Cryogenic Hydrogen Technology
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Lecture 33
Cryo Hydrogen Storage

Welcome to this lecture on Cryogenic Hydrogen Technology. We were talking about the hydrogen storage. We have talked about the hydrogen storage vessel. Now, in this lecture we will be talking about the pressurization ah of a closed hydrogen container. And then of course, we will in that context we will also discuss about the storage of cryogen in an open Dewar. In continuation to that we will also talk on the adsorption storage process or the possibility of storing hydrogen in a adsorbed condition which the basic of that adsorption process we have learned the basic ah I mean processes of adsorption and desorption techniques we have talked about in an earlier class.

Now, today in this class we will try to ah talk about the storage of hydrogen in ah in carbonaceous material. So, to start with this is the ah topic of this ah today's lecture hydrogen storage at cryogenic condition ah. And then that I mean keywords are like cryogenic storage vessel and its pressurization or ah I mean ah how this is hydrogen is getting ah coming out of this storage vessel ah. If it is a open storage ah it is stored in open condition.

Then ah comes the cryosorption storage as I have already talked about. Now, ah if we are storing in general the cryogen in open condition for example, we have talked about ah you know ah while talking about the liquefaction process, we have talked about a storage of liquid nitrogen at reduced pressure or sometime we you know ah allow the liquid to boil at normal boiling point or keeping it at atmospheric pressure. So, but it is not always possible for ah all the cryogens we keep it in open ah pressure or open condition. By open condition what I mean is that in no time we allow the ah pressure to increase ah you know ah or ah whatever vapour that will be generated will be allowed to escape keeping the or maintaining the pressure inside this annular space or sometime we call it isobaric storage condition ok. So, that means, this annular space sorry this ullage space will always have ah the vapour at a particular pressure.

So, now, if we ah look at this storage condition it may so, happen that this container is ah closed with the base I mean valve and you know if necessary we will allow it to open up to you know take the liquid out or you may have to while in filling it up you know we will open it. Otherwise ah when it is in stationary or moving condition basically ah I mean depending on the situation we will allow it to ah stay as it is ok. Now, if as we have learned in the previous classes that depending on the type of insulation we are using ah in a storage tank ah there would be some finite amount of heat that is going to go I mean coming inside or heat in leak be there. And that will tell you what is the kind of overall performance for this storage vessels are having. And often you will find that we are expressing this storage I mean parameter or you know the performance parameter or effectiveness of this storage vessel in terms of it is evaporation rate that evaporation rate is mostly ah determined in terms of it is ah percentage change per day.

So, if it is a 100 litre storage in the valve and every day if it is you know ah 1 litre of liquid is getting evaporated. So, we can say that it is having 1 percent of evaporation rate per day. So, that is how it goes. So, ah, but again ah it has to be I mean ah if it is liquid nitrogen ok fine we do not mind keeping it in open condition because that ah vapour that will be coming out is going to ah be there in I mean in the atmosphere it is freely going. But if it is in if it is a liquid hydrogen or liquid oxygen we have to be careful about the accidental release of or I mean the release continuous release of this vapours into the atmosphere.

So, now, if we look at if it is a hydrogen ah you know we have to keep it in closed condition preferably, but if it is in open condition how the pressure is getting changed with the the ah what is called ah time I mean with the insulation what is happening some finite amount of heat is going in and if it is ah you know ah open condition that will try to evaporate the liquid and the liquid will constantly you know ah from the this surface this liquid will try to evaporate and the there would be some boil-off gas is moving out. So, if we are storing the liquid at open condition and if the liquid is getting evaporated then we will find that we can draw an equivalent ah picture for this ah storage like you know at some point of time t we have the vapour at Tg bar and this is at the saturation point and this liquid is at it is saturation condition Tf. So, imagine that in time t prime some other time as time has passed you know this gas is at some other temperature average temperature Tg prime and this liquid is still at Tf there is not appreciable you know change in temperature ah I mean we are neglecting ah any change in the liquid column ah and of course, since this ah excess gas which has been evaporated you know is coming out the leaving the temperature on this space different, but ah this saturation temperature is remaining same because this pressure in this annular space is remaining constant. So, at some point t to t prime what is the change in the annular space ah sorry in the ah vacuum in the ah ullage space temperature change how it is evolving that is what we are going to ah monitor because this liquid will be steadily depleting because ah you know constantly heat is coming and the liquid is getting evaporated ah, but ah there is no change in pressure because we allow the excess vapour to move out keeping the pressure constant. So, there would be constant boil up you know condition.

So, here we will be writing some you know ah of this equations ah here this is the rate at which this boil-off gas will be coming out there is a small amount of liquid if it is getting evaporated and that is also giving rise to some change in the mass of the ah vapour space ok that will also change. Basically, if you look at this is the delta L ah length and the corresponding cross sectional area that is the amount of liquid getting evaporated and that will cause some amount of change in the volume in the vapour space and that is exactly that is dmg part and the amount of liquid that is getting evaporated is delta mf part and this two are different because there is a change in the density of the liquid and the change I mean there is a difference between the density of the vapour and the liquid part. So, now let us look at the ah other part where you know this mass is getting evaporated because of the total amount of heat going into the system. Then comes ah if we ah take an energy balance for the entire ah you know ah gas part this was for the liquid part and this is for the gas part of course, taking care of the amount of ah you know mass which is getting evaporated from the top layer of the ah liquid surface and this is coming from you know the T saturation temperature to ah the Tg temperature and finally, it is coming out of the system. So, with this ah ah I mean basic equations ah you will find that we can ah you know calculate the temperature rise in the space ah related to ah the temperature of an earlier time Tg and then finally, this will be related to the hfg then the amount of total heat that is going in and of course, ah the you know ah it is basically the time step dependent part ah where delta t you know if it is changing with time then you know the amount of heat going in is also changing that will change the phi and eventually the temperature in the annulars I mean in the ullage space will be determined.

So, that is about this expression ah I would suggest you ah sorry I I would suggest you reading this particular ah paper ah it is ah like ah I mean you can study this ah like a self study in the self study mode and if you have any difficulty in understanding we will be ah discussing it in the ah along with the TA in the live session. So, in cryogenic storage vessel as we have ah learned in the previous slide we have conducted an experiment ah and this is liquid nitrogen this has been done with the liquid nitrogen and this liquid nitrogen is stored in this vessel and we have measured the temperature along the length of this liquid stored ah this is covered with ah you know small ah lead and we have measured the temperature ah initially all these senses were ah kept inside the liquid, later on we did some experiment with the partially filled liquid nitrogen. And it is basically ah vacuum insulated ah the bar and the heat in leak is good enough to evaporate ah some of the liquid. So, this liquid nitrogen will be vented out from this ah tank with time. So, these are the kind of temperature ah profile what we will find the once this you know initially all this temperature senses were inside the liquid and they are giving you know 77 Kelvin value, but as time passes this liquid will be layer will be coming out and this sensor will you know ah basically monitor the temperature of the ullage space with time.

You can see there is a steady rise in the temperature with this first sensor then after some time when the liquid is coming below this ah level you will find that the temperature of this ah second sensor is gradually going up and so on as time passes you know this is the third one. So, ah with the help of this ah you know theory just ah we have ah talked about in the earlier slide we can try to explain this ah temperature profile and these are the you know experimental and the theoretical ah values corresponding to the ah you know theory that has been ah proposed in the earlier slide. Then of course, as I told you that we have started an experiment where initially ah you know it these sensors were kept ah I mean out of this liquid or it was not filled up completely it was partially filled and then we found that the initial temperature that was here it is you know going like this. Similarly, this is ah the second sensor this is the third one, but the fourth one was initially 1, 2, 3, 4th one was initially dipped in liquid and after you know one and half hour nearly ah one and half hour we found that it is you know getting exposed to the vapor space and this average temperature I mean of this vapor space at this located at this point. So, when it is depleted to this level this is the kind of temperature rise it is having.

So, that can also be explained with the help of this theory, but please mind that this is in ah in the vessel is you know in open condition. So, this is particularly has been done for ah nitrogen we could allow the ah easy escape of this gaseous vapor nitrogen vapor into the atmosphere. So, with this ah analysis we have done a parametric studies where we have seen that this will be the this is predicting the average temperature in the annular space, but look at the temperature scale this is of course, done for the liquid ah hydrogen storage and initially the liquid was stored at 20 K and with time the ah I mean this is these are for the average annular ah spaced ah sorry average ah ullage space temperature and this is the liquid stored in the container how it is getting depleted ah with the ah time and this these lines are basically telling you the stored liquid as it is you know as time passes they are getting evaporated and coming out and if the ullage space is 10 percent of the total volume then we have you know we can retain it for a longer time and this would be the kind of temperature rise in the ah ah I mean ullage space, but when we have 50 percent ah ullage space I mean half of that container is back end you will find that we are getting depleted or getting rid of this liquid very quickly and the average temperature rise in the ah I mean in the space or in the ullage space is quite fast ah. This is about the liquid hydrogen storage condition if it is you know stored in open condition. Now, ah this is ah this can be in a different completely different situation where as I was telling earlier that this container could be ah quite closed and in the closed condition we ah stored this liquid and what is the temperature ah ah in the ah ullage space that again ah this time the difference is that we are not allowing this vapor to come out of the system, but it will be remaining inside and not only that we will see that this is going to increase the pressure on top of the liquid.

So, accordingly ah for this closed system we will have a different equation slightly than the ah open condition storage of the liquid nitrogen sorry liquid hydrogen and this will become you know the these are the governing equations for this ah this is this comes out to be the total the liquid content which is having the liquid part as well as the vapor part and this is ah where we assume that if we differentiate it with respect to ah you know ah this equation we will find that there is both the you know change in the vapor as well as there is a change in the density and the density change is always associated with the pressure rise. So, that will lead to this equation will lead to ah a change in the vapor space and not only that it will also be associated with the density of this liquid. Now, comes the part of this liquid is getting evaporated and that is getting transferred into the vapor. So, this will become the other equation and associated you know ah equation the energy balance equations are like this. So, ah I will suggest you again ah doing a self study for this particular ah you know equations and if you ah it would not be that difficult to understand.

So, if we have a total amount of heat transfer ah into the entire vessel we can put in divide it into a part which is going to the liquid and the other part is going to the ah vapor. So, depending on the difference in temperature between the ah vapor space and the liquid and the outside temperature that is the remaining constant. So, that constitute the total amount of heat going into the system a part of it is you know going to ah evacuate ah sorry evaporate the liquid and there is you know the same ah temperature there is there would be a change in the temperature in the liquid because we have a change in the pressure and accordingly this you know the boiling point of the liquid is going to change. So, finally, we can write a equation ah like this ah because the mass will be evaporated and that will move from a temperature T saturation to the you know temperature in the ah ah ah ullage space. So, that will constitute a temperature ah at a time at a time t prime ah initial while the initial time was t and this temperature rise and will be expressed by a ah expression like this.

So, if we parametrically try to look at this ah these are the type of temperature rise with time and this is the corresponding rise in the pressure. So, similarly this is of course, with the different heat ah I mean amount of heat that is going to get in and this is with respect to the different ullage space or different initial filling level of the container. So, initially if we are having 10 percentage of you know liquid or ullage space sorry 10 percent of the vapor space or ullage space then this is the kind of you know the temperature profile we have whereas, the pressure will be given by the corresponding value. So, ah again I would suggest you reading this particular ah paper and look at this ah parametric study this is particularly when the storage vessel is in closed condition. Now, we come to the adsorption storage ah container ah discussion where ah we have talked about the liquid hydrogen storage ah sorry gaseous hydrogen storage in ah carbonaceous material and the gases are basically ah getting adsorbed or physisorption is taking place.

So, let us start with a small problem based on the earlier studies we have made and here we are supposed to find out the amount of hydrogen that is to be stored in 10 kg of activated carbon and the carbon density is given as 502 kg per meter cube and the operating pressure and temperature are 3.5 MPa nearly 35 atmospheric pressure, but at liquid nitrogen temperature. So, we have been asked to use the Langmuir isotherm to calculate the storage capacity and here this is the you know the constants for the ah temperature dependence of this ah Langmuir coefficient and the storage capacity is ah given here. In the above equation this is T and K are in the units of Kelvin and kPa respectively. So, let us now go to the calculations part ah here is the temperature this is the Langmuir constant this unit would be ah in terms of 1 by kPa ah you can try calculating it this Nm that is ah coming as ah this is the expression that has been given here and accordingly this is coming as millimole per gram ok.

So, this millimole per gram ah when it is converted into ah mole per kg of activated carbon it is remain the same because this is in millimole and this is in gram. So, we have converted into mole per kg of ah activated carbon. So, then we have 10 kg of ah activated carbon. So, the total ah amount would be basically ah this multiplied by 10 and then comes ah we have this many mole of nitrogen. So, from there we calculate the the amount of ah you know sorry this mole of hydrogen.

So, accordingly we have this many gram of hydrogen ah stored in 10 kg of ah activated carbon. So, this 10 kg of activated carbon if we look at this carbon density we will find that this is the ah volume it will occupy and these are the expression for that. So, from there we can calculate the liter this many. So, liter of ah activated carbon will be able to store something like 540 gram you know ah amount of activate sorry hydrogen. So, that means, in 1 liter at 77 Kelvin and 35 bar pressure you will be able to store ah you know 5 half a kg of hydrogen.

So, ah you can compare the same thing at 77 Kelvin and 35 35 bar pressure because here you see we have put ah the corresponding pressure here. And we can see ah that this is the half a kg of hydrogen that could be stored in 10 kg of activated carbon, but if it is not stored in ah I mean in activated carbon is not there if it is gaseous hydrogen compressed to 35 atmospheric pressure at 77 Kelvin. So, what is the amount ah corresponding amount of hydrogen that can be stored. So, you can try that ah definitely this value will be 546.5 ah or nearly half a kg of ah hydrogen is more than the corresponding value of the compressed gaseous hydrogen.

So, ah that is about the adsorption capacity, but ah I just I would like to mention about this ah this is the summary of this part if you are trying to do it you ah and if you are finding this value just check these ah values ah these are the values ah of this calculation ah if it it should be of this order. And ah this is an example where we have ah talked about the equilibrium adsorption capacity because we have said that ah while storing the hydrogen in carbonaceous material this equation that we have talked about we have assumed that it is in the equilibrium condition. By equilibrium condition what I mean is that ah when we are adsorbing the gas and we are instantaneously able to remove that heat of adsorption and this is at 77 Kelvin, but in reality we will find when the gas is getting adsorbed it will rise the temperature of the adsorbent bed not only that while you know desorption is taking place then there would be non-uniform temperature ah you know drop in the entire bed in a desorbing bed ah. So, ah that also happens with the ah compressed storage of hydrogen when the entire vessel is compressed you know there would be ah non-uniform temperature rise in the vessel and of course, there would be non-uniform temperature drop when the ah gaseous hydrogen is withdrawn from a pressurized container. So, here in case of adsorption ah storage system we have this is a schematic of the cryosorption storage basically ah it is needed to design a storage container which will be cooled with the liquid hydro liquid nitrogen and ah this is the activated carbon which will be a filled in with the gaseous hydrogen and when you know the storage is complete we will close this valve and open this valve to take out this gaseous hydrogen.

So, you can see what is the kind of you know ah time versus adsorption bed pressure rise it is not instantaneously it is ah done ok it will take some nearly about 5 minutes and accordingly we will find that there are at the entry region we have some kind of temperature rise, but there is temperature non-uniformity along the entire bed and this is changing with the time. So, this is again for the average bed pressure when we are taking or withdrawing the liquid. So, there would be lot of non-uniformity in the bed and that is again going to change the adsorption capacity because the ah there is a lot of non-uniformity in the bed temperature. So, these are some of the references you can look into. So, particularly this paper ah where you know there is a activated carbon AX-21 has been talked about for storing gaseous hydrogen and some of the other papers particularly for ah the pressurization and depressurization of the liquid storage container.

So, these are the conclusion open and closed storage cryogenic pressure and temperature rises are different ah in the storage conditions are the cryogenic pressure temperature rises are different and adsorption could be a good storage option at moderate temperature and pressure ah. So, thank you for your attention.