Cryogenic Hydrogen Technology
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Week - 03
Lecture 15
Thermochemical Process

Welcome to this lecture on cryogenic hydrogen technology. We were talking about the production of hydrogen. So, in that context have talked about the electrolysis of water. Then we have now moved towards another important aspect of this hydrogen production that is called thermochemical process. This is different than electrolysis, but we are having the same source water and that we are trying to decompose into its constituent hydrogen and oxygen. It is not electrolysis, we have learned about electrolysis, we have a requirement of ΔG and that ΔG was supplied in terms of the electricity and that electricity come you know may come from different sources or you know generated with the help of some primary energy resources. Here in this thermochemical as we can understand that there are two terms thermo and chemical that means, we have to apply heat and there has to be some chemical reactions involved with it is not only water there has to be other you know chemical compounds in it.

So, let us look into that ah we have the concept that will be covering is the thermochemical water splitting and then of course, we will be talking about ah the one step thermochemical and two step thermochemical process and then finally, we will be talking about the multi-step thermochemical processes. So, in the one step that means, you know in a single step water will be decomposed ah we have looked into it already H_2O was you know decomposed into H_2 and half of O_2 that is what is the single ah step reaction that we have already talked about in the earlier lectures. But ah in contrast to this ah what is the disadvantage of this process that we are now trying to ah or if we look into this one step process we will find that if this is the initial point and this is the final point say this is I and this is F ah this can be reached from this point to this point ah keeping the temperature constant or we can follow a path like this this path B or let us call it as path A. So, these two paths can be followed ah and we can understand this is on the TS diagram the temperature and entropy diagram the between the process one ah I to F there is an entropy enhancement and in the single step process we have seen that ah the when water is decomposed into it is constituent ah we have the water at 26 degree and 1 bar pressure and between 1 ah sorry sorry I to F we had ah you know a requirement of ah Δthe work that is done you know between 1 and 2.

$$\Delta G = \Delta H - T\Delta S$$

If the temperature is remaining constant we have ΔH minus T ΔS and that is equals to in terms of electrical energy or the Gibbs free energy we have ΔG. This ΔG we were supplying in the form of electrical ah voltage and that we have learnt that you know in presence of this ah external heat input we need nearly about 1.23 volt and if it is you know below I mean if it is the thermal neutral that means, there is no assistance from the environment we have seen it to be 1.48. So, that means, we are supplying 1.48 or 1.23 volt of electrical energy to achieve this you know ah reaction to take place the water will be there and from there we will be able to generate hydrogen and oxygen. Now what happens if we follow a path B that means, we will increase the temperature and that means, we will have some elevated temperature and we will still reach the point B, but will there be any ah you know advantage in terms of this voltage that we you know have to put from outside.

$$\Delta\, W_H = \Delta H - \int_I^F T dS$$

So, ah for ah a process where it is taking place at high temperature we find that between I to F ah the temperature is not constant and we have to put this you know this integral ah which was coming as TΔS. Now we have the integral TdS between point I to F and there obviously, ah when we compared with the this if it is the path A this is for path A and this is for path B, if we look at we can understand that ah this corresponding ΔG_H that will be ah less in this be a step B because this is the shaded area part that is getting deleted from this work required ΔH.

$$\Delta G_H = \Delta G + \int_T^{T_H} \frac{\partial \Delta G}{\partial T} dT$$

So, we will have less requirement of ΔG if we are working at high temperature. So, let us try to look at this ΔH or ΔG part how it is associated with and in that connection what we will find that we can write this ΔG_H that is you know the Gibbs free energy ah the requirement at higher temperature if this you know reaction is taking place at ah T_H in as compared to the temperature T. So, we have we can write this ΔG_H at elevated at an elevated temperature as a part of combination of ΔG plus then you have the ΔG ΔT at dT, but this ΔG ΔT is ah associated with we can write ΔG ΔT is equals to minus ΔS and ah we can ok it is already written ΔG ΔT is minus ΔS. So, if we put that in that equation we find that and finally, we subtract this 2 we get the difference in the energy Gibbs free energy change or with when it is occurring at temperature T and when it is occurring at a temperature T_H whether there is a change in this ah Gibbs free energy. And ah assuming that this ah this equation will come only when we assume that this ΔH part or ah say ah this ΔH and this ΔS they are independent of temperature.

So, ah with this ah I mean there would be obviously, associated ah ΔQ_H minus ΔQ and that will be equal to this part there would be associated energy requirement I mean we have to provide this thermal energy to reduce this ΔG_H part. So, this is about this reaction now let us try to look into this ah I mean what would be the requirement of this ΔG_H corresponding to ah I mean a higher temperature what would be the kind of temperature that will be necessary to split water into a in a single step reaction. So, in a single step water ah splitting ah we want this H2O and we will provide the thermal energy. So, that you know it will get into H2 and O2. So, in a single step reaction what we have learned earlier is basically we need an electrical energy input, but here only the thermal energy that we will provide we will not provide any electrical energy.

$$\Delta G_H = \Delta G - \Delta S(T_H - T)$$

So, what would be the kind of thermal energy at what temperature do we need to provide this energy. So, that ah you know that T_H or basically what we need to find out is this T_H ah corresponding to this reaction or you know this equation that we have learned in the earlier ah slide the ΔG minus ΔS into T_H minus T that is what is ΔG_H. So, this is earlier we were providing ah this ΔG_H in terms of the electrical energy. Now, now you ah please note that we are trying to make it 0 because we are providing the thermal energy in terms of the thermal energy we will provide. So, that you know this thermal energy will make this T_H sufficiently large and what happens actually this ΔH or the change in entropy once the water is going you know beyond 100 degree centigrade as it moves from water to the steam at ah T_H equals to ah 100 degree centigrade we do not have much large change with respect to ΔS or the entropy change is not that high.

So, that means, we have to ah change the temperature T_H. So, let us look at the temperature T_H corresponding to which we will have very I mean one step ah water splitting and that means, we will provide thermal energy and water will break into its component hydrogen and oxygen. So, this is the ah I mean ah percentage of water splitting that we can achieve at the different temperature in Kelvin. Look at this temperature 4300 Kelvin if we provide at that temperature you know it is we do not need any electrical energy input by thermal energy you know itself we can split water into ah its constituents water I mean hydrogen and oxygen. But as we reduce the temperature the percentage of you know conversion of this ah percentage of water splitting will be gradually less and around 2000 ah Kelvin you can see that only 1 percent of the water will be spitted into ah hydrogen and oxygen.

So, that will not be able you know we will not be ah able to ah that will not basically serve our purpose. So, we can understand that one step process for dissociation of this water ah without any electricity or electrical input is ah not that ah efficient we have to go to very high temperature in a single step. In that case we have to look for a two-step or multi step processes where we can probably reduce this T_H temperature. So, in that case you know if we have to ah in that connection there are several reactions ah we can say that if we have a compound say AB ah and where you know water is mixed with it or and we provide the steam then we will have the oxide formation along with that hydride. So, this hydride will be forming and this BO or oxide will be formed.

So, here this A this ah you know metal I mean hydride part again with respect to heat ah it will decompose into A and you know hydrogen. Then this BO will be heated up to give us the component B and O2 and this B and A will combine together with the help of again heat to give us the you know same AB that with which we have studied our reaction. So, that means, we do not have any this component AB will be ah we do not need any replenishment. It is just trying to help ah taking ah I mean dissociating the water into it is component hydrogen and oxygen. And ah if we can have in different kind of reactions if we can identify different reactions with high ah I mean percentage of conversion percentage or high efficiency ah of the reactions then it is ah I mean with the help of heat itself you know and without any electricity we would be able to generate or split the hydrogen and oxygen, but it will be in a reduced temperature as we have learned in the earlier slides that it needs very high temperature 4300 Kelvin to dissociate it completely into hydrogen and oxygen.

We want to reduce it to a or we want to achieve that ah I mean splitting at a lesser temperature ok. So, the reaction numbers have to be you know minimum. So, we have shown here 4 step reactions. So, the higher the ah number of reactions involved it is the overall efficiency of the process will be reduced. Say if we say that each one is having say 0.9 ah percent or I mean ah efficiency is 90 percent then you can say that you know 0.9 multiplied by 0.9 and then it becomes 2 step you know it would become 0.81 or 81 percent. Though individually this reaction are 80 percent efficient that sorry 90 percent efficient the 2 step process which are you know individual processes are point 95 90 percent efficient the 2 step in a 2 step process the overall efficiency becomes 81 percent.

Along with that again if it is 90 and 90. So, all this will be ah multiplied to have 0.9 into 0.9 and 0.9 and 0.9. So, it will become nearly around say 0.64 or 64 percent ah you know ah efficient. So, like that ah I mean the equations are to be chosen such a way that there is no by product. Here you can see other than hydrogen and oxygen there is no other product and what we have is ah the water as the input heat as the input and we have this is as a product this is also as a product this AB etcetera or whatever you know they are coming and they are going back to it is original ah process. So, here one has to also look into that there is no intermediate ah product and if there is any intermediate product that handling or separation has to be safe and the reactants of the materials are to be low cost we should not have ah obviously, very high cost materials.

So, that is about the I mean requirements ah for such kind of you know thermochemical reactions and there are plenty of such reactions out of that we will be you know choosing only 2 in this lecture ah those which are you know bit promising ah. So, one such reaction is called ah you know where the ZnO which will be ah this is a 2-step process. So, in a 2-step process now we understand that ah it has now ah that ΔG corresponding ΔG_H that we have you know talked about the temperature will now come to from 4300 it is now it is coming to 2300 degree centigrade and so, here this is these are the 2 steps we have the zinc oxide which will be decomposed into this ah zinc and half of O2 this is this O2 is ah basically ah a product and what we have is that this zinc will be reacting with the water at 700 degree centigrade to give us again the ZnO and H2 as a product. So, this ZnO will be going back ah and again further reaction will be taking place. So, these are the 2-step reaction process now how do we ah achieve in a practical ah system let us have a look into it.

So, we have the solar radiation and this solar in the solar reactor what we have is this zinc oxide that will be ah you know coming in presence of the inert gas they will be mixing together ah they will be fused in this solar reactor to give us the zinc and the oxygen. Now, as we can understand that we have this ah zinc ah in the form of liquid or there will be small droplet kind of stuff, but ah this is mixed with the the inert gas and the oxygen. So, what we need is a quick quenching process and this product as you can understand it is mixed with this 2 are the gases the inert gas and the oxygen and this zinc is you know will be taken ah for ah of course, it has to be first ah it has to be quenched and as well as you know it has to be separated. The separation will be done in terms of the inert gas and oxygen and on the other side we need this zinc you know to carry ah forward the other reaction at 700 degree or 700 Kelvin. So, here this oxygen and inert gas is getting separated then we have this zinc which will be reacting with the water.

So, here comes the water splitting reactor where this water is coming and reacting with the zinc to give us the ah hydrogen and ZnO. So, this ZnO ah will go back to it is ah you know ah this first step where we have studied with this ZnO and the inert gas, but here we get hydrogen as the product. So, here ah in this 2-step process you can understand that we are not using any ah electricity, but just by ah providing the thermal energy we are able to split water into oxygen and hydrogen, but the temperature maximum temperature that we have learned earlier in a single step where the 4300 Kelvin there was the kind of temperature that was required ah to carry forward this reaction. So, it is reduced to nearly about 2300 maximum temperature that we need. So, the associated material and this separation process and etcetera ah these are still you know ah I mean costlier or it is not that cost effective as compared to the electrolytic process, but one good part of it is that we are able to use this solar radiation to ah I mean ah use it for generation of hydrogen and oxygen, but other than that you know we need there are separation process then ah it here also we need ah a separation of ZnO and then we also need to separate the zinc and the $O2$ and ah the inert gas.

So, compared to all this you know it is still not that competitive with respect to the electrolysis process. So, now let us look into a multi step process again ah there are several such reactions which are possible. So, here we will be talking about the multi step process where it is ah the sulphuric acid and iodine process ok ah. Here comes ah there are these 3 processes ah one is taking place at 1123 Kelvin and the other one is 723 Kelvin, the third one that Bunsen reaction that is taking place at 393 Kelvin. So, these are the ah processes involved.

So, now, here we have 3 steps ah in the first step we are decomposing the sulphuric acid into it is component like ah SO2, H2O and half of O2. This half O2 is a product and then this half O2 is coming out then we say that this SO2 and H2O ah basically ah they will be combining this SO2 is coming from here and water will be supplied from outside and this iodine that iodine will come from this HI basically this HI will be formed with the help of SO2, H2O and I2 that is the Bunsen reaction it will give 2 acids ah, but 2 acids they are not miscible immiscible acids. So, one is lighter than the other and it can be separated. So, hydroiodic acid and H2SO4 will be generated and you know they will be separated then this hydroiodic acid will be decomposed into iodine and hydrogen. So, this iodine is going back to this Bunsen reaction this SO2 is coming back to this Bunsen reaction and we have this H2 as a product. So, here we can understand that we are supplying water and then in that water you know is getting decomposed to the half of O2 and H2, but this is multistep reaction it is not a single step reaction we have understood that the single step reaction needs very high temperature.

If we want to reduce the high temperature to a moderate temperature, but without any electricity. So, you can understand that this kind of temperature we can probably create ah I mean or we can have it ah associated with the nuclear nuclear power plants. So, if we are able to you know ah achieve this kind of what we can make the other processes we will talk about that what are the other complexities we have associated with these processes. So, this achieving this kind of temperature on earth is not that difficult particularly when we have the nuclear power plants. So, we can think of using this thermal energy without any electricity we can what I mean decompose water into it is constituents.

Now, here ah we have the sulphuric acid ah decomposition that is ah this reaction this is taking place at 1173 Kelvin. So, what we are getting here is basically the SO_2 and H_2O and half of O_2. It is not like that it will be only you know ah giving us this, but there will be some ah part which is ah the H_2SO_4 will also be mixed with it this ah this H_2SO_4 will also be mixed with this part. So, ah we will try to cool it and separate them out into it is constituent that is ah O_2, O_2 will be one on one side and H_2SO_4 and H_2O on the other side. So, this H_2SO_4 and H_2O will be going back and here we need ah sulphuric acid ah concentration ah it has to be concentrated.

So, that you know this is ready for this sulphuric acid decomposition. So, this is one side the other side we have this SO_2 and O_2 part which will go back and this finally, you know this O_2 will come over here finally, it will be separated as a product. What is happen to this SO_2? This SO_2 is coming to this Bunsen reaction. So, ah other than that this one is this SO_2 that is what is required then what we have the you know what is needed is the water of course, this water supply will be ah given from outside H_2O will be given from here and from that H_2O it will be coming over here in the Bunsen reaction. This SO_2 is coming from this decomposition of H_2SO_4 along with that this iodine will be coming from the hydroiodic acid decomposition.

So, this hydroiodic acid decomposition will give directly this hydrogen as product and here this iodine will go to the Bunsen reaction, but what is the source of this ah hydrogen hydroiodic acid? This acid comes from the Bunsen reaction where we will have all this safe H_2O, I_2 and O_2 and on this side, we have 2 liquids ah a hydroiodic acid and the H_2SO_4. So, as we have understood that this 2 are immiscible ah I mean ah acids and they can be separated ah depending on it is ah you know one will be settled at the bottom other will be settled at the ah top. So, from there we can ah take out this ah this H_2SO_4 and hydroiodic acid this separation will be taking place at this point. So, this separation will give H_2SO_4 and H_2O on this side and this sulphuric acid again will be decomposed. On the other hand this hydroiodic acid will be coming over here to give us the hydroiodic acid ah decomposition and it is not only that you know the separation part that Bunsen reaction if you look at we have both iodine O_2, H_2O and this separation is only to take out the oxygen from this process and once that is separated out then we have the separation of this hydroiodic acid and the H_2SO_4 along with that we have the iodine and the H_2.

So, H_2SO_4 and ah water is going to that side along with that you know this is ah aqueous solution. So, basically hydroiodic acid and water along with the iodine will be going to this ah hydroiodic this you know reaction. So, the overall reaction if you look at the complexities are involved with it is that not only it is the temperature, but it is the separation of acids that is to be done. Obviously, acidic solutions are not very easy to be separated out and that to at high temperature. So, in terms of it is material in terms of it is ah composition I mean in terms of it is ah separation processes all these are quite challenging to ah give us a complete commercial solution for these multistep processes.

Multi step process, but we could understand that if we can handle this ah you know these processes or we can commercialize it it will be a good source of ah ah hydrogen energy because we have this kind of ah temperature available ah in the associated with the thermal ah nuclear power plant ok. So, that is about the multi step process. So, let us look into the references you can read this reference of ah particularly for the ah thermodynamics that we have talked about and the other book will give you this process. There are plenty of books ah particularly dealing with this ah this is basically the futuristic process. So, we can understand that one step process needs to high ah to conclude with we need a very high temperature in a single step process, but multiple step or two step processes are ah you know can reduce this temperature and ah of course, to ah make them commercially compatible to the the electrolytic process ah we need to ah improve the overall processes ah to ah a large extent.

So, that is all. Thank you for your attention.