Cryogenic Hydrogen Technology
Prof. Indranil Ghosh
Cryogenic Engineering Centre
Indian Institute of Technology Kharagpur
Week - 03
Lecture 11
Hydrogen Production (Electrolysis)

Welcome to this lecture on cryogenic hydrogen technology. So, we were talking about the hydrogen production and in continuation to that today we will be looking into the process ah which is known for long that is electrolytic hydrogen. I mean if we electrolyze the water ah the or the water electrolysis if we are doing then we can produce both hydrogen as well as oxygen and we will try to see ah what is the ah I mean basics of this electrolytic hydrogen. Today in this class ah if we ah continue ah we will find that ah this is the concept we will be covering today and the keywords are like basically what are the minimum cell voltage and what is the Gibbs free energy in this connection ah how it is related to this electrolytic production of hydrogen. So, in continuation to our earlier discussion when we have talked about ah this non-renewable ah or renewable energy. So, here ah when we have say said I mean we are looking about the hydrogen production we have talked about the different you know primary. So, we have talked about different primary sources of energy like natural gas, coal, nuclear energy and from there we are generating the electricity that is the secondary energy and from there you know using that secondary energy and water we have said that you know ah it is ah used on the ah third level you know ah for the I mean using the conversion technique electrolysis we can produce non-renewable ah energy ok. So, these are ah basically the when we are using the fossil fuel ah even you know if we are using the renewable energy resources ah where we have talked about say be it biomass or solar energy or you know the tidal or the wind energy etcetera. We are generating the secondary energy in the form of electricity and that electricity is finally, used you know to you know do the electrolysis of water. So, from these two ah I mean slides we can understand that be it renewable or non-renewable energy we have if we have to generate the hydrogen from electrolysis of water.

So, it has to come you know first of all we have to have this secondary energy which may come from the renewable or non-renewable energy or the primary and the secondary energy resources. So, we are heavily dependent on this two energy resources to you know ah generate this ah ah hydrogen from water. So, we will try to see what are the actual you know thermodynamic restrictions ah that will limit or you know ah I mean that will bound our hands to dissociate water ah and produce the hydrogen ah based on this electrolysis. So, I think it would be ah just basically a recapitulation for many of you ah if we say that this is an electrolytic cell where this details of course, we will talk later on just today we know we will try to analyze the thermodynamics of it and ah just if we say that you know we have an electrolytic cell and where we have water and we have put two electrode and we have put a cell in between. So, you know it is ah the positive potential and here you will find it is generating ah O_2 oxygen will be generated in this and on this side, we will have the hydrogen.

So, basically if we look at we will find that we are taking water that is H_2O this is in the form of liquid and from there we are getting the H_2 and half of O_2. So, if we have taken one mole of water from there we are getting one mole of hydrogen this is in gaseous condition and half mole of O_2 is coming this is also in gaseous condition. So, we have started from liquid from there we are getting you know two gaseous product one is hydrogen another one is oxygen half a mole of oxygen. So, ah this is you know there has to be some separator in between. So, that they are not mixing with each other etcetera and you know there has to be ah I mean some you know cell potential minimum cell potential that is to be applied.

So, let us try to look into it ah into that point of view ah. So, our initial point is you know water and from there we are getting two gaseous products. So, if it is so, ah let us you know try to look at the thermodynamics of it I mean how much would be the change in I mean how much energy do we need to put in. So, these are the you know ah if we look at it say we have one mole of water we have as if you know we have taken one mole of water and ah that water is at 298 Kelvin temperature and it is at atmospheric pressure. So, these are the ah I mean initial conditions at which water is there.

So, if we have one mole of water from there as we have said that there is ah you know ah half of O_2 and H_2. So, what is the change in the enthalpy and in the entropy? So, these are the you know ah data we have taken from this reference you can refer to this for this detail of these values. So, if we have this ah you know ah values ah let us try to go one by one what are the changes in different you know thermodynamic potentials. So, say first of all let us try to look at the change in enthalpy for example, what is the change in enthalpy if we calculate? So, from here ah if we look at the enthalpy of water is 285.83 with a negative sign and the final product that is oxygen half of oxygen and half of hydrogen.

So, if we finally, calculate the ΔH that is you know the change in enthalpy change in enthalpy that is change in enthalpy that is final enthalpy minus initial enthalpy final enthalpy is you know 0 plus ah 0 minus of minus 285.83 and that is kilojoule per mole. So, we have taken 1 mole of water. So, for 1 mole of water this comes out to be 285.83

kilojoule.

So, the change in the energy sorry enthalpy that is 285.83 kilojoule. So, if we want to electrolyze this water we you know expect a kind of change in enthalpy by this amount 285.83 kilojoule. So, you know some of these numbers we will try to remember and time and again we will be using these numbers ok.

So, next is if we want to ah you know calculate what is the PdV work why this PdV work is coming in play because we have said that you know this water is getting converted into half a mole of oxygen and 1 mole of hydrogen. So, this will evolve in the form of bubbles ah you know if we go back to our earlier slides. So, here this will you know come out as bubbles ah from the electrode and they will evolve like this. So, here it was water and you know they are finally, coming out as bubbles. So, we can understand that ah you know there would be some amount of PdV work because there is change in volume of this gases ok.

So, if we want to calculate that ah PdV work let us ah try to look into it. So, what is the pressure we have we have ah you know 101.3 kPa is the atmospheric pressure and what is the ΔV. So, try to let us try to calculate that P is equals to 101.3×10^3 Pascal. So, this is this many 101.3 kPa and ΔV let us try to calculate. So, initially we had you know ah we have started with ah 1 mole of hydrogen and finally, how much did we get we get ah ah you know 1.5 ah sorry 1.5 mole of you know total hydrogen plus you know oxygen.

So, in that case ah what we have is this ah, but you know this water was in the liquid form and in the gaseous form both this hydrogen and nitrogen was there. So, we can say that 1.5 mole of hydrogen and nitrogen multiplied by you know we have 22.4 liters per mole of you know gases at NTP or STP this is ah that is mean that means, you know at 1 atmosphere and ah 273 Kelvin. So, that is what is the volume occupied by 1 mole of gas and here we have 1.5 mole of gas. So, we have 22.4 liters we will convert it into the meter cube later on. So, these many liters of ah gas and 1.5 mole then comes ah that is the pressure P 101.3×10^3 Pascal and there is a change in temperature you know we have worked at ah what temperature we have worked at ah you know 298 Kelvin, but this you know it is that taken as 273.

$$\mathrm{PdV} = \frac{1.5 \times 22.4 \times 10^{-3} \times 101.3 \times 10^{3} \times 298}{273}$$

So, it will come as 298 by 273. So, if you evaluate this value you will find that it comes out to be 3.715 kilo sorry this kilojoule ok. Only thing is that this liter has to be changed to meter cube. So, 22.4 liters will become 10^{-3}. So, this if you finally, put in.

So, how much will it come this is 1.5 then 22.4 into 10^{-3} multiplied by 101.3×10^3 Pascal multiplied by 298 by 273. So, this number comes out to be 3715 joule 0.4 joule and this is you know in terms of kilojoule we put it as 3.715 kilojoule. So, this much amount of PdV work has to be there.

So, if we ah you know try to now calculate the change in internal energy. So, how much will it be change in internal energy will come out to be this is a ΔH,

$$H = U + PV$$

H equals to U plus PV ok.

$$\Delta H = \Delta U + PdV$$

$$\Delta U = \Delta H - P\Delta V$$

And from there we can say that ΔH is equals to ΔU plus PdV we have not changed any you know pressure the pressure remains constant the temperature also remains constant. So, now, you see already we have this parameter known to us and we have estimated this PdV work also. So, we can estimate this change in the internal energy that is ΔU that comes out to be ΔH - PΔV.

So, this much amount of internal energy that has to you know be associated when we have this reaction. So, how much is it? It is 285.83 minus we have estimated it to be 3.715 kilojoule. So, for this would come out to be 282.1 kilojoule. So, this much amount of internal energy change will occur for converting 1 mole of water to half a mole of oxygen and half 1 mole of hydrogen. So, this is about the internal energy and the enthalpy change. Now, there comes another parameter which we call it as the Gibbs free energy. Why do we want to calculate this Gibbs free energy? Because finally, we will see that how much you know energy we can take from the environment and how much you know we are supplying it in the form of electrical energy. So, in the cell as we have told you that or the electrolytic cell that I mean that we are providing some you know electrical input that electrical input we now want to estimate how much you know minimum cell potential that we should apply and for that we need to calculate the ΔG.

So, let us try to do that if we look at ah that ΔG calculation we ah let me erase it first. So, we have estimated ah the internal energy ah or change in internal energy from the PdV work. We have also calculated ah we have also calculated ah the change in the enthalpy. So, let us try to put that ΔH is equals to 285.83 kilojoule. Then we have estimated ΔU that is equals to 282.1 kilojoule and we have estimated PdV work also that is 73.715 kilo joule. Out of this you know using this values ah can we estimate ah the ΔG. So, ΔG is will come from which relation G is related to the H and the TS. So, that is the enthalpy temperature and the entropy. So, if we want to calculate then ΔG ah we need to you know calculate also T remains constant we have said that that there is no change in temperature and there is no change in pressure. So, we have to calculate the ΔS. Now, for calculating the ΔS we have to go back to that ah earlier slide when we have talked about ah these values.

So, the entropy values of water was 69.95 kilo joule per mole per kelvin and that of hydrogen is 130.68 and for oxygen it is 205.15, but please note that there is you know half a mole of oxygen present in that reaction. So, now, based on this ah values we can try to calculate the TΔS. So, if you have to calculate the ΔS what we will find that is the final enthalpy minus the initial enthalpy multiplied by the I mean temperature.

So, if we look at it. So, it has to be 130.68 plus half of 205.15 that is the final entropy and initial entropy is 69.95. So, that we have to subtract and this whole thing will be multiplied by the temperature 298 K.

So, let us try to look into it ah this is ah as I told you that 298 is the number, 298 is the temperature and the final enthalpy is 130.68 plus half of 205.15 that is the entropy of oxygen and half is coming because it is ah half of mole of half mole of oxygen is involved. Then we have to subtract how much 69.95. So, this number is supposed to be ah from this value you will get as 48664 you can calculate do the calculation and since we have one mole of you know one mole of water associated with this you know work. So, we have 48.66 kilojoule of T ΔS this is what this is basically we try to calculate this number this is temperature T this has come like this and this is the entropy of hydrogen entropy of half mole of oxygen and this is the entropy initial entropy that was of water. So, this is the change in entropy this is ΔS and this is T.

So, T × ΔS comes out to be 48.66 kilojoule. So, now we have this number ΔH already we have calculated and T ΔS just now we have estimated. So, based on that you know we can find out ΔG that ΔG would come as how much was ΔH, ΔH we can put as 285.83 kilo joule minus we have estimated it to be 48.66 kilo joule this many kilojoules and the ΔG comes out to be if you estimate this value you will find it to be 237.17 kilojoule. So, this much amount of Gibbs free energy has to be associated when we want to break this water into hydrogen one mole of water we want to break into ah you know half a mole of oxygen and one mole of hydrogen. So, how this ΔG is useful for us we have seen that we need a total change of this ΔH that is 285.83 kilojoule that much energy has to be you know ah that much change in energy has to be associated with this change of water to hydrogen and oxygen. But we have estimated it to be this ah you know Gibbs free energy we have estimated it to be ah 237.17 kilojoule and since this reaction you know is taking place in an environment which is in connection with our I mean atmosphere.

So, that means, there is a possibility that this much energy would be supplied from the environment or since this temperature 298 Kelvin and this you know this ah container it is in connection with the it is in connection with the atmosphere this $T\Delta S$ will be supplied as if from the environment. So, it is in communication with the environment and this $T\Delta S$ is being supplied from the surroundings. So, that we are just you know the minimum potential that we have to apply will be only this you know to supply this ΔG what does it mean? That means, that if we are supplying this in the form of electrical energy we can you know I mean show that this ΔG is basically the Δwork and that Δwork is non-PV work there is one PV work and there is one non-PV work. This non PV work that we are supplying that is coming in the form of electrical electrical energy. So, this non-PV work ah we are supplying in the form of electrical energy then ah if we look at this electrical energy part we can ah you know try to put it in this form that how many number of electrons those are sorry the how many charge that is in the flowing and what is that potential.

So, that is what is the electrical energy. So, now, if we want to put it in that forms and if we say that there are ah so, please try to remember this number this is 237. ah 237.17 kilojoule of Gibbs free energy we need and now we are trying to calculate or we try to you know equate it with ah this number ΔG with the electrical energy where we have said that there are ah you know n number of mole sorry n number of electrons flowing per mole ah ok and n number of moles of you know electron is flowing and if F is the Faraday constant that is ah you know the number of charges per unit mole. So, you have n into F and the voltage related to that. So, this is what is that you know electrical energy and here we have 237.17 kilojoule and that is electrical equivalent say we have two number of electrons and the Faraday constant is 96485 these many coulombs per mole and we have this voltage. So, based on these values we can now try to calculate this 237.17×10^3 divided by 2×96485. So, if you evaluate this value we will find it to be 1.229 volt or approximately this is 1.23 volt. So, that is the minimum you know voltage that you have to apply if you have started with 1 mole of water at 298 Kelvin and 101.3 kPa that is atmospheric pressure this is 298 Kelvin and 1 atmospheric pressure you have started and you have to apply this voltage at least 1.23 volt to dissociate it into water and sorry a half a mole of oxygen and 1 mole of hydrogen. So, that water was in as I told you that it is in the liquid form from there you will get half a mole of O2 plus you know 1 mole of H2 and these two are in the gaseous form. So, we have seen how much amount of PV work is associated with it and how much is the electrical input that is you know coming as non-PV work.

So, based on these calculations we could understand that we have you know at least we have to apply 1.23 volts. So, this is a summary of this calculation we have 283.83 kilojoule of ΔH, PV work we have estimated and ΔU we have estimated and also the ΔG. So, finally, we could conclude that we need ah these are the references ah I mean you can take it from ah the different values we have taken and this is the conclusion that we have a minimum potential of 1.23 approximately if we want to dissociate water into oxygen and hydrogen. So, thank you for your attention.