Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 46
Metal Hydrides for Solid State Hydrogen Storage - Part-1

In the previous class we have seen the different adsorption based materials, where the hydrogen it gets adsorbed on to the surface of adsorbent and the bond formed was weak Van der Waals bond. Now, in this class we will look at another class of materials, which are absorption based materials. Wherein the bond formed is a stronger bond compared to the materials we have seen earlier.

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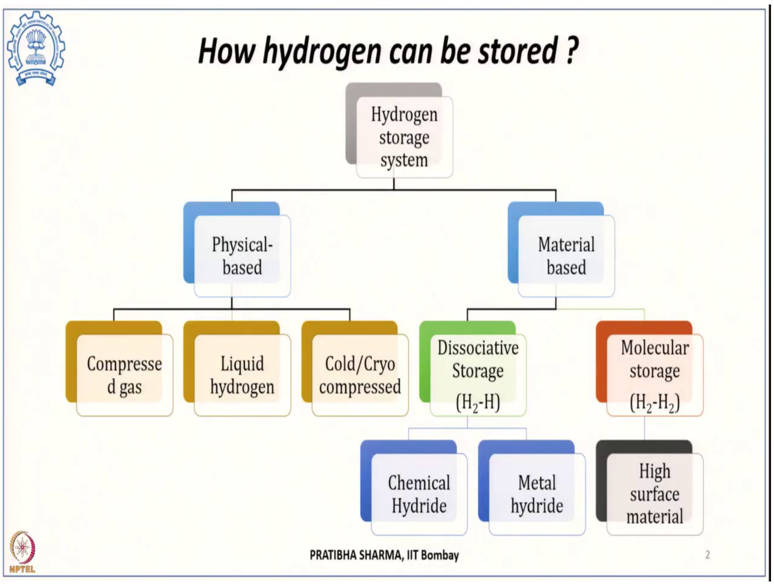

Now, this is just a repetition to mention that different, among the different hydrogen storage materials that we have we will be looking at, we have already seen where we can store hydrogen as a molecule without dissociation it into hydrogen atoms. And that can be done on the surface of high surface area materials or the porous materials with high porosity and pore volume. This we have already studied.

Now, in this class we will start with the other category of materials used for solid state hydrogen storage, where in the hydrogen molecule it disintegrates or dissociates to form hydrogen atom and that hydrogen atom that forms a bond with the material. So, the class of materials that we will look in today's class is metal hydrides.

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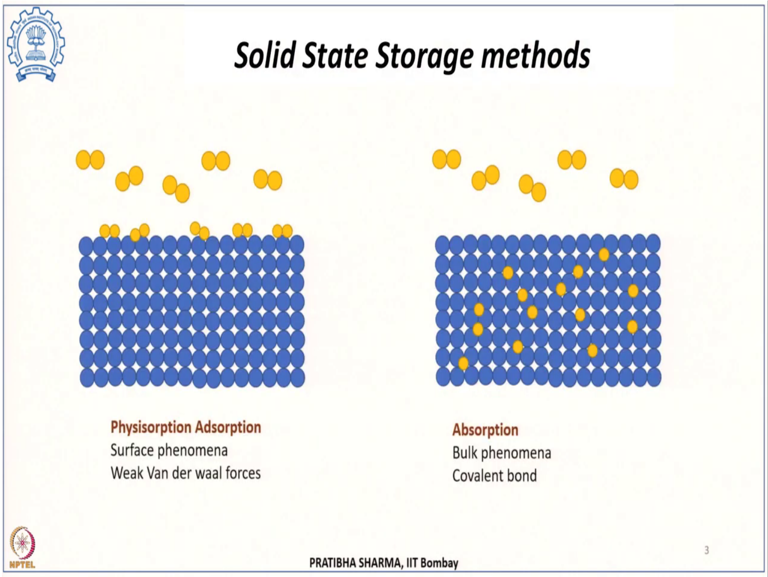

Now, we have already seen that the different solid state storage methods, wherein these could be either physisorption based or adsorption based where the molecule of hydrogen that sits onto the surface of these materials and it forms a weak bond. That we have already studied.

Now, today we are going to look at the absorption based material and here in the molecule it dissociates into hydrogen atom, gets into the interstitial sites and this is a bulk phenomena compared to the adsorption based phenomena, which was a surface phenomenon. And here the bond formed comparatively is a stronger bond.

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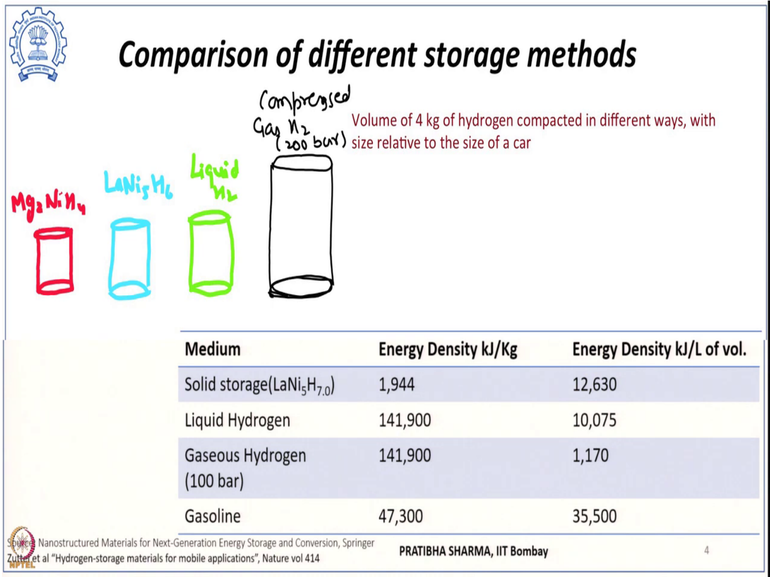

A paper which is reported in nature and this is a very good comparison which shows that, if we have to store hydrogen in different ways, like whether it is liquid state or solid state or gaseous state. How the volume of the tank, how the size of the tank will vary? Now, let us say if we want to store 4 kg of hydrogen for a vehicle which has to be driven for a 400 kilometers and then we can store hydrogen either in a compressed form, then the tank size at when it is storing at 200 bar will look like something this.

If however, we liquefy hydrogen then this will be the tank size; however, if we store in the form of metal hydride that will even reduce. So, on a volume basis this is reduced further if we store in one of the metal hydride form that we are going to learn which is $LaNi_5$ or it can further reduce depending upon what is the capacity of these materials, metal hydrides which we are using.

Let us say if we use Mg_2Ni, then the size further reduces. So, this is a very good pictorial representation of how the size of the tank it reduces as we move from compressed to liquid to solid state storage. Thus, like if we have for example, compared to gasoline, which is having an energy density 47.3 megajoule per kg and an energy density 35.5 megajoule per liter here with solid state storage if we compare, this is volumetric energy density is about 12.63 megajoule per liter. So, this is how the comparison goes.

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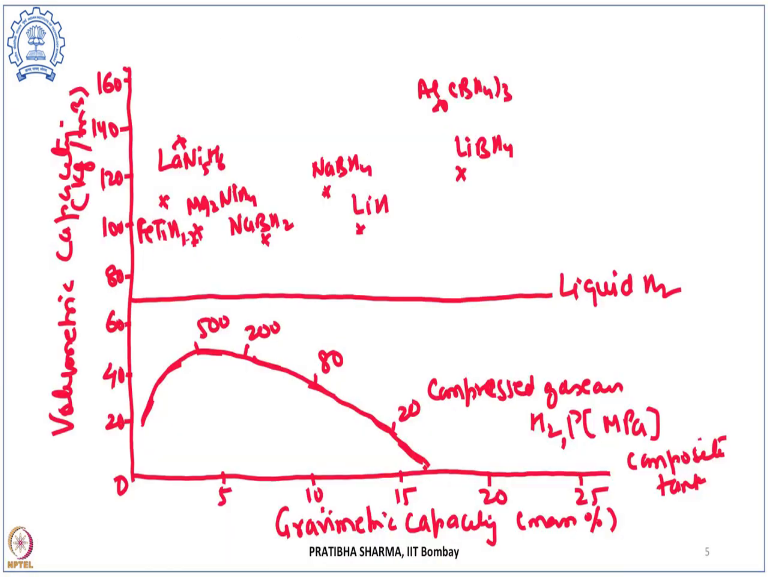

Now, if we plot together the volumetric and gravimetric storage capacity for different ways of storing hydrogen, we can see that the capacities for a pressurized container at a metal tank or type 1 tank this is lower. If it is pressurized with a composite tank, then the capacity of storage it increases.

But compared to the method of either liquid state storage, here in this shows 70.8 is the typical volumetric capacity of hydrogen being stored in the liquid form. So, all the materials based storage or the solid state storage they have a higher volumetric capacity.

But then we will also see that they have, some of the materials they have good gravimetric capacity also, but at the same time the materials which we are going to learn like the metal hydrides they have good volumetric capacity, but because of their own weight the gravimetric capacity is relatively lower. So, the solid state materials we can see definitely they have advantage when it comes to volumetric hydrogen storage capacity, but then depending on what materials we are using their gravimetric capacity definitely vary over a wider range.

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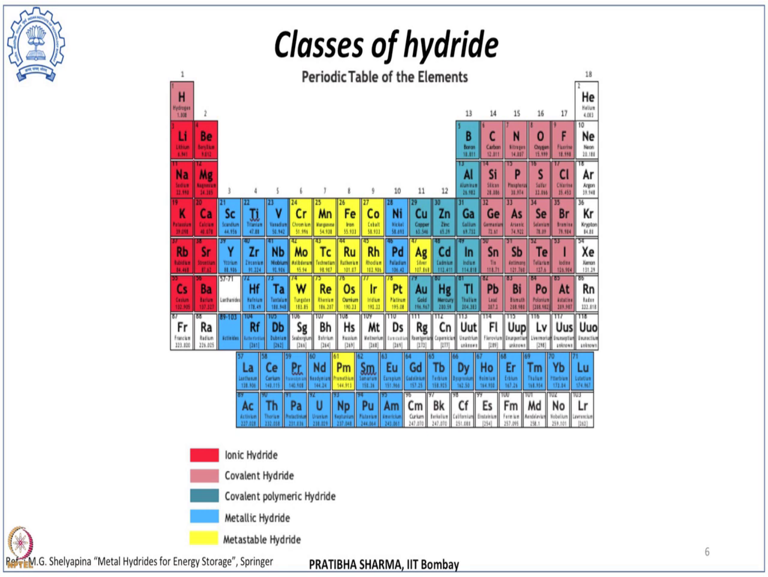

Now, hydrogen in the very first class we have seen that it has one electron and that one electron in the 1s orbital that is reactive and can react with the many elements; so, almost all elements of the periodic table. Now, depending upon what sort of bond it is forming, these can be the hydrides which are formed they can be classified.

Like for example, the elements highlighted in red form ionic hydride, elements highlighted in pink they form covalent hydride, those in blue they form metallic hydride, in teal they form covalent polymeric hydride and those which are in yellow they form metastable hydride. So, depending upon what is the metal to hydrogen or the element to hydrogen interaction the bond formed, we can classify these metal hydrides into different classes.

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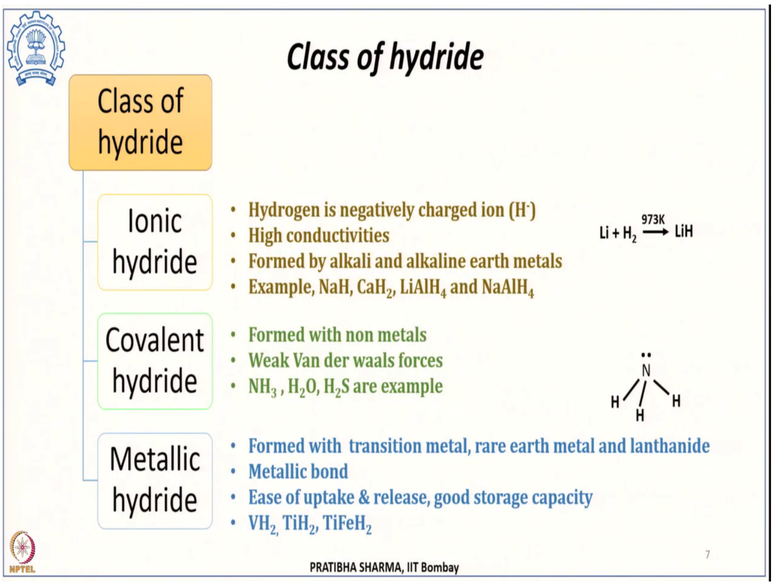

Like the ionic hydrides these are formed by hydrogen being reacting with the alkali or alkaline earth metals. These are usually formed when the electro negativities of the two atoms, these are very much different. The hydrogen in ionic hydrides usually found as negatively charged ion.

And these materials, the ionic hydrides where the element to the hydrogen bond or the bonding is ionic in nature they have high conductivities, either below or at the melting point. Now, typical examples the binary hydrides with which are the ionic hydrides are sodium hydride or calcium hydride or there can be complex hydrides, like lithium aluminium hydride or sodium aluminium hydride.

Now, the other class of such hydrides is the covalent hydride. These hydrides are formed when the electro negativities are almost similar. So, in that case the sharing of electron takes place and then the formation of hydride occurs. So, usually these hydrides are formed with non metals and the interaction is involved is a weak Van der Waals force. As like these covalent hydrides are usually not usable for hydrogen storage.

The reason being most of these hydrides these are having low melting point, these are low melting point solids or low boiling point liquids or these are gases. And they have toxicity, they can have even like low thermal stability. So, as such they are usually not used for hydrogen storage purpose. Some of the typical well-known examples like ammonia, water or H_2S. The next category of such hydrides is the metallic hydride and these metallic hydrides are formed when hydrogen reacts with either transition metals or rare earth metals or lanthanide actinide series.

So, based on the nature of the bond form, these are known as metallic hydrides. So, the bond formed is metallic and because of the very easy uptake and good reversible capacity of these materials, the taking up of hydrogen, release of hydrogen is relatively easier. As such these are most widely used for hydrogen storage application. Some of the examples like vanadium hydride or titanium hydride or titanium iron hydride of this class of hydrides.

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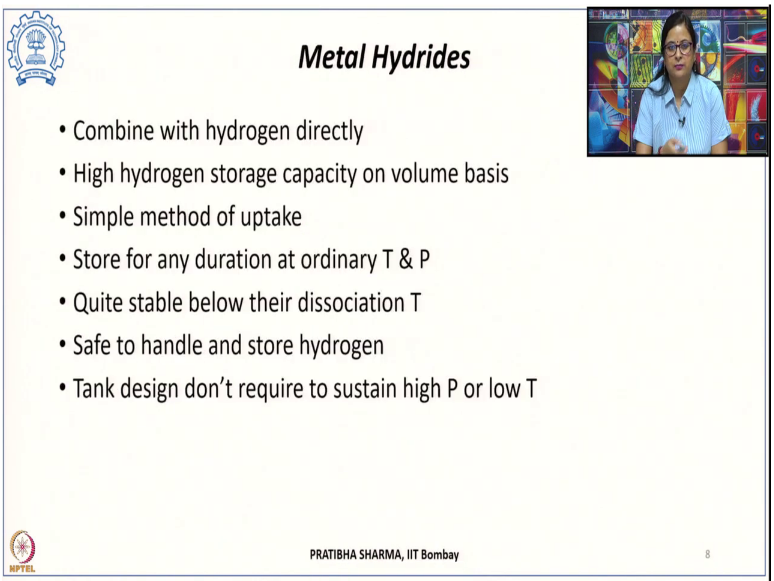

Now, the important category of absorption based materials is the metal hydrides and they are specifically of interest, because of their reversible capacities. These are simple in the sense, they can combine chemically directly with hydrogen when these materials are exposed to hydrogen at certain pressure temperature conditions, they form hydrides. So, the uptake as well as release of hydrogen is simple with these metal hydrides. So, it is a simple method subjected to temperature and pressure changes we can have hydrogen being stored and released from these metal hydrides.

They also have good storage capacity and that is high on the volume basis for such metal hydrides. In fact, this is higher than the liquid state hydrogen storage. This is about 60 percent higher than the liquid storage in case of metal hydrides. At the same time with these metal hydrides we can store hydrogen for any amount of time.

So, for long durations we can store and that too at ordinary temperature and pressure conditions. By ordinary temperature and pressure conditions we mean we have variety of metal hydrides, some of the metal hydrides which can even store at room temperature or ambient pressure conditions. Now, this becomes important when we compare this method of storage as against the compressed state storage, where we have seen that the storage of hydrogen occurs at very high pressure 700 bar.

However, in metal hydrides, we do not require very high temperatures, at the same time the pressure the temperature required are also close to room temperature or it could be higher depending upon which metal hydride we are selecting. But unlike the liquid state storage, when the storage was carried out at 20 kelvin here the temperatures involved are not that low.

At the same time the metal hydrides are very much stable, they can be stored for longer much longer durations and they are quite stable below their dissociation temperature. Important thing here is that until the temperature is raised or let us say if there has been a leak in a metal hydride based storage system, the reaction of release of hydrogen is endothermic.

And because of that a self cooling effect may arise and that will further reduce the temperature of the metal hydride because of the endothermicity of the reaction and that will stall the reaction or the release of hydrogen. So, it is very safe to handle and store hydrogen.

And since we are not using very high pressures or very low temperatures for storing hydrogen as such the tank design are not that sophisticated as we have used in case of compressed hydrogen tank, where the pressure required were high, requirement was very high or like the liquid hydrogen tanks where super insulations were required so as to reduce the heat flow. But since the temperatures of operation and the pressure of operations are moderate here, we do not require such sophisticated tank design.

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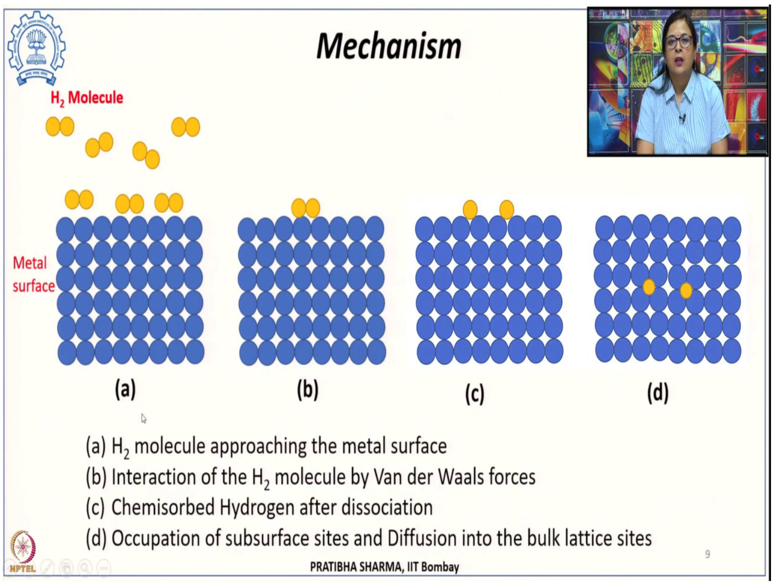

Now, let us look at the mechanism of hydrogen uptake in these this class of material which is metal hydrides. Now, the first figure it shows hydrogen molecule far away from the surface and as it approaches the near to the metal surface, in that case in the second figure this hydrogen molecule it interacts with the surface atoms.

And initially that interaction is by means of weak Van der Waals forces, thereafter the hydrogen molecule it dissociates into hydrogen atoms. And these hydrogen atoms get chemisorbed after dissociation in the third step. After that hydrogen enters into the matrix of the material, it occupies the subsurface sites, further it diffuses deep into the bulk and then it occupies the bulk lattice sites. So, this is how the hydrogen uptake in these metal hydrides take place.

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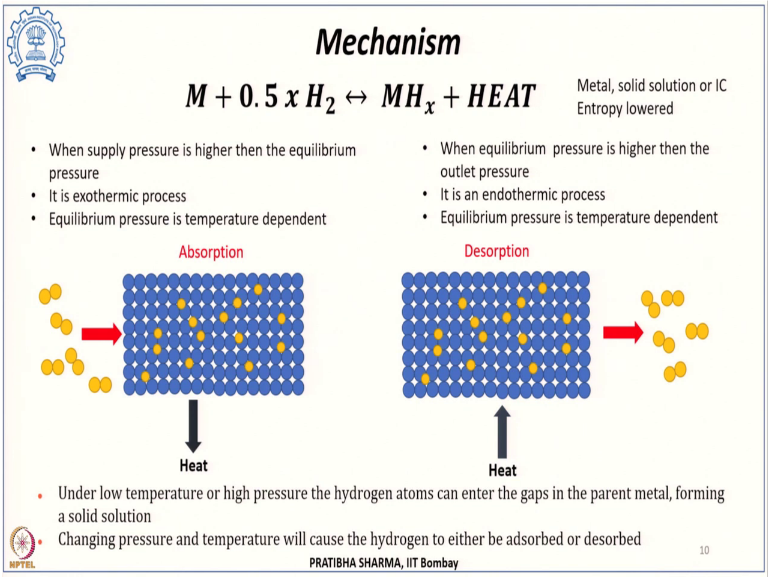

Now, if we see the mechanism of hydrogenation or dehydrogenation in these type of materials, a simple reaction can be written. The metal now this M is either a metal or it could be it could form the metal, it could be a metal hydride, it could be a solid solution or it could be intermetallic compounds that can be used.

So, metal on reacting with hydrogen molecule, like this is $(x/2)H_2$ forward reaction forming metal hydride plus certain amount of heat is being released. Now, since the metal hydride which is being formed, that has a lower energy compared to the metal and the hydrogen molecules. So, a heat is released in the forward reaction. So, the formation of metal hydride from metal and hydrogen is an exothermic reaction, heat is released.

However, the reverse of it that is getting the hydrogen or release of hydrogen from these metal hydrides is an endothermic reaction. That means, we have to supply the heat to the metal hydrides in order to get this hydrogen back. So, the discharging process or the reverse reaction is an endothermic reaction. Now, the conditions of absorption and desorption or the uptake of hydrogen is absorption here and the release of hydrogen is desorption.

So, the conditions are like for absorption, when the supply pressure it is higher than the equilibrium pressure, now what is this equilibrium pressure we will see a little later. So, provided that the supply pressure it is higher than the equilibrium pressure absorption of hydrogen into such metal hydrides take place. And this process as I mentioned it is an exothermic process. However, this equilibrium pressure that also changes, if there is a change in the temperature.

So, this equilibrium pressure also depends upon temperature. Similarly, the desorption is an endothermic process, wherein heat has to be supplied for releasing these hydrogen being stored from the matrix to get hydrogen molecules. So, whenever the equilibrium pressure, equilibrium pressure is higher than the pressure outlet pressure we can get the desired hydrogen.

And this process since we know that it is an endothermic process and all at the same time the equilibrium pressure we know that it is also temperature dependent. Now, changing the pressure and temperature will result into either absorption or desorption of hydrogen, in these materials. Now, let us look at the formation of metal hydrides in little more detail, how the process takes place.

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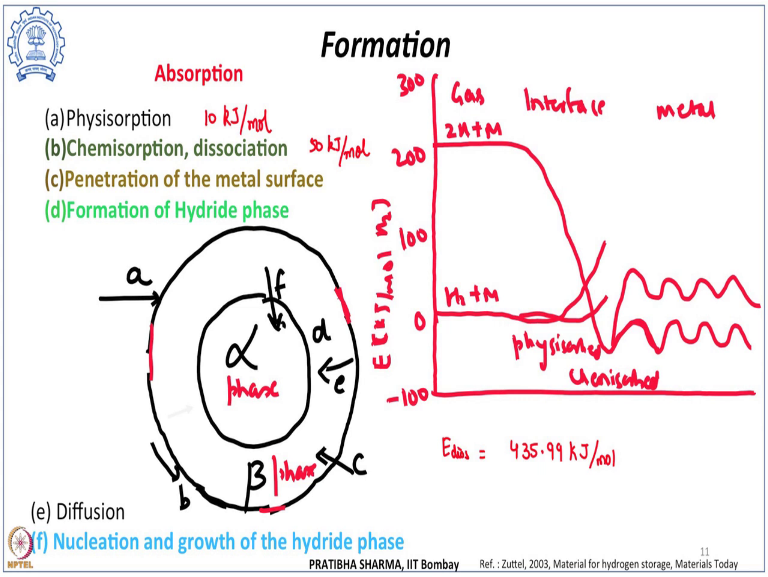

Now, this can be represented on a potential energy diagram, now this is how the distance is increasing from the metal. Now, far away from the metal surface, where there is hydrogen molecule. Now, the if we see the potential energy difference between the hydrogen molecule and when it dissociates into 2 hydrogen atoms, this is 435.99 kilojoule per mole, that is the dissociation energy for hydrogen.

Now, the first attractive interaction that the hydrogen molecule when it approaches onto the metal surface that it observes is the weak Van der Waals interaction. So, that is the weak Van der Waals force it observes and it gets physisorbed onto the surface. So, the first step is physisorption that occurs onto the surface of the metal.

And at that time like the distance is about 1 hydrogen molecule distance and the heat of adsorption for this physisorption is about 10 kilojoule per mole. Now, there is a difference or there is an activation barrier between the hydrogen molecule and its dissociation into hydrogen atoms. Also there is a barrier towards hydrogen being chemisorbed onto the surface of the metal so, chemisorption of the hydrogen.

So, now, these activation energy barriers these needs to be overcome and that then the process occurs. So, that requires sufficient energy to be supplied for overcoming this activation energy barrier. Now, what happens is on to the surface of the metal the hydrogen, once it gets dissociated into hydrogen atoms, that hydrogen atom forms a bond with the surface atoms. And this the electron transfer or the electron sharing occurs with the surface atoms.

And then it gets chemisorbed onto the surface. So, this dissociation and chemisorption occurs at the surface and usually this energy involved is about 50 kilojoule per mole in the process this is roughly around 50 kilojoule per mole. Now, these hydrogen atoms which gets chemisorbed onto the surface these have high surface mobility. And they interact with the other surface atoms they form different phases and thus that gives rise to a very high surface coverage.

Now, after they get chemisorbed, they enter into the subsurface they penetrate inside the metal surface and they enter into the matrix or the interstitial positions that we have seen in the previous slide. They enter into the metal matrix. So, they penetrate into the metal surface and they start to form hydride phase by means of diffusion. And finally, they further diffuse undergo bulk diffusion and then occurs the nucleation and growth of the hydride phase.

So, this is how the entire process of formation of metal hydride is. So, starting from physisorption on to the surface of the metal atom, it undergoes dissociation, chemisorption, penetration into the metal surface. Finally, forming a hydride phase and that hydride phase or the hydrogen diffuses inside forming hydride phase and further the nucleation and growth of the hydride phase occurs.

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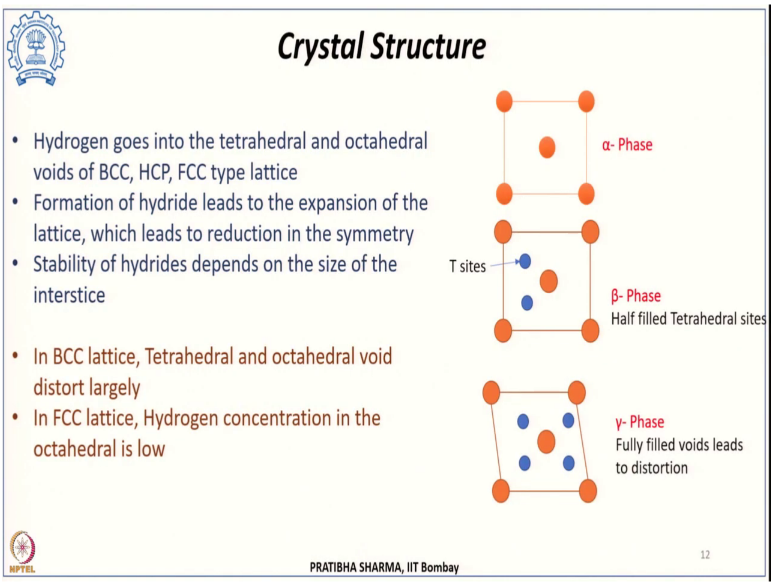

Now, this hydrogen which enters into the metal matrix or the material and sits into the interstitial position, that goes into the different voids of the different lattice; like, they can go into either tetrahedral or octahedral voids of the different structures like BCC or HCP or FCC type of lattice.

Now, when it enters into the lattice, then when the concentration of hydrogen is lower into the metal matrix it exothermically it enters into the lattice and that leads to expansion, that entering into the lattice leads to expansion of the lattice. That also leads to reduction in the symmetry.

Like typically that expansion which is considered is like 2 to 3 angstrom cube per hydrogen atom. Now, thereafter the problem is that the stability of these hydrides that also depends upon the size of these interstitials. Now, in the BCC lattice like, tetrahedral and octahedral voids they get distorted largely and in FCC hydrogen concentration in the octahedral sites is comparatively lower. So, in alpha phase where it forms a sort of solid solution, it starts to form hydride that enters into the tetrahedral sites, these are half filled here in another phase these are fully filled voids and that leads to significant distortion of the lattice.

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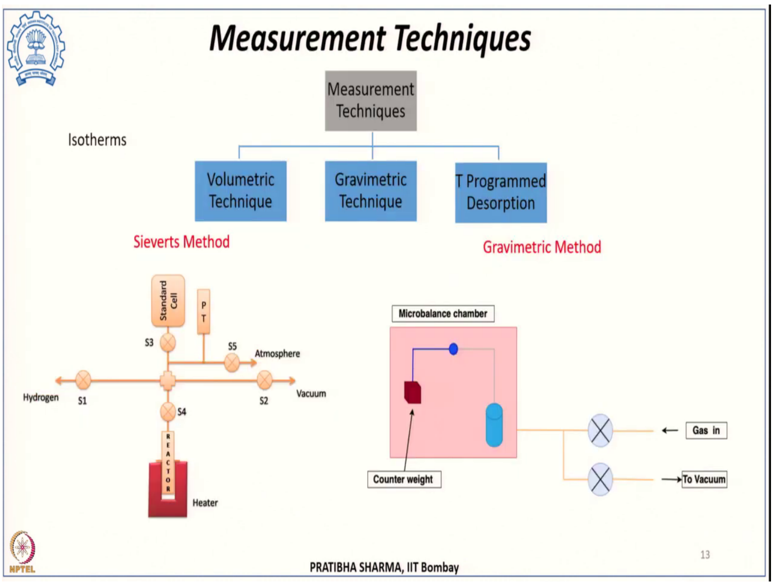

Now, if we want to know how much amount of hydrogen has been taken up by a material, then there are different ways of finding that. So, there are different measurement techniques which exist. Now, these measurement techniques are like they can be divided into either volumetric technique or gravimetric technique or temperature programmed desorption.

Now, we usually in these measurement techniques like the two volumetric and the gravimetric technique, we draw isotherms. Now, these isotherms they are plotted showing the hydrogen uptake for different pressures at constant temperature. Now, in the first method which is the volumetric technique usually what we do is we introduce known a liquids of hydrogen into a known calibrated volume and after that the hydrogen absorption that will cause a decrease in the pressure.

So, because we know the pressure, all the volumes in the systems these are calibrated and we introduce hydrogen at a certain pressure and that reduction in the pressure because of absorption or taking up of the hydrogen by the material will result into a drop in pressure. And that change in pressure is measured at a known volume and then we can use the different state equations to find out how much amount of hydrogen has been taken in.

Similarly, we can do for desorption. So, there was a decrease in pressure during absorption; however, when we supply the required heat, so that the hydrogen comes out in the reverse process that is desorption. The increase in the pressure can be measured and then we can find out the hydrogen released amount. So, this is in the volumetric technique. Now, the another method is the gravimetric method where in instead of recording the change in pressure we see the change in mass.

So, a very well calibrated microbalance and a sensitive microbalance is used for measuring the change in mass subjected to different hydrogen gas pressures and then the major problem lies is that of buoyancy. And the third method is instead of keeping here the samples at constant temperature, here we can change we can see the desorption of the material subjected to different temperatures. So, these are the different methods in which using which we can measure how much is the hydrogen uptake.

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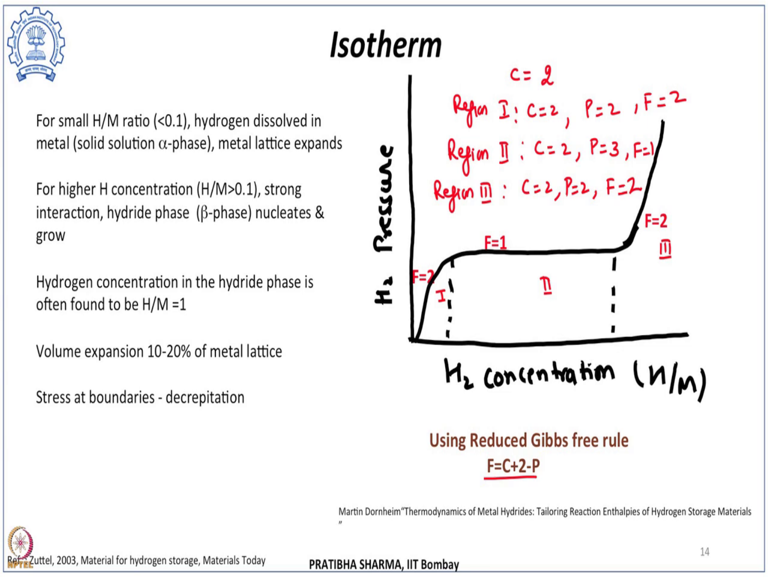

Now, when we measure how much is the hydrogen uptake what we do is we plot like the isotherms which are like this is one of the isotherm an ideal isotherm shown here as a function of concentration of hydrogen so, the amount of hydrogen being taken up by the material H/M, hydrogen by metal ratio and as a function of pressure.

Now, what happens is when we have low amount of hydrogen in the beginning, when we have smaller amount of hydrogen to metal ratio for say less than 0.1, the hydrogen it gets dissolved into the metal and this is a sort of exothermic process and then it forms a solid solution, which is known as the alpha phase. In this process the metal expands, as I mentioned like the expansion is about 2 to 3 angstrom cube per hydrogen atom.

However, what happens is when the hydrogen concentration it increases, it goes beyond say 0.1. So, the strong hydrogen-hydrogen interaction occurs hydride phase starts forming, that starts to nucleate, that starts to grow and that leads to distortion in the metal, distortion in the metal matrix. Now, usually the hydrogen concentration in the hydride phase usually is considered as H/M equal to 1.

Now, it is observed that when this higher concentration the volume expansion of the lattice is significant and that is approximately even 10 to 20 percent of the metal lattice, which introduces large number of large amount of stresses on to the phase boundaries. And because of these stresses the decrepitation of the material can result and the material can become brittle. And so particle size can also reduce.

Now, if we see the typical and ideal pressure temperature isotherm, then there are three regions we can see. The 1st region which is here shown as alpha phase, 2nd where the hydrogen is formed as a this is a solid solution phase, the 2nd region where both the alpha and beta phase are co-existing beta is the hydride phase. So, alpha and beta phase both coexist and the 3rd phase where it is only the beta phase.

Now, if we apply the Gibbs phase rule which is the number of degrees of freedom that is equal to the number of components, here the components are 2. There are 2 components the metal and the hydrogen. So, c is equal to 2 in this case. Now, if we apply the Gibbs phase rule for the 1st region, which is the alpha region. Now, here if we see then this Gibbs phase rule, if we apply there are two phases there is hydrogen and alpha.

So, for the region 1, we have 2 components and then we have 2 phases. If we put in this equation $F = C + 2 - P$ then we get the number of degrees of freedom equal to 2. That means, our concentration varies with the pressure. This is in the 1st region. Now, if we see the 2nd region where the 2 phases are coexisting, region 2 again the number of components is same, but the number of phases are 3.

So, there is hydrogen, an alpha phase and a beta phase. So, as such the number of degrees of freedom for region 2 is 1 and that is why we get a plateau. So, the concentration changes here at a constant pressure and this we will see we will define in the next class that equilibrium pressure is given by this plateau pressure. So, in the 2nd region the number of degrees of freedom is only 1.

However, if we now look at the 3rd region again we have 2 components and 2 phases, hydrogen and beta phase. So, as such the number of degrees of freedom is again 2 and thus there is a rise in the pressure as the hydrogen gas pressure rises and here is also a change in the concentration. So, this is a typical and ideal isotherm. Now, there are irreversibility involved there are several changes are involved in these isotherms that we will see in the next class.

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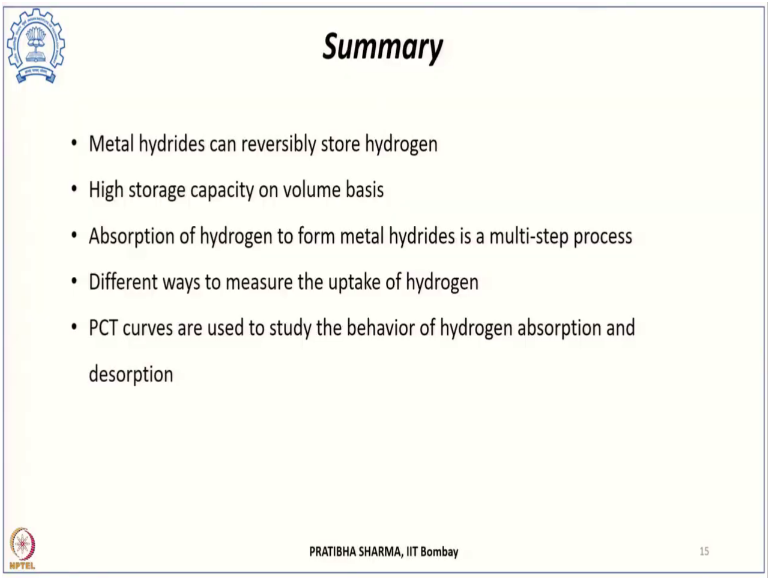

To summarize what we have learnt in this class, we have seen the metal hydrides a special class of material which can store hydrogen reversibly and that is the biggest advantage of these materials. They show a high storage capacity on the volume basis and hydrogen can absorb on these metal hydrides and we have also learned what are the different steps involved in absorption of hydrogen in these materials.

We have seen that there are different ways in which we can measure the uptake of hydrogen, like the volumetric method or the gravimetric method or it could be TPD. And thereafter we can get the different PCT curves. So, the series of PCT curves we will see in the next class. These PCT isotherms or curves these are used to study the behavior of hydrogen absorption and desorption. And what more information we can get from these PCT that we will see in the next class.

Thank you.