Cryogenic Hydrogen Technology

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Week - 03
Lecture 12

Electrolytic Hydrogen

Welcome to this lecture class on Cryogenic Hydrogen Technology. We were talking about the production of hydrogen through electrolysis. So, in this ah class we will try to learn about the production of hydrogen using the alkaline electrolyzer and solid polymer electrolyzer. And before that ah if we recapitulate some of the things that we have learned in the last class, we have tried to calculate the potential or the voltage that will be necessary to split water into its constituent hydrogen and oxygen. So, we have calculated it on the basis of the thermodynamics and we have learned ah certain numbers and today we will continue from that point onward. So, it is basically a continuation of what we have learned in the last lecture class and it is electrolytic hydrogen and this concept will be covered today along with that we will look into the I mean basically it is the water electrolysis.

And if we look at or recapitulate what exactly we have learned in the last class, we have said that this water we are trying to dissociate it into water I mean hydrogen and oxygen in the form of gas and the energy that is needed or the enthalpy that will be necessary is 285.83 kilojoule per mole of hydrogen. So, if we have to produce 1 mole of hydrogen, we will need 285.83 kilojoule of energy.

So, that you know along with that we have also calculated that you know if we have water in the form of liquid and we are trying to get it in the form of gaseous oxygen and gaseous hydrogen, we need to spend nearly about $P \Delta V$ work of 3.7 kilojoule per mole and that will constitute or you know ah reduce the basically the ah enthalpy part by sorry the internal energy part will be reduced to ah by 3.7 kilojoule per mole. So, the internal energy would be about 281.1 kilojoule per mole.

But at the same time if we look at we have also said that we you know we are taking help of the assistance or it is communicated with the connected with the environment. So, this environment is also supporting some amount of energy or providing some amount of $T \Delta S$ amount of energy which will reduce the ah ah ΔG or the Gibbs free energy which is directly related to the self voltage that will be necessary. So, that corresponds to 1.229 Volt. So, this we have learnt, but ah there is another point say if we think that you know this ah 2.8 ah 48.7 kilojoule of ah ah kilojoule per mole of energy which was coming from the environment if it is not available. So, we call it as thermo neutral voltage if you look at in contrast to the earlier one that was the thermodynamic voltage that is necessary to split water into its constituent. But now we are talking about thermo neutral where we will see that there is no ah communication with the environment. That means, we will not have any energy ah from this ah environment we will not get the support.

So, ah obviously, there would be there would not be any T ∆S or this assistance is not available in that case what will happen ah we will not have this T ∆S part.

$$\Delta G = \Delta H$$

So, only we will have ∆G equals to ∆H now there is no T ∆S part in it. So, the amount of electrical energy that we have to ah get earlier it was much less because we were getting some assistance from the environment and T ∆S was supplied and it was reduced from ∆H minus T ∆S and that equivalent was you know 1.229 Volt. But when we have you know this entire energy has to be supplied from the through the electrical you know ah energy you can understand that the corresponding voltage would be say ah 285.83 divided by n equals to this is kilojoule per mole and you know this is 2 number of this part electrons and we have the Faraday constant 96485 coulomb per ah mole. So, this will be ah you know will constitute if you calculate this value of course, kilojoule has to be converted into ah joule and if you take this this will be 10 to the power 3 part would be there instead of this k and accordingly we will find that the voltage necessary is 1.48 volt. So, that means, ah you know there is some potential or neutral I mean thermo neutral voltage earlier we talked about 1.229 Volt now it has increased to 1.48 Volt. So, there is a lower limit and there is an upper limit for this ah you know this ah voltage that will be necessary to split water into its constituents. So, ah, but does it depend on the temperature because we have talked all these calculations that we have done is based on the temperature 298 and pressure atmospheric pressure. So, does it depend on the temperature and pressure ah the answer is ah yes it depends largely on temperature. So, if we look at this ah temperature dependence of this voltage you will find that as we keep on increasing this ah temperature and we try to calculate this energy needed to split water we will find that you know there is a line from here nearly we calculated it to be 285.83 kilojoule per mole this is for the ∆ah h that the total energy requirement and there is a jump ah here this temperature is around 100 degree centigrade that is you know when ah this water is changing its phase from the ah liquid to the steam condition and evaporation of this you know energy will be ah necessary.

So, there is a step jump here ah at around 100 degree centigrade. So, this is the curve for the total energy ∆H and as we find that of course, ah it is ah dependent on the temperature it slightly ah reduces up to 100 degree centigrade, but in from beyond 100 degree to high temperature its slightly increasing it is not a strong function of the temperature. But there is another part where we find that this T∆S or this assistance from the ah environment or because we are supplying this water at high temperature since we have this energy heat input T∆s accordingly this Gibbs free energy will also change and this Gibbs free energy will with the increase in the temperature this will ah decrease. So, we have earlier ah calculated this Gibbs free energy and correlated it with ah n into f into the voltage. So, accordingly we can calculate based on this curve or based on this ah you know input we can calculate the voltage necessary in the ah cell to dissociate this water into its constituent hydrogen and oxygen.

So, this will be the cell voltage, but we have put an ideal cell voltage ah because all the conditions are ideal ah we will talk about it later on what non-ideality will come in play ah. So, this is the voltage that we have calculated if you remember this was the cell voltage necessary nearly around ah what is called at 26 degree centigrade and atmospheric pressure we have calculated it to be 1.229 Volt and the thermo neutral you know voltage we have calculated it to be 1.48 Volt at around ah 26 degree centigrade and atmospheric pressure. So, we find that as the temperature is increasing ah this there is a small jump at this ah 100 degree centigrade as we have learned that there is a change in the state from water to ah the steam and we have this region ah the now we have 3 regions 1, 2 and 3 and they are separated by the thermo nuclear thermo neutral potential and then you know we have ah this voltage necessary.

So, below this curve there is a you know this part is generation of hydrogen with the absorbed heat from the environment, but there is a generation of heat if you are putting a potential or voltage more than this voltages there would be generation of heat with the ah generation of heat would be there along with the generation of hydrogen, but ah I am sorry there is a no generation of oxygen ah sorry no hydrogen will be produced if the voltage is you know below this part. So, no hydrogen generation would be possible ah even if you are putting it at high temperature, but you know at around say you know this 500-degree centigrade if the cell voltage is less than 1 Volt we will find there is no ah hydrogen generation. So, this ah hydrogen generation part and the dependence of this voltage on temperature has been noted here. So, with this ah background knowledge let us move forward. So, ah let us look at the real scenario where you will find that ah you know there is a lot of practical problems will arise as we have learned that we have put 2 electrode one is the cathode and anode and we have connected it with the cell.

So, this is the voltage where you know we were talking about so far. So, what is that minimum voltage that we need to apply if we if this cell is connected with the environment or if it is not connected with the environment. If it is getting that assistance T ΔS that will give you one kind of cell voltage if it is not if it is not connected then it will be different. But let us look at the practical problems ah what are the typical resistances we have in a cell. So, first of all there would be the electrical resistances this ah resistances at ah the ah positive terminal as well as in the negative terminal.

Because the cell will be connected finally, with this electrode with the help of certain ah connectors and this connected positive some amount of the resistance. So, some voltage drop will be occurring in this ah you know in this lead connectors. Then we will have also this ah electrodes those are also basically ah metals and it will have it is own resistance. So, we have the cathode resistance then we have ah the resistance or ah basically the electrochemical reduction resistance. That means, ah here this ah hydrogen ah you know ah coming as ion and they are transferring their charge they are becoming you know their nucleation of the bubble will start finally, they have to come out of this surface and evolve as gas from this surface near to the ah you know outside.

So, this is ah there is a finite electrochemical reduction resistance. And then we have this electrolyte ah we will talk in details about this electrolytic part we have so, far talked about only water as if we have put the water and water is getting dissociated into H+ and O- OH- or hydroxyl ion. But we will see later that it this electrolyte also ah probably you know that this water is a conductor of electricity yes, it is true, but ah that is having you know finite resistance and that is the electrolytic resistance we try to minimize it. Then ah next, we will have similar to that you know cathode resistance or cathode electrochemical resistance we have the electrochemical oxidation ah resistance on the anode part. So, here ah this resistance is again you know ah we we cannot avoid this resistance on this anode part or on the anode.

And of course, this ah you know this hydroxyl ion will come over here they will again ah you know dissociated to its constituent parts. So, finally, you will find that it is evolving as ah oxygen from this ah anodic surfaces. So, this charge transfer bubble formation and nucleation and finally, ah detachment from this ah this anode surface all this will occur in the surface and ah that will ah determine the kinetics of this total reaction. So, we have to look into that part and this resistance is equally important. So, finally, we have ah this anode resistance because of the finite metallic resistance of this anode and the lead resistance of this which is connecting the anode with the positive terminal of the cell.

So, these are the kind of resistances we have ah in the ah I mean in the whole cell ah and we have talked about this voltage and its dependency on the temperature. But finally, we find that if we are putting this voltage we will never be able to achieve the dissociation of this energy or dissociation of this water. Because there is finite you know resistances ah you know offered by this the ah connecting where be it cathode or the anode or the electrolyte and of course, this R_3 and R_5 are something which is you know giving us basically the dissociation of water into hydrogen and oxygen. But all the other resistances say from R_1, R_2, R_4, R_6 and R_7. So, all these resistances we try to minimize because these 2 you know then we want to you know have that complete you know dissociation of oxygen and ah this ah oxygen and hydrogen ah I mean basically water will be dissociated because of this ah this throughout the important part other are basically the losses.

So, ah this is about the electrolytic resistances. So, we understand that this ah resistances all these resistances will give us ah finite over potential. So, or over voltage basically what we ah understand that this is we have estimated this ah thermodynamic ah voltage or thermo-neutral voltage, but we need to put in excess of what we are giving in this ah cell voltage. So, accordingly we will find that ah there is R3 and R5 that we have said which are the most important part. So, we have the reaction resistances if we categorize them into ah you know different categories we will find that the reaction resistances and then transport resistance.

So, what we have looked into is in between we have the separator. So, the separator is basically is separating the ah products here you have hydrogen products evolving as vapor and here we have oxygen vapor which are moving out they are separating this, but they will allow the ah migration of this ions, but they will not allow the ah vapor bubbles ok. So, transport resistance we have the membrane and this membrane will be there then ion will be moving from one end to the other. So, we have the transportation resistance and other than that we have the electrical resistances we as we have ah understood that this is a finite ah anode and cathode resistance and the lead resistances. So, accordingly ah we can see that this ah over voltage E equals to E_0 this is the you know ideal that thermodynamic voltage, but we need because of this finite you know current that will be flowing through it and the resistance it is the electrical resistance and we have this charge ah you know transfer over voltage eta A and eta C that is for one for the anode and the for the cathode which is related to you know R_3 and R_5, but most importantly what we find is that we are putting some value j which is nothing, but the ah I mean current density or the current per unit area.

So, that means, ah so far we are talking about ah that we will just you know connect a cell and with some voltage we will be connecting and we are expecting you know the hydrogen and oxygen to come out from this cell, but it is ah of course, it will come, but the amount ah which is to be the amount of hydrogen generated from here or you know the oxygen is equally important ah if we want to separate them out and in a finite quantity we must put some good amount of current. So, now we it is ah there is another ah requirement we have the current and ah the current density. So, how much area will be ah I mean involved with this reaction because we have learned that this ah charge will be coming over the surface and, on the surface, it will transfer its ah you know the charges and this ion after transferring the charge they will become ah nascent kind of you know we will talk about that in detail. So, they will become the nascent hydrogen or nascent oxygen and from there it will produce the molecule of hydrogen and oxygen finally, they have to leave the surface and come out as ah gaseous form. So, all this ah dynamics has to ah take place on the electrode and we have to give a very large amount of surface area.

So, we have the current as well as ah you know the surface. So, current ah density or the area density or current ah you know surface area per unit surface area is equally important. So, we will ah try to see how practical ah things are you know possible. So, there are unipolar electrolyzer ah I mean that means, we need large number of ah cells to get meaningful amount of ah hydrogen and oxygen. So, one of them is ah you know this configuration which is called the tank type or the unipolar.

So, here what we have is ah the 1, 2 and 3 cells they are connected in ah parallel. So, here all this ah cathode and anode this is the cathode they are connected with the negative voltage ah potential and here this all these anodes are connected with the same potential. So, here this is say if it is 1.6 Volt if we have applied and this is on the negative part and this 1.6 Volt all this anode and cathode are ah you know ah connected with the same voltage.

So, here we will have on the cathode we will find um hydrogen and, on this side, we will have the oxygen. So, all this cells ah say cell number 1, 2 and cell number 3. So, all of them will be connected in parallel and we have the same you know 1.6 Volt applied to it, but as you can understand that since there in parallel connection. So, everybody will need some amount of current flowing it here and it will be coming like this and going back.

So, like that we will have the current requirement will be depending on the number of cells fine. So, ah in contrast to this unipolar electrolyzer ah we have another ah called the bipolar electrolyzer where you will find that the cathode and anode are connected back to back and we have the electrolyte on this here we have the electrolyte electrolyte solution and here we have the cathode and then you know it is the anode on back to back they are connected and on this side we are putting ah positive and on this side we have the negative terminal of the cells. So, here we will have the hydrogen generated and, on this side, it is the oxygen they are separated each cell are separated by ah a separator this is a separator here this is also separator this is also separator. So, we have cathode here then this is another cathode this is another cathode and these are the anodic surfaces this is anode this is anode this you know all these are anodes. So, this is sometime also called bipolar because this on the same plate we have on one side we have the cathode on the on other side you have the anode.

So, 2 polarities are there on the same plate we call it bipolar or filter press type ah electrolyzer. So, this ah if we look at ah the I mean if we take a comparison we will find that we are applying the same voltage say V and the amperage would be the if there are n number of cells. So, we need n into I amount of current on the contrary here what we have you know since the cells are in series the voltage will depend on n × V and the amperage would be ah the same amount of current will be flowing through the all the cells. So, I would be ah the same, but the cell voltage would be you know that voltage that you have to apply ah will be depending on the number of cells. And here as in contrast as we have said that the same voltage will be applied over the all the cells, but amperage would be ah definitely high.

So, here the current requirement is high for a low voltage here the voltage requirement is high with a small current. So, this is ah you know the requirement wise for the unipolar and bipolar electrolysis. And on the ah, I mean if anything goes wrong with this unipolar ah electrolyzer it is easy to repair, but you know if anything goes wrong you have to dismantle the entire assembly and you have to then again ah repair it and then put it back. So, we will find application for both this type of electrolyzers in practice. So, these are the references we have ah you know used in this lecture you can also ah use it.

And there are ah I mean in conclusion we can say that voltage depends on the temperature voltage means the cell voltage to be applied on this electrolyzes it depends on temperature that we have learned. And this sub valve voltage is necessary because there is some finite ah you know reaction taking place and there is an also the ah different resistances offered by a practical ah cell has to be overcome. So, we need ah some excess voltage in addition to the thermodynamic voltage that also we have learned. And the cells can be connected in parallel or tank type connection and they can also be connected in series which is called the filter press connection and filter press configuration. So, thank you very much for your attention.