Cryogenic Hydrogen Technology
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Week - 01
Lecture 03
Slush Hydrogen, Ortho-Para H2

Welcome to this lecture class on cryogenic hydrogen technology. So, in continuation to our earlier lectures on this hydrogen properties, today we will try to cover the slush hydrogen production and then ortho para conversion and I mean what is ortho and para hydrogen. So, let us start with the slush hydrogen. In the last class we talked about the hydrogen properties and we have seen that hydrogen is basically ah low density ah when it is it is a very small molecule and it is on the first it is the first element in the time I mean in the periodic table. So, it is density in the gaseous form is very low. So, we have to densify it while storing it and one of the storage means is as we have learned that we can compress it and another form of storage is the liquid hydrogen, then liquid hydrogen is denser than the compressed hydrogen.

Another form of hydrogen is the solid hydrogen. So, that is the third phase of hydrogen and, but we can completely make it solid, but that will not be very convenient thing to transport from one point to the other. So, often what we do is that we make a slurry of solid and liquid. So, this is these are the some of the keywords we will talk about the Auger method, then we will talk about the Freeze-N-Thaw technique, then we will come to ortho hydrogen and para hydrogen.

So, now let us talk about the slush hydrogen as I was talking that it is the slurry of solid and liquid. So, this solid and liquid ah I mean we can vary the quantity of solid in the liquid hydrogen and that will ah I mean that will determine the density of the resultant solid liquid slurry. So, if we have about 50 percent of solid in the liquid, we will find the density of the resultant slurry is about 15 percent higher than the liquid hydrogen at normal boiling point. So, it is we have the benefit of course, at the cost of you know additional refrigeration, but when we are going to use this solid liquid slurry or the slush hydrogen, we will find that we can have an additional refrigeration of 82.7 kilo Joule per kg.

So, if we have some amount of liquid hydrogen, I mean mixed with solid hydrogen. So, that is somewhere in this region, we can we have talked about it that this is where you know solid liquid part would be there and this solid liquid slurry is basically what we are looking for for having higher density and with the additional refrigeration. Now, if we look to the methods of producing this solid liquid slurry, we will go back to our earlier discussion when we have talked about a storage of some amount of liquid hydrogen in a container and we said that it is a double walled container and, in that context, we tried to you know find out what is the vapor pressure and the boiling point relation. So, if we you know along with in the phase diagram, if we see that this is where is the ah this is where is the critical point and this is the triple point. So, if we have some normal boiling point the liquid at normal boiling point, so that is the atmospheric pressure and it is at the corresponding you know 20.3 Kelvin temperature. So, now if we have this liquid ah and if we reduce the pressure on top of it or you know if we reduce the pressure on top of it, it will follow this line. So, what will happen the boiling point of the liquid will gradually decrease and it will keep on decreasing till it reaches the triple point temperature. So, that is 13.9 Kelvin.

So, at this point all these 3 phases will coexist, we will have some amount of solid hydrogen, we will have liquid hydrogen as well as we will have vapor. So, that is exactly what we will do in this case and in the last class, we have also tried to solve how this temperature and pressure is varying. So, what we have to do is that we have to somehow reduce the pressure on top of this ah liquid hydrogen. So, if we are able to take it out this vapor that will you know change the ah temperature of this liquid or the boiling point of this liquid and we will be able to create some amount of solid. So, let us look how we can do it.

So, this is ah you know if we plot ah the temperature sorry the pressure versus time, the time is on this axis and the pressure is on this axis. So, I hope you understand that this pressure would be 7.2 kPa that is the triple point pressure at which the liquid will exist in the 3 phases and the corresponding temperature would be about 13.9 Kelvin. So, initially what we will do is that we will connect it with the vacuum pump to reduce the pressure on top of this liquid. So, what will happen at the triple point temperature you know ah or actually it has to be slightly below the triple point pressure.

So, we will reduce the pressure below 7.2 kPa with using the vacuum pump and at that time what will happen some amount of solid will be forming on top of this liquid. So, after sometime when the solid is has formed on top of it we will find that you know it is becoming difficult to I mean take out the vapor. So, at that time what will happen we have to increase the pressure above 7.2 kPa. So, in one cycle we are reducing the pressure in the other cycle we are increasing the pressure around 7.2 kPa. So, at that time if we consider that this is the solid hydrogen that has formed that will come inside. So, here you know this arrow is downward arrow that means, we are slightly pressurizing this system above 7.2 kPa and that is how this solid hydrogen is coming below and that is how we will produce depending on the requirement of the solid you know hydrogen in the slurry we have to again start this process we have to you know decrease the pressure below 7.2 kPa and again increase it. So, if we look at the you know diagram it is taken from this cryogenics journal by C. Sindt in 1970.

So, you can see that these are the kind of slurry that has been or solid hydrogen that has been produced inside the this is the double walled vessel and this has come below and some part is you know on at the middle some of the liquid and solid hydrogen at the top. So, this is how it is produced for laboratory scale you know of slush hydrogen, but for bulk you know production of this slush hydrogen we may have to take a different route we call it auger method. So, ah for producing slush hydrogen as we understand that it has to come to nearly 13.9 Kelvin or below 14 Kelvin. So, that this hydrogen will be existing in the solid phase. So, if we have a system or a pipe say for example, or a tube ah which is cooled by say liquid helium. So, we are you know it is a coil wrapped around this tube and we are sending liquid helium liquid helium is colder than hydrogen. In fact, it is the lowest you know boiling point naturally occurring liquid and this is liquid helium it is normal boiling point is 4.2 Kelvin. So, if we send this liquid through this coil this will be cooling this inner surface to and this is coming out as gaseous helium when it reaches to the top. So, we have some surface you know this is the surface which is cooled by liquid helium indirectly of course, this surface is maintained nearly at 4.2 K. So, now, if we pour liquid hydrogen from the top it will try to come in surface of in contact to this surface and it will you know create ah solid hydrogen layer on top of this tube. So, if we keep on pouring liquid hydrogen from the top this will increase the layer of this solid hydrogen it will keep on increasing and at some point, we will find that this passage is getting blocked.

So, what we need to do is that we have to remove this solid hydrogen from time to time. So, for doing that what we do is we need to have some kind of cutter we call it auger and this auger is I am sorry ok. So, this is cooled by this inner surface is cooled with the liquid helium and this liquid hydrogen is coming through this ah you know top surface and then we are we are trying to add one cutter through this. So, this is basically a rotating cutter and this is the actual picture we have taken from this paper ah. So, if you have to introduce a kind of rotating device to cut the you know solid hydrogen from this surface what we need to do is that we should have the associated you know bearing attached to the ends of this cutter.

So, we have to put some bearing here we have to add now the liquid from the top as usual the liquid helium will be coming from here and it will become gaseous helium. To cool this inner surface when this liquid hydrogen is coming contact to this surface inner surface this liquid hydrogen is becoming solid hydrogen and this cutter will cut and the solid hydrogen will come out from the bottom you know through this surface and whatever be the amount of solid hydrogen that you need you can add it to the liquid hydrogen to generate the solid liquid slurry. So, this is the commercial way of ah making the slush hydrogen for you know densification of the liquid hydrogen. This is another ah you know part of ah solid I mean the solid hydrogen or solid hydrogen solid liquid hydrogen ah mixture. Then comes other properties like ah often we will find that we are talking about normal hydrogen then we are talking about ah equilibrium hydrogen.

So, what is that? Basically if you look at we will find that ah probably you are familiar with the isotopes of hydrogen you might have heard that there are ah 2 isotopes one is ah called deuterium another one is tritium or sometime if it is ah I mean this deuterium is also I mean deuterium water often is called that it is ah heavy water and that is used in the nuclear power plant to ah decelerate the fast moving neutrons. But this is something different these are spin isomers if those isotopes are having different mass numbers here the mass number remains same, but its spins are different. So, now let us look into this hydrogen atom first. So, there is a new I mean electron revolving the nucleus we have one proton inside this nucleus of this hydrogen atom. This hydrogen atoms will have a spin of this nucleus there is a spin for this electron also we are not going to talk about the electronic spin at this moment we are going to talk only about the spin of the nucleus.

So, when we combine this 2 hydrogen atom you know this basically they are spin half particles or fermions and this 2 spin half particles when they can you know combine or when they will form a hydrogen molecule they can have a total spin of one and this this particular combination I mean is having you know both spin up or both spin down or you know basically the degeneracy would be 2 I plus 1 that is 3. So, it will have m equals to 0 plus 1 and minus 1. So, there are 3 degenerates 3-fold degeneracy with this and this is called the ortho hydrogen. The other possibility is I equals to 0 or the total spin would be 0 and this is basically ah what is called para hydrogen. So, this is what is known as ortho hydrogen and this is what is known as para hydrogen.

So, along with this ah total spin they also have the rotational quantum number J. I will not get into the details of this ah, but what we just want to mention that this para hydrogen and this ortho hydrogen there I mean the difference lies with the J equals to 0 state and J equals to 1 state these are the you know the lowest state for the ortho hydrogen and the para hydrogen and this ortho hydrogen is having 3 fold degeneracy. So, mostly they will be existing in the J equals to 1 or J equals to 0 will be populated because this difference in temperature would be more than 5 16 ah Kelvin in terms of the temperature. So, here the this is the lowest energy state and if we want to move from lower energy state to higher energy state what we need is to add heat, but just in opposite way if it is at higher temperature if you have to go to this lower I mean lower state you have to decrease the temperature. So, that is what exactly will happen you will see that this ortho hydrogen at room temperature if it is there and if you at low temperature if we bring it it will be mostly a para hydrogen. So, this ortho hydrogen and para hydrogen they are I mean basically coexisting at room temperature and with a particular ratio.

So, as I have said that this total pin being I equals to 1 and it has 3-fold degeneracy and this is I equals to 0. So, 2 I plus 1 is basically the single you know degeneracy. So, total is 4. Out of this 4 you know three-fourth is ortho hydrogen and one part is para hydrogen at room temperature. So, that means, the ortho hydrogen and para hydrogen concentration would be something like this and it will vary with temperature. So, at this point so, let us look into this ortho para hydrogen concentration.

So, we can understand that at nearly 300 Kelvin we have 75 percent of ortho hydrogen of OH 2 and remaining 25 percent of para hydrogen. So, this is what we call it as normal hydrogen. So, this normal hydrogen at this is at gaseous condition because this temperature is 300 kelvin and if it is pressurized or non-pressurized it will be in the gaseous state. And if we now try to liquefy it using any liquefier or at bringing it to somehow to normal boiling point at 20 K we will have almost all 99.8 percent of para hydrogen and remaining about 2 percent is ortho hydrogen.

So, you can understand this complete gas has been converted into the liquid state and if it is coming to an equilibrium then this equilibrium concentration equilibrium concentration should have been 98.99.8 percent para hydrogen and 2 percent ortho hydrogen. So, what it is called that this is you know how this concentration is going to vary and if it follows that as the temperature of this gas is lowered say at about 80 Kelvin if the you know it is supposed to have 50 percent ortho and 50 percent para. So, if it is able to convert itself from ortho to para by this amount we call it as equilibrium hydrogen.

It may so happen that this gas you have brought it quickly to the liquid state and then still it may have this 75 percent ortho and 25 percent para it is also possible. But at that time what will happen this you know ortho hydrogen will slowly try to convert itself to para hydrogen as a result it will I mean release some amount of heat and that heat will try to evaporate the liquid which is been you know produced. So, that is not desired. So, we have to you know look into ah I mean we should try to convert this normal hydrogen to equilibrium hydrogen. So, that you know as we are liquefying the gas or as we are cooling the gas we must take care of this conversion which is a basically a slow process.

Based on our discussion what we understand that this ortho and para hydrogen is not only it is important because of this release of heat, but it is also having quite different you know C v. C v of this ortho and para are quite different and you know if we plot try to plot it you know this is ah 1.5 and this is say 2 and this is 2.5 and this is sorry 2.5 and 3. And in this temperature scale ah we will be having you know about 350 around this is 150 K or so. So, this is for the ortho hydrogen this ortho hydrogen C v by R ratio will be like this. So, if you look at the para hydrogen you will find it is something like this and it is coming around say 150 and it will be something like this. This is for the para hydrogen and on this side, you know the normal hydrogen would be in between and something like this. So, this C v being different you need to know exactly whether it is in the para hydrogen you are dealing with or you are dealing with the ortho hydrogen or you are dealing with the normal hydrogen.

Accordingly, this C v will be different and that will that may change the design of your equipment etcetera. So, now let us try to conclude. So, these are the references you can look into the Barron's book or Thomas Flynn and these are some of the papers we have referred to also you can look at this book by matter and method at low temperature by Powell. So, conclusion is like that we have talked about the slush production slush hydrogen production by Freeze-N-Thaw technique as well as Auger method which is a commercially I mean if you have to produce a slush hydrogen in bulk you should go for a you know Auger method. Then we have also tried to understand what is slush I mean what is ortho hydrogen and what is para hydrogen and the importance of this ortho and para. So, thank you for your ah attention.