Cryogenic Hydrogen Technology
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Week - 06
Lecture 30
Cryogenic Liquefaction – Contd.

Welcome to this lecture on Cryogenic Hydrogen Technology. And we were talking about the hydrogen liquefaction. In that connection in this lecture we will try to talk about the hydrogen liquefaction, but we will look into two aspects one is that how do we do the ortho para conversion. So, we may have to recapitulate bit which has been talked about long back I mean initially in the first or second lectures we have talked about the ortho para conversion that something some phenomena which occurs with this hydrogen or gaseous hydrogen. Then we will come back to this you know practical system where this particular aspect is taken into account when talking about the liquefaction.

So, the topic is basically if we look at it is cryogenic liquefaction cycles, but it is basically the practical systems and also, we will look at the ortho para conversion you know that is you know done in this practical system how they are taken into account. So, first of all we have so far talked about the different refrigeration system and in that connection, we have talked about the pre-cooled Linde Hampson liquefaction system which is entirely based on the isenthalpic expansion. Then we have also talked about the I mean these are the liquid yields and the expression for the ah work requirement. And then we have talked about the Claude cycle where we have seen this is the kind of improvement that gives which is basically based on the isenthalpic and isentropic expansion combination.

And here there is some benefit in terms of the turbine output if we are taking it to assist the compression process. This is the Claude liquefaction cycle where we do not need any pre-cooling, but if we add this pre-cooling we have seen that the precooled Claude cycle will also enhance the liquid yield and this is the practical system. But these are the kind of basic cycles and in practice you will find that we have also you know a combination of several such systems ok. So, we have talked about this pre-cooled Linde Hampson pre-cooled Claude cycle then we have talked about the dual pressure systems. So, in principle we have learned about the liquefaction cycles, but in practice you will find there may be several combinations of such ideas we will look into that part later on.

So, the basic idea is that we have to compress the gas we have to expand this gas ah and basically ah that will you know this with pre-cooling without pre-cooling sometime it will be mandatory sometime it is not mandatory. But in all these processes we have not talked about ah what is the I mean a basic necessity this is this is the basically these are basically the ah I mean liquefaction cycle for any cryogenic processes. But in addition to that for hydrogen liquefaction we have to take a special you know ah concern relating the ortho para conversion. So, what is that ortho para conversion? It is basically ah the ortho hydrogen and para hydrogen ah we have learned about it in the previous class just we will try to recapitulate and we will see that ok this is the ah I mean liquefaction related to the pre-cooled Linde Hampson cycle these are the liquid yield and the expression for the work requirement. And here comes the ortho para conversion part we have talked about it in previously that this is basically a half spin particle hydrogen atom.

And when they are combined ah they are either you know spin one particle or it is basically a spin 0 particle ok. So, they are either ortho if they the spins are aligned parallelly I mean in the same direction when they are in opposite direction ah I mean it is the nuclear spin that we are talking about. And this total spin if it is one we call it ortho hydrogen and the total spin 0 it is called the para hydrogen. The point is that we have also discussed about this part that the ortho and para hydrogen are 75 25 percent ah at room temperature. So, if you are given some amount of hydrogen you be sure at room temperature they are having 75 percent ortho hydrogen and 25 percent para hydrogen this combination as we have learned earlier that we call it as normal hydrogen.

So, the normal hydrogen concentration ah you can see that ah at room temperature it is ah 75 percent ortho hydrogen this is with respect to this ortho hydrogen concentration. This comes out to be 75 percent at room temperature, but as the temperature goes down you will find that it is coming almost negligible to I mean negligible ortho hydrogen. So, maximum or the entire thing is basically para hydrogen. So, how does it matter basically that also we have talked about this reaction or this conversion from ortho hydrogen to para hydrogen is an exothermic reaction. And the heat of conversion is more than the heat of evaporation of the liquid hydrogen.

What does it mean? That if we are you know allowing this conversion to take place in the liquid hydrogen condition you will find that you have liquefied hydrogen you have kept it and stored it without converting the ortho to para it will slowly you know ah convert get converted from ortho to para. And in the process what will happen it will liberate the heat of you know conversion and basically this will try to you know reduce the I mean the quantity of liquid hydrogen because it will evaporate the liquid because it is liberating heat. So, this ortho to para conversion is basically should be taken into account while liquefying the hydrogen. But is it to be taken care always basically if I say ok fine I am producing liquid hydrogen and I will you know use it within few minutes or few hours then we do not need to convert it at all. Because if I am not storing it for long this conversion is not going to take place instantaneously.

If you look at this ah I mean all this previous liquefaction system that we have talked about the hydrogen that normal hydrogen that is 75 percent ortho and 25 percent para we are you know feeding into the system or feeding into the liquefier. And how much time it is spending in the liquefier it is if it is in a steady state condition it will you know take few minutes or hours to get converted into liquid. So, within that short time if it is you know getting converted it would not be sufficient. So, whatever liquid that you have you know generated out of these liquefiers will be primarily the normal hydrogen at low temperature. I hope you got my point that we have the liquefier that where we are you know putting 75 percent ortho hydrogen and 25 percent para hydrogen.

So, this combination will be coming inside this liquefier by the time it is say this is at 300 Kelvin . And here this is almost all you know 99.9 percent of say para hydrogen we have learned about this is the entirely almost you know this is para hydrogen and small part of the ortho hydrogen would be there. So, now this is what it is supposed to be, but you will find that when you have liquefied it to 20 Kelvin it is almost having the similar kind of ortho hydrogen and para hydrogen because it is not instantaneously getting a chance to ah this is para hydrogen. So, almost it will retain the same kind of composition as the initial one.

What does it mean? That means, we have the liquid at this composition, but it is supposed to be at this condition. So, it is supposed to have you know not 25 percent para hydrogen, but it is supposed to have 99.9 or you know even ah I mean 99.9 percent of para hydrogen. So, that means, this conversion will now you know take place if you have kept it in this condition.

So, if you remember we have tried to solve one numerical problem where we have you know calculated ah this expression for that mass fraction which is remaining ah if we are starting with say 75 percent ortho and 25 percent para and after say this many hour 1000 hour it would be only this fraction ah it is getting you know remaining in the storage vessel rest of it is basically getting evaporated we have also tried to calculate the expression for that. But imagine in contrast to that if the initial composition of the ortho hydrogen is only 25 20 percent you will find that after 1000 hours this liquid is being stored and it is still you know some ah I mean about 80 percent of the liquid could be retained. It would be nice if we can completely do the conversion and store it. So, that you know no conversion for this ortho to para will take place and it will generate some internal heating and evaporate. Some amount of additional external heat leak will always be there in the storage vessel that we also try to ah you know reduce as much as possible in a good storage river, but that can always not be I mean always possible to ah reduce it to 0.

But ah what we are telling is that this ah I mean you have also learned about this part when we have talked about this ah initial composition. So, initial composition that is normal hydrogen will always be 75 percent 25 percent, but before we you know stored it for long time we have to ensure that this conversion has taken place. So, that is the ah I mean ah importance of ortho para conversion ah I think it is already been discussed long back just we have recapitulated it once. Now we will look at the ah I mean how do we do in practice ah while taking care of the liquefaction of hydrogen. In this context I would like to ah mention that this ah ortho para conversion are some you know ah basically their rate equations this dx0 ortho hydrogen ah rate of change of ortho hydrogen is some constant k x0 square this is what we have used in this connection.

But this can also be such that these reactions can be in presence of some catalyst and all this can be ah some other constant and x0 and then you know it is in the liquid condition it can be some other constant and it can be a completely constant. So, dx0 dt can be made a constant. So, in presence of the catalyst we can change the rate of this ah you know conversion. So, that is what is ah is necessary because this conversion is basically what we understood is that very slow process, but we have to add some catalyst and that catalyst will enhance the rate of conversion, but you cannot avoid the heat of conversion. So, now, we have to decide at what temperature we will do this conversion.

Do we do it at liquid nitrogen temperature some other temperature or we have to do it at liquid hydrogen temperature. So, that we will see in this lecture. So, now, ah let us ah talk about the practical system how do we ah achieve this. This is ah first there are 2 ah steps we will talk one by one. This is basically the liquid nitrogen precooling.

So, here comes this the gaseous hydrogen let it be completed ok fine. So, this is gaseous hydrogen that is coming in passing through this catalytic bed and this is dipped in liquid nitrogen as we have said. Why liquid nitrogen for that we have that ah I will come back to that part ah. So, this is passing through the gaseous nitrate I mean sorry this gaseous hydrogen is coming and passing through this bed of catalyst dipped in liquid nitrogen. Then it comes to the heat exchanger then it is getting evaporated and here we have the liquid sorry liquid ah hydrogen and this liquid hydrogen is being stored in this container.

So, this liquid hydrogen finally, is passing through another catalytic bed. So, finally, this is where we have getting the liquid hydrogen and this is supposed to be almost all para hydrogen ok and this ah vapor is going back. So, you can understand that in all the practical systems or liquefaction system wherever we have talked about that a part has to be added where you know this gaseous hydrogen before it is expanded a part of it will be you know converted in a liquid nitrogen precooled catalyst catalytic bed and finally, the conversion has to be done in the liquid hydrogen container or liquid hydrogen temperature. So, the reason is like this if you remember that graph we have shown this is ah with the concentration this is with the temperature and this is concentration is for ortho hydrogen. This ortho hydrogen concentration versus temperature we have plotted at around room temperature 300 K we have seen it is 75 percent and ortho hydrogen and 25 percent para hydrogen.

If you look at that graph if you go back you will find that nearly around what is called 75 sorry at 77 Kelvin that is the boiling point of liquid nitrogen or around you know that value you will find that it is concentration is about 50 percent or slightly less than 50 percent if we can go below 77 Kelvin or around 70 Kelvin if it is. So, that means, if we are able to you know get it cooled or if we put the catalyst in ah liquid nitrogen-based container or inside a liquid nitrogen vessel or cooled by the liquid nitrogen ah then what will happen the heat of conversion say 50 percent of this conversion will take place at 77 Kelvin. That means, ah this will liberate the heat at 77 Kelvin and the heat will you know evaporates some amount of liquid nitrogen. So, it is advantageous because this liquid nitrogen is cheaper than the liquid hydrogen ok. First of all it is not that abundantly available this hydrogen in atmosphere whereas, this nitrogen is you know it is a basically comes from the air and it is relatively cheaper with respect to the helium.

So, we can afford to you know evaporate the liquid nitrogen compared to the liquid hydrogen, but you will find that finally, we are you know ah converting completely complete conversion has to be done at liquid hydrogen temperature we cannot avoid that, but if we are not doing it that conversion would have taken place at 20 Kelvin at it would have you know evaporated lot more hydrogen. So, you are producing hydrogen and getting evaporated because of this conversion which could have been you know taken at the 77 K. So, if we remove this what is called liquid nitrogen ah you know pre-cooling and this conversion of ah ortho to para at 77 Kelvin we will find that it is costing a more on the liquid hydrogen part. But when it comes to you know the liquid hydrogen has already ah you know been generated and it is at 20 Kelvin. So, this you know liquid hydrogen is taken inside this ah catalytic bed finally, whatever conversion that has to take place will be taken place and the heat of you know conversion will be liberated at liquid hydrogen temperature.

So, that will be I mean taken care by the liquid hydrogen and initially it will be taken into account by the liquid nitrogen. So, there is another arrangement for this ah ortho para conversion when we will find that it is coming ah and a part of it is basically ah I mean there are two type of expansion. First of all one expansion is directly producing the liquid hydrogen this is LH2 and this is of course, the LN2 here again initially as I said that we will be converting a maximum or maximum conversion from 75 to 50 percent or 55 percent ortho to para will be converted at liquid nitrogen temperature and rest of it has to be done at liquid hydrogen temperature this is at 20 K. So, here a part of it will be directly expanded the second part will be expanded through the JT valve this is the JT valve and from there it will directly go to the catalytic build and then it will come out as liquid hydrogen this is also liquid hydrogen, but this liquid hydrogen is having ortho hydrogen almost 0 this is nearly 0, but the I mean all this conversion of ortho to para has already been.

So, taken care. So, nearly you know 99.9 percent of it is basically the para hydrogen what it should be before we store it. So, this liquid hydrogen can be stored ah for longer time. Here we have directly I mean this is different from this because it is you know this expansion is taking place out of this and here this is taking place inside this container where it is basically a double expansion both are JT expansion and this is supposed to be more efficient than the other one. So, this is about this ortho para conversion ah you can understand ah that we have this liquid nitrogen requirement this liquid nitrogen requirement is basically to reduce the pressure on say ah this liquid hydrogen boil off and I mean in practice you will find that it is not only that it is done at constant temperature we also have the practical system where adiabatic kind of ah catalytic bed conversion is also ah you know likely.

So, this is the catalytic bed and what are the catalyst that are ah you know used ah let us have a look into that. So, we have mainly ah quite different kind of you know catalytic ah catalyst those are the possible. So, one is the hydrous ferric oxide that is commonly used in this liquefaction ah or ortho para conversion then we have the chromic oxide and charcoal or silica gel and then nickel base catalyst. So, these are the typical catalyst those are in use and you will find that some of the ah components if it is present in the hydrogen then they become you know ah become poisonous for this catalyst. For example, there are ah if the methane is present or say carbon dioxide or mono oxide is present we will find that that is ah I mean basically ah doing harm to this catalytic bed, but that harm may not be the permanent one, but if there is sulfide or you know chloride say hydrogen chloride or hydrogen sulfide if it is present or ah I mean basically HCl if it is present then you will find that this chlorides and or chlorine if it is then it they will be ah doing ah I mean permanently ah make this things ah ineffective ok.

So, you have to be very careful about removal of all those impurities from this ah this ah ah hydrogen gas here this is the hydrogen gas. So, we have to ensure that they are free from all those poisonous things for the catalytic bed. So, that is about the ortho para conversion. Now let us have a look into this practical system this is the practical system you have seen this is we can see it from you you can refer to this to ah you know papers and the book. So, where this has been taken from that book itself.

So, here ah if you look at this the ah papers you will find a enlarged version of it and a good combination of all the system that has been talked about in the previous liquefaction lectures. So, this is the practical cycle. Now you see ah here this is the feed from PSA, PSA is pressure swing adsorption and this is where from we are getting the gaseous hydrogen. This gaseous hydrogen if you follow bit carefully if you follow that this is an absorber then comes this LN2 bath with catalyst. So, this is where the first stage of removal of the or basically this liquid nitrogen bed will take care of the evaporation caused by the heat of conversion from ortho to para.

So, this is the first stage where this conversion is taking place then comes you know these are the heat exchanger 1, 2, 3, 4 like that 5 they are the different plate fin heat exchangers. And you see ah there basically this is as I told you that this is at liquid nitrogen bath this is this conversion is taking place at liquid hydrogen bath, but additionally there are ortho para catalytic conversion is ah taking place adiabatically. So, these are not dipped in either liquid nitrogen or you know any other ah ah I mean liquid, but they are getting cooled by this process say here this is the heat exchanger. They are coming over here this is the gas which is coming over here then passing through this catalytic bed passing through the ah I mean heat exchanger and coming back. So, basically this gas when it pass through this adsorber they will be heated up then it will be cooled down again it will be coming over here heated up cooled down and coming like this.

So, this so, this is the feed gas which is coming getting you know ah cooled by the LN2 catalyst then you know this adiabatic condition and then finally, it is you know being cooled and then it is coming through this catalytic bed to be stored in the liquid hydrogen container. Now, at this point you can see that ah I mean there is basically a part which is not getting compressed or any only thing is that there is a small JT valve here that JT valve you know you have already compressed it will cooled by liquid hydrogen and then it is being stored. So, that means, there is something this is basically the liquefaction part the other part is basically ah refrigerated part maybe that is what is the hydrogen ah hydrogen liquefy sorry hydrogen refrigerator itself and what kind of refrigerator it is it is the dual compressor ah refrigerator that we have talked about. So, this is the main compressor where you will find this compressed gas is coming over here, let me use a different color for this. This is the main you know gas which is coming through this then it is you know you see a part of it will be ah expanded these are the expanders and this is expanded sometime maybe in series and this expander can also be in parallel.

So, these two are in parallel, but they are in ah sometime ok this is also in parallel because this is coming over here getting cooled and then again it is getting expanded and then you see this is coming over here to this intermediate pressure. What is about this other part let us have a look. So, this part you see a remaining fraction which has been expanded this is coming to atmospheric pressure and the low pressure you know gas is returning to the suction of the low-pressure compressor. So, this is how ah you know this is the first stage, this is the second stage of the compression process and that means, the one which we are going to store for long time will only be you know passing through these catalytic converters. So, where ortho para conversion will be done only for this system, but not with these refrigerators or where you know instantly this liquid is being used and it is basically trying to cool this.

So, this system this green and blue colored one or this compression part is basically constituting a kind of refrigerator because there is no replenishment here except you know if something is going evaporator or if there is any kind of leakage or etcetera that is all we has to be replenished otherwise this hydrogen system there is no in this part there is no ortho to para conversion because this hydrogen which is being liquefied will almost instantaneously will be used because we are adding heat by this conversion of ortho to para, but this part is getting you know stored in the liquid hydrogen container and that is you know getting converted into ortho to para and then finally, it will be transported. And whatever this ah small amount of nitrogen or impurities that are coming over here they are putting in into the stack and then finally, they are released to the atmosphere and sometime they will be you know ah burned out ok. So, this is the practical system you can have a look into these references to have a clear picture about this system. So, that is about the ah I mean practical hydrogen liquefaction system and then we will ah look into these references. So, these are the references you can go through and in conclusion we find that the ortho para conversion is needed for whenever it is stored for longer time and ah this conversion done using catalyst because this ah I mean these reactions are ah basically slow reaction in presence of the catalyst they we try to ah make it this conversion as much as possible faster.

And preferably we should do the conversion at ah we should take advantage of the liquid nitrogen because a part of it are almost 50 percent of the conversion can be done at that temperature because otherwise that will unnecessarily ah load the liquid hydrogen. So, thank you for your ah attention.