Cryogenic Hydrogen Technology
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Week - 04
Lecture 20
Adsorption Storage of Hydrogen

Welcome to this lecture on cryogenic hydrogen technology. We were talking about the storage of hydrogen. And in this lecture, we will look into the sorption storage of hydrogen. And basically, in this lecture, we will be talking on the adsorption storage and in general adsorption and desorption. Later on, we will look into the specifically for hydrogen and what are the adsorbents necessary for this storage of hydrogen. And the keywords are like adsorption, desorption, equilibrium adsorption capacity.

So, let us start with the nomenclature where we will find that this adsorbent, it is basically the solid porous surfaces and which will be exposed to the gases or the liquids. And particularly in this application, we will be looking into the gas adsorption. And adsorptive is basically the molecules which are or gas or gas molecules which are not which are not adsorbed yet, but they are present in the gaseous form. So, this adsorbent is as I have said earlier that it is a micro porous or porous or basically ah there we will define what is micro porous and what is mesoporous or macro porous.

But these adsorbents are basically porous substances and these are the gaseous molecules or it may be in the liquid phase. So, these are adsorptive, but the moment when they are going inside these pores and they are attached to the surface by weak Van der Waals gas in Van der Waals equation or force rather weak Van der Waals force, it is called adsorbate ok. So, from adsorptive it is becoming you know adsorbate. So, these are the different nomenclatures we will be following in this lecture. And we have let us look into the definition of adsorption and desorption basically.

So, the moment you know it is coming this is what is you know from the gaseous state it is coming and getting adsorbed and they become adsorbate. And when this adsorbate is moving out of this these pores and they are going into the gaseous phase again then it becomes desorption. So, this is what is adsorption and desorption I am sorry ah. So, this is when it is going out of this ah what is called the pores to the gaseous phase it is called desorption. So, this adsorption is basically a phenomena ah we see that it is molecules getting adhere to the surface by weak Van der Waals force.

And the reverse is when it is there these adsorbed molecules are coming out of the solid surface and going to the gaseous phase they are called it is called this phenomenon is known as a desorption. So, there is a basically ah dynamic ah situation that some molecules will be getting adsorbed, some molecule will be getting ah desorbed. So, it is not like that which are sticking you know on the surface it is like more like when we talk about the liquid vapor ah equilibrium that some of the molecules will always leave the ah top liquid surface and they will go to the ah vapor phase. And similarly, some of the vapors will you know they condense and come to the liquid phase. So, like that there would be an equilibrium and here ah similar in a similar fashion. So, if we ah you know take it as an equivalent that this is a kind of liquid phase this is also you know in the adsorbed phase we call it. So, in the adsorbed phase and the desorbed phase ah there is a kind of ah equilibrium. So, some molecules are always getting adsorbed and some of them are getting desorbed. So, there is a dynamic equilibrium and that is what is adsorption equilibrium we call it. So, with these definitions and the nomenclature let us go ahead.

So, here ah the I mean ah what is a porous adsorbent first let us look at there are plenty of ah adsorbent which are we are familiar with knowingly or unknowingly we use of ah I mean we use them as a very common one is of course, the silica gel which is used particularly to absorb the moisture ah. And for ah I mean we have already given that example earlier that when we buy any costly electronics goods and a computer or camera like that you will find a small pouch containing ah very small salt like structure or white colored you know structure and those are basically the silica gel to capture the moisture. And again, that silica gel is ah I mean porous ah material we are also familiar with ah the I mean in our household we have the water purifier there also we have you know charcoal adsorber, but that charcoal and this charcoal is you know charcoal for ah adsorbing the gaseous nitrogen is quite ah different we will come to that part later on. So, let us look at the pore size and the pore volume distribution. So, what is the pore size there are ah I mean depending on the dimension of the pore ah we have a micro pore mesopore and macro pores.

So, the micro pore is basically ah the one with which you know the dimension is less than the pore size is less than 20 angstrom unit and for mesopores it is 20 to 500 angstrom and ah for macro pores it is more than 500 angstrom unit. So, we will follow this nomenclature for this ah pore size and a typical ah I mean micro pores element for ah this gaseous hydrogen adsorption ah is it will look like this where it it gives you a pore volume ah versus pore width ah I mean this is on this scale on the x axis you find that 5, 10 this numbers are nothing, but the pore and the corresponding value on the y axis gives you the pore and it is unit is cc per gram. So, it is it may look you know surprising that the volume we are talking about, but it is unit is cc per gram basically this talks about ah the cc or volume per gram of activated carbon this is basically this is for activated carbon and this activated carbon looking at this pore size distribution we can tell confidently that this is basically ah micro porous ah substance or micro porous adsorbent because we find that the majority of the pores or pore volume ah belongs to you know between ah 5 to 8 or 5 to 7 angstrom unit. So, ah basically this is a kind of micro porous, but you see when it is going higher and higher there are this pore sizes are you know slowly I mean there it is dispersed and we do not have higher or macro pores or mesopores are mainly absent here. So, ah what is the I mean advantage with these microporous adsorbents it is basically ah if we now if we compare it with our say domestic activated carbon which are used for purifying water you will find that if we employ those kinds of adsorbent ah for this ah purpose you will find that the hydrogen is not ah adsorbed to a good extent.

So, it is basically because the ah activated carbon that we use in our household is basically ah mesoporous or macro porous because the type of ah you know purification that is necessary or the pollutant that we want to capture in the those activated carbon are basically large in size whereas, this ah the gas when we want to ah you know adsorb they are quite small in size and obviously, we need micro porous material to you know adhere get them adhere to this ah surface. So, this is the typical I mean pore size. So, whenever we ah want to ah adsorb ah this ah basically adsorption storage of hydrogen we look for particularly in the carbonaceous material like activated carbon or charcoal. So, we must look for the pore size and there are ah I mean we will talk about that how do we get into this kind of ah you know pore size distribution how do we get. So, this will tell you ah as I told you that the pore volume and the I mean with the pore ah width.

So, this will tell us the nature of the adsorbent way that we can utilize it for you know storing the hydrogen storing hydrogen or not. So, now let us look what is the amount of ah gas or hydrogen that can be captured in ah activated carbon or any adsorbent. So, there are isotherms. So, this is another I mean ah definition of isotherm is basically if we look at that tells you ah at a particular temperature iso iso means same and therm is the temperature. So, at a particular temperature what is the adsorption capacity and how it varies with the ah pressure.

So, that tells you know this whole graph will tell you about that adsorption capacity and basically there are different type of I mean isotherms depending on the type of adsorbents. As a matter of fact, you will find that there are 5 to 6 ah nearly number of or types of adsorbents ah this isotherms which we are talking about is basically Type-1. So, this for a Type-1 ah adsorbent this typical ah adsorption capacity versus pressure this pressure is of course, you know normalized with respectance to a standard value like atmospheric pressure and all. So, we will have this kind of graphs you know ah particularly at different temperature. So, ah the I mean this is at a low temperature this is ah I mean higher than T1 and T3 is again higher than ah both T1 and T2.

So, here that means, T1 is less than T2 less than T3. So, which means that as we are increasing the pressure and as we are lowering the temperature the adsorption capacity is ah becoming larger. So, but with the very high pressure I mean when we increase the pressure beyond a certain point we will find that there is not much increase in the adsorption capacity we call it that it has come to a saturation level. But in this range when we you know from 0 or say you know when we start pressurizing or charging it we find that the gas you know adsorption capacity is increasing ah gradually and if we are able to maintain that temperature at a particular value we find that it is coming to a saturation after some time when the pressure is increasing beyond a certain value. Similarly, we will have a different curve like this ah when we have a different temperature.

So, the adsorption capacity again if you look at the ah unit you will find that it is given in either mole per mole of carbon or it is the gram of adsorbate ah say for example, if we are storing nitrogen this much mole of nitrogen and per mole of ah activated carbon or the adsorbent. Similarly, it can also be written in terms of this many grams per gram of activated carbon or kg of you know hydrogen ah per kg of carbon like that it goes and this pressure will be either in MPa or in atmosphere or bar depending on the ah I mean choice of the units. So, now, ah if this is the isotherm ah how do we explain it I mean how do we ah is is there any equation which will be able to ah tell us what is the Type-1 adsorption capacity or every time we need to ah experimentally determine this adsorption capacity. So, let us look into that what are the isotherms we have one such isotherm is called the what is called is Langmuir isotherm. Here you can see that this green coloured molecules which are adhered to the surface ah of the adsorbent in the porous body it is called ah I mean it is in the adsorb phase, but there is also ah gaseous phase it is not these molecules are not in ah I mean adsorbed state.

$$n_t = n_a + n_g$$
$$n_a = n_t - V_g \rho_g$$

So, there is only mono layer has been formed which is you know on the ah particularly in the in the it is in the adsorbed state, but rest of it is in the gaseous state which has not been ah adsorbed. So, now, the total adsorption is ah nt equals to the adsorbed state plus the gaseous state. So, we have to find out say if we want to know what is the adsorption capacity. So, this is the total and minus ah this gaseous state which is in the gaseous condition and we ah Vg minus ah Vg into ah rho g that is ah the density of the gas at that temperature and pressure. So, this is what is the ah the condition that this only the mono layer will be formed and only one layer of adsorbent adsorbate can you know ah is possible there are no successive layers ah that is possible in the adsorbent.

$$\theta_1 + \theta_0 = 1$$

So, with this ah assumption we can look at the ah basic ah I mean the equation ah which is possible for the Langmuir isotherm. So, here ah you know if this is from the kinetic ah theory of gases we can say that ah N_A is the Avogadro number. So, the number of molecules striking ah the adsorbent surface ah depending on the pressure and temperature are given by this relation and ah this is ah the number of molecules striking part centimeter square per second. Now here if we say that ah if there is if this total surface if the surface is not entirely covered say this θ_0 is basically the uncovered surface ah and that is you know if we multiply it with this factor. So, that is is the striking rate per centimeter square and we have θ_0 empty or un unoccupied space or you know that is still it is not yet ah the monolayer has not yet formed and ah obviously, you can understand that ah the total ah if we say that there is θ_1 which is occupied and θ_0 that is unoccupied some total would be ah 1 ok this is the in the dimensionless form.

So, this is ah then you know we can ah simplify it with this ah this we have taken as a constant because this we are talking about an isotherm. So, T is constant R is constant this M bar is also constant molecular weight Avogadro number is ah constant. So, this is the basically k is a constant. Now ah if ah you know this is the rate at which the molecules are striking on the surface. So, there is a probability A1 that it will adhere to the surface.

$$N_{des} = N_m \theta_1 v_1 e^{-(\frac{E}{RT})}$$

So, the number of molecules getting absorbed ah is ah you know k into P into θ_0 into A1 where A1 is the coefficient of ah condensation coefficient we can say or the sticking coefficient we can say. And ah similarly ah ah on the other side as we have learned that there would be a tendency for the molecules to come out of the surface and that will be given by Nm into θ_1 $v1$ e to the power minus E by RT. So, E is the ah basically the adsorption ah energy and Nm is the number of adsorbate molecules ah on the complete monolayer. So, if there is a monolayer we will have Nm number of molecules and θ_1 is the fraction of surface which is covered ah with the adsorbed molecule and R is of course, the gas constant T is the temperature and $v1$ is the ah frequency vibrational frequency in the normal ah to the surface. So, this has a you know these molecules are ah vibrating it is not there you know completely stationary.

$$\theta_1 = \frac{KP}{1 + KP}$$

So, they are getting adhere to the surface and this is the vibrational frequency of the molecules when it is you know ah normal to the surface. So, in equilibrium what will happen ah this will be ah in ah I mean there will be a dynamic equilibrium and that is how these two are equal. And in that case ah we have if we ah you know put this condition now what we want to know is how much is the adsorption capacity depending on the I mean if if we put this relation from here to here we will be able to find out this θ_1 and with this substitution k equals to this value we can say that θ_1 is KP by 1 plus KP. So, this is what is called the Langmuir isotherm. So, it is frequently in use particularly for Type A and there are I mean according to this Langmuir isotherm we can also try to calculate ah the what is called the Langmuir surface area ah, but it is not that popular ah there are different models ah according to that ah you know we change we actually calculate the surface area for this small I mean these adsorbents.

$$\theta_1 = \frac{N}{N_m} = \frac{W}{W_m} = \frac{KP}{1 + KP}$$

$$\frac{P}{W} = \frac{1}{KW_m} + \frac{P}{W_m}$$

So, here we can with a little you know modification we can rearrange this equation ah this N by Nm the theta ah is θ_1 that is what we have talked about. So, Nm we have said that this is a monolayer number of molecules in the monolayer and N is the at any time what is that number of molecules that is present and W is the corresponding weights in the monolayer as and the uncovered surface. So, this is what is that coverage ah part and if we rearrange it we can have this ah you know graph and as a function of pressure if we plot this we will find that the slope and the ah you know intercepts would be like this if we plot it P by W as a function of P then the intercept is 1 by KWm and this is ah you know the slope is 1 by Wm. So, from this slope and you know sample surface area we can find out once we know that Wm from the slope ah we can calculate the ah sample surface area here N_A is again the Avogadro's number and this a is basically the cross-sectional area of the adsorbate whereas, this M is the molecular weight of the adsorbate. So, you can understand that we can have an estimate of the ah Langmuir surface area though it is based on certain assumption that there is only monolayer formation, but ah you know ah there are different models.

So, like other isotherms one popular isotherm is BET isotherm where ah this ah you know restrictions which has been imposed on the ah Langmuir isotherm that there is only monolayer possible no successive layers are possible. So, that restriction if we release and if we assume that ah you know only the ah the ah surfaces which are most energetic will be first covered and the successive layers are possible and the last layer which will be you know in the dynamic equilibrium with the gas in that case this is the BET isotherm will come and from the BET isotherm ah we generally do the surface area calculation just you know in the similar procedure will be followed and most of the time this adsorbents will be characterized by this BET surface area. So, then we have ah the two other isotherms popularly known as DR equation or the DA equation where this is this a is basically ah related to the adsorption potential.

$$A = -RT\ln(\frac{p}{p_s})$$

So, that means, it is an assumption that this molecules or gas molecules are assumed that they are in a ah potential well and that is the adsorption potential given by this value minus RT ln P by Ps and there are two isotherm based on this two often ah we you know ah use this DR and DA equation sorry this would be DA equation ah and this two equations are ah often used to characterize the adsorption of hydrogen and in activated carbon or in other carbonaceous materials. So, we will not get into the details of this ah those who are interested can just have a look into this two books ah for ah this adsorption isotherms.

So, now, let us get back to the equilibrium adsorption capacity. That means, as you can understand that we were increasing the temp I mean pressure and ah say we have a bottle filled with ah adsorbent and we are charging it with the gas or adsorb ah bit. So, in that case ah what will happen ah it will keep on increasing its capacity. So, at a particular temperature if we are able to maintain the temperature of the bed ah we need to know what is the amount of gas that we can you know you know stored in that or basically we are trying to densify the gas. Say for example, here in this case ah we are trying to store hydrogen in activated carbon or in other carbonaceous material.

So, we need to know what is the amount of gas that we will be able to ah you know ah store in a particular amount of adsorbent. What is the adsorbent that will be necessary to store this ah hydrogen? So, if we want to look at we have ah you know ah different ah adsorption capacity ah measurement techniques of this is called the ah volumetric technique, then there is another called gravimetric technique. We will not get into that details again. So, here we will talk about the volumetric ah I mean ah method this is simple and you have two adsorbent I mean two bottles of similar size one is empty the other one is filled with ah you know the adsorbent. So, this one is with the adsorbent and ah initially we ah evacuate we ah keep this valve closed and we evacuate it. So, that this adsorbent is fresh and ah then we close this valve or vacuum pump then ah independently this you know this is called the gas volume. This will be ah filled in with a particular pressure the high pressure P1 and this volume is V0 is known. So, we know what is the amount of gas which has been kept in this ah reference volume. So, this is the valve we will open to allow the gas to come in and then ah this valve is of course, closed and once we it has come to this volume we will ah store this valve and open this valve. So, what will happen the gas from the high pressure in a bottle will come to the adsorbent bottle there that bottle there would be you know an equilibrium between this two.

$$n_1 = \frac{P_1 V_0}{ZRT_1}$$

$$n_2 = \frac{P_2 (V_0 + V_g)}{ZRT_2}$$

$$n_{ex} = \frac{n_1 - n_2}{M_{ads}}$$

So, once that equilibrium is reached ah we can ah you know this pressure will be same on both sides and we know ah what is the volume V0 we have to estimate ah this adsorbent volume or the ah porous volume I mean basically if we look at this is the I mean an ah enlarged part of a particular say you know portion. So, here these are the adsorbents this we have assumed that they are granular in nature. So, we have this ah inter particle volume that’s where you know this gas is getting stored. So, we need to find it out and we will talk how do we do that. So, once we know this Vg or the gas volume we can say that the number of molecules you know ah in ah I mean in the adsorb state is basically P2 into V0 plus Vg by Z R T2 and we are maintaining the T1 equals to T2.

So, we have an iso-thermalizer to maintain this temperature. So, initial number of molecules are known to us now what we have is you know a situation where ah this two has come to an equilibrium and the number of molecules now have reduced because this pressure ah you know from P1 it has ah reached to a lower pressure P2 and from there we can now calculate the number of moles n2. So, from this difference we can say what is that you know excess adsorption we call it or you know basically this is the amount which has gotten or adsorbed. So, here ah as we have learned earlier that this is ah the number of molecules which has been adsorbed in the gaseous I mean in the ah adsorbent. So, this na can also be written as ah Vg we need to know what is the Vg ah here ah to find out this how do we ah to calculate this Vg basically we need some gas which will not get adsorbed.

So, most of the time we use the gaseous helium I mean the same experiment will be repeated with the gaseous helium and assuming that the gaseous helium is not going inside the you know or it is not getting adsorbed ah in the adsorbent. So, that means, it will fill up all this empty volume or this gas volume. So, I mean there is no adsorbed state only thing is that is there is nt equals to Vg into gh. So, if we equate it to 0 we can find out the number of this is nt,H and this is equals to ah the rho g,h the density of helium. So, from there we can calculate this Vg and this Vg will be used here to calculate the equilibrium adsorption capacity.

So, this is very important particularly to know exactly what would be the amount of ah I mean activated carbon or the other adsorbent that is necessary to stood a particular amount of activated carbon. So, there is also some heat of adsorption that means, whenever we are trying to ah you know store ah this hydrogen or any other gas there will be release of heat and that can there are two types of heat of adsorption one is basically the isosteric heat when we have you know a constant capacity and we are trying to you know ah I mean move from one temperature to other temperature. So, the amount of heat that is given in so, that will release some amount of the ah I mean ah hydrogen from the adsorbed state to the desorbed state, but the total one is remaining constant. So, then in that case it is the isostatic heat of adsorption and this can be ah easily obtained from this ah this equilibrium adsorption capacity chart and there is also a differential heat of adsorption say when we are charging it the adsorbate capacity I mean this capacity is also changing it is not ah I mean the capacity is not constant. So, with the change in the capacity ah there is also release of heat that is what is called the differential heat and they are related to ah this value I mean this relation.

So, that is about this ah I mean adsorption basic basically these are the basics of ah the adsorption and based on this later on we will of course, talk about the cryosorption storage of hydrogen particularly for vehicular application and also, we will look into the cryo ah I mean ah you know what is called cryo crumpet hydrogen later on sometime when we have finished the cryogenic liquefaction part and all. So, so these are the references you you can follow and let us look into the conclusions. So, we have the we have learnt that the suction capacity depends on the temperature and pressure and of course, ah for a particular ah adsorbent and adsorbate and adsorption has ah you know has to be ah in the ah adsorption has to be microporous for gas adsorption I mean this adsorbent basically has to be ah microporous and there are different isotherms as we have come to know ah studying from the Langmuir isotherm BET isotherm DR or DA equations ah those will be used to you know useful for describing this adsorption isotherms. So, ah thank you.