Hydrogen Energy: Production, Storage, Transportation and Safety

Prof. Pratibha Sharma
Department of Energy Science and Engineering
Indian Institute of Technology, Bombay

Lecture - 44

Fundamentals of Adsorption based on Materials for Hydrogen Storage

In the earlier classes we have studied in very much detail the compressed state hydrogen storage and liquid state hydrogen storage. Where the goal has been towards making the hydrogen molecules as close as possible to store it compactly increasing the volumetric density and at the same time using as little additional material as possible. Like for this purpose we have to provide certain amount of work to compress the hydrogen gas or to liquefy it or maybe we have to reduce the repulsion between the various molecules by using different materials.

Now there is another method of hydrogen storage which is a hybrid of both these compressed as well as liquid state that is known as cryo compressed method of hydrogen storage. Now this is having advantages of both the methods compressed and liquid state storage and the tanks are designed in such a way that they can hold compressed cryogenic fluids. Now, since we have already studied in very much detail the compression liquid state storage we will just touch upon this particular method.

Now in this method of cryo compressed storage, there are several prototypes that have been also been demonstrated like BMW demonstrated a prototype where they could achieve using a cryo compressed tank gravimetric capacity of 5.48 percent and volumetric energy density of 4 mega joules per liter and a boil off of 4 to 7 grams per hour. There was another prototype which was demonstrated wherein hydrogen was stored at 40 to 80 kelvin and 300 bar.

Now the method of storage of cryo compression has advantage in the sense that we can curb the boil off losses. Now the inner tank which is a type 3 tank which could hold pressure say of 300 or 350 bar is having an outer vacuum and then multilayer insulation so, as to prevent the heat losses as well. Now, in this method of storage since we are not going to very high pressures like 700 bar in case of compressed hydrogen tank we have already seen as such the strength of material or there is a saving in terms of the material.

While we are also not considering storage at liquid hydrogen temperatures 20 kelvin rather the temperatures are above that temperature as such the super insulation requirement that also is relaxed and we can save in terms of that. At the same time as we have seen in the liquid state storage that because of the heat loss, because of evaporation there is a pressure build up and liquid hydrogen tanks they do not have as much of strength to bear very high pressures.

So, at that time boil off or loss of hydrogen is unevitable, but in case of cryo compressed tank since the inner tank can hold a higher pressure as such the dormancy period can be extended and boil off can be curved. So, as such there are several advantage of cryo compressed storage and that is another way of storing hydrogen. Now in this class we are going to start with the solid state hydrogen storage methods.

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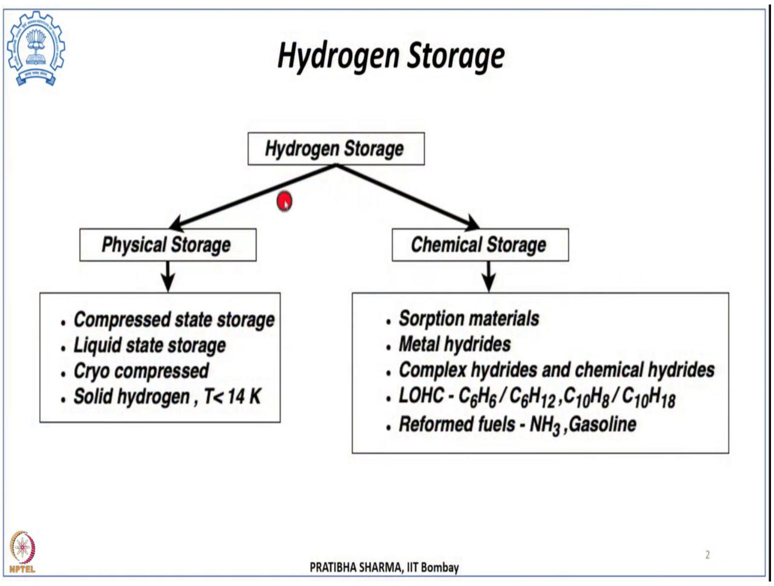

Hydrogen Storage

Hydrogen Storage

Physical Storage

- Compressed state storage
- Liquid state storage
- Cryo compressed
- Solid hydrogen , $T< 14$ K

Chemical Storage

- Sorption materials
- Metal hydrides
- Complex hydrides and chemical hydrides
- LOHC - C_6H_6/C_6H_{12}, $C_{10}H_8/C_{10}H_{18}$
- Reformed fuels - NH_3, Gasoline

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Broadly, hydrogen storage can be categorized into physical storage and chemical storage. Now in physical storage hydrogen is constrained by the boundaries of a storage media or storage tank or storage vessel. The difference is that the hydrogen in this method of storage do not interact with the storage media.

So, this method of storage we have seen like compressed state storage, liquid state storage, cryo compressed method of storage and then if you further cool it down below the boiling point like the liquid state storage temperature was 20 K. If we further cool it down to less than 14 K, then we can achieve solid hydrogen. So, herein in this method hydrogen is stored in the molecular form and it is confined within the boundaries of a storage vessel or container with which it does not interact or it is not desired that it should interact.

In the other method of storage which is chemical storage. In this particular method of storage hydrogen atoms or molecules they in fact, interact with the storage media or they react or they form a bond with the storage material which is being used for storing hydrogen as such forming certain compounds or a different material. So, in the chemical storage method comes the different sorption based materials that we are going to start to learn today.

Metal hydrides, complex hydrides and chemical hydrides liquid organic hydrogen carriers including C_6H_6, C_6H_{12}, $C_{10}H_8$, $C_{10}H_{18}$ then there are reformed fuels different reformed fuels can also be used like converting it into form of ammonia or different Fischer tropsch liquids and then can be stored.

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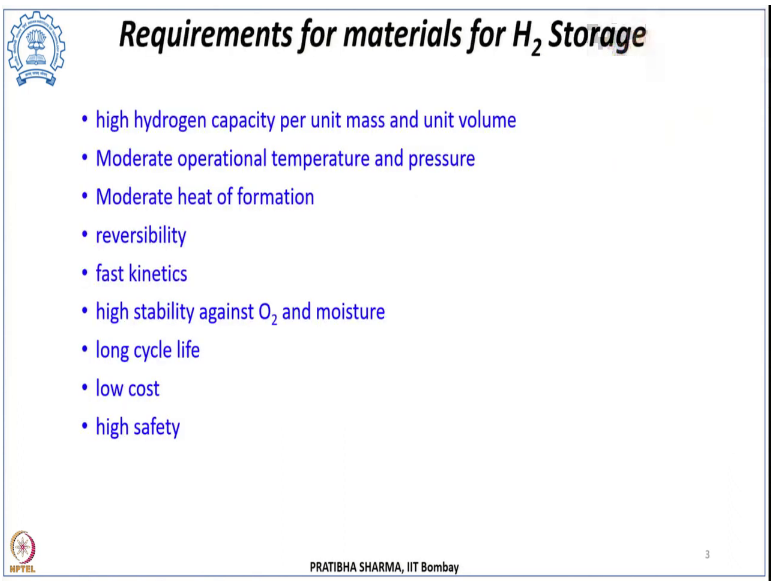

Requirements for materials for H_2 Storage

- high hydrogen capacity per unit mass and unit volume
- Moderate operational temperature and pressure
- Moderate heat of formation
- reversibility
- fast kinetics
- high stability against O_2 and moisture
- long cycle life
- low cost
- high safety

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Now, we will start with the adsorption based material today; now, when we when it comes to solid state hydrogen storage there are certain characteristics, which are required for the materials if they are to be used for hydrogen storage. So, the basic requirements for material to be used to be hydrogen storage is that the material should have high hydrogen capacity and that capacity should be both per unit mass and per unit volume and that can be expressed in the form of either gravimetric energy density or gravimetric hydrogen storage capacity or volumetric storage capacity.

So, the gravimetric capacity can be defined as the mass of hydrogen being stored divided by the sum of mass of hydrogen and the storage media. And same way volumetric storage capacity can be defined as mass of hydrogen per unit volume of the storage media. It should be able to store hydrogen under moderate conditions of temperature and pressures unlike the compressed state storage where the pressures were very high 700 bar or 350 bar or either it should be very low temperatures like in case of liquid hydrogen which was 20 K.

So, the operational temperatures and pressure should be moderate. There should be moderate heat of formation and desorption sorption desorption should be associated with such materials by moderate heat of formation we mean the thermal management should not be very restrictive or very strict this is because if undergoing a reversible hydrogen storage. If certain amount of heat is also released during the cycling process in that case that should not be very high and if that is very high there are lot of thermal management issues will be there,

The material should be reversible. By reversible we mean, once the hydrogen is used from such materials then putting back hydrogen to get the initial state of material should be relatively possible. By reversibility we mean there are ways of doing making the material reversible or there are it could be either on board reversible it could be off board reversible.

By onboard reversible we mean that at a certain temperature and pressure if we put hydrogen into the material which has already desorbed hydrogen then it should take back that hydrogen and get back to its initial state that is we can do on board. However, there are certain materials that we will see that take up hydrogen again at very high temperatures or pressures or very strict conditions.

They can also undergo certain set of chemical reactions to so, that the used material gets back to its initial state; that means, they can be off board reversible. But reversibility is a must for sustainable hydrogen storage. The next characteristic required is fast kinetics. Now fast kinetics plays an important role when we are getting hydrogen from the such materials so, that is when the hydrogen is being released or when hydrogen is being charged into such materials.

So, that becomes important during the refueling of such materials or during the withdrawal of hydrogen. These materials should be highly stable against the environmental conditions, they should be stable against the oxygen, they should not form oxide, they should be stable when in the presence of even moisture and that means, that it should not degrade or the performance should not degrade when exposed to such conditions; that means, they should have a long cycle life.

So, there should not be any performance degradation with cycling, they should be definitely low cost and high safety. Although, this is a long list for any material to satisfy; however, there are different materials which can be used for hydrogen storage.

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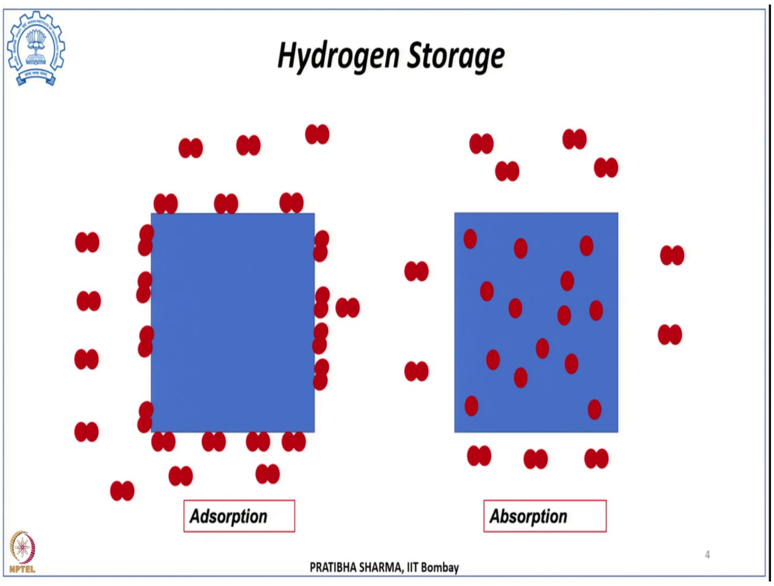

Hydrogen Storage

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Now in this class we are going to learn in more detail the fundamentals of hydrogen storage in physisorption based materials. Now, before we go on to looking at those materials and the concepts, let us understand some of the basic things that we have already studied in the earlier classes like what is adsorption what is absorption.

Now the first figure which shows adsorption when the atoms or molecules of a substance here in our case it is hydrogen, when it sticks on to another material surface and either it gets sticks adhered or it gets accumulated on the surface of another substance, in that case the process is known as adsorption.

So, the molecules which adhere on to the surface are known as adsorbate and on the surface of which the substance on the surface of which these molecules adhere is known as adsorbent. Similarly, if the molecules or atoms of one substance they enter into another substance. So, the blue colored is another substance if they enter into another substance they permeate into this substance.

Then they get assimilated into the internal volume or they get completely diffuse into the volume or internal structure or dissolved into this material in that case the process is known as absorption. So, the material which gets into is known as absorbate it and the material into which these molecules get inside is known as absorbent in our case these red colored molecules these are representing hydrogen gas.

However, the blue colored matrix is the material or the hydrogen storage material into which the hydrogen gas dissociates and enter in the atomic form so, this is what is absorption. So, we can see that adsorption is surface phenomena while absorption is bulk phenomena.

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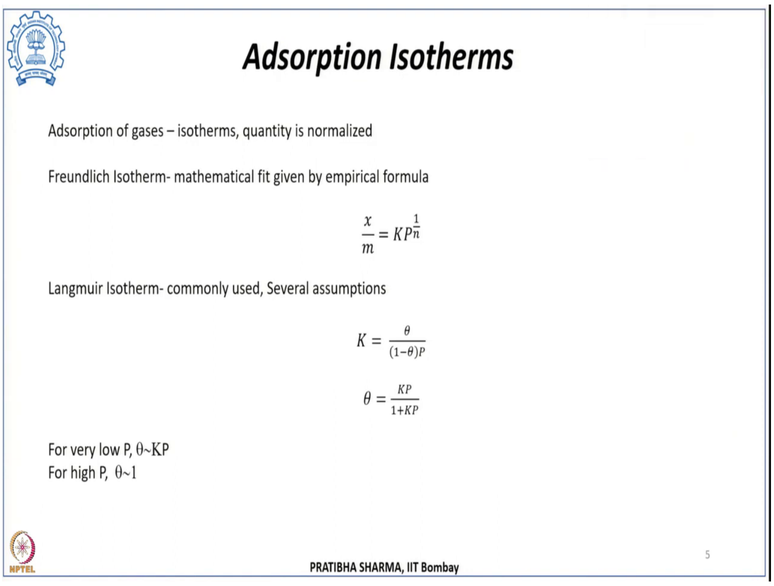

Adsorption Isotherms

Adsorption of gases – isotherms, quantity is normalized

Freundlich Isotherm- mathematical fit given by empirical formula

$$\frac{x}{m} = KP^{\frac{1}{n}}$$

Langmuir Isotherm- commonly used, Several assumptions

$$K = \frac{\theta}{(1-\theta)P}$$

$$\theta = \frac{KP}{1+KP}$$

For very low P, $\theta \sim KP$
For high P, $\theta \sim 1$

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Now in order to describe the adsorption of different gases there are different isotherms that can be plotted. Now these isotherms in fact, represents the amount of adsorbate on the absorbent as a function of pressure at a constant temperature.

Now, this amount of adsorbate that has to be normalized this quantity needs to be normalized with respect to the mass of absorbent and this is required if we want to compare the different materials. Now there are different isotherms which are available where which we can quantify the amount of adsorbate, which is stored in a particular sorbent material.

Now the Freundlich was the first one. So, Freundlich-Coster they came up with the isotherm Freundlich isotherm and that was in fact, a mathematical fit that they provided to the adsorption isotherm and that was fitted using an empirical relationship. So, this empirical relationship is x/m, with where x is the mass of the adsorbate, m is the mass of the adsorbent and that is equal to $KP^{1/n}$, where, P is the gas pressure, K and n these are respective coefficients constants which are associated with a pair of adsorbate and adsorbent.

The another isotherm set of isotherm is being provided by Irving Langmuir and Irving Langmuir was the first one to derive scientifically these adsorption isotherms and in fact, he modeled the adsorption of gases on to the solid surface and this was in fact, kinetically based and this was derived using statistical thermodynamics.

However, there were several assumptions which were there in Langmuir isotherm and these assumptions are like the adsorption sites these are all equivalent and the each adsorption site is occupied by a single molecule, there are no phase transitions, the surface is energetically homogeneous at the same time the adsorbents they do not interact the adsorption takes place in the form of a mono layer. So, these are several assumptions all these to be followed are very difficult.

The reason being the surfaces may have their own imperfections, the adsorbent may not be always inert, it may not be possible that always a mono layer is formed there could be multilayer formation, which is actually taken care of in the next set of adsorbents which is BET by means of BET theory. At the same time, it is also the first molecule when it gets adsorbed and the last molecule when it adsorbs the conditions not be similar.

So, it is not possible always that all these assumptions may hold true. Now the relationship between K and Θ here is that $K = \Theta/[(1-\Theta)\times P]$. So, P is the pressure, Θ is the surface coverage. So, Θ, surface coverage is given by $KP/(1 + KP)$. Now for very low pressures theta is approximately equal to KP and for high pressure, Θ is approximately equal to 1 in the Langmuir isotherm.

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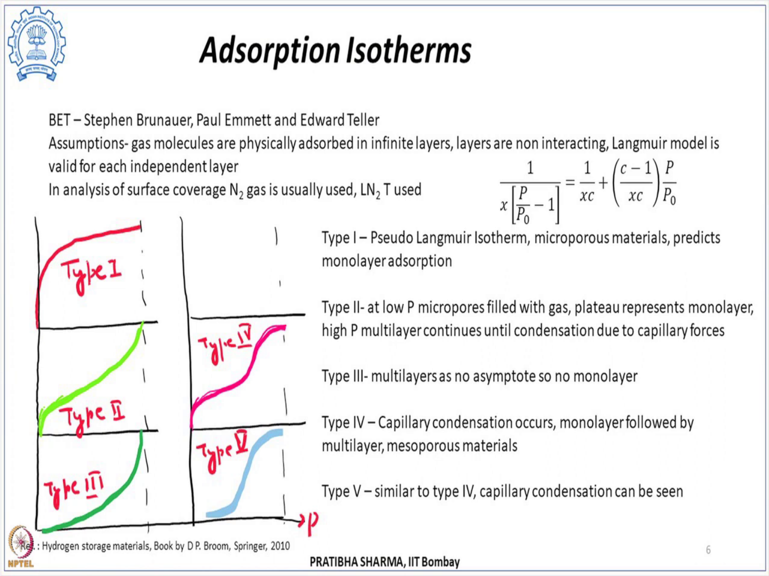

Adsorption Isotherms

BET – Stephen Brunauer, Paul Emmett and Edward Teller

Assumptions- gas molecules are physically adsorbed in infinite layers, layers are non interacting, Langmuir model is valid for each independent layer

In analysis of surface coverage N_2 gas is usually used, LN_2 T used

$$\frac{1}{x\left[\frac{P}{P_0}-1\right]}=\frac{1}{xc}+\left(\frac{c-1}{xc}\right)\frac{P}{P_0}$$

Type I – Pseudo Langmuir Isotherm, microporous materials, predicts monolayer adsorption

Type II- at low P micropores filled with gas, plateau represents monolayer, high P multilayer continues until condensation due to capillary forces

Type III- multilayers as no asymptote so no monolayer

Type IV – Capillary condensation occurs, monolayer followed by multilayer, mesoporous materials

Type V – similar to type IV, capillary condensation can be seen

Ref.: Hydrogen storage materials, Book by D.P. Broom, Springer, 2010

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The another set of adsorption isotherm was being given by Stephen Braunauer Paul Emmett and Edward Teller and this is the BET theory. Now, this BET theory is in fact, an extension of Langmuir theory and it is applicable for multilayer adsorption. The basic assumption that goes in the BET theory is that the gas molecules they are physically adsorbed in the form of infinite number of layers.

So, as such it is applicable for multilayer adsorption these layers are non interacting and individual layers for them Langmuir model is applicable is valid for each of these independent layers. Now, when we analyze the surface coverage to form the isotherms, the gas which is used usually is nitrogen.

This is because it is inert pure and then cost effective; however, at the ambient conditions at the room temperature pressure conditions since the adsorption involves very weak forces as such very small amount of gas gets adsorbed. So, as such to get a detectable amount of gas being adsorbed liquid nitrogen temperatures are being used.

Now, the expression that relates is $1/[x\ (P/P_0 - 1)]$, where P/P_0 is the relative pressure, x is the amount getting adsorbed is equal to $1/xc + ((c - 1)/xc)(P/P_0)$. So, this is a relative pressure where c is a coefficient, which is related to the heat of adsorption. Now from the BET theory there are five different types of isotherms which are possible.

Now if we look these one by one then Type-I isotherms where we can see at lower pressure there is a steep rise in the mass of gas adsorbed and then it flattens to form a plateau. Now this Type-1 is a sort of Pseudo Langmuir isotherm and this holds true for microscopic materials; however, it predicts the formation of a mono layer adsorption. The second isotherm is we can see a sharp rise steep rise at the very low pressures then a sort of linear rise and then it peaks.

So, this Type-2 isotherm this is at low pressure there is sort of micro pores filling that is taking place with the gas being adsorbed then a slight plateau that is arising because of the mono layer being formed and at higher pressures their multilayer adsorption occurs and that multilayer adsorption continues until there is a condensation, which takes place due to capillary forces. So, this is the Type-2 type of BET isotherm. Type-3 we can see that there is no plateau being observed, there is no asymptote also.

So, in this there is a multilayer adsorption only that takes place there is no mono layer formation or we can say from the beginning the multilayer formation adsorption takes place, it begins before even the mono layer adsorption gets over. Type-4 type of isotherms these represent here in fact, the capillary condensation occurs a monolayer adsorption takes place and that is at a lower pressure and that is followed by a multilayer adsorption. And this is usually obtained in case of mesoporous material. The last one which is Type-5 this is almost similar to Type-4 and here also capillary condensation can be seen.

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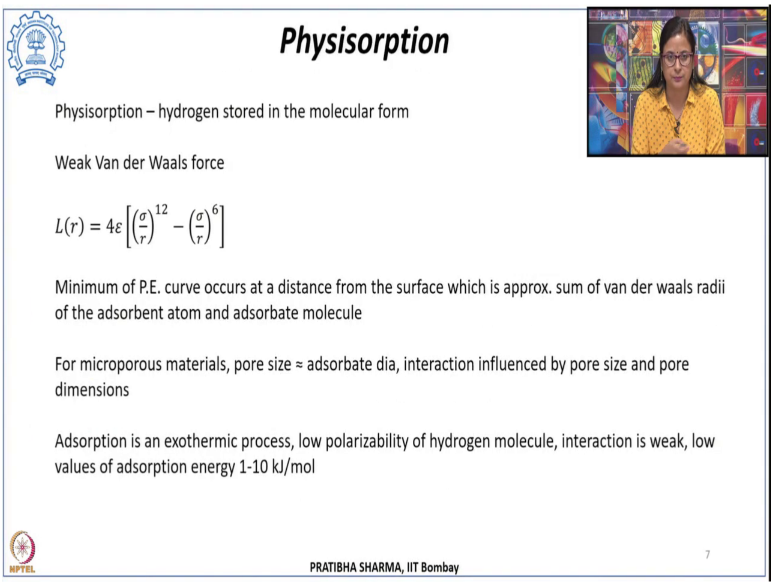

Physisorption

Physisorption – hydrogen stored in the molecular form

Weak Van der Waals force

$$L(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Minimum of P.E. curve occurs at a distance from the surface which is approx. sum of van der waals radii of the adsorbent atom and adsorbate molecule

For microporous materials, pore size ≈ adsorbate dia, interaction influenced by pore size and pore dimensions

Adsorption is an exothermic process, low polarizability of hydrogen molecule, interaction is weak, low values of adsorption energy 1-10 kJ/mol

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Now these are the different isotherms if you want to measure the hydrogen uptake in case of physisorption based material then these isotherms are much helpful. Now when it comes to hydrogen storage in the sorbent materials physisorption is the basic process. In physisorption hydrogen is stored in the molecular form and this is stored in the molecular form on the surface of the different sorbents materials and these are interacting with the surface of the sorbent by means of weak Van der Waals forces.

Now these weak Van der Waals forces these arise because of the dipoles which are created because of the random fluctuations in the charge distribution that results into the weak Van der Walls forces or we can say the absorption and the attraction between the different gas molecules and the surface or repulsion between the gas molecules can be represented by the potential energy curve, which is given by the Lennard Jones potential.

So, the potential is given by 4ε, this is the depth of the potential well times so, r is the distance between the atom and the sorbate, ε is that finite length distance at which L(r) becomes 0. $[(\varepsilon/r)^{12} - (\varepsilon/r)^{6}]$this is the potential energy relationship.

Now if we draw this potential energy relationship its minima occurs at a distance from the surface, which is approximately equal to the sum of the radii of both adsorbate and adsorbent. So, it is minima occurs at a distance from the surface which is sum of Van der Waals radii of the adsorbent atom and the adsorbate molecule.

Now, when it is a micro porous material in that case the pore size is very small and we know that it is say less than 2 nanometer in that case the pore size is almost equivalent to that of the adsorbent dia. Now in that case the interaction gets very much affected by the pore size and pore dimension. Physisorption is we have already seen that it is a surface phenomenon.

Now in surface phenomena what is the requirement is that a high specific surface area should be there, it is dependent upon what is the pore geometry, what is the pore dimension, what is the pore volume, what is the porosity of the material all these determine the adsorption of the adsorbate onto the adsorbent.

Also this adsorption process is an exothermic process and this is because of the low polarizability of the hydrogen molecule the interaction which is taking place by means of weak Van der Waals forces is weak in the case of physisorption or sorption based materials.

Now, that means, adsorption energy is very small, the value of adsorption energy typically lies in the range of 1 to 10 kilo joules per mole. This is unlike in case of the materials which work on the principle of chemisorption where the bond formed is more stronger and there the adsorption energy can be even an order of magnitude higher than this particular adsorption energy.

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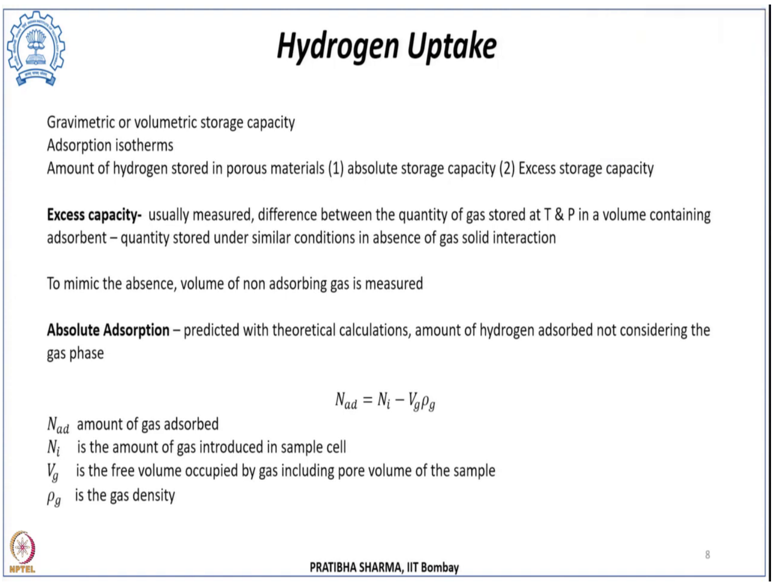

Hydrogen Uptake

Gravimetric or volumetric storage capacity
Adsorption isotherms
Amount of hydrogen stored in porous materials (1) absolute storage capacity (2) Excess storage capacity

Excess capacity- usually measured, difference between the quantity of gas stored at T & P in a volume containing adsorbent – quantity stored under similar conditions in absence of gas solid interaction

To mimic the absence, volume of non adsorbing gas is measured

Absolute Adsorption – predicted with theoretical calculations, amount of hydrogen adsorbed not considering the gas phase

$$N_{ad} = N_i - V_g \rho_g$$

N_{ad} amount of gas adsorbed
N_i is the amount of gas introduced in sample cell
V_g is the free volume occupied by gas including pore volume of the sample
ρ_g is the gas density

Now if we want to measure the hydrogen uptake there are different ways of measuring hydrogen uptake either it could be gravimetric or volumetric storage capacity could be monitored. So, as I mentioned that the gravimetric capacity is mass of hydrogen being stored divided by the mass of hydrogen stored plus the material mass or the mass of the storage media and volumetric storage capacity is the mass of hydrogen stored per unit volume of the storage media.

Now, in order to find the hydrogen uptake in these porous materials the best way could be to find the adsorption isotherms. Now this adsorption adsorbed amount of hydrogen in these porous materials can be mentioned by either finding out the absolute storage capacity or excess storage capacity.

So, these are the terms that can be used for deciding on to how much is the hydrogen uptake in a particular class of material. Now this term access storage capacity is in fact, what we measure experimentally using the different experiments and this excess capacity if we try to define then it is the difference of the gas which is being stored at a particular temperature and pressure in a volume which already has adsorbent minus the quantity of hydrogen which will be stored in the same condition same temperature, pressure, same volume in the absence of gas solid interaction.

Or we can say that excess capacity is the amount of hydrogen being stored at a certain temperature pressure in a volume wherein adsorbent is there in the presence of gas solid interaction minus in the absence of gas solid interaction. Now, but the how to measure this quantity which is stored in the absence of gas solid interaction and that is very difficult to obtain.

Now in order to mimic that quantity which will be corresponding to absence of gas solid interaction what is being done is non adsorbing gases taken, which does not interact with the solid surface and the volume of this non adsorbing gas is being measured to find the second term in the excess capacity. The another term is absolute adsorption. Now this absolute adsorption as such is difficult to find out this is actually predicted by means of different theoretical calculations and what it tells is the amount of hydrogen which is adsorbed when we are not considering the hydrogen in the gas phase.

So, this adsorbed amount of gas $N_{adsorbed}$ can be given by $N_i - V_g\rho_g$. N_i is the amount of gas which is introduced into the sample cell the total hydrogen which is introduced into the sample cell minus the free gas which is there in the sample set. So, this is given by the product of free gas volume occupied by the gas inside the pore volume of the sample times the gas density. So, that gives the absolute adsorption.

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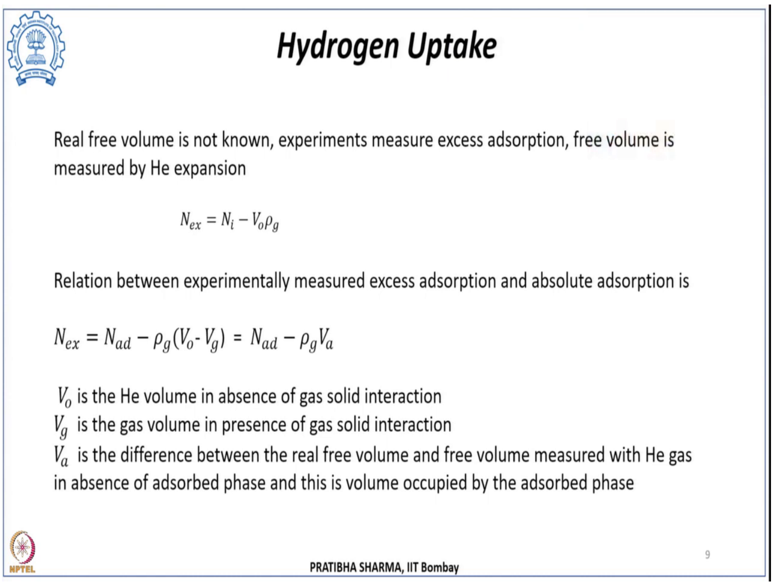

Hydrogen Uptake

Real free volume is not known, experiments measure excess adsorption, free volume is measured by He expansion

$$N_{ex} = N_i - V_o\rho_g$$

Relation between experimentally measured excess adsorption and absolute adsorption is

$$N_{ex} = N_{ad} - \rho_g(V_o \text{-} V_g) = N_{ad} - \rho_g V_a$$

V_o is the He volume in absence of gas solid interaction
V_g is the gas volume in presence of gas solid interaction
V_a is the difference between the real free volume and free volume measured with He gas in absence of adsorbed phase and this is volume occupied by the adsorbed phase

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Now it is very difficult to find out what will be the real free volume it is not known. What experimentally we can find out is excess adsorption now to find out the free volume we usually do the helium expansion and find out. Now what we get is the excess adsorption that excess adsorption is given by $N_i - V_0\rho g$. Where N_i is the hydrogen which is introduced into the sample cell or the measuring cell minus V_0 is the helium volume which is being taken up in the absence of gas solid interaction because that is a non adsorbing gas and the gas density ρ_g.

So, this is the excess adsorption and the earlier one was the absolute adsorption. So, there is a relationship between the experimentally measured excess adsorption and the absolute adsorption and that is given by the excess adsorption is given by the absolute adsorption $N_{adsorbed} - \rho_g \times V_0 - V_g$ where, V_0 we have seen this is the helium volume in the absence of gas solid interaction while V_g is the gas volume in the presence of gas-solid interaction.

So, the difference of two can be represented by Va and this is the difference between the real free volume and the free volume which is measured by the helium gas in the absence of adsorbed phase. So, this is the volume occupied by the adsorbed phase and this is how we can calculate the hydrogen uptake.

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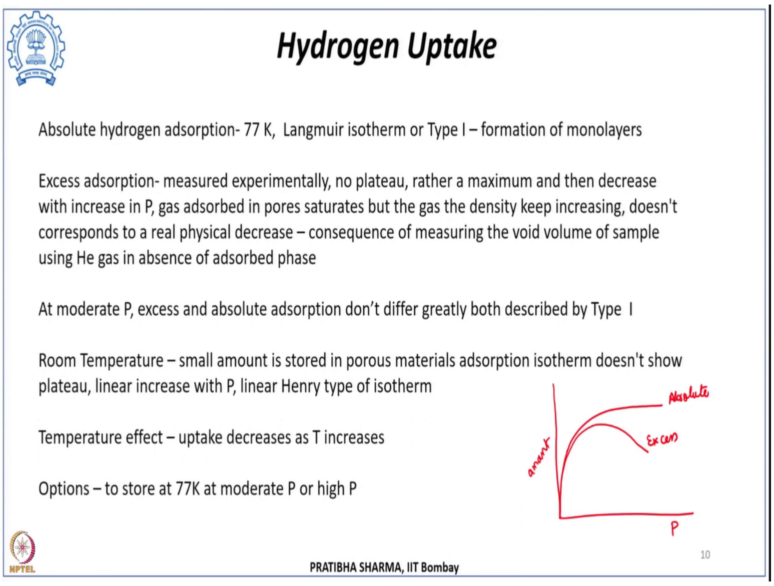

Hydrogen Uptake

Absolute hydrogen adsorption- 77 K, Langmuir isotherm or Type I – formation of monolayers

Excess adsorption- measured experimentally, no plateau, rather a maximum and then decrease with increase in P, gas adsorbed in pores saturates but the gas the density keep increasing, doesn't corresponds to a real physical decrease – consequence of measuring the void volume of sample using He gas in absence of adsorbed phase

At moderate P, excess and absolute adsorption don't differ greatly both described by Type I

Room Temperature – small amount is stored in porous materials adsorption isotherm doesn't show plateau, linear increase with P, linear Henry type of isotherm

Temperature effect – uptake decreases as T increases

Options – to store at 77K at moderate P or high P

Now if we see the absolute hydrogen uptake at a temperature of 77 K that is actually given by a Langmuir isotherm or Type-I type of isotherm and that shows the formation of monolayer. So in fact, if we plot the amount of gas adsorbed as a function of pressure at a particular temperature then we will see there is a sharp rise and then it becomes constant.

So, that is the absolute adsorption at 77 K. So, it follows a sort of Langmuir type of isotherm or Type-I type of isotherm and that shows the formation of monolayers; however, the other term which we have studied is the excess adsorption. This excess adsorption we know that can be measured experimentally; however, the variation does not show a plateau. So, there is no plateau if we plot the excess adsorption initially it remains consistent with the absolute adsorption; however, it peaks and then it decreases.

So, there is a peak and thereafter there is a decrease in the adsorption. So, maxima is reached and this decrease in the with the increase in pressure and then thereafter it is the decrease with the increase in pressure. Now, it can also become 0 or it can also become negative. Now as such it is not corresponding to the real physical decrease. So, this is because the gas is adsorbed in pores.

So, this nature is because the gas is adsorbed in the pores and that it gets saturated, but the gas density it keeps on increasing. So, actually this decrease does not corresponds to real physical decrease of the adsorption capacity rather it is the consequence.

Because we have measured the void volume of the sample using the helium gas expansion that was in the absence of adsorbed phase that is the reason why we are getting this dip in the adsorbed amount. At moderate pressures both we can see that the absolute and excess they are similar they coincide there is not much of difference between the two and they can directly be represented by the Type-I type of isotherms; however, there is a difference that occurs at a higher pressure.

So, we can see the deviation that takes place at a higher pressure. For absolute there is a plateau is reached; however, for excess after peaking that there is a dip in the excess adsorption. Now this was the effect of pressure now if we consider these adsorptions we are considering at a liquid nitrogen temperature; however, if we consider at room temperature then the amount of hydrogen uptake will be very small.

So, a very small amount of hydrogen will be there being stored in such porous materials and the adsorption isotherm in that case will not show any plateau there will be in fact, a linear rise that will be observed and that will continue to even higher pressures and if it is room temperature adsorption then the isotherm, which is we obtained is a linear isotherm that is a Henry type isotherm that we will be getting.

Now, the temperature effect for most of these type of physisorption based material as the temperature increases the adsorption capacity decreases and the reason is since the hydrogen gas molecules they are attached on to the surface of sorbent by means of weak Van der Waals forces at a higher temperature or at room temperature.

The thermal motion energy is also equivalent to the Van der Waals forces and as such the capacity or the adsorption potential decreases as the temperature increases. However, if we want to store hydrogen in an appreciable amount either we have to reduce the temperature of the gas like 77 K liquid nitrogen temperature is preferably used for storing hydrogen in such adsorption based materials at ambient pressure.

So, if we see the excess adsorption capacity of many of the materials this peaks at around 77 kelvin and maximum like 4 MPa it can we can obtain the highest capacities. The other choice if we want if we do not want to reduce the temperature or we do not want to cool it down or have insulations then the other method could be pressurize the gas so, as to increase the adsorption potential.

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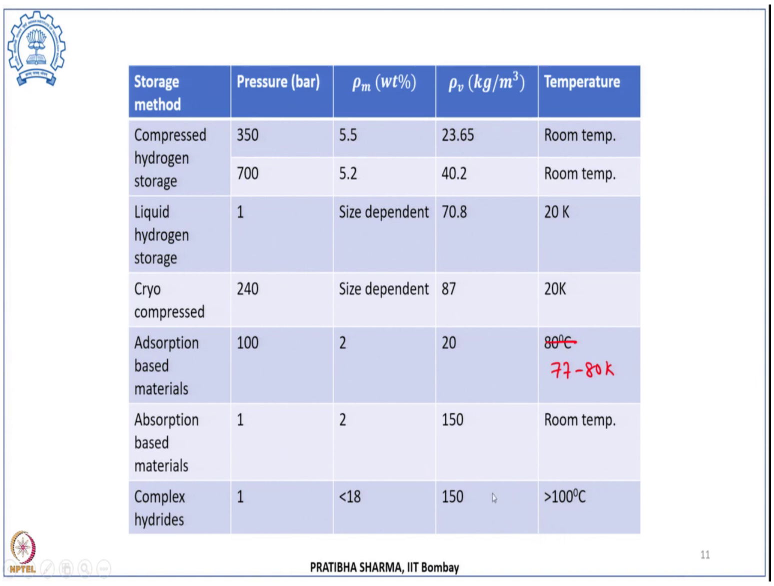

Storage method	Pressure (bar)	$\rho_m\ (wt\%)$	$\rho_v\ (kg/m^3)$	Temperature
Compressed hydrogen storage	350	5.5	23.65	Room temp.
	700	5.2	40.2	Room temp.
Liquid hydrogen storage	1	Size dependent	70.8	20 K
Cryo compressed	240	Size dependent	87	20K
Adsorption based materials	100	2	20	~~80⁰C~~ 77-80K
Absorption based materials	1	2	150	Room temp.
Complex hydrides	1	<18	150	>100⁰C

PRATIBHA SHARMA, IIT Bombay

Now if we quickly compare with the other methods like we have already seen the compressed hydrogen storage at 350 bar and 700 bar then the weight percent gravimetric capacity can be 5.2 to 5.5 weight percent, volumetric capacity can reach to 23.65 kg per meter cube when compressed hydrogen is stored at 350 bar and for 700 bar, this is 40.2 kg per meter cube, but these both these are at room temperature condition storage.

In case of liquid hydrogen storage when the pressure is held at 1 bar the gravimetric capacity will depend upon size the volumetric density could be 70.8 kg per meter cube and the temperature of storage we have already seen is 20 K. Same was for cryo compressed that the temperature of storage can be 20 K or higher the volumetric capacity could even reach 87 kg per meter cube, which is even higher than the liquid storage when it is being stored at 240 bars with the materials, which we are going to see adsorption based materials the pressure can be at 100 bar the gravimetric capacity is 2 weight percent.

Typically, 2 weight percent there are materials which have higher than 2 weight percent as well the volumetric density is 20 kg per meter cube and the temperature could be 77 to 80 kelvin. Now there are other class of materials which are based on chemisorption there could be absorption based materials where the pressure could be close to 1 bar or even higher the gravimetric capacity that can be reached is 2 weight percent.

And the volumetric energy density volumetric capacity is 150 kg per meter cube and they can store hydrogen even close to room temperature or higher temperature. Complex hydride again they can store at 1 bar or higher pressure their gravimetric capacity less than 18 percent, volumetric capacity even 150 kg per meter cube can be achieved but the temperature of operation will be greater than 100 degree centigrade.

So, there are different class of materials in the todays class like we have seen the different fundamentals associated with these materials what are the ways in which we can measure, what are the ways in which we can express the hydrogen uptake, these type of materials they have certain advantages as against the chemical hydrides that they have a very fast kinetics.

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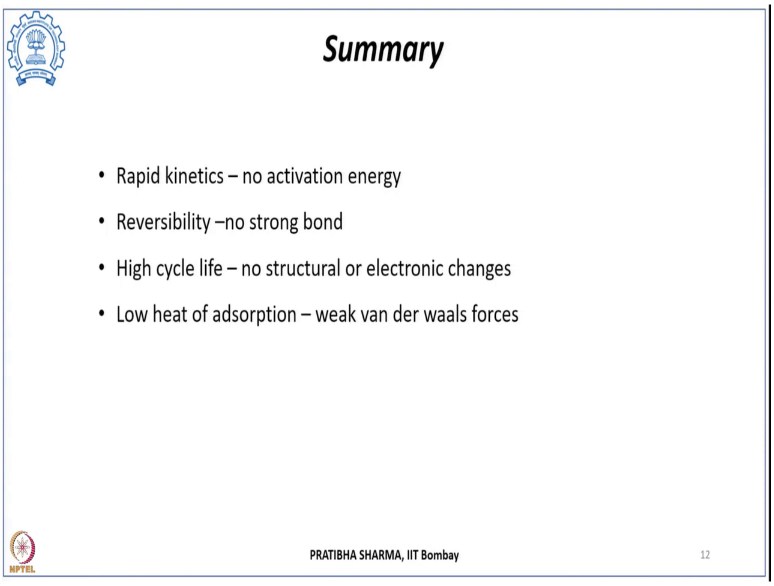

Summary

- Rapid kinetics – no activation energy
- Reversibility –no strong bond
- High cycle life – no structural or electronic changes
- Low heat of adsorption – weak van der waals forces

PRATIBHA SHARMA, IIT Bombay

The reason for fast kinetics of such materials is, since there is no activation energy involved as such the uptake of hydrogen or release of hydrogen is very quick because the bond in these materials is a weak bond. Now the reversibility of these materials is very high. The reversibility is an important criterion when selecting a hydrogen storage material, the reason of reversibility is there is no strong bond with the storage media.

Now, this is an advantage for such materials that we can get a reversible hydrogen store. At the same time the cycle life of such materials is very good because there is no diffusion of hydrogen into the molecule, no permeation of molecule, no formation of strong bonds into the molecule, not getting up into the internal structure of the sorption materials.

So, as such there is no structural changes which take place or no electronic changes that can occur, no perturbation of the electronic charge that can occur as such the cycle life of such materials is higher. There is a low heat of adsorption which is associated which is with the weak Van der Waals forces and that becomes an advantage when it comes to designing a hydrogen storage tank. So, in the next class we will see in more detail what are these materials, what are the different classes of such materials which store hydrogen by means of physisorption.

Thank you.