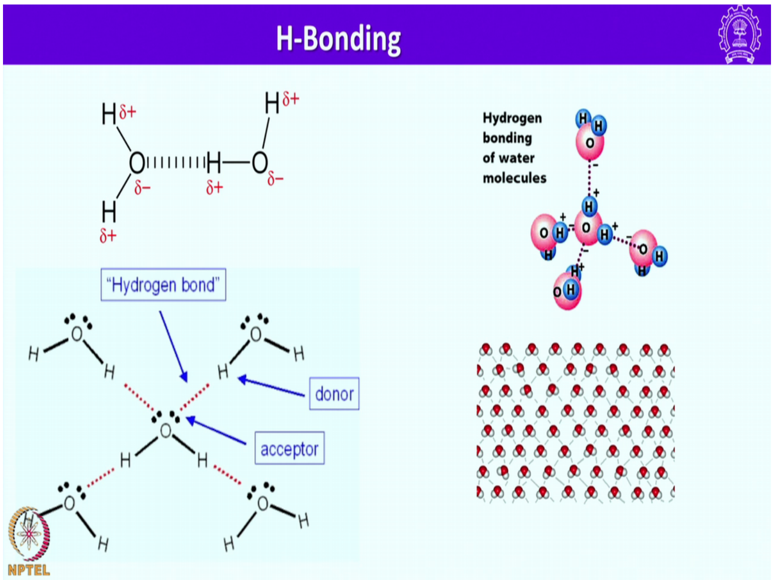

H-Bonding

"Hydrogen bond"

donor

acceptor

Hydrogen bonding of water molecules

As a result of this one what happens all this water molecules come very close to each other and they are held formally and as a result what happens enormous energy is required to melt these molecules to separate this molecules. So, hence they show very high melting and boiling point compared of hydrides of rest of the elements in the corresponding groups.

So, one can also represent hydrogen bonding in this fashion. So, these interactions individually if you take these interactions are very weak collectively these interactions are enormous in case of water molecules due to the infinite number of hydrogen bonding interaction that we come across. So, this brings this molecules close to each other and increasing their density and increasing their boiling point and melting point and you can see how this molecules are arrange in the lattice.

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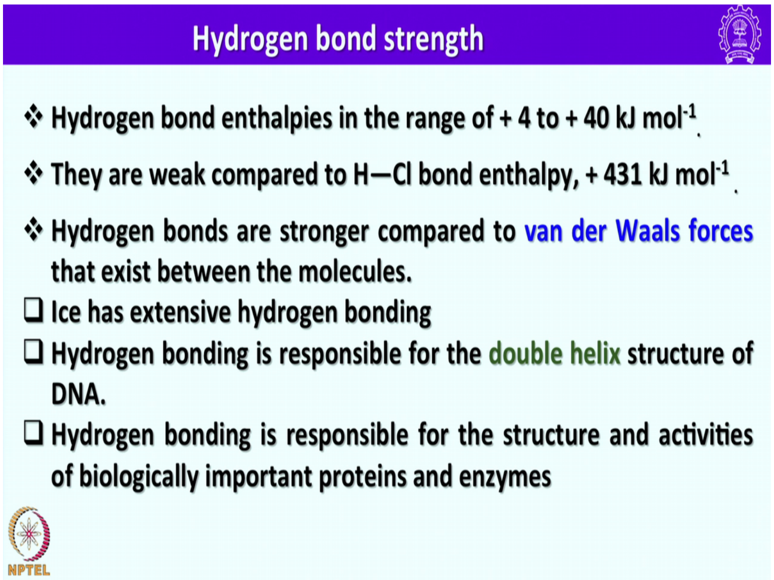

Hydrogen bond strength

❖ Hydrogen bond enthalpies in the range of + 4 to + 40 kJ mol^{-1}.

❖ They are weak compared to H—Cl bond enthalpy, + 431 kJ mol^{-1}.

❖ Hydrogen bonds are stronger compared to van der Waals forces that exist between the molecules.

❑ Ice has extensive hydrogen bonding

❑ Hydrogen bonding is responsible for the double helix structure of DNA.

❑ Hydrogen bonding is responsible for the structure and activities of biologically important proteins and enzymes

So that means, hydrogen bond enthalpies in the range of plus 4 to plus 40 kilo joules per mole they are weak they are weak compared to HCl bond enthalpy of 431 kilo joules per mole. Hydrogen bonds are stronger compared to van der Waals forces that exist between the molecules. Hydrogen bonding interactions are much stronger than van der Waals forces that exist between the molecules such as a methane molecules or ethane molecules etcetera. And ice has extensive hydrogen bonding. And hydrogen bonding is responsible for the double helix structure of DNA and hydrogen bonding is also responsible for the structure and activities of biologically important of proteins an enzymes.

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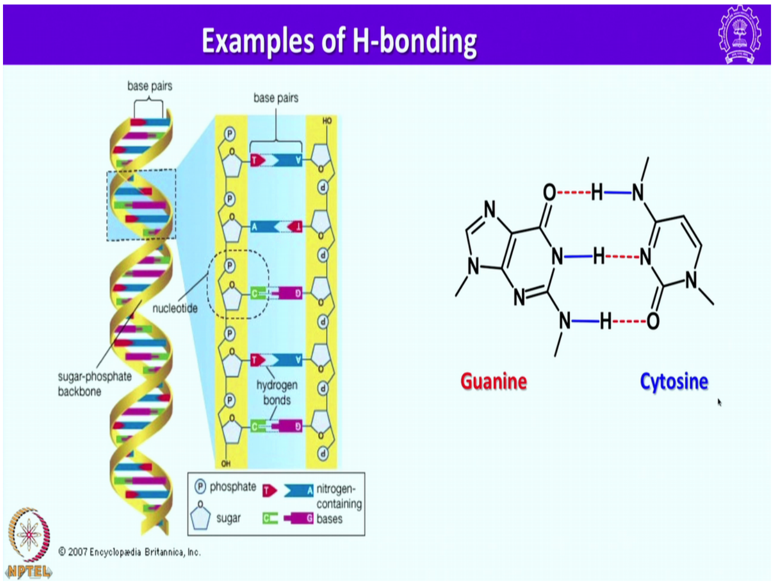

Examples of H-bonding

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And you can see here helical structure happens because of intense hydrogen bonding between 2 such DNA strands that gives twisted conformation and one of the representative hydrogen bonding is shown here between guanine and cytosine. And when we talk about van der Waals often students make mistake in writing the name and one should remember van der Waals full name is Johannes Diderik.

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Johannes Diderik van der Waals

van der Waals

So, this is the full name of van der Waals that is called Johannes Diderik, van der Waals and when we write shortly we have to write only this one; that means, we should remember small v and small d and capital W. So, this is how one should write one should not forget about this one often I have seen student making mistake while writing his name.

So, let us look into one more important compounds of hydrogen that is hydrogen peroxide. Industrial production of hydrogen peroxide involves the antraquinone auto oxidation process where an antroquinonol dissolved in an organic solvent is oxidized using air to the corresponding antraquinone and hydrogen peroxide is formed. The hydrogen peroxide obtained is recovered by extracting the organic solution with water and then the antraquinone that is formed is then reduced back to the antroquinonol using hydrogen and a palladium catalyst. This process is repeated many times giving a catalytic cycle. Let us look into it how it is made, it is called auto reduction.

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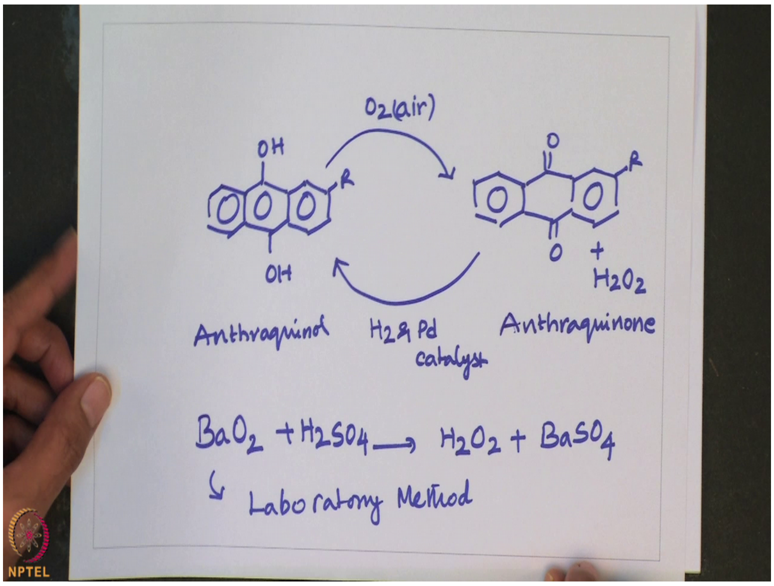

So, this one on aerial oxidation forms antraquinone plus H 2 O 2 is formed and this one is in the organic phase when it is treated with water H 2 O 2 comes into water and that can be separated from organic layer. And again to get back this one this is antraquinone.

So, to convert this antraquinone back to antraquinonol one should use hydrogen and palladium catalyst has a reducing agent.

So, you can get back and again plus hydrogen. So, this can be repeated several times to produce H 2 O 2. And of course, laboratory method involves simple interaction of barium oxide barium peroxide with sulfuric acid. So, this is laboratory method. So, in case of industrial method antraquinonol is taken and it is treated with oxygen to undergo aerial oxidation to form antraquinone and H 2 O 2 is formed this H 2 O 2 is extracted by treated this organic medium with aqueous so that H 2 O 2 moves to the aqueous layer and then it can be separated. And treating antraquinonol with hydrogen under catalytic condition using palladium catalyst one can reduce this back to antraquinonol and repeat this cycle to get H 2 O 2, and in laboratory method one can simply treat barium oxide barium peroxide with sulfuric acid to form H 2 O 2 and BaS O 4 is formed it (Refer Time: 16:11) out and this can be taken.

When crystals of compounds especially a coordination compounds are grown from a solvent they may contain solvent of crystallization if the solvent is water; that means, if the crystallization is carried out in a aqueous medium the compounds all often get hydrated. The formula of the solvated compounds shows the molar ratio in which the solvent of crystallization is present.

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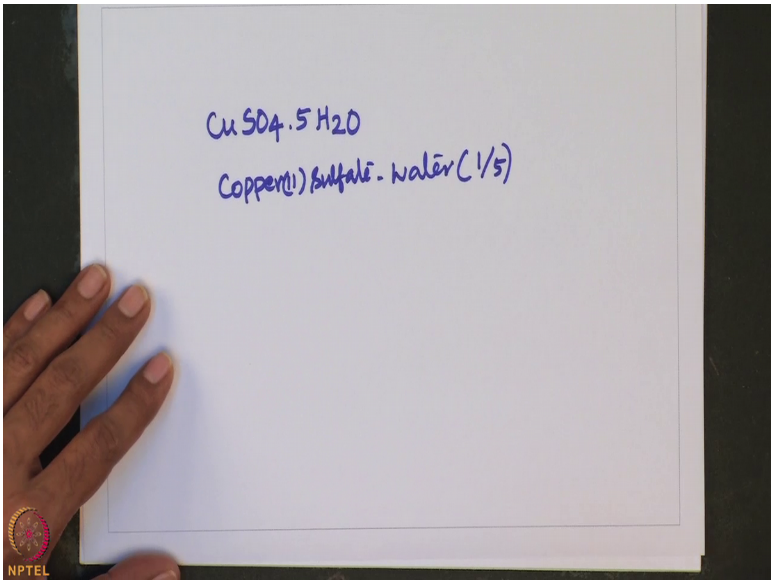

$CuSO_4.5H_2O$

Copper(II) sulfate . water (1/5)

For example, if you look into copper sulfate often we come across the formula is written in this fashion or it can also be pronounced as copper to sulfate pentahydride or one can also write. So, it represent the ratio is 1 is to 5. And what are the importance of hydrogen in biology?

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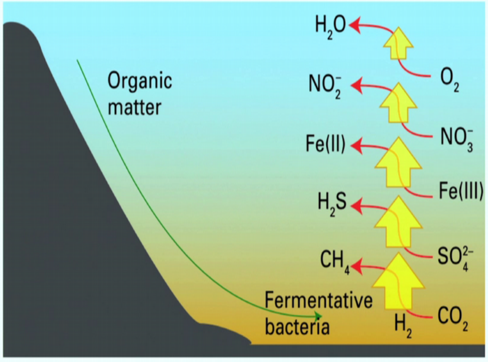
The biological hydrogen cycle

- ☐ Hydrogen is cycled by microbial organisms using metalloenzymes. Example: nitrogen fixing bacteria which yield H_2 as a byproduct of ammonia formation.



Hydrogen is cycled by microbial organisms using metalloenzymes for example, nitrogen fixing bacteria which yield hydrogen as a byproduct of ammonia formation. We can see those things here various biological cycles in which hydrogen is formed as a byproduct is shown here.

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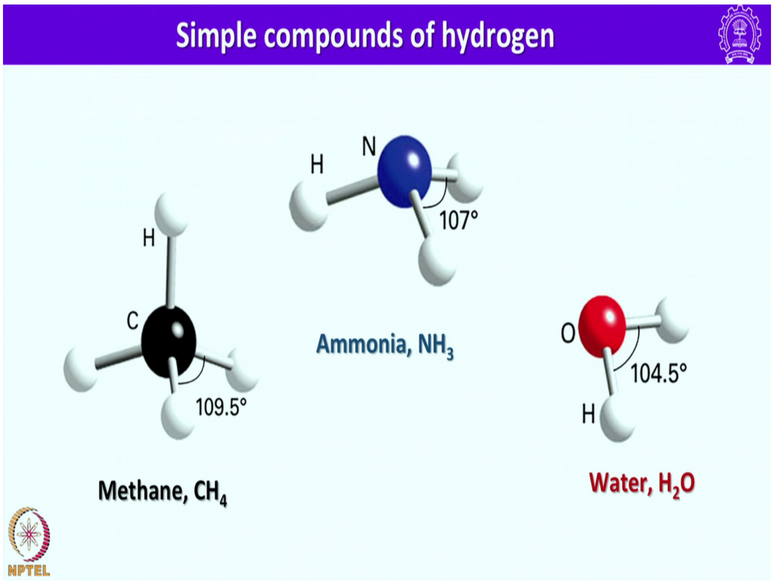

Simple compounds of hydrogen

Ammonia, NH_3

Methane, CH_4

Water, H_2O

And some of this simple compounds of hydrogen are shown again here. The simplest once are methane in case of group 14 and ammonia in case of group 15 and water in case of group 16 and also they respective shapes and also the geometries also you can see here.

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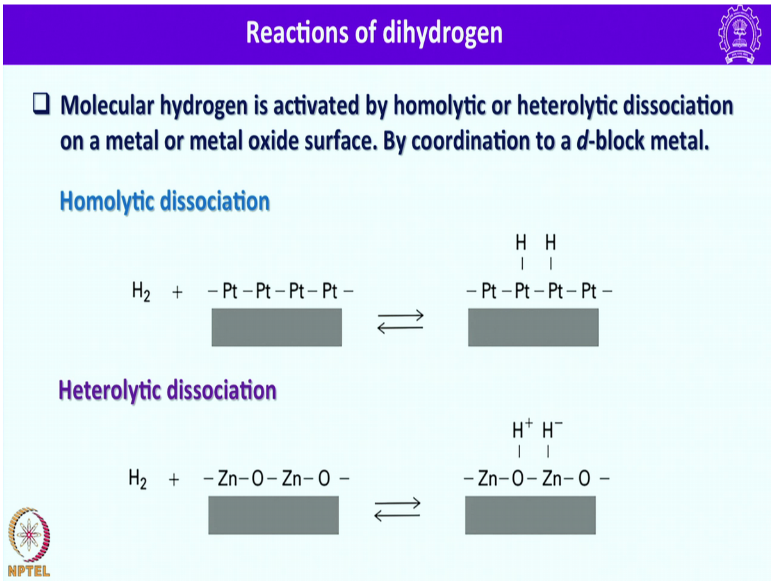

Reactions of dihydrogen

- ☐ **Molecular hydrogen is activated by homolytic or heterolytic dissociation on a metal or metal oxide surface. By coordination to a *d*-block metal.**

Homolytic dissociation

$$H_2 + -Pt-Pt-Pt-Pt- \rightleftharpoons -Pt-\overset{H}{\overset{|}{Pt}}-\overset{H}{\overset{|}{Pt}}-Pt-$$

Heterolytic dissociation

$$H_2 + -Zn-O-Zn-O- \rightleftharpoons -\overset{H^+}{\overset{|}{Zn}}-\overset{H^-}{\overset{|}{O}}-Zn-O-$$

And let us look into the reactions of dihydrogen and molecular hydrogen is activated by homolytic or heterolytic dissociation on a metal or a metal oxides surface essentially by using d-block metals. That means, if you want to do hydrogenation of unsaturated organic compounds one can generate the active species from molecular hydrogen.

For example, in case of homolytic dissociation one can take on metal surfaces what happens is hydrogen is split homolytic dissociation happens and it forms platinum hydrides; that means, both are H minus they are formed by reaching out one electron from platinum and it forms like this. And then in case of heterolytic dissociation what happens for example, if you take hydrogen over zinc oxide here it shows heterolytic where H plus and H minus are simultaneously formed and as expected H minus will be binding to O and H plus binding to O and H minus will be binding to zinc and later these H plus are H minus can be transferred to the substrates in the process we call it as hydrogenation reaction.

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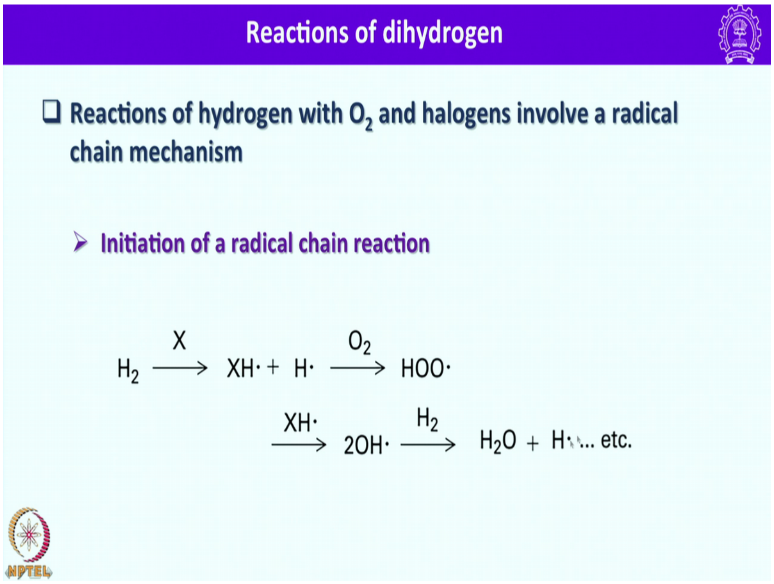

Reactions of dihydrogen

- Reactions of hydrogen with O_2 and halogens involve a radical chain mechanism
  - Initiation of a radical chain reaction

$$H_2 \xrightarrow{X} XH\cdot + H\cdot \xrightarrow{O_2} HOO\cdot \xrightarrow{XH\cdot} 2OH\cdot \xrightarrow{H_2} H_2O + H\cdot \ldots \text{etc.}$$

And reaction of hydrogen with oxygen and halogens also involve often radical chain mechanism. Of course, when we talk about radical chain mechanism we have to remember 3 steps initiation of a radical chain reaction and in here essentially what happens if H 2 when its treated with halide it generates the 2 radicals I have shown there, 2 radicals are shown here and these 2 radicals in presence of oxygen molecule form HOO dot and then this HOO dot again reacts with this radical here to form 2 O hydroxyl ions and this hydroxyl ions are combination with H 2 molecule gives H 2 and H dot and this H dot again participates and this radical chain reaction continuous.

So, now let us have some questions. Classify the following compounds into ionic covalent and metallic hydrides.

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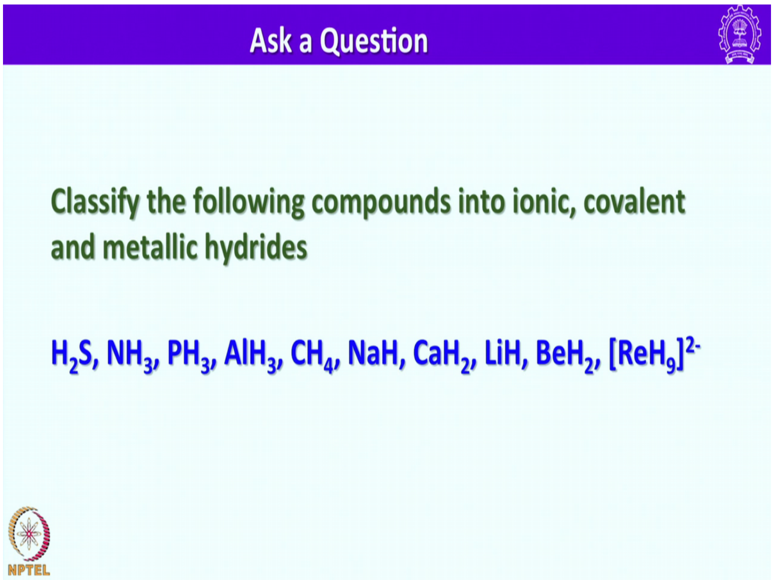

Ask a Question

Classify the following compounds into ionic, covalent and metallic hydrides

H_2S, NH_3, PH_3, AlH_3, CH_4, NaH, CaH_2, LiH, BeH_2, $[ReH_9]^{2-}$

We all know that alkali metals and alkaline earth metals form ionic hydrides because they are extremely high, extremely electro positive elements whereas, p-block elements form covalent hydrides and transition metals form metallic hydrides. So, based on this information we can classify for example, hydrogen sulphide, ammonia, PH 3, alluminium hydride, all of them here up to here all covalent hydrides and here they can be polar or non polar covalent hydrides whereas, sodium hydride, calcium hydride, lithium hydride, beryllium hydride, beryllium hydride as some covalent character, but never the less they are all ionic hydrides and ReH 9 2 minus is metallic hydride. In fact, this is one of the rare example of homolytic transfer metal halides here rhenium exist in plus seven oxygen states and having 9 hydrogen atoms and the geometry of this one is tricapped trigonal prismatic geometry.

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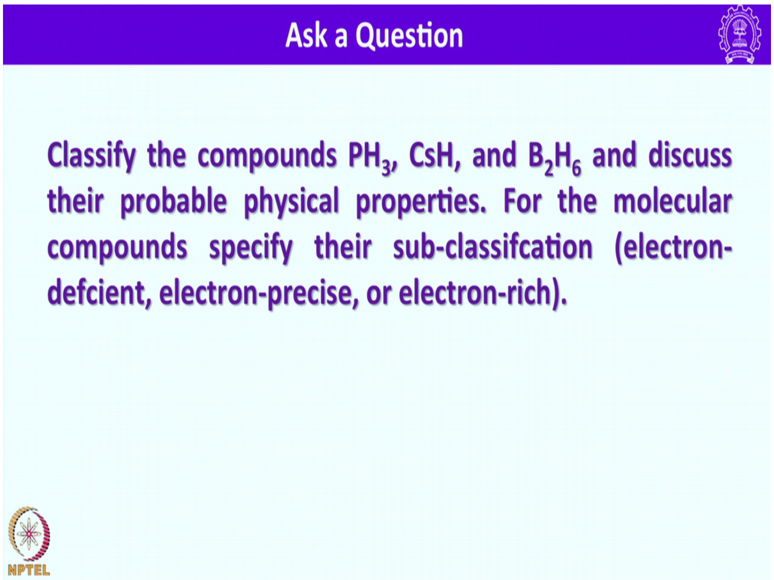

Ask a Question

Classify the compounds PH_3, CsH, and B_2H_6 and discuss their probable physical properties. For the molecular compounds specify their sub-classification (electron-deficient, electron-precise, or electron-rich).

So, now let us look into another question here. Classify the compounds such as PH 3, cesium hydride and diborane and discuss their probable physical properties. For the molecular compounds specify their sub classification so that means, whether there are (Refer Time: 22:05) electron precise electron rich by simply looking into the hetero atoms that is present in the hydride we should be able to tell based on the knowledge we have about this hydrides. For example, phosphine phosphorous is not trivalent state and phosphorous still has a pair of electrons intact so this is essentially electron rich compounds. So, it can act as electro, it can act as Lewis base.

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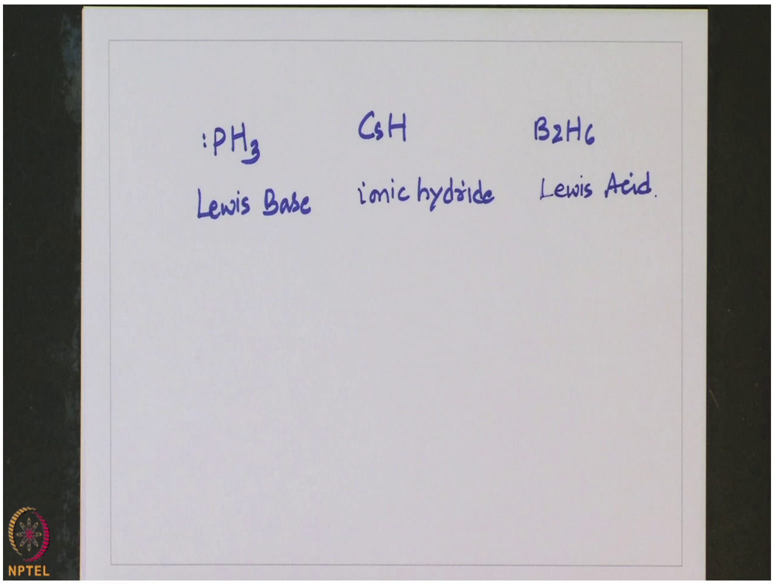

$:PH_3$ CsH B_2H_6

Lewis Base ionic hydride Lewis Acid.

This is Lewis base and cesium hydride it is electron precise, but ionic hydride whereas, B 2 H 6 it is electron deficient so it acts as a Lewis acid. So, this how we can classify by looking into the hetero atom and its electronic configuration.

And let me summarize overall the chemistry of hydrogen I had discussed so far. Lightest elements and the most abundant elements in the universe, hydrogen is the lightest elements and the abundant elements in the universe and 3 isotropes are known for it I essentially having one proton one proton 1 neutron and 1 proton, 2 neutron, protium, deuterium and tritium.

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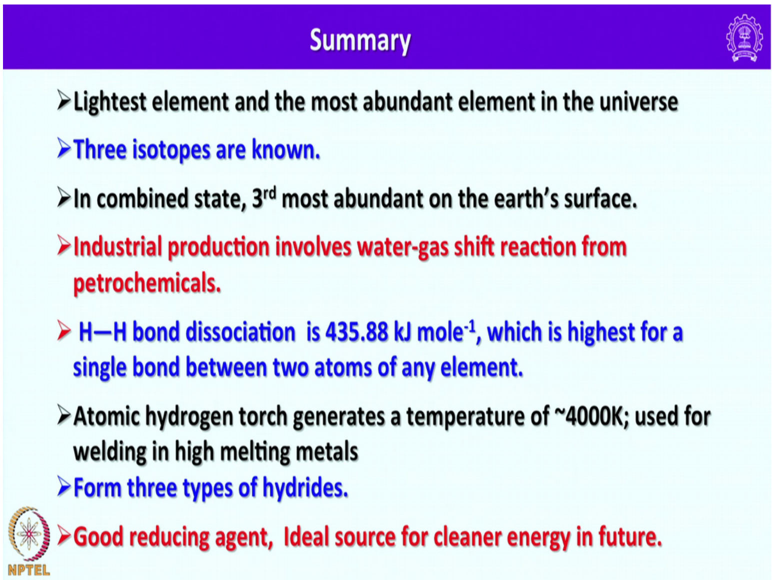

Summary

- Lightest element and the most abundant element in the universe
- Three isotopes are known.
- In combined state, 3rd most abundant on the earth's surface.
- Industrial production involves water-gas shift reaction from petrochemicals.
- H—H bond dissociation is 435.88 kJ mole^{-1}, which is highest for a single bond between two atoms of any element.
- Atomic hydrogen torch generates a temperature of ~4000K; used for welding in high melting metals
- Form three types of hydrides.
- Good reducing agent, Ideal source for cleaner energy in future.

In the combined state third most abundant on the earth surface essentially in the form of water or hydrated minerals. In the shell production involves water gas shift reaction from petrochemicals the bulk of the production of H 2 comes from petrochemicals all the views electrolysis and other methods and hydrogen hydrogen bond dissociation is very high it is about 435.88 kilo joules per mole which is highest for a single bond between 2 atoms of any elements for that matter. And atomic hydrogen torch generates a temperature of 4000 Kelvin used for welding in high melting metals.

For 3 types of we come across 3 type of hydrides when hydrogen interacts with any elements in the periodic table they are ionic hydrides, covalent hydrides and metallic hydrides and all hydrides are good reducing agents and they are ideal source for cleaner energy in future. I wish I had time to discuss about hydrogen fuel cells for renewable energy as an alternate source of energy; however, before I complete this course I shall talk about hydrogen fuel cells at some point of time.

With this I conclude the chemistry of hydrogen. In my lecture I will be focusing on the chemistry of group 1 elements that is the chemistry of alkali metals.