Cryogenic Hydrogen Technology

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Week - 01

Lecture 04

Ortho-Para H2 Conversion

Welcome to this lecture on cryogenic hydrogen technology. So, we were talking about the hydrogen properties and today we will try to learn about the ortho para hydrogen conversion. In our last class we have talked about the ortho and para hydrogen and there we have seen how this ortho and para hydrogen concentration is varying with the temperature. At room temperature it is 75 percent ortho hydrogen and 25 percent para hydrogen, but as we lower the temperature we will find that this ortho hydrogen will completely convert itself to para hydrogen by changing it is spin and that is an exothermic reaction. So, it has to I mean when we are doing this conversion it will release some amount of heat. So, the keywords are ortho hydrogen, para hydrogen and ortho para conversion.

So, let us start with a small recapitulation of what we have learned in the earlier class. So, this is what is the ortho hydrogen concentration and initially at nearly room temperature or slightly higher temperature you will find that it is 75 percent ortho hydrogen and 25 percent para hydrogen. Then this is for the ortho hydrogen concentration we have ortho hydrogen concentration ah we have written and in terms of para hydrogen it would be something like this. This is the concentration of para hydrogen.

We can understand that as we have learned earlier that this ortho hydrogen to para hydrogen this is what is called the normal hydrogen and in equilibrium condition say for example, at you know 80 K around as we have told earlier that it is a normal I mean hydrogen is supposed to have 50 percent para hydrogen and 50 percent ah ortho hydrogen. So, at this point it is supposed to be at equilibrium at with a 50 percent ortho and 50 percent para. If it deviates I mean it will be you know it will try to come back to that concentration level slowly. Now, this reaction this reaction rate ah $\frac{dx}{dt} = -kx^2$. Where x is the concentration of ortho hydrogen at any instant of time. So, x is the concentration of ortho hydrogen at any instant of time at any instant of time t and it is variation with time is the second order equation where k is the rate constant.

So, you can understand that this you know if x is the concentration it is varying with the concentration of square of the concentration level. This is what is happening you know if you are not putting any kind of catalyst in the during the cool down time, but if you ah allow some you know catalyst to put in we will find that we this reaction rate $\frac{dx}{dt}$ can also be you know $-kx$ it will be varying with the concentration just directly it will be proportional with the concentration in contrast to what we have learnt that $\frac{dx}{dt} = -kx^2$ when there is no catalyst. In presence of catalyst in the gaseous condition we will find that the reaction will be you know different and this concentration this constant k 1 will be depending on the temperature pressure and the catalyst present in the system. It can also go to $\frac{dx}{dt}$ is equals to some just a constant without varying with the concentration level that is also possible and it will be in this catalyst will be in the liquid I mean ah the when you are mixing the catalyst in the liquid state of hydrogen. So, this is these are the typical you know variation of the concentration of ortho hydrogen we have taken at an instant of time and how it is varying the rate I mean what is the rate reaction ah they are changing with the concentration level.

So, with this ah basic information let us now try to ah solve ah you know a situation where we have imagined that we have liquefied some amount of ah hydrogen normal hydrogen we have taken and we have liquefied it, but we have not you know put any kind of catalyst. So, it is gradually you know trying to ah I mean convert itself to equilibrium hydrogen. So, it has converted from say 300 Kelvin to its normal boiling point at 20 Kelvin and we have not added any catalyst. So, that means, you know it is almost instantaneously or within a very short time you know we have in maybe it may be few hours or so, it has been converted to the gaseous state to the liquid state, but it has not the same I mean it is ah with 75 percent ortho hydrogen and ah 25 percent para hydrogen. That means, it is in the normal condition it is the normal hydrogen and in the liquid state also it is trying to convert itself from 75 percent to you know different concentration and at the same time it will release heat and what will happen to the liquid content.

So, now, imagine a situation that we have a container where we have kept ah you know that liquid that is you know that is ah 75 percent ortho hydrogen and 75 percent para hydrogen. We have taken some gas we have been able to liquefy it and we have stored it and it is imagined that it is the very you know good container with very excellent you know insulation there is no ideally there is no heat leak from outside. So, if there is kind any kind of heat generation then only you know that will convert this liquid into ah I mean it will evaporate that liquid. So, that means, what would be the content of this you know container ah after several hours if we have not done anything just we have liquefied normal hydrogen and kept it as it is. So, the rate reaction would be $\frac{dx}{dt} = -kx^2$ and if we have some initial mass m_0 we would like to find out what would be the mass of this liquid hydrogen after several hours and of course, we have to tell that you know we are not you know keeping it confined.

So, it is always that the always the pressure is maintained at the same pressure. So, the amount of liquid that will be remaining inside this or say basically m by m_0 we are trying to find out. So, let us try to look into this problem. So, we have $\frac{dx}{dt} = -kx^2$. So, if we try to integrate it what will happen ah $\frac{dx}{x^2} = -kdt$ and if we integrate it between the ah I mean it will be minus $-\frac{1}{x} = -kt + A$.

So, what is the boundary condition or initial condition at t = 0, we have said that the concentration this x is the concentration of ortho at any instant of time as we have learned this $x = x_0 = 0.75$. So, we have initially 75 percent of ortho hydrogen. So, let us now put it in this. So, x becomes minus 1 by you know 0.75 is equals to minus k equals to 0. So, it is equals to A. So, A = $-\frac{1}{0.75}$ or this is equals to $\frac{4}{3}$. So, 1.33 roughly we can say. So, with this one we can now write that x is equals to 1 by 1.33. So, the resulting equation becomes $1.33 + \mathrm{kt}$ this is you know if we put this value of A in this equation it becomes $1.33 + \mathrm{kt}$. So, that is what is the value of x you know with time it is varying. Now, we have this container with certain amount of mass initially at initially it was m_0 at any instant of time at any instant of time at any instant of time t let the mass be small m. So, if there is m mass and the rate is of conversion is $\frac{dx}{dt}$. So, you have $m\frac{dx}{dt}$ amount of ortho hydrogen generation ok. So, in that case $m\frac{dx}{dt}$ is the ortho hydrogen that is being generated.

So, this reaction being exothermic. So, if Q is the amount of heat released per unit conversion of ortho to para we have $m \times \frac{dx}{dt} \times Q$ amount of heat generation ok. So, this is the amount of heat that will be generated if you know m mass is getting converted at a rate of $\frac{dx}{dt}$ and the heat of conversion is Q. So, with this amount of heat generation what will happen this will try to evaporate the liquid. So, what is the evaporation heat of evaporation now h_{fg} is the heat of evaporation.

So, that will come in picture. So, if we look at it ah we have this is the amount of heat that is generated and this is the heat of evaporation. So, if we try to correlate this two you know we can find out what is the rate at which the you know mass is you know converted or mass is evaporating. So, this is the amount of heat and this is the heat h_{fg} heat of you know evaporation. So, what would be the resulting ah you know ah ok.

So, we have h_{fg} heat of evaporation and $m \times \frac{dx}{dt} \times Q$ that is the amount of heat being generated. So, if we divide it by $\frac{1}{\mathrm{hfg}}$ then $m \times \frac{dx}{dt} \times Q$ that would be the generation of rate of change of evaporation of the liquid. So, we have this equation now. Now we will try to replace this $\frac{\mathrm{dx}}{\mathrm{dt}}$ from this equation. So, in that case we can write it as $\frac{\mathrm{Q}}{\mathrm{hfg}}$ into m we will take to this side you know and this would become $-\mathrm{kx}^2$ then this is $\frac{1}{\mathrm{m}}\frac{\mathrm{dm}}{\mathrm{dt}}$.

So, now we have obtained one equation where this x can also be changed we have earlier obtained $\mathrm{x} = 1.33 + \mathrm{kt}$. This is you know for a situation when the initial concentration is 75 percent of ortho. So, if we replace this equation in this equation the value of x what we will find is $\frac{\mathrm{Q}}{\mathrm{hfg}}$ into there is a negative sign k into $\frac{1}{(1.33+\mathrm{kt})^2}$ equals to $\frac{1}{\mathrm{m}}\frac{\mathrm{dm}}{\mathrm{dt}}$. Now we can integrate it on both sides and we can find that this integration will give you $\frac{\mathrm{Q}}{\mathrm{hfg}}$ into k will cancel out.

So, $\frac{1}{1.33+\mathrm{kt}}$ and then you will have this is logarithmic this t will be coming to this side of course, it would be you know this would be dt this would be this would not be there here. So, $\frac{\mathrm{dm}}{\mathrm{dt}}$ will be logarithmic of m plus constant of integration say let us call it as logarithmic B. So, this would be the integration part and if you ah you know try to now put the initial condition with respect to the mass we will have ah something like this that Q we have taken all the terms Q, m ok fine. So, what is the initial condition at t = 0 we have m = m_0 mass was there. So, if we substitute it here we will find that this becomes m_0 and this becomes $\frac{\mathrm{Q}}{\mathrm{hfg}(1.33)} = \ln(\mathrm{m}_0) + \ln(\mathrm{B})$. So, we now have the value of ln B with us and if we substitute it in this you know equation that we have obtained ah you know it is supposed to give us the resulting ah expression is supposed to be ah $\frac{\mathrm{m}}{\mathrm{m}_0}$ you can try to calculate it and if you are finding something different then you can tell me. So, this b would be supposed to be $\frac{\mathrm{m}_0}{\mathrm{e}^{\frac{3\mathrm{Q}}{4\mathrm{h}_{\mathrm{fg}}}}}$ and the resulting expression is supposed to be $\mathrm{e}^{(\frac{\mathrm{Q}}{\mathrm{h}_{\mathrm{fg}}(1.33+\mathrm{kt})}-\frac{3\mathrm{Q}}{4\mathrm{h}_{\mathrm{fg}}}}$. So, this is supposed to be the final expression and if we you know try to plot this we will come to that part in the next slide that this would be the expression form by m 0 if the initial concentration of ortho hydrogen x equals to x_0 is equals to 0.75. If it is other than 0.75 initially this expression is going to change accordingly fine. So, based on this information now let us try to calculate a problem where we have $\frac{m}{m_0}$ for the initial concentration different initial concentration it if it is given say initially it may be 0.75, 0.6, 0.5 and so on and we have been given the value of Q equals to that is the heat of conversion that is you know 141416.9 joule per mole and h f g that is heat of evaporation that is 900 joule per mole. So, what we need to find out is $\frac{m}{m_0}$ or you know up to 1000 hour basically what we are trying to look at that if we have liquefied hydrogen with this initial concentration 0.75 or you know if we are varying with different initial concentration of ortho hydrogen by you know by suitable method we will talk about it while talking about the liquefaction of hydrogen. So, what is the kind of you know $\frac{m}{m_0}$. So, what fraction of the initial mass will be there after 1000 hours.

So, ah we have you know we have done the expression or we have calculated the expression for you know 0.75 you are you can calculate it it would not be very difficult to you know for calculated heat with the initial concentration of 0.6, 0.5, 0.3 and 0.2 and 0.3. So, with those concentration levels if you are solving this ah you know ah this kind of equation if you have ah you can plot it this fraction with ah you know up to 1000 hours. So, this is supposed to give you a kind of ah you know graph like this and here this is the on this side we have the time scale and, on this side, we have the fraction $\frac{m}{m_0}$ or we call it as the remaining mass fraction. So, if we have started with an initial concentration of 0.75 or if I mean it is basically you know finally, the normal hydrogen. If you have stored the liquid in the normal condition I mean you have taken normal hydrogen, you have liquefied it, you have not done any kind of conversion and you know finally, if you have stored it in that condition itself you know after 1000 hour you will find that just doing anything you have you know only about say more than about 35 percent or so, is in the liquid state.

So, rest of the hydrogen has been converted you know from ortho to para and that ortho to para conversion has evaporated the liquid. So, you can understand the loss that means, you have taken some amount of hydrogen, you have spend energy to convert it into liquid, but you have not taken adequate means to convert this normal hydrogen or you have not converted the ortho hydrogen to para hydrogen and you have just like that if you have stored it, it will result in a you know only about more than some 30 percent of liquid hydrogen at the end. Rest of the hydrogen it has converted try to convert the ortho to para and in that being an exothermic reaction that has evaporated and that is more than actually if you look at in the previous expression where we have talked about the h_{fg} that is the heat of evaporation of you know this liquid hydrogen that is around 900 joule per mole whereas, this heat of conversion that is 1416 joule per mole. So, that is way higher I mean than the evaporation heat of evaporation so that means, if this ortho to para is getting converted it will generate adequate heat to evaporate the liquid ok. So, but now let us look into the situation as we are keeping on you know decreasing this ortho concentration initial ortho concentration say for example, this is with the 0.6 if it is reduced from 0.75 to 0.6 you can understand that after 1000 hours you will find that the concentration is about more than 40 percent. So, so on I mean if in the finally, if we our you know liquefaction process is such that the resulting you know conversion is having only when we have taken normal hydrogen and then we have liquefied it and changed the concentration of ortho or we have converted ortho to para and ortho concentration is only about 0.20 percent in that resultant liquid and if you have kept that liquid in that condition you will find that about you know 80 percent of the liquid could be stored and you know after say 1000 hour in contrast to you know the 35 percent or slightly more than 35 percent with the initial concentration of 0.75. So, what we can understand from this ah you know you you have to what you have to do is that for 0.6 to 0.2 you have to find out this expressions as we have derived earlier and you have to calculate this lines you can plot it in excel graph and then you can ah try to ah ah I mean reproduce this graph and you can also try to find out the ah that expressions for that $\frac{m}{m_0}$. So, this shows ah the I mean ah how important it is to ah convert this ortho to para when you are converting this or when you are ah liquefying hydrogen you know from gaseous state to you know the ah liquid state fine. So, these are the references you can look for the Barron book and then you know Thomas Flynn and Pobell these are the books you can refer to. So, in conclusion we can tell that this ah conversion of ortho to para is an exothermic reaction and if it is ah not converted while you know storing the liquid for longer duration then one must you know have to pay the penalty in terms of evaporation of the liquid. So, thank you for your attention.