Course on Phase Equilibrium Thermodynamics
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Lecture 10
Thermodynamic network (Contd.)

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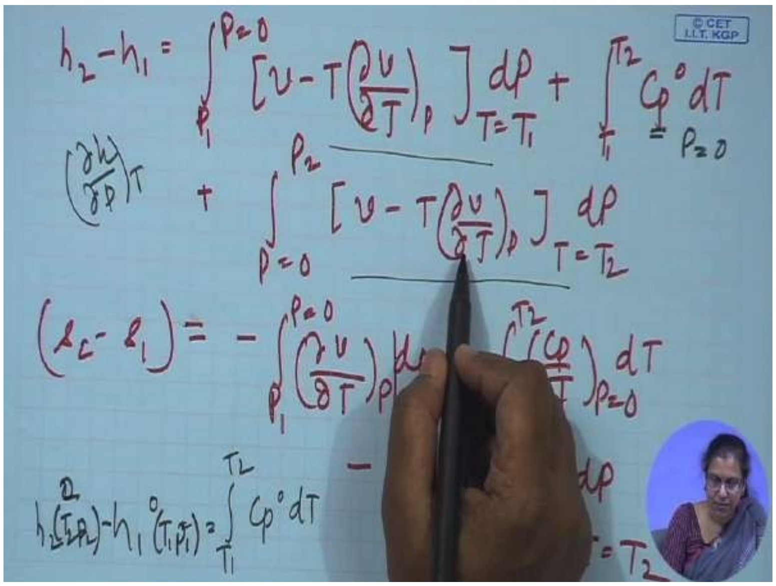

Well, so we continue with our discussions on finding out the enthalpy of any particular real gas when it is going from pressure T rather from condition P1T1 to a condition P2T2. Now I had already written down the equations in the last class where I had shown that I may need data of Cp0 at the ideal gas this particular data this is for P equals to 0 and for other than that what I need is? I need the 2 particular relationships of del h del P at constant T, this particular relationship I need for 2 temperature conditions, one is at the lower temperature the other one is at the higher-temperature.

And we found out that if we can just evaluate these 2 and find out Cp0 then we shall be in a position to find out h2 minus h1. The same is applicable for s2 minus s1 as well. Now just look at the equations very carefully, when you look at the equations what do you find? What is this term? This particular term is nothing but the change of temperature of an ideal gas at from T1 to T2. What is this? This term basically arises if you think logically had the gas been ideal would we have this particular term or this particular term?

This term and this term would not have been there if the gas would have been ideal, suppose for an ideal gas say for instance for an ideal gas if I write h20 minus h10 then only this term would have been there Cp0 dT from T1 to T2 where h10 is at T1 P1 h20 was at T2 P2, right? So therefore we find that these 2 terms they arise just because the gas is not ideal the gas is real. So therefore can we not see we try to find out h of T2P2 the change of state or the change of h when a gas travels from T1P1 to T2P2, now we can take it by several processes. We have already discussed 3 processes and selected one among the 3 just because it was convenient or the data was available on by that particular process.

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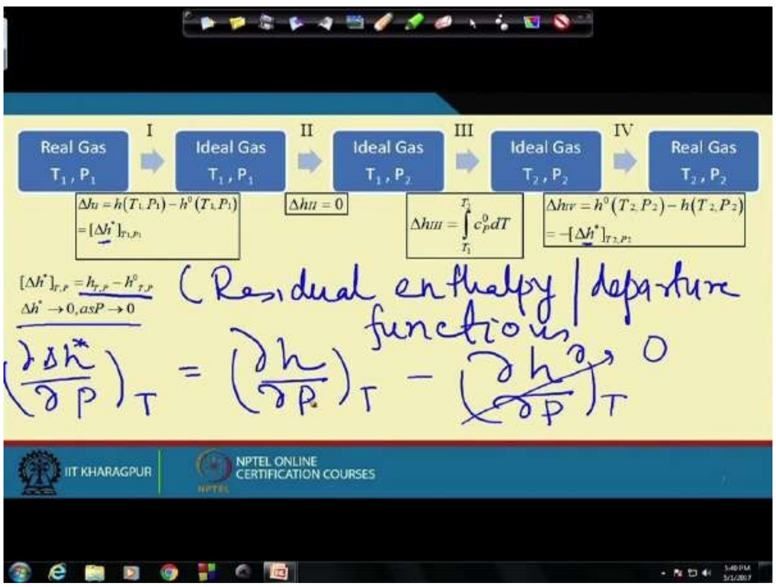

Now let us see if we can go for a Fourth process as well. Well, what is the fourth process if we see? It is the fictitious path let me tell you but it hardly matters because the initial state and the final states are actual and we would like to go from the initial state to the final state.

From this initial to this final we had already devised 3 parts earlier, one was an isobaric process followed by an isothermal the other one was an isothermal followed by an isobaric and the third one which you had adopted was an isothermal expansion of the gas to P equals to 0 than i it was an isobaric heating of the ideal gas and then it was an isothermal compression to the real gas state to T2P2.

Let us see this fourth particular state what is this? You have a real gas at T1P1, say for example by some means we can just convert this real gas to the ideal gas at the same conditions of temperature and pressure. Once we have done this then after this we take this ideal gas from T1P1 to T2P2. Once we are taking this we know what should be the enthalpy changes for each of these and at T2P2 I change the ideal gas to the real gas condition, right?

Now in the entire process we find that the only hitch in the process is to find out the enthalpy change involved when the real gas is changed to the ideal gas conditions at T1P1 and when the ideal gas is changed to the real gas conditions at T2P2. Now this particular enthalpy change is nothing but the enthalpy change associated with the gas because it is real.

So therefore this can be written down as a different function between the actual enthalpy of the gas and the enthalpy of the gas had it been ideal. These particular terms which I have used here and here these are basically they are known as the residual properties this is known as the residual enthalpy or they are also known as the departure functions, why? Because they show the departure of the property from its ideal gas value and if you have to define the residual properties or the departure functions we need to specify one or the value at one particular limiting condition.

The limiting condition for each case is that, for example for Delta h star it was that Delta h tends to 0 as P tends to 0. So therefore when we try to find out Delta h star at any condition other than P tends to 0 then in that case it is quite natural that del of delta h star versus delta P at constant T this is nothing but del of del h del P at constant T minus del h 0 del P at constant T and we know that this term is equal to 0. So therefore what do we find? We find that the variation of the departure function with pressure is nothing but the variation of the actual function with pressure and we already know what this particular function is.

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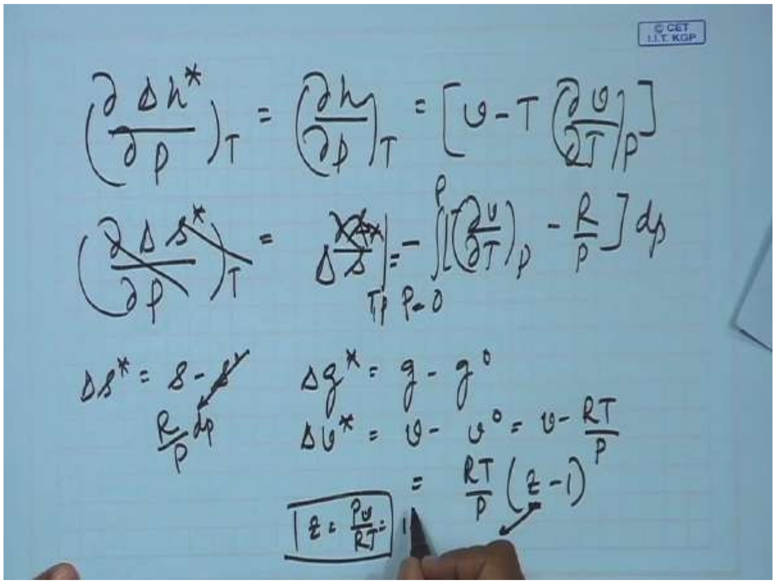

This particular function as we have already mentioned this is nothing but, so therefore del delta h star delta P at constant T since it is nothing but equal to del h del P at constant T. So therefore this is nothing but equal to V minus T del v del T at constant P and nothing else, isn't it? In the similar way we can also write down suppose we would like to find the departure function for entropy in this case also it is nothing but the difference between this delta s star is nothing but the difference between the actual value and the ideal value in this case we need to remember that the entropy of an ideal gas it is not 0.

It has a nonzero value if you remember this nonzero value this is nothing but equal to R by P dp, right? So therefore for this particular case also we can write it down in the form as del s or in other words I will write the final expression I leave it to you for that deriving, this will be equal to P equals to 0 to P del v del T at constant P minus R by P dp this is equal to delta s star at T and P, right?

Therefore delta s star at T and P, this is nothing but equal to this particular expression, so therefore from here what do we find? We find that the entire botheration of finding out the properties they simply boil down to finding out the departure functions. If the departure functions can be found out then and the departure functions can be found out once we know how those particular properties vary with pressure at a constant temperature?

In this particular way we can define all sorts of departure properties, for example we can define delta g star as g minus g0. We can define the residual volume as v minus v0 and what is v0? All of us know it is RT by P, so therefore if we substitute this as v minus RT by P we find that the residual volume is nothing it can be expressed in terms of compressibility factor where this particular z it is nothing but the deviation of the actual volume from the ideal gas volume.

So therefore this is nothing but Pv by RT which is equal to 1 for an ideal gas and it has got some value greater than 1 for a real gas. So in this particular way what have we done?

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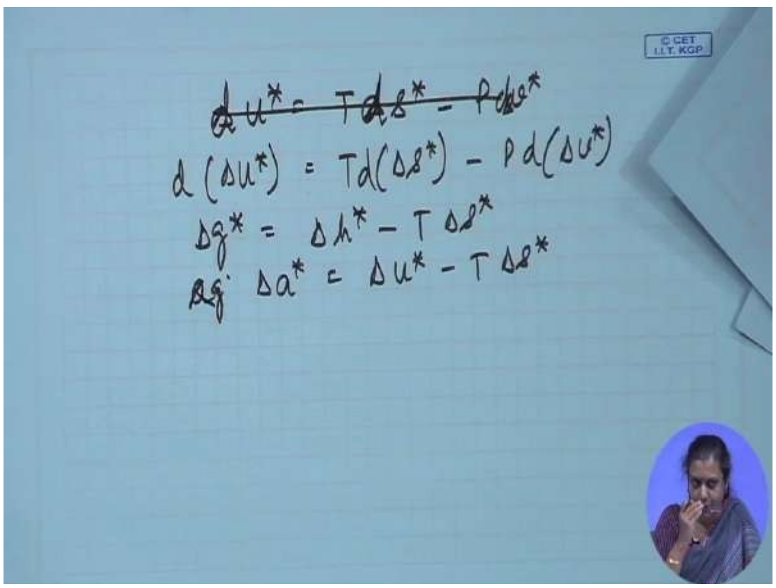

We have first defined the total properties then we have defined the molar properties than we have define the residual properties and again I would like to remind you, we can have two sets of residual properties, total properties and molar properties and whatever relationships that we have defined for the total properties are also applicable for residual properties, for example we can very well write down that Delta u star equals to T Delta s star, sorry let me write down in terms of du star is equal to d T delta the ds star minus Pdv star.

Just I will write it down properly once more d of delta u star equals to T of delta s start minus Pd of delta v star the same way we can write down delta g star equals to Delta h star minus T Delta s star we can write down Delta a star and equals nothing but and we can continue like this it was just to show that whatever equations we have derived till now they are applicable for total properties, they are applicable for molar properties, they are applicable for total residual properties, they are also applicable for molar residual properties as well.

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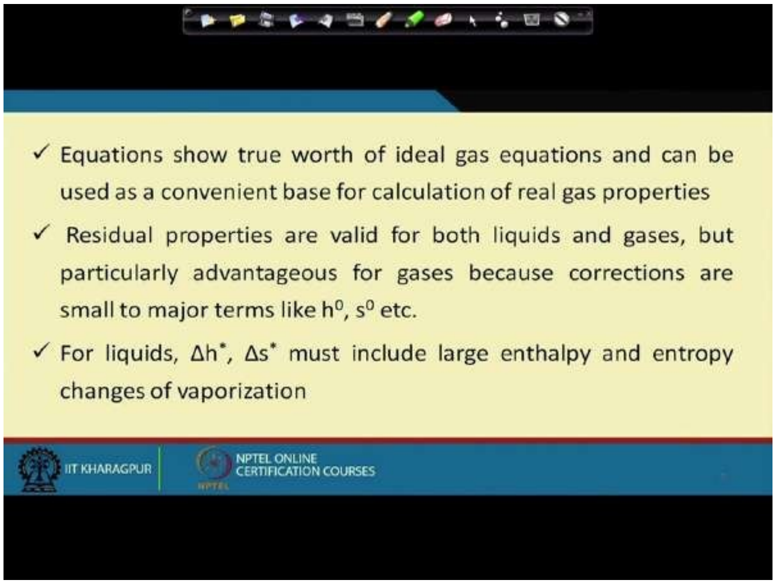

Well, after this the next thing which I would like to, so from here there is one particular thing that we could very much appreciate what was the thing? The thing is from here we could appreciate the true worth of ideal gas equations because we found out that from here that the ideal gas equations they can be used as a convenient base for calculation of real gas properties that is quite evident from here

The next thing is residual properties you must remember that they are particularly advantageous for the gases although they can be valid for condensed phases as well as for the gases but they are particularly advantageous for gases, why? Because for gases we find that the corrections are usually small to all the major terms, right? So the corrections to the ideal gas value since they are small for real gases so therefore residual properties are particularly advantageous for gases. For liquids we find that the residual properties they must include large enthalpy and entropy changes of vaporization, so therefore they are not very much useful for those particular conditions.

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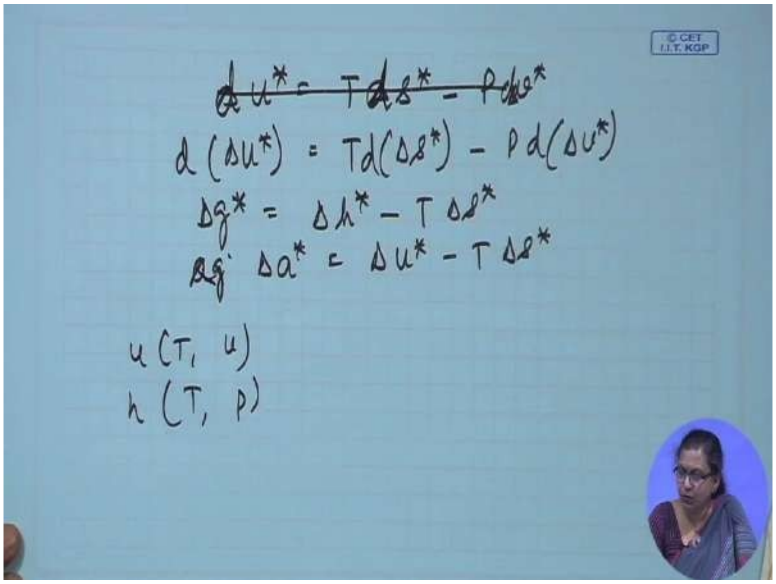

Now let us try to derive some other types of equations we have already derived some equations for example we have shown you how u varies with T and v, we have also shown you how h varies with T and P and we have also found out some very important rather we have also found out some very important things which you had already known we have found out the, that for an ideal gas h and u both of them are unique functions of temperature pressure etc.

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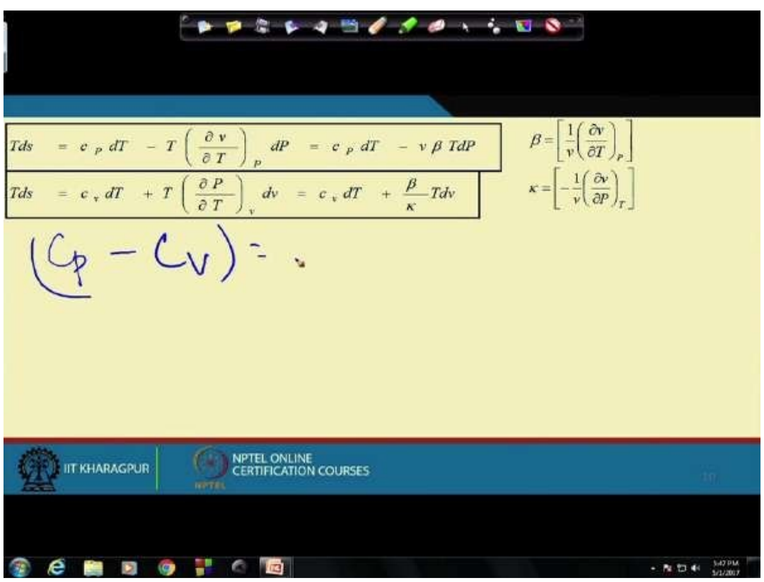

Now I would like to derive certain other things again from the basic Tds equations that we have found out, now from the basic Tds equations which are already written down here if you observe the 2 basic Tds equations we find we can find out some very important things, for example suppose I would like to find out Cp minus Cv equals to from this particular equation, what do I get in this particular case?

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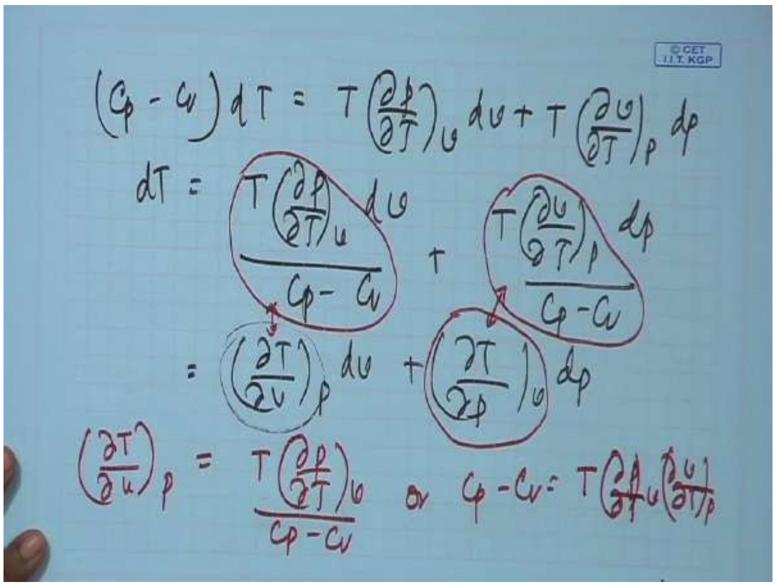

I get Cp minus Cv dT this is equal to T del p del T at constant v dv, just see that, no matter how much I am writing? I am not going to use uppercase alphabets showing that every time I am using or rather every time I am dealing with molar properties. In the same particular way can I not write it down as dT equals to T del P del T at constant v dp by Cp minus Cv plus again this particular term by Cp minus Cv.

Just see what I have done in this equation I have expressed T as a function of V and p that is only thing that I have done and I know that all of these are properties, so all of these are exact differentials, right? So therefore by this equation should be equivalent to the equation del T del v at constant pdv plus del T del p at constant vdp, isn't it?

So therefore this particular term and this particular term the coefficient of dv these 2 should be equal again this particular term and this particular term these 2 should be equal, isn't it? So in that particular case I should be able to write del T del v at constant P this is equal to T del p del T at constant v by Cp minus Cv or in other words from here I should be in a position to write down

Cp minus Cv, what is Cp minus Cv in this particular case you tell me? This is nothing but equal to T del P del T at constant v, del v del T at constant P.

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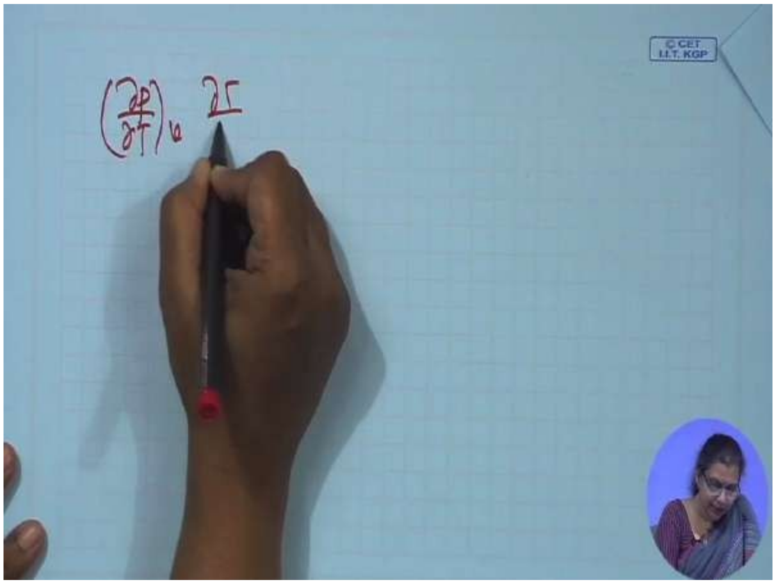

Now let us adopt the cyclic rule, what was the cyclic rule if you remember? Cyclic rule was del P del T at constant v. Just that the normal cyclic tool del v del p at constant T equals to minus 1.

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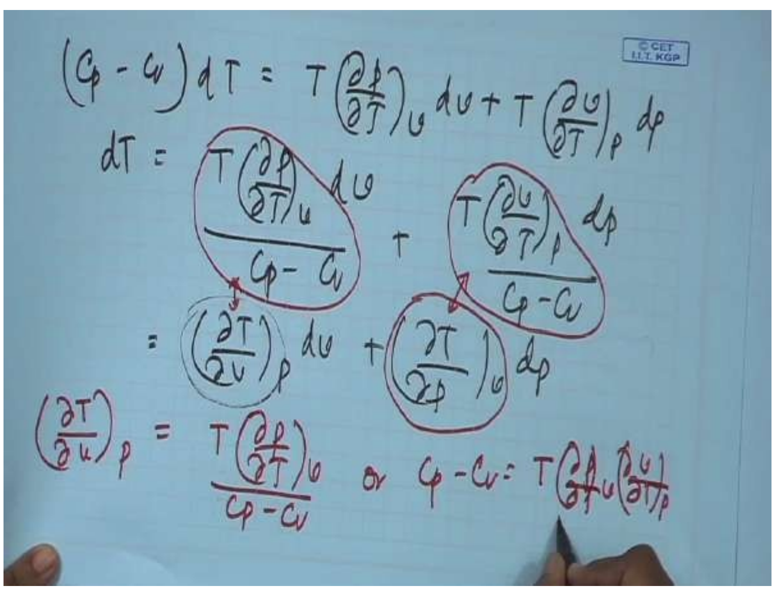

So therefore using this particular equation we should be in a position of substituting this particular equation or rather this particular term, if you substitute this term then what do we get?

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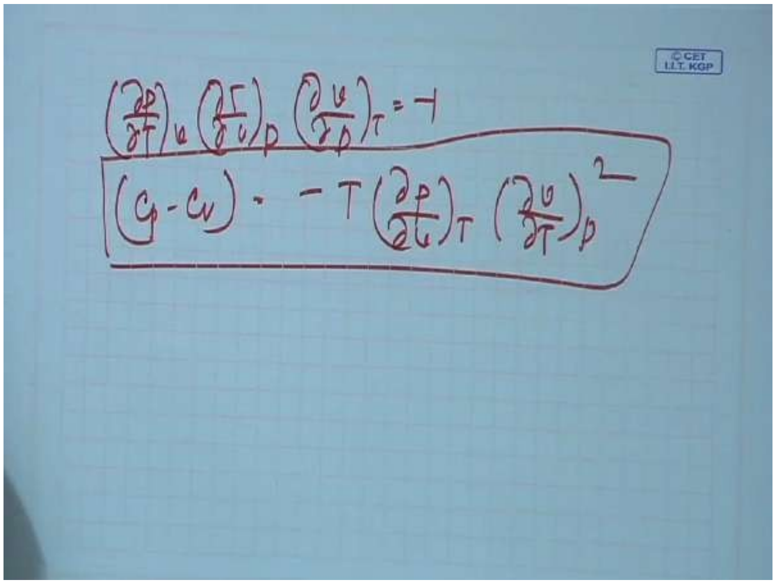

We get Cp minus Cv this will be equal to minus T del P del v at constant T, del v del T at constant P whole square. Just look at this particular equation, this equation I should say this equation is extremely important.

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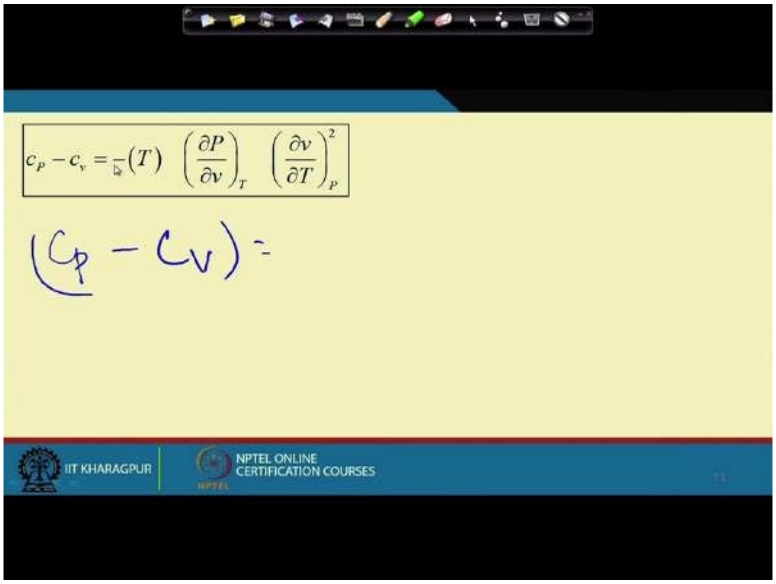

Let us see what is the importance of this particular equation? If you observe this equation what are the important points that we see? The first thing which we see is, that if you observe this term there is a minus here, right? And this term always has to be positive this particular term, okay.

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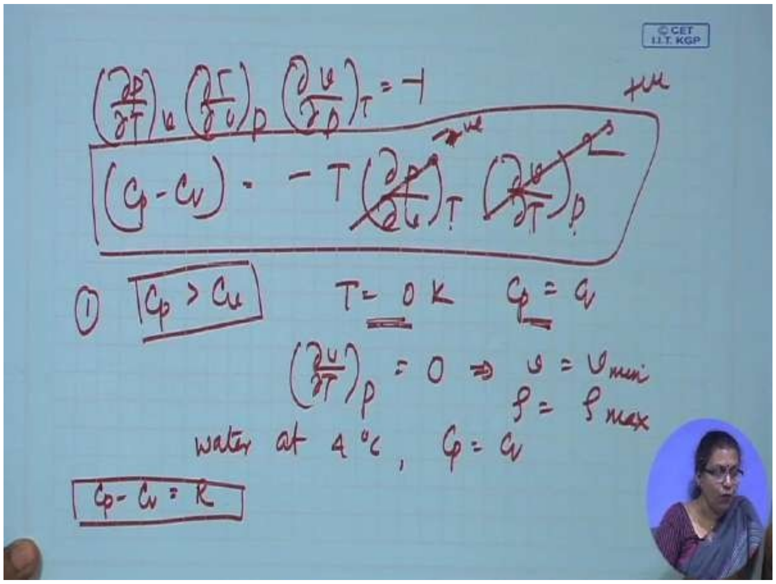

We will continue it here, so therefore if you observe here what do we find? We find that this term is always positive and this term it will be always negative, isn't it? So therefore this whole particular expression on the right-hand side this will always be positive as a result of which Cp is always greater than Cv which you have been knowing so long. So this is the first observation that we get and this is evident because Cp includes the flow work or the work of expansion on or compression which Cv does not include.

What other useful things does it show? Let us see what are the other useful things that we can see from here? The other useful things are suppose at T equals to 0 degrees Kelvin, Cp becomes equal to Cv. Can you tell me under what other conditions Cp can become equal to Cv? Definitely at T equals to 0 Kelvin Cp can become equal to Cv there is one other condition when del v del T at constant P this becomes equal to 0.

When does this happen? This happens for a condition where v equals to v min which automatically implies rho equals to rho max. Or in other words can this not happen for water at 4 degrees centigrade where we know that water has got the maximum density, under that particular condition Cp equals to Cv and therefore we take a constant value of the specific heat capacity of water usually assuming it to be at 4 degrees centigrade and again if we substitute Pv equals to RT and we try to find out del p del v at constant T and del v del T at constant P then for an ideal gas what do we get?

You can substitute it and you can find it out, for an ideal gas this reduces to Cp minus Cv equals to R again something which you have already known so long, right? And I leave it as an exercise to you to express Cp minus Cv in terms of beta and Kappa. So this was one very interesting thing that we have observed.

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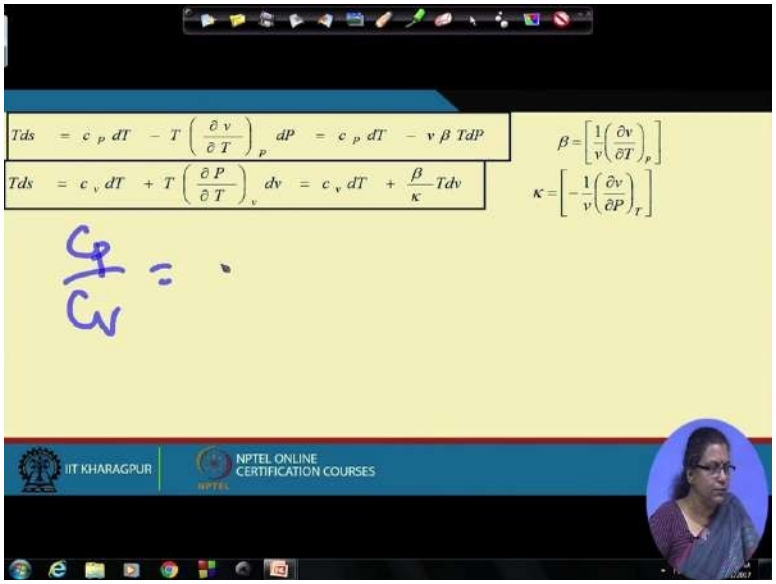

Let us see there is certain other interesting things also which we can find out by using the Tds equations in this particular case. What can we do? Initially we have done Cp minus Cv, let us see what is Cp by Cv in this particular case? Just divide one equation by the other under constant entropic conditions; what do you get for that that particular condition?

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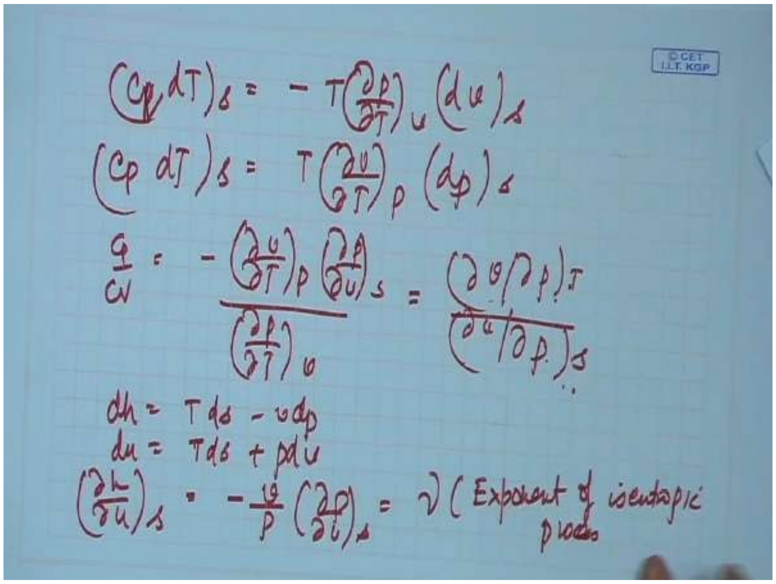

Just divide and tell me what you are going to get in this condition? So at constant entropy conditions we can write down CpdT at constant entropy this is nothing but equal to minus T del P del T at constant v dv at constant s, sorry this was Cv I wrote. CpdT again at constant S, can we not write it down as T del v del T at constant p dp s. Now if I divide 1 by the other under constant entropic conditions, do I get something like minus del v del T at constant P, del P del v at constant s considering these 2 terms divided by del P del T at constant v, right?

So switch again if we use the cyclic rule we can derive it and we find that this is nothing but equal to del v del p at constant T divided by del v del p at constant s. So what is it? It is basically the isothermal compressibility divided by the adiabatic compressibility and we know that this, what is this adiabatic compressibility? This is nothing but the exponent of an isentropic process. Let us see what is the exponent of an isentropic process if we take down the basic equation dh equals to this again we take down the basic equation du which is equal to Tds plus Pdv again for constant entropic conditions we can write down del h del u at constant s this is nothing but equal to minus v by P, del P del V at constant s this is the term which we need here.

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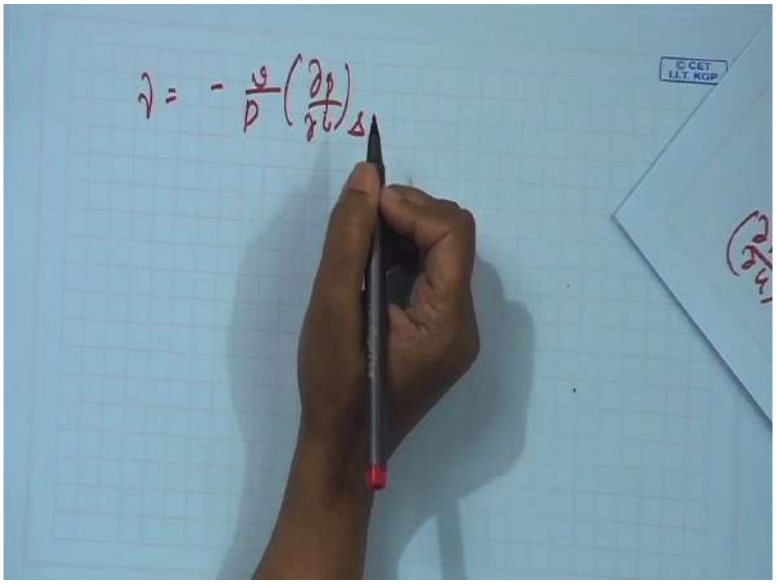

And we know what is del u del h at constant s, this particular term is nothing but the exponent of an isentropic process, so therefore from this what do I get? From this I get gamma is nothing but equal to minus v by p, del P del v at constant s, right? Now this has got some 2 very important implications the first implication is that for an ideal gas suppose we substitute it in this particular form.

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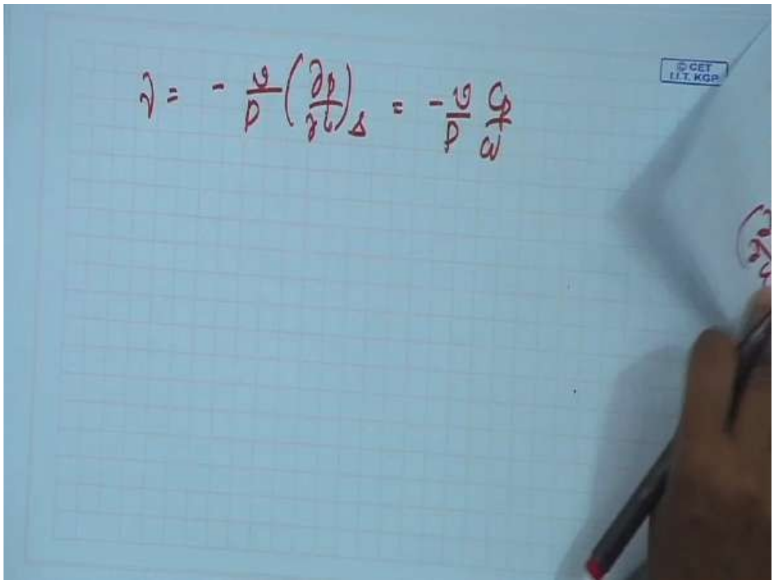

This can be written down suppose from this particular equation Cp by Cv.

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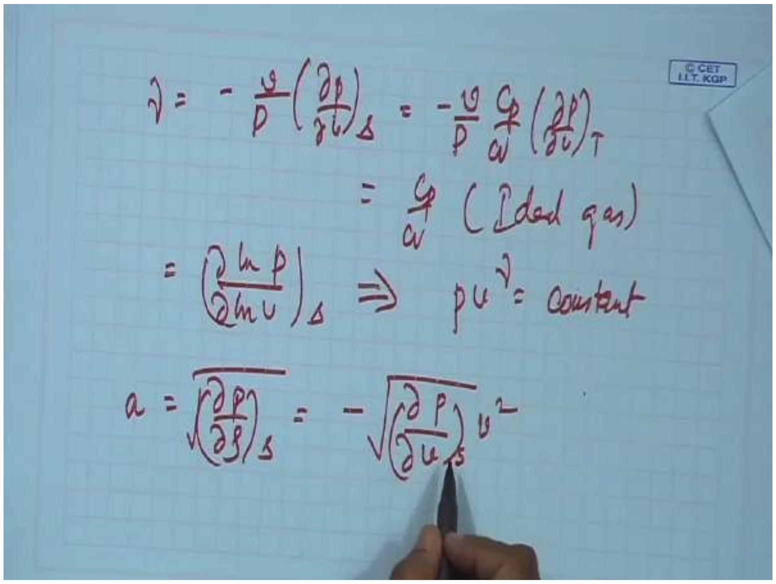

So therefore for an ideal gas I can write it down as del p del v at constant T which reduces to Cp by Cv for an ideal gas and you already know that for an ideal gas Cp by Cv equals to gamma this is one important implication of this equation.What is the other thing? Can we not write it down as del ln P del ln V at constant s which tells you the equation of an isentrope which is Pv to the power gamma equals to constant, right? So therefore there are certain other things also that we can derive from this, for example say the thermodynamic velocity of sound, how do we define the thermodynamic velocity of sound let us see? This is equal to del p del rho at constant s, right?

Now how in terms of specific volume we can write this down? In terms of specific volume what do we get? This is del P del v at constant s into v square, right? Or in other words can we not write this del p del v at constant s.

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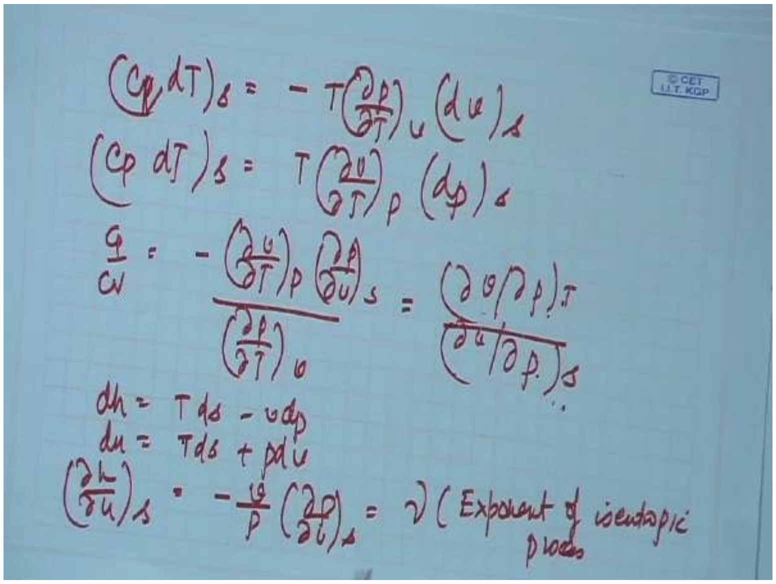

We have already found out its expression del p del v at constant s can be expressed in terms of gamma and can be expressed in these terms.

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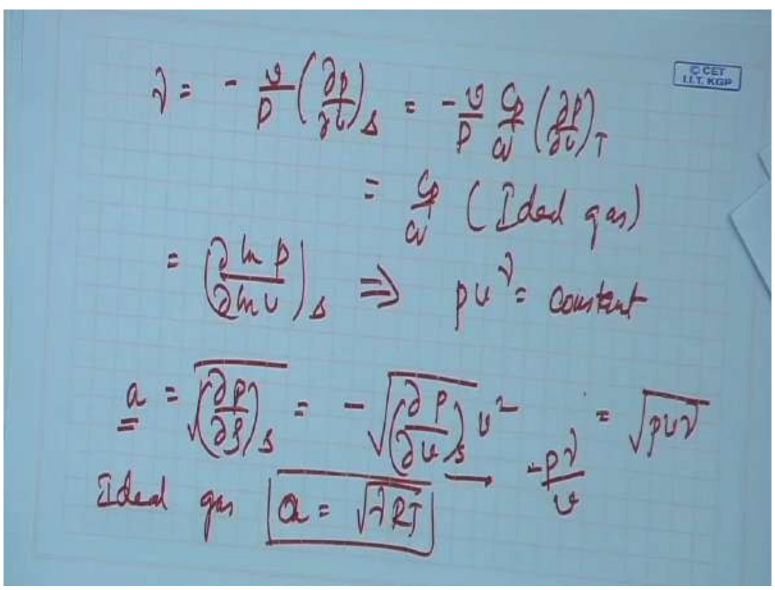

So therefore what is this term equals to? This term is nothing but equal to P gamma minus v gamma by v. If we substitute instead of this minus P gamma by v then what is the thermodynamic velocity of sound equal to? This is nothing but equal to root Pv gamma for an ideal gas we can write it down as, a equals to root gamma RT another equation which you already know.

So therefore we find that we can come across a large number of interesting derivations by using the Maxwell's equations. I will be not going into great details through all the derivations what I would just suggest is, you can find out the effect of heating or the effect of cooling when you would like to cool or rather by expansion by using an isentropic process, isenthalpic process keeping constant internal energy etc.

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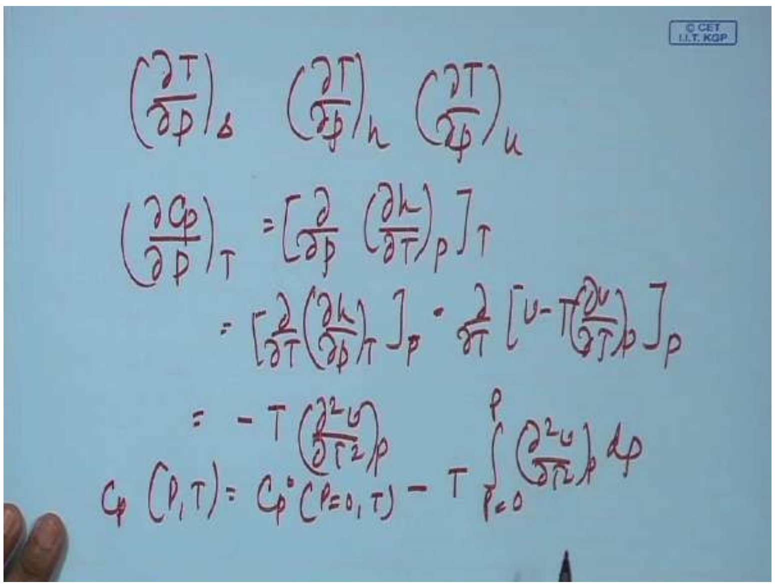

What I mean to say is, it would be interesting if you can find out del T del P at constant s, del T del P at constant h, del T del P at constant u and you can compare which particular process is more effective in affecting cooling by expansion. So therefore there are lot of other things that you can do as well but I would not be going into the details there is just one thing which I would like to discuss before I end this class on the relationships between measurable and non-measurable properties.

Initially I had already told you that usually Cp values they are available at low pressures then the gas behaves ideally. Suppose we would really need Cp values at higher pressures, would we then stop the computer shell or stop the process or in other words we should have some particular equation to deduce Cp at higher values from the ideal gas values. we are going to get that equation rather you are going to get some sort of that relationship if you can predict the property del Cp del P at constant T, what is this particular property let us see?

Can we not write it down in this particular way? Now we know that h it is a, this is at constant T we know h again it is a property. So therefore we can also write it down as del del T of del h del P, we can just invert the order of differentiation and we know what is del h del p at constant T, what is it? So this is nothing but equal to del del T of v minus T del v del T at constant P this is also at constant P and then if you expand this particular differential what do we get?

We get this del v del T, del v del T cancels out we get minus T del 2 v del T square at constant P. So therefore Cp at any particular pressure temperature this is nothing but Cp0 at P equals to 0 T minus T integral P equals to 0 to that particular pressure P, del 2 v del T square at constant P dp.

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In a similar way we can also find out del Cv del v and try to find out Cv at conditions other than the ideal gas condition.

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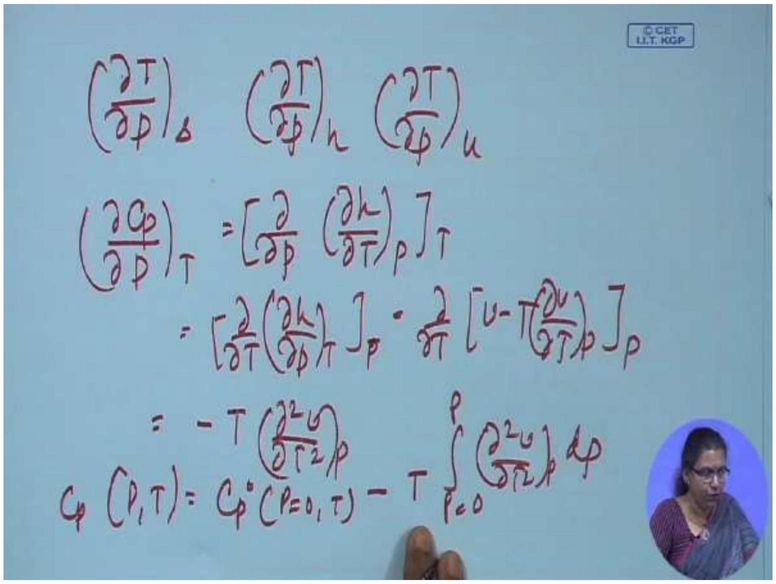

I would not be elaborating further here I stop here on these particular derivations but I would just like to impress upon you that if you are aware of the PvT behavior of the gases than using the PvT behavior of the gases we will be in a position to find out all particular non-measurable properties in terms of the measurable properties and we can quantify them and we can find out what are the energy changes associated with the process? Whether the process will be feasible or not by calculating the entropy change and so on and so forth.

So therefore the next class will be on how to or rather we will be on the discussion of the PvT behavior of gases, there is nothing to discuss about the PvT behavior of ideal gases we will be taking up the PvT behavior of real gases, we will be seeing the most of equations that are available. We will be discussing the equations in brief so that once you are aware of those equations we will be in a position to use those equations and find out changes in enthalpy entropy etc by using the PvT behavior of the gases, have a good day