Cryogenic Hydrogen Technology

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Week - 01
Lecture 05
Deuterium Production

Welcome to this lecture on cryogenic hydrogen technology. Today we are going to learn about deuterium production. This deuterium is an isotope of hydrogen and we are familiar with other ah isotope of hydrogen that is ah deuterium and tritium and of course, this deuterium production is not directly linked to our ah I mean hydrogen technology for ah the hydrogen technology for fuel and ah, but it is in a in a broader aspect if we look at it this hydrogen can be treated as this deuterium separation and production is of course, a part of the cryogenic hydrogen technology. So, we will go to ah this today's concept is ah basically the deuterium production and we will find that deuterium production will involve lot of cryogenic activities in it. So, let us look into it and first of all we will ah these are the keywords ah we will see hydrogen enrichment, then hydrogen deuterium ah separation and then hydrogen catalytic decomposition. So, first of all we need to understand what is the deuterium and how is it different from the hydrogen.

So, in the last class we have talked about the isomers of hydrogen and that is ortho hydrogen and para hydrogen where we have seen that those are having the same atomic mass, but they are different in with respect to their spins or nuclear spins. But here these are the isotopes of hydrogen where the atomic mass of hydrogen is different and they are basically as I told you that ah with the atomic mass 1 it is hydrogen, with the atomic mass 2 that means, this deuterium ah will be having atomic mass 2, where one is the proton the other one is the neutron. So, with this 2 it is the deuterium and it symbol is D and there is another ah isotope of hydrogen that is tritium with the atomic mass 3 and basically this is an isotope ah, but with a very short ah half life and we are not going to discuss about the tritium at this moment, but the deuterium separation will be discussed in this lecture. So, deuterium and hydrogen both are diatomic molecules, but in the atmosphere this hydrogen is I mean hydrogen and deuterium is forming a hydrogen deuterite it is in a diatomic molecule, but it is mixed and ah it is available with hydrogen is to hydrogen deuterite with a ratio of 3200 is to 1.

So, you can understand that the presence of hydrogen deuterite is very small in atmosphere or I mean natural hydrogen. So, if we have to decompose this hydrogen deuterite into it is 2 constituent hydrogen and deuterium we need to first concentrate this hydrogen deuterite and then we can think of separating it. Now, this hydrogen deuterite and hydrogen ah I mean normal boiling point of hydrogen we have seen that it is 20.27 Kelvin, deuterium boiling point is 20. 23.67 Kelvin and hydrogen deuterite that is the another diatomic molecule is boiling point is 22.13 Kelvin. Now, why are we talking about this boiling point is because the concentration or separation of this hydrogen deuterite from ah you know this hydrogen mixture is needing a kind of ah first of all as I said that concentration will be necessary and then you know it has to be separated from hydrogen and then only we can decompose it into hydrogen and deuterium. Now, how to separate this hydrogen deuterite from hydrogen? It is one of the separation process is by you know cryogenic distillation. So, we will not go into the details of the distillation in this class, but we will talk in a nutshell about this hydrogen deuterite separation from hydrogen and how this distillation works in in this I mean in cryogenic domain.

So, just ah I will try to briefly give you an example like say we have a mixture of ah two component say imagine that A and B are the two components which are of which you know A is the lower boiling point component lower BP and B is with the higher boiling component higher boiling component. So, if they are mixed together and if we have to separate and if they are in liquid form. So, there comes the you know hydrogen deuterite and hydrogen which is you know available in normal hydrogen as a mixture of say if it is 3200 this will be only one you know. So, this is the kind of ratio it maintains in the gaseous condition this is normal hydrogen and this is hydrogen deuterite. So, if we have to separate them from this if we have to separate this hydrogen deuterite we first need to make a liquefaction of these two components and obviously, it has to be brought down to the boiling point of this of this order of 20 K or so.

Now, if in case of A and B this this is say the lower boiling point it is having the higher boiling point. So, if this liquid mixture if it is heated up what will happen the lower boiling component will try to move up and the higher boiling component will be remaining at the bottom. So, if we look it as an example like you know say alcohol and water mixture we will find they are having widely different boiling point and if you are heating it up the lower boiling component that is the alcohol which will be travelling up and leaving aside the water at the bottom. So, you cannot exactly tell that the vapour that you have obtained is you know free from any water in a ah you know mixture of water alcohol as I have told. So, in a AB mixture this A which has come up as a lower boiling point you know vapour it cannot be said that it does not contain any vapour in it ok. So, similarly we cannot say that B is completely pure B it can also have some amount of A mixed with it, but mostly the vapour which has come up it will be mainly A and which is there at the bottom that is mainly B. Now, if we collect this vapour A from the top again if we liquefy it or if we make a liquid of this heat it will be reach in the A component at the top and B component at the bottom again if we you know put some heat and it will find that the A component is coming you know on the top. So, depending on their relative boiling point or what we call ah I mean ah relative volatility what we call depending on the difference in their boiling point it would be easier or difficult to separate. So, similarly ah as we have seen that you know we have separated this component A similarly we are separating this component B again we will put some you know heat in it. So, we will always try to separate them in terms of A and B successively.

So, this is what is called you know fractional distillation and we will find that this lower boiling component will be you know in the form of vapour and it will be gradually on the top we will find it is reached in ah lower boiling component and at the bottom we will find that the higher boiling component is more you know ah I mean it it will be preferred mostly the lower boiling component higher boiling component. So, now, here ah this two will be separated like this in and in a distillation column. So, we I am not going into the I mean ah packed bed column or the tray column in that details, but mostly what we can understand that sometime we need to heat it up and this you know vapour that you have collected again it is to be condensed. So, that we can heat it up and generate the A and B or separate it as A and B. So, like that this distillation column you know works and we can separate the ah you know ah it is constituents.

Here in this case we have the hydrogen and hydrogen deuterite. Now, in that case let us see if we remember that the boiling point of hydrogen deuterite was around ah this was the boiling point of hydrogen deuterite 22.13 and in deuterium is 23.67 and hydrogen is 20.27. So, they are pretty close to each other. So, obviously, what we need to understand that this distillation will be quite difficult in nature, but we will again as I said that we will not go into the details of this distillation column only thing is that we will assume that we have the refrigeration available around 20 k to make it liquid and we have the adequate heat which is not difficult you know particularly for cryogenic engineering anything you know which is in terms of the room temperature it can easily pick up the heat from the room temperature and ah you know heat addition is very simple in case of cryogenic engineering operation. So, assuming that the heaters are easily available and we have the refrigeration process available around the ah 20 K we can now try to look into the enrichment process of this hydrogen deuterite and then you know to the ah hydrogen deuterite separation. Now, this hydrogen and hydrogen deuterite this mixture will be first compressed and then it will be expanded and a part of it will be cooled in the heat exchanger. So, I am not going into that details, but what it will give you is you know we will put it in the column as I told you in a rectification column ah it will be giving or separating it ah you know into its constituent that is in the hydrogen and hydrogen deuterite.

So, it may not be possible to separate them in a single column. So, sometime we need more than one column this is the primary column we call it and then you know we can primary ah column and then we will have a secondary column. So, from where you know this enriched hydrogen deuterite say this is about 3 percent of the hydrogen deuterite will be taken to the second column or secondary column where again it will be separated primarily into HD and H 2. Now, on this part this hydrogen deuterite it will be about 95 percent hydrogen deuterite and on the top it will be hydrogen deuterite I am sorry hydrogen. So, this hydrogen will again be taken back into appropriate location, but what we will do is that now we have sufficiently enriched hydrogen deuterite and we now can you know take out this hydrogen deuterite though it will be in the liquid condition we will take the vapor part from heat and then we will put it into a heat exchanger.

So, in this heat exchanger what will happen this will be taken into this reaction where hydrogen deuterite will be decomposed into deuterite and hydrogen. So, from here ah what we will try to do is that this deuterite will be taken back into another column and this deuterite will be going back while going back again it has to you know be cooled down and it will come over here in this deuterium column. So, this is going back to this and here it will be separated into deuterium and hydrogen finally. So, this deuterium is in the liquid form. So, if we want it in the gaseous form again we will put it into that heat exchanger.

So, from here we will have the deuterium you know for the deuterium product. So, if anybody wants it in the liquid form one can you know take it out from here itself if it is needed you know in the form of ah deuterium in the gaseous form one can you know put it through the heat exchanger and it will be coming like this. Now, the question is why did we do this decomposition ah you know I mean why did we use this heat exchanger to heat it up because this reaction you know is favoured at higher temperature. So, typically you know 250 to 300 Kelvin depending on its application will be you know it will be cooled down or heated up depending on this heat exchanger and the operation. So, particularly we will try to now look into this reaction where hydrogen deuterite is broken into hydrogen and deuterium.

So, its equilibrium constant will be you know if it is known we can look into this reaction how it is you know giving how it is giving us the two products. So, let us now look into this equilibrium composition of hydrogen deuterite it will break into the hydrogen and deuterite. This reaction as I told you it occurs at elevated temperature and its equilibrium constants are known to us. So, this is the ah equilibrium constant it gives you the it is related to the concentration of HD and D2 and the hydrogen this y stands for the ah composition in the vapour phase. So, ah this y Ke or the equilibrium constant will be known to us and if it is known then we can try to look at a particular problem say if you remember that this hydrogen deuterite was composition in the column was 95 percent hydrogen deuterite and sorry HD along with that we had 5 percent of H2.

So, this 95 percent HD and 5 percent H2 is you know coming here in this reaction and then in presence of the catalyst it is going to decompose into deuterium and hydrogen along with that some portion of the you know hydrogen deuterite will also be present. It is not like that we have taken the hydrogen deuterite and everything is getting converted into hydrogen and deuterium. So, this reaction there would be something like this and if it is say as I told you that 95 percent hydrogen deuterite and 0.05 you know is the composition of hydrogen and what would be the composition of C_1, C_2 and C_3 and that is for C_1 is for the hydrogen and C_2 is for deuterium and C_3 is for hydrogen deuterite. So, we need to look into the ah composition of the ah I mean gas which is this product you know ah concentration if we want to find it out how do we do that.

So, let us look into that part ah ok. So, this can be done by ah let us look into this ah first of all we can do the hydrogen balance in this equation if we look at this is 0.95 for the hydrogen and then it would be ah 0.05 I am sorry this is not there 0. 95 plus 0.05 into 2 that is for the hydrogen on this side. On this side we have 2 C_1 and on this we have C_3 that is what is the you know if we try to make and balance for the hydrogen. So, this will become an equation ah involving C_1 and C_3. So, C_3 can be written as C_3 equals to ah 2 C, I am sorry this is 2 C_1 and this is C_3 H. So, it becomes $C_3 = 2C_1$ with the minus plus 1.05. So, if we add this 2 on this side and on this side it would be $2C_1$ and $C_3 = -2 C_1 + 1$. So, this is one equation which involves C_3 and C_1. Similarly, if we try to balance the reaction with respect to the deuterium we will have point ah let me change the color of this pen. So, this is 0.95 for the deuterium on this side what we have is there is no deuterium on this side. So, it can be written as $2C_2$ and we have $1C_3$. So, C_3 $2C_2$ like this this equation would be there. Now if I try to replace it and put everything in terms of ah C_1, what it would give is equals to $- 2C_1 + 1.05$. So, this can be written as C_2 equals to ah you know ah it is $C_1 - 0.05$. So, this is another equation we have obtained. So, all together we will have you know 3 component this $C_1 + C_2 + C_3 = 1$. If we combine this 3 if we look at $C_1 + C_2$ is 2, I am sorry $C_1 - 0.05$ and $C_3 = -2C_1 + 1.05$. So, combined together you will find this is equals to 1 and that is equals to the C_m. Now, ah if we you know look into it ah we have 3 unknowns and we have gotten 3 equation. One is equation this one is equation this these are the 2 equation the third equation I am yet to tell, but already you have told about this. So, this will give you the third equation and as I said that K_e would be known in this case K_e is given as in the form of $\ln K_e = 1.1848$. So, that K_e can be taken as 3.27. So, this K_e is 3.27 in that case what will happen ah we will have another equation. So, this y[HD] is basically C_3^2. Let us change the color this K_e that is known K_e is equals to y[HD] that is

$C_3{}^2$ divided by y[D_2] that is equals to C_2 and this is equals to C_1. So, we have this third equation given as $K_e = \frac{C_3{}^2}{C_2 \times C_1}$.

So, now these 3 equations can be solved to find out C_1, C_2 and C_3. So, to obtain the equilibrium composition of this reaction. So, if we solve it we will find that ah I am sorry this is ah let me just erase it ah we will find that C_1 is coming to be this is coming to be C_1 is supposed to come as 0.288 you can try to solve it C_2 equals to 0.238 and C_3 is equals to 0.474. So, that means, when it is you know ah this reaction is taking place with this you know this equilibrium constant this is temperature dependent this reaction is taking place at 300 Kelvin and at this temperature this concentration part in the product steam C_2 is supposed to be 0.238. So, this is what is there in the product steam along with that you will have some amount of hydrogen present in it and a product I mean hd will also be there. So, from here this deuterium in the column you know it will come back to the this whole mixture will come back as such in from the catalytic converter and it will be cooled down and again go to the deuterium column. So, this is how it takes place in actual system and with the ah ah as I told you that with the adequate refrigeration and heating we can separate it out ah or first of all we can enrich the hydrogen deuterium and from there we can get this deuterium fine.

So, these are the references only it has been taken from the Barron's book of cryogenic systems and let us look into the conclusions then. So, we have seen that deuterium is not available freely ah I mean in nature it is mixed with hydrogen and it is available in the form of hydrogen deuterite and that too it is available in very minuscule quantity. So, first of all if we have to separate this deuterium we need to ah have considerable amount of hydrogen deuterite present in the ah mixture and that can only be done by you know using ah cryogenic column where ah I mean particularly one of the rather you know ah mostly commonly employed technique is the cryogenic ah distillation column. We can enrich it to nearly about as we have seen with an example to 95 percent depending on the column you know ah construction . And once we have the enriched deuterium we can you know decompose it in using a catalytic decomposition.

So, that will give you ah the hydrogen and deuterite and hydrogen deuterite the I mean hydrogen and ah deuterium they will be you know separated, but it is basically in in the catalytic reaction we have seen basically it is a mixture of hydrogen deuterite and hydrogen deuterite hydrogen deuterium and hydrogen deuterite. So, this mixture has to be separated out again in a cryogenic column and from the bottom product of that column would be the deuterium and that deuterium can be taken as liquid as well as if anybody wants it to be in the gaseous form it has to be warmed up in a heat exchanger and separated it ah and taken out as a product . So, this is about the deuterium production and thank you for your attention.