Cryogenic Hydrogen Technology
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Week - 05
Lecture 22
Coefficient of Expansion

Welcome to this lecture on Cryogenic Hydrogen Technology. We are talking about the liquefaction of hydrogen. In that context, we have talked about the I mean ideal liquefaction cycle. So, we will continue on that ah and in that respect today we will be talking about this is basically a continuation of the cryogenic liquefaction process. So, today we will try to cover the following things and in that connection ah I mean in the connection of hydrogen liquefaction and in particular ah I mean cryogenic liquefaction ah we will look into the coefficient of expansion and the maximum inversion temperature which we will find its most relevant for any cryogenic liquefaction process and in particular ah hydrogen liquefaction process. So, let us ah slightly recapitulate and where we have talked about the ideal refrigeration and the ideal liquefaction cycle in the last lecture ah this is the Carnot refrigeration cycle and we said that a half of that cycle is good enough for us to make a ah ideal liquefaction cycle.

So, in that context I have forgotten to mention ah the heat I mean some conventional things that we generally follow in this lecture ah that heat addition to the system we considered it to be positive and heat rejection by the system is considered to be negative. Then ah similarly work done by the system is positive whereas, work done on the system we considered it to be negative and in that connection if you look at we have also calculated this ah ideal work requirement where we will find that minus W by mdot that is the work requirement per unit mass of gas compressed or per unit mass of gas liquefied that is ah for ideal liquefaction cycle its one and all the same. But look at the negative part where we have negative sign we have put ah its basically that takes care of that negative ah I mean this indicates that it is work done on the system and work done on the system is basically negative. So, ah this negative of you know this quantity finally, you will get as a positive quantity, but since this minus W by mf or W by mdot that takes care of that negative part of it indicates that it is work done on the system.

So, ah this is an ideal liquefaction cycle where we have the starting point I mean as one and we want to come back to this finally, you know ah saturated liquid this is ah saturated liquid f and this is saturated vapor g. So, ah it is not practical in the sense we have said that state point 2 will be lying ah in a it is in the gaseous state and this is in some ah you know this pressure would be some giga Pascal and not only that from point 2 to ah I mean f if we have to ah just you know expand the gas in an isentropic expansion. So, from ah completely gas to completely liquid there is no expansion engine which can take or you know it can ah produce such a kind of ah thing from completely gaseous state to completely liquid state it would not be able to generate and so, it is not practical, but ah we understand that ah ok we have to compress the gas and then we have to expand it. So, there are ah 2 ways of expanding the gas ah. So, it is the basically the steps towards the practical liquefaction cycles.

So, we have the isobaric lines. So, these dotted lines are this line is isobaric line, this is an isobar, this is another isobar and we have also learned that these are the ah isenthalpic lines. So, the H remains constant ah on this blue colored line is the isenthalpic line, this is also isenthalpic line, this is another isenthalpic line. So, from state point 1 say nearly we are ah I mean we have we will be given some gas at nearly the room temperature and the state point 1 would be ah at some atmospheric pressure most of the time. Then we have to compress the gas and let it is ah you know we ah compress it assuming that it is isothermal compression that means, we are rejecting the heat of compression here ah.

So, from state point 1 to 2 is isothermal compression and now there will be definitely some ah line passing through it ah that means, the isenthalpic line would be there. So, this compressed gas generally what we do is that we confine it within a container high pressure container and if you have to depressurize the easiest way of ah doing it is just open the valve and the gas will try to expand freely. We call it free expansion or joule thumption expansion ah and what will happen the enthalpy remains constant there is no work done in this process ah. So, if if we expand the gas from state point 2 I mean if the enthalpy remains constant and isenthalpic line it will follow. So, it will come from state point 2 to state point this point it will come and maybe this is called 3 or 4 whatever.

So, from high pressure line it is coming to the low-pressure line and the degree of cooling is this much this much delta T you can have ah. That is about the isenthalpic expansion, but there is another way of doing it ah maybe you know this will be compressed slightly to lower pressure earlier we were taking it to still higher pressure. So, here we have compressed it again this is an isothermal compression. So, this heat of compression is rejected and from state point 2 we can do an isentropic expansion. So, keeping the entropy constant you know if we just drop a line vertically this is on the T S plane we are talking about the entropy is remaining constant we can vertically go below to this state point 3.

Now, here you can understand that the degree of the temperature difference I mean the is quite high or the temperature drop we can achieve with the isentropic expansion is way higher than the isenthalpic expansion. And not only that this entropy remaining constant is a good thing I mean the reversibility is less with this process, but why do you go for ah then you know isenthalpic expansion at all ah. When you know we know that we are going to get a large temperature difference in an isentropic process why should we go for an irreversible you know process like isenthalpic expansion. We will get that answer later, but for time being let us look at these two expansions and whether you know we can ah I mean how do we take advantage of this process. Now, as we have said that we understood that we have moved from ah an ideal liquefaction cycle where it was compressed to a very high pressure and followed by an isentropic expansion, but now we are talking about both I mean the isenthalpic as well as isentropic expansion, but we have not compressed it to very high pressure in case of isentropic expansion, but isenthalpic expansion relatively we have taken it to ah state point 2 which is higher pressure relative to this you know this process fine.

So, let us look in details about this ah isenthalpic expansion we will come back to this isentropic expansion later. So, ah in case of isenthalpic expansion as we have understood that we are compressing the gas and the gas is getting expanded just by opening the valve and ah let us look at the PV diagram in that case. So, what happens if we ah have some gas we have compressed it we have you know put it put it at some temperature just in the previous slide you have seen that we are following some isentropic lines this is on the TP plane this is temperature versus pressure plane and if we are somewhere here on this line for example, and if we have this this is constant enthalpy H remains constant here. So, all these are H is equals to H1 this is H2 and some other H equals to H3 like that ah and so on H equals to H0. So, these are the constant isenthalpic lines and we are following that isenthalpic line.

So, we have we have compressed it at a particular temperature. Now, if we are expanding it what we find is that as we are reducing the pressure the temperature is rising, but if it is below this point you know then we because of this expansion we are finding there is a decrease in temperature, but if you were somewhere here ah and you are expanding the gas it will result in ah what is called and heating effect whereas, if you are on this side I mean if you are in a different ah I mean enthalpy line if you are following then it would be something different. So, corresponding to this ah line in enthalpy line you will be ah you know following this path and again like this. So, you can understand that this temperature is shifting from lower to higher temperature as we move you know with the enthalpy lines. But the more interesting part is that that is if we are expanding the gas in an isenthalpic process it ah is possible that it may result in heating it may ah you know generate cooling also.

So, we have to be ah careful and this is what is called the for a particular isenthalpic line this is called the inversion temperature. So, this corresponding temperature is the inversion temperature and this dotted red color curve is called the inversion curve. So, you can understand that there is a change in the slope of this curve and that is basically the del T delP is the ah I mean and H constant of course, that gives you the slope of this curve and this slope of the curve we want a positive slope because we are looking for a cooling when we expand the gas. That means, as we are reducing the pressure the temperature we expect that the temperature will drop and we would get cooling. So, we must have you know this slope of this curve in the positive region ok.

So, we must be we can understand that we must be there inside this graph. So, we should be you know confined our self to this line and you can understand that if we are you know beyond this point whatever be the enthalpy whatever be the pressure and if we are trying to expand it no time we will have any ah you know cooling. So, that is what is called the maximum ah inversion temperature corresponding to P equals to 0. So, we understand that something ah coming in ah picture that is called the maximum inversion temperature. So, we have to operate ah or you know we have to ah work within that temperature and if we have to get ah I mean expand cooling out of this isenthalpic expansion.

So, fine. So, we will have a look into this isenthalpic expansion in details ah. You have already seen ah on the T S plane this is we have talked about the temperature pressure ah diagram just now, but ah already I have told you this is for you know the para hydrogen and this chart you have seen this is from the Barron's book and if you look at these are the isenthalpic lines. So, this is the line you will be following say at a particular temperature and pressure corresponding to say 40 or 50 bar pressure this is the 50 bar pressure line and if you are somewhere here at you know this is 84 K ah. So, this 84 K this is the enthalpy line. So, from here if you are expanding the gas to P equals to 1 atmosphere this is the kind of you know cooling we can achieve, but look at this temperature we are starting point is 84 Kelvin, but from 84 Kelvin you are going to about you know something like 78 Kelvin or so.

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$$

So, this is the kind of delta T you can expect from say when we expect expand the gas from 50 atmospheric pressure to nearly 1 atmospheric pressure ok. So, that is about this ah isenthalpic expansion, but we understand that we have to now look at this temperature that is called the maximum inversion temperature we should operate it always below that temperature. So, now let us try to quantify it and we will do some I mean small mathematics. So, we call it as a joule function coefficient or this slope of the curve that we were talking just now that is basically the delT delP at constant enthalpy. So, ah with you know little bit of algebra you would be able to ah do this ah I mean it can be ah you know shown that mu JT equals to 1 by cp into T into delv delT at constant P minus v.

I will not derive this expression I will give you some hint and with that hint you are supposed to ah try to derive this expression if you are not able to do it will be supplying you that ah you know in the I mean at some point or ah in the tutorial class it will be given to you. So, the hints are like this ah you can use this hint this is from the calculus and this is the Maxwell's thermodynamic relations. So, you have to basically use these two things along with that of course, the enthalpy ah H equals to U plus ah H equals to U plus Pv that relation you use and ah this Maxwell thermodynamic relation appropriate thermodynamic relation you will be able to ah sort it out if you are trying to do that derivation. So, now, we have this mu J T equals to 1 by cp and that expression delv delT at constant P and then you have minus v. So, this is what is that expression for the isenthalpic expansion of or coefficient of isenthalpic expansion or JT expansion coefficient.

$$\mathrm{pv} = \mathrm{nRT}$$

$$\mu_{JT} = \frac{1}{c_p}(\mathrm{T}\left(\frac{\partial v}{\partial T}\right)_p - v)$$

Now, ah what happens let us look if we are following the ah ideal gas law. So, in the ideal gas law we will write it as Pv equals to RT this is the v is basically ah the molar volume earlier we were writing it as Pv equals to nRT basically this is v by N and this is the small v ah ok. So, PV equals to nRT. So, in that case if you look at that delv ah del T at constant P you will find that we are getting that is equals to R by P. So, if we put R by P inside ah this is ah 1 by cp multiplied by ah T into R by P minus v.

So, that gives you the mu J T. So, mu JT is equals to 1 by cp and then ah RT is basically nothing, but Pv and ah if it ah you know you write it this will give you v minus v that is equals to 0 or mu J T for ideal gas if the gas was an ideal gas mu JT would have been 0 there would not have been any kind of ah isenthalpic expansion would not ah you know result in any cooling because you have seen that mu JT equals to 0 is the inversion curve where there is no change in slope and there is no cooling no heating. So, that means, ah ah ideal gas would not have given you any cooling upon isenthalpic expansion, but fortunately it is not. So, the gas and gases are not ideal gas and the non-ideality will of course, increase as you are moving towards the I mean the ah I mean lower temperature as well as higher pressure. So, the this is about the ideal gas behavior and ah that is I mean when we try to relate it to the joule function coefficient we find that the mu JT is equals to 0, but what is about the real gas equation.

$$(p + n^2 \frac{a}{v^2})\left(\frac{v}{n} - b\right) = \mathrm{RT}$$

$$\mu_{JT} = \frac{\left(\frac{2a}{RT}\right)\left(1-\frac{b}{v}\right)^2 - b}{c_p[1-\frac{2a}{vRT}]\left(1-\frac{b}{v}\right)^2}$$

Now, let us look into that ah one such equation we have already talked about that is the Van der Waals gas equation and if we ah you know ah this is the Van der Waals gas equation in the earlier ah I mean context we have talked about and if you just slightly modify this equation you will find that we are finding it to be P plus a by v square minus v minus b equals to RT. So, where R and sorry R, a, b are given like this these are the values for R and a, b and if we use now this equation ah and if we put ah this you know if we calculate this delv delT ah with the pressure constant ah you would get it would result in this expression 2a by RT into 1 minus b by v whole square minus b and this ah in the denominator you will have all this terms. So, this basically tells you that ah you know this mu JT it can be 0, but ah it can be positive or negative depending on the temperature. So, what happens ah for ah basically if we ah have this high molar volume ok. So, this very ah large value of v and then we can say that b by v is nearing 0 and we can write mu JT equals to ah we can write it as 2a by RT minus b and in the denominator, we will have cp.

So, this large for a large specific volume v you know we can ah neglect this b by v term or compared to 1. So, we have mu JT equals to 2a by RT minus b. Now if 2a by RT minus b if it is greater than 0 then mu JT is positive and this is positive that is what we are looking for that means, if T is less than 2 A by RT ah then we have mu JT equals to positive. But if we you know on the other side if we write that mu JT ah equals to 2 A by RT minus b if it is less than 0 that corresponds to T greater than 2a by ah bR I am sorry this is bR ok and 2a by bR if ah this T equals to T greater than 2a by bR then we have ah this mu JT is equals to negative. So, for this ah you know temperature greater than this ah you have no cooling effect, but if temperature is less than 2abR we have the positive JT expansion and then we can have expect cooling upon ah you know expansion by isenthalpic process.

$$T_i = \frac{2a}{bR}\left(1-\frac{b}{v}\right)^2$$

$$T_{i,max} = \frac{2a}{bR}$$

So, let us try to find out ah I mean the I mean curve for which will follow this ah you know or the temperature line which ah corresponds to this inversion curve ah. So, we can write it as mu JT equals to 0 that will correspond to mu JT equals to 0 will give you the inversion curve and then we have 2a by RT I mine into 1 minus B by V square ah equals to B that would corresponds to mu JT equals to 0. So, from here we can have this value of Ti equals to 2a by b into R into 1 minus b by v whole square that is is the that is the expression for the maximum inversion temperature. Now, ah this value ah you know from here ah we can try to calculate that maximum inversion temperature. So, if you remember that curve we have said it is like this temperature versus pressure on this side and this is on the temperature and there was that dotted line and this is P equals to 0 and this is where is the maximum inversion temperature that corresponds to b ah I mean P is very small ah or P equals to 0 that means, the ah ah ah specific volume is very high that means, b by V equals to 0 or the Ti max ah will be ah given as say we can write it as 2a ah by b into R.

So, if you ah now put for ah hydrogen we have the value of this B and A value are known to us if you ah this R value is also known to us. So, if you calculate this value ah you know just by putting this ah it would come nearly around 220 Kelvin or so. So, you put this value and check the I mean whether it is ah the temperature k is coming as unit ah or not. So, this is what is called the maximum inversion temperature of ah this hydrogen ah this is for hydrogen of course, these values are for hydrogen and of course, for different gases these constants ab will be different. Now ah this is of course, a slight approximation and if you look this book you will find that the T inversion maximum inversion temperature according to this book is about 205K for hydrogen.

So, which is a pretty close to this our approximation that we have used a real gas equation ah like ah what is called the Van der Waals gas equation that gives us ah the value of Ti max or the maximum inversion temperature of 220 Kelvin. So, you have to remember this value or 205 you have to remember ah because this will be ah used later on. So, on the TS plane ah as we understand that somewhere here ah around for this is for hydrogen of course, around this 220 Kelvin or 205 Kelvin there would be the almost there would not be any change in the ah I mean isenthalpic line, but below that you will find that there ah like this and like this, but on the other side when it is above ah 220 K you will find constantly this lines are becoming like this. So, if it is ah you know ah this is up to 100 Kelvin from 14 Kelvin to 100 Kelvin on the lower part of the this isenthalpic sorry this TS diagram, but we have also shown you the other part that is ah the upper part that is ranging from 80 Kelvin to 300 Kelvin and you can see the change in the ah I mean slope of the curve at around 205 you can find that they are almost like a straight line ah as you move from one end to the other end. So, this has some implication ah and we will consider it while doing a practical expansion ah cycle ah based on this isenthalpic process.

So, now let us try to ah look at the other expansion coefficient that is the isentropic expansion coefficient or new ways we call it. So, here what remains constant that is the entropy that remains constant. So, we have delT delP at ah at constant S earlier we were calculating delT delP at constant H now we have delT delP at constant S. So, obviously, this will change the calculation and we have ah now 1 by cp ah T into delv delT at constant pressure. So, again ah you follow the ah I mean hints that has been given earlier to calculate this value, but now look at this term delv delT at constant pressure.

So, does it remind you something familiar ah that is basically the volumetric coefficient of expansion. So, that is beta, beta is basically ah 1 by v delv delT and at constant pressure. So, that is what is the volumetric coefficient and that means, this delv delT at constant pressure is nothing, but ah beta v. So, we can ah write this to be 1 by cp and then T and beta v. So, if you look at this mu S value you will find that since this specific volume is never 0 or negative value.

So, all these parameters are positive and that means, the isentropic expansion will result in ah cooling always. So, mu S will always be greater than 0 ah that means, always we will have expansion I mean expansion by ah you know isentropic process would result in cooling. So, this also we have to keep it in mind and we will while designing the actual liquefaction cycle we will ah consider these two facts. So, now, let us look at the ah references these are the two references you can follow and all these things you will be ah getting in details there.

So, now, let us conclude. So, we have talked about ah the isentropic expansion, but we found that cooling is not guaranteed ah if we are following the isentropic expansion and we have identified that you know there is something called maximum inversion temperature and if the expansion is done below that maximum inversion temperature then only we have the possibility of getting cooling and isentropic expansion always ah generates cooling. So, thank you for your attention.