Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
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Lecture 18
Property Estimation from PVT Behavior

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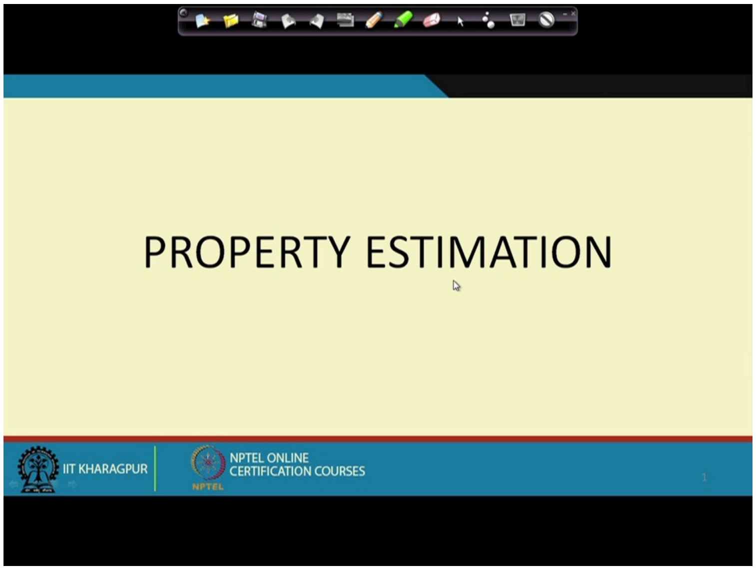

PROPERTY ESTIMATION

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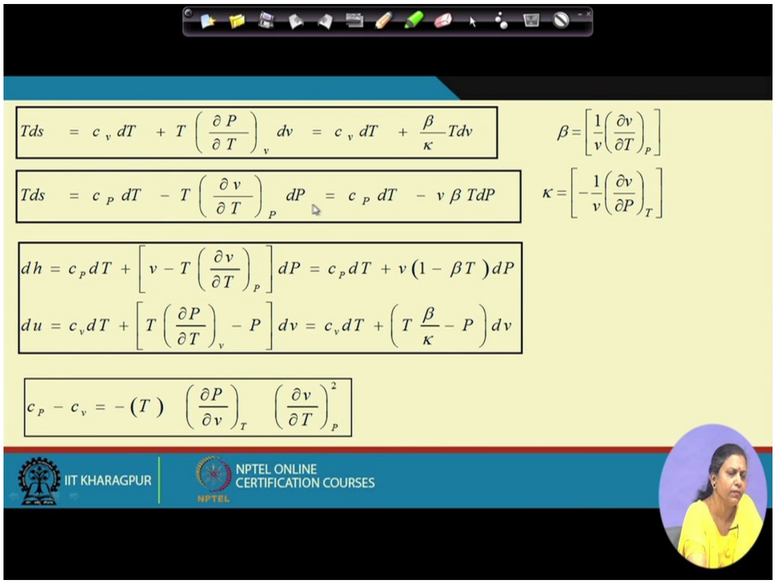

$$Tds = c_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv = c_v dT + \frac{\beta}{\kappa} Tdv$$

$$\beta = \left[\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P\right]$$

$$Tds = c_P dT - T\left(\frac{\partial v}{\partial T}\right)_P dP = c_P dT - v\beta TdP$$

$$\kappa = \left[-\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T\right]$$

$$dh = c_P dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP = c_P dT + v(1 - \beta T)dP$$

$$du = c_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv = c_v dT + \left(T\frac{\beta}{\kappa} - P\right) dv$$

$$c_P - c_v = -(T)\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P^2$$

Well, so today we are going to discuss the property estimation of real gases and other substances of course but they will be primarily confined to real gases. Now to a quick recap before we go for the property estimation part if you remember in the last class or rather few classes before this, what did we do? We used the Maxwell's equation in order to express certain non-measurable properties in terms of measurable ones.

What were the different non-measurable properties? We tried to express the change in entropy with change in measurable properties primarily T and P or T and V they are given by the first 2 equations here, then from there what we tried to do? We tried to find out the rather we tried to express the change in enthalpy and the change in internal energy again in terms of the PVT behavior of the gases and also the Cp Cv the specific heat property data and after that we also did a few other things for example we tried to express Cp minus Cv in this term we tried to express Cp by Cv and so on and so forth.

We had tried to derive several such properties in terms of the PvT behavior of gases and then we found that unless we know the PvT behavior we will not be in a position to exploit these equations further, so therefore we had discussed the PVT behavior of gases we had discussed both the mathematical equations as well as the graphical representations and of course I have mentioned that there are some tables as well which can be used for this purpose.

Now once we are aware of the PvT Behavior of gases now we can use whatever information we have at hand in order to find out or rather in order to express your enthalpy, entropy, internal energy etc in Cp Cv etc in terms of the PVT behavior of the gases.

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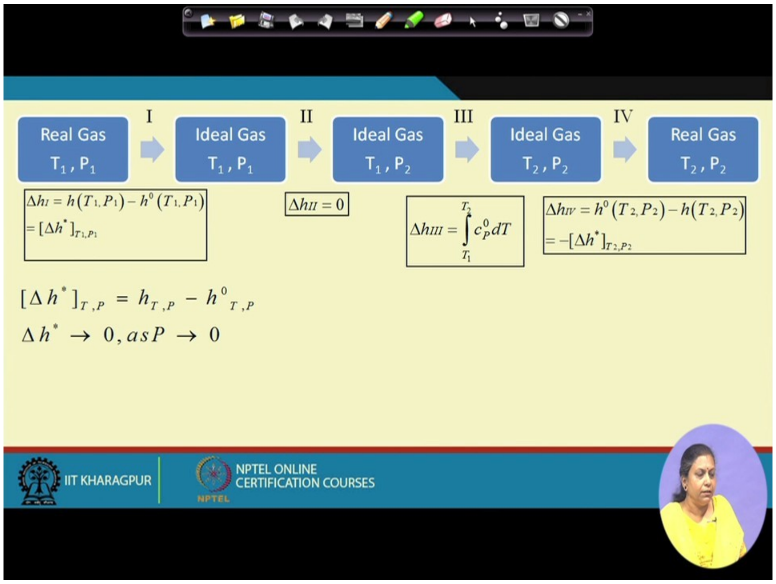

$$\Delta h_I = h(T_1, P_1) - h^0(T_1, P_1) = [\Delta h^*]_{T_1, P_1}$$

$$\Delta h_{II} = 0$$

$$\Delta h_{III} = \int_{T_1}^{T_2} c_P^0 dT$$

$$\Delta h_{IV} = h^0(T_2, P_2) - h(T_2, P_2) = -[\Delta h^*]_{T_2, P_2}$$

$$[\Delta h^*]_{T,P} = h_{T,P} - h^0{}_{T,P}$$

$$\Delta h^* \rightarrow 0, as P \rightarrow 0$$

Now I would also like to remind you that while we were discussing this we found out that the behavior of real gases can very well be described with respect to the ideal gas behavior with the definition of residual properties or departure functions.

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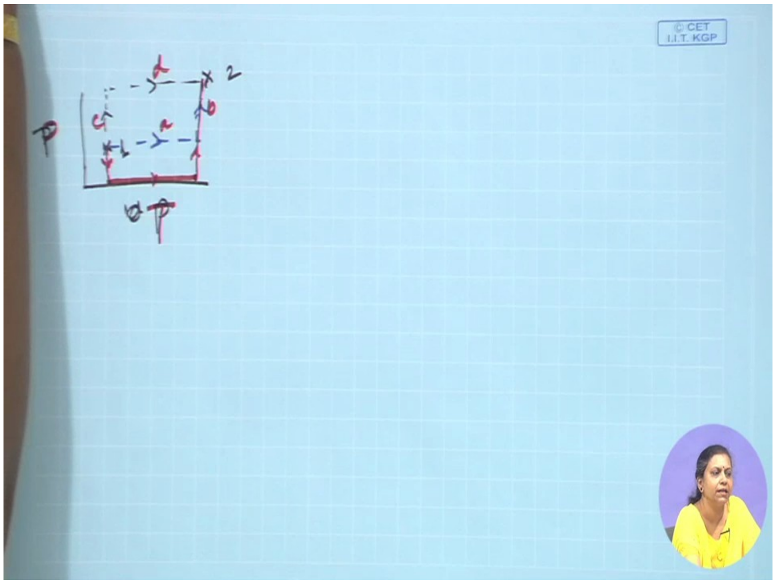

We had discussed how the evolution or the definition of these departure functions if you recollect what I had done was, I had initially proposed that on a Pv plot I have some particular or on a PT plot if you take it was a TP plot as far as I remember. We have some particular gas at 1 and we need to take it to 2.

So therefore I have proposed which path are we going to adopt, is it going to be this path or it is going to be this path and then finally we found out that it does not matter whichever paths we take but if we have to consider the availability of data then we would not accept or rather we would not like to adopt either path AB or path CD rather we would like to go to the low-pressure range, sorry.

We would like to go to the low-pressure range and at this low-pressure range we would like to find out the enthalpy change or the entropy change due to temperature change and then from here we would like to reach state 2. So this was the path which we had preferred the only reason being that we knew the Cp or rather the Cp values are available at low pressure and the gas behaves ideally and then I had also proposed another path for performing this particular computation.

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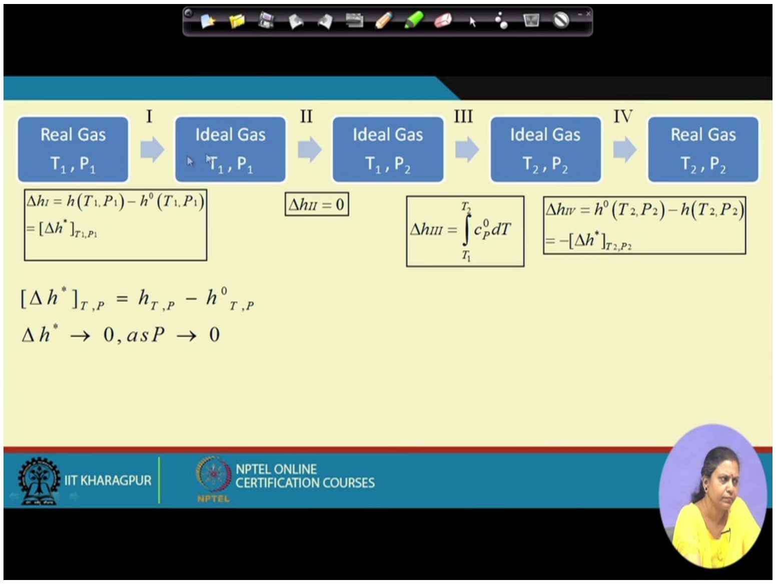

Real Gas T_1, P_1 → I → Ideal Gas T_1, P_1 → II → Ideal Gas T_1, P_2 → III → Ideal Gas T_2, P_2 → IV → Real Gas T_2, P_2

$$\boxed{\begin{aligned}\Delta h_I &= h(T_1, P_1) - h^0(T_1, P_1)\\ &= [\Delta h^*]_{T_1, P_1}\end{aligned}}$$

$$\boxed{\Delta h_{II} = 0}$$

$$\boxed{\Delta h_{III} = \int_{T_1}^{T_2} c_P^0 dT}$$

$$\boxed{\begin{aligned}\Delta h_{IV} &= h^0(T_2, P_2) - h(T_2, P_2)\\ &= -[\Delta h^*]_{T_2, P_2}\end{aligned}}$$

$$[\Delta h^*]_{T,P} = h_{T,P} - h^0{}_{T,P}$$

$$\Delta h^* \rightarrow 0, as P \rightarrow 0$$

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And this path is already provided here, in this path most of the states that we have intermediate except the first in the last state they are fictitious ones but it hardly matters because if we start from one state and end in another state, if these 2 states are the same then it hardly matters whether we are going from state one to state 2 through a fictitious part or through a practical path it hardly matters. The property changes that we are going to compute they will remain the same no matter what path we adopt if the initial and the final states are the same.

Of course if you ask me what is going to happen regarding the energy interactions? Definitely they are going to be different but at the moment we are just dealing with property estimation. So therefore the path of execution is not important for us, the initial and final states are important.

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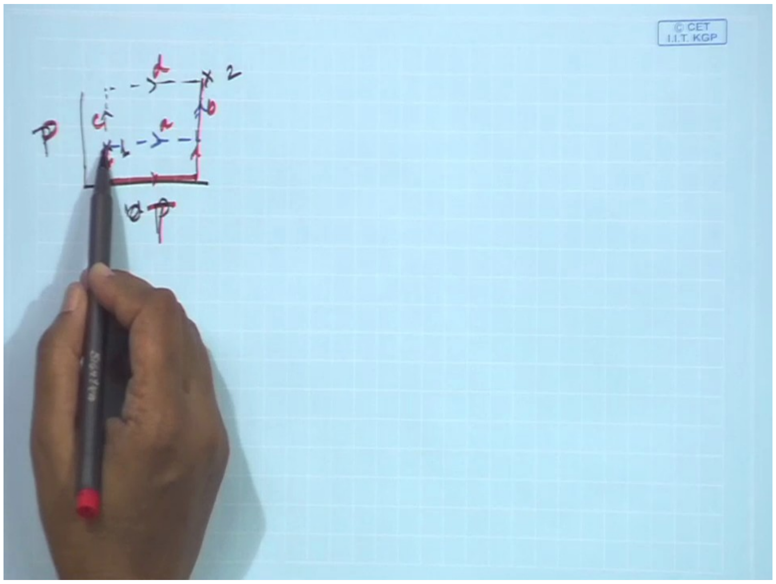

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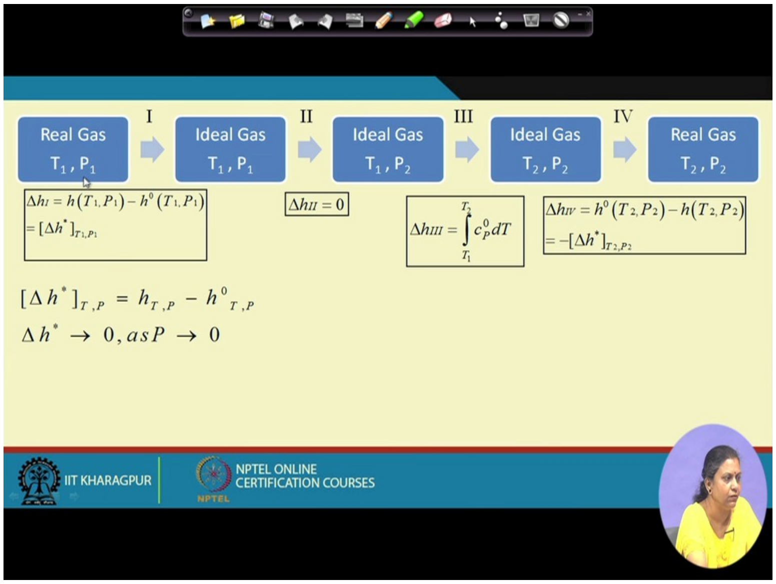

Real Gas T_1, P_1 → I → Ideal Gas T_1, P_1 → II → Ideal Gas T_1, P_2 → III → Ideal Gas T_2, P_2 → IV → Real Gas T_2, P_2

$$\Delta h_I = h(T_1, P_1) - h^0(T_1, P_1) = [\Delta h^*]_{T_1, P_1}$$

$$\Delta h_{II} = 0$$

$$\Delta h_{III} = \int_{T_1}^{T_2} c_P^0 \, dT$$

$$\Delta h_{IV} = h^0(T_2, P_2) - h(T_2, P_2) = -[\Delta h^*]_{T_2, P_2}$$

$$[\Delta h^*]_{T,P} = h_{T,P} - h^0{}_{T,P}$$

$$\Delta h^* \rightarrow 0, as P \rightarrow 0$$

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So instead of adopting this particular path and going from state one to state 2, I had proposed an alternative path where we are converting the real gas at T1P1 an ideal gas at T1P1 then we perform the entire computation that we desire over the ideal gas we take it from T1P1 to T2P2 and after that we convert this ideal gas to the real gas at T2P2.

So therefore all these intermediate conversion say from this state to this state and this to this path 2 and 3 they are very well-known and they are very easily computed the only hitch for the entire problem was to execute path 1 and to execute path 4 both of these are fictitious paths they cannot be performed in practice, what are these? We are converting a real gas to the ideal gas and we would like to know the property change for this case.

Here we are converting an ideal gas to a real gas, we would like to know the property change for this case. Here we would like to compute the property change at T1P1 here we would like to compute the same property change at T2P2, right? So therefore if you observe what are we basically trying to find out in path 1 and path 4? We're trying to describe the property of a real gas with respect to an ideal gas under the same conditions of temperature and pressure.

Definitely at high-pressure low temperature conditions we cannot have an ideal gas state. So therefore the ideal gas state here and here they may be fictitious but it hardly matters because what we are interested to find out is, if the gas could have existed as an ideal gas under any particular temperature and pressure condition then what would have been the property difference?

Now every time this particular thing it was motivated from the fact that if this property change can be calculated then the rest of the computations can be done under the ideal gas conditions and which simplifies the computation to a large extent. Second thing is suppose we can define this particular property at any temperature and pressure we can use this definition and find out this property for other conditions of temperature and pressure.

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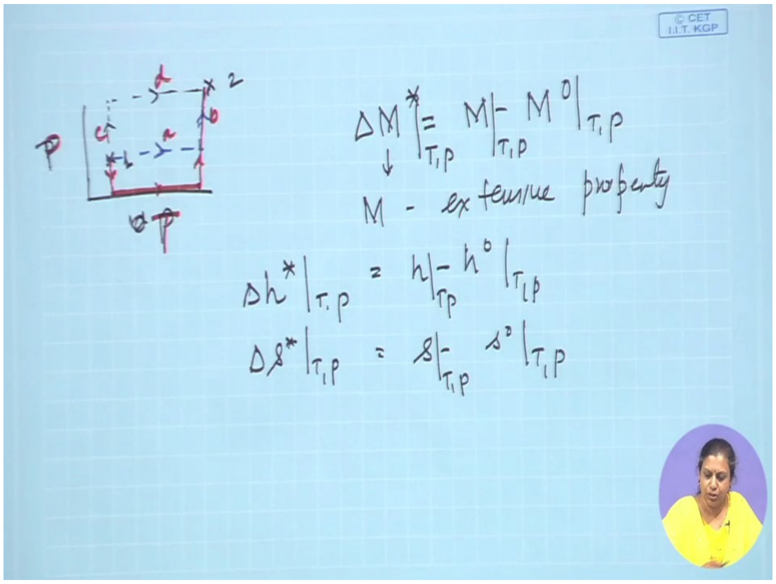

$\Delta M^*|_{T,P} = M|_{T,P} - M^0|_{T,P}$

M - extensive property

$\Delta h^*|_{T,P} = h|_{T,P} - h^0|_{T,P}$

$\Delta s^*|_{T,P} = s|_{T,P} - s^0|_{T,P}$

And therefore we had defined this particular property change here or this particular change we had defined this as a departure function or a residual property and we had denoted it with Delta M star where M is any extensive property we have already discussed these things. So if M is an extensive property then Delta M star Delta means a difference, M star is the deviation from the ideal gas value.

So this is nothing but M minus M0, where M is an extensive property and suppose this has to be done at some temperature and pressure. So this and this are at the same temperatures and pressures this we can define for any extensive property. In this particular lecture we will be primarily be confining our attention to the estimation of enthalpy and entropy keeping in mind that from this we can also compute other properties at our wish.

In this particular lecture we will primarily be confining our interest to the estimation of Delta h star at any Tp and Delta s star at any Tp these are the departure functions for molar enthalpy and molar entropy this is defined by h at Tp minus h0 at the same Tp this is defined as s at Tp minus s0 at the same Tp. So once we are in a position to define these properties then definitely the rest of the computations become quite easy.

So naturally this class will be confined to finding out or to predicting the departure functions primarily of enthalpy and entropy. So that we can use this in order to compute the change of state or rather to compute the entropy and enthalpy changes when a gas undergoes a change of state from any initial to any final state. Now let us see how we are going to do it.

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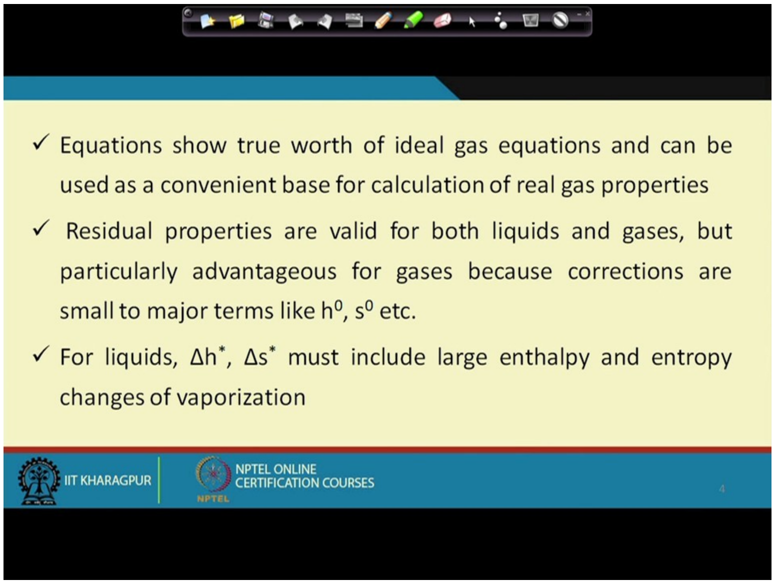

- ✓ Equations show true worth of ideal gas equations and can be used as a convenient base for calculation of real gas properties
- ✓ Residual properties are valid for both liquids and gases, but particularly advantageous for gases because corrections are small to major terms like h^0, s^0 etc.
- ✓ For liquids, Δh^*, Δs^* must include large enthalpy and entropy changes of vaporization

I think I had already discussed some part of it earlier and I'll just be proceeding in finding out the discussion once I have the expressions for Delta h star and Delta s star and before that I would just like to remind you this also we have discussed earlier that this concepts of residual properties or the equations which define residual properties they just show the true worth of ideal gas equations and they just show that the ideal gas equation can serve as a convenient base to estimate real gas properties and it is also important for you to remember that we can have residual properties for gases for condensed phases as well as for gases but they are particularly advantageous for gases, why?

Because if you're trying to find out the residual properties of condensed phases with respect to an ideal gas at the same temperature then pressure, the value of the properties will become very large. So our idea was to find out the properties changes from ideal gas equation and then incorporate small corrections to account for the deviation of the behavior of the substance from ideal gas behavior.

Usually any such corrections they are desirable when the deviations from the ideal gas behavior are small. So naturally if you're computing these residual properties for condensed phases the corrections will be very large and it's not very worth in that particular case, they are primarily useful for finding out the property changes in real gases. Along with that I would also like to remind you that all these residual properties they arise just because the real properties are functions of pressure and for most of the cases the ideal properties are not functions of pressure.

So therefore this difference between the real and the ideal gas property primarily for both the cases the variation of temperature are more or less the same it's the variation of pressure which is important and for condensed phases they hardly varies the property hardly vary with pressure. So with everything put together residual properties or departure functions you may use any term at your convenience they are primarily applicable to real gases and real gas mixtures.

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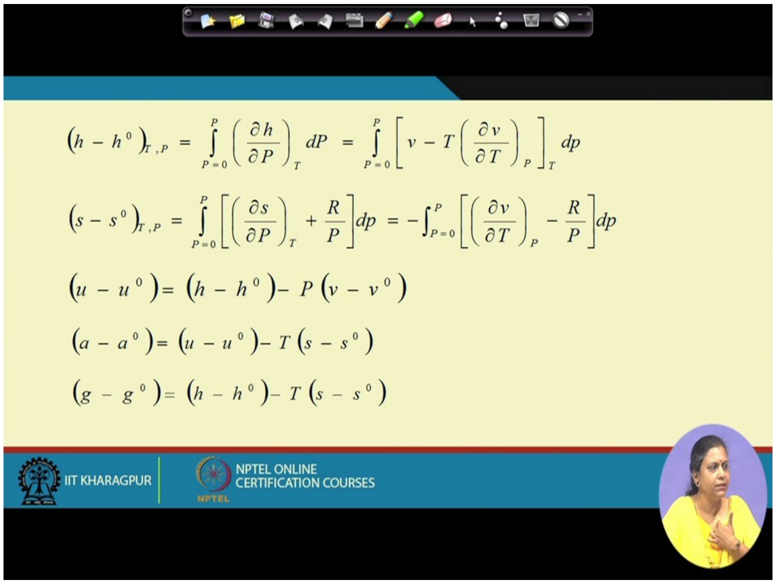

$$\left(h - h^0\right)_{T,P} = \int_{P=0}^{P} \left(\frac{\partial h}{\partial P}\right)_T dP = \int_{P=0}^{P} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]_T dp$$

$$\left(s - s^0\right)_{T,P} = \int_{P=0}^{P} \left[\left(\frac{\partial s}{\partial P}\right)_T + \frac{R}{P}\right] dp = -\int_{P=0}^{P} \left[\left(\frac{\partial v}{\partial T}\right)_P - \frac{R}{P}\right] dp$$

$$\left(u - u^0\right) = \left(h - h^0\right) - P\left(v - v^0\right)$$

$$\left(a - a^0\right) = \left(u - u^0\right) - T\left(s - s^0\right)$$

$$\left(g - g^0\right) = \left(h - h^0\right) - T\left(s - s^0\right)$$

We will be dealing with property estimation for real gases in this class, real gas mixtures will be dealt later on, right. And after this if you recollect we had also defined h minus h0, how had defined h minus h0? We found that in variation with the temperature that remains the same for both the cases, right. So therefore the residual property it primarily arises because h is a function of P I believe I had already done the derivation earlier and therefore we know this expression this expression is obtained from this particular equation that we had already discussed earlier.

So this is the expression for the departure function for enthalpy and this is the expression for departure function for entropy, once we can find these 2 we can use any particular equation or rather all the other properties can be found out from these 2 departure functions and maybe the departure function for volume etc which can be easily obtained we can find out all other non-measurable properties.

So therefore the main challenge of finding out Delta h star and Delta s star is to compute this particular integral or to compute this particular integral, how to do this? One thing is we find that this integral it is a function of let me see if I can write down this integral we find that this integral it is going to be a function of the PVT behavior of gases, isn’t it?

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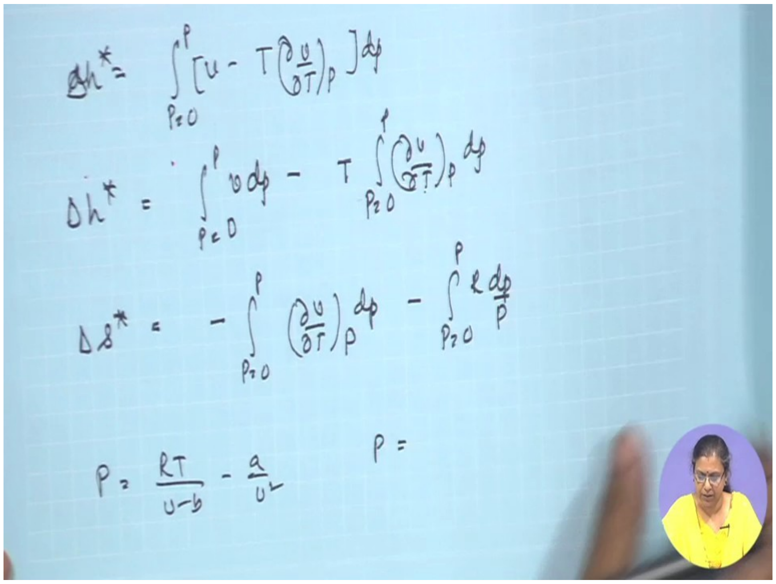

$$\Delta h^* = \int_{P=0}^{P} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right] dp$$

$$\Delta h^* = \int_{P=0}^{P} v\,dp - T\int_{P=0}^{P} \left(\frac{\partial v}{\partial T}\right)_P dp$$

$$\Delta s^* = -\int_{P=0}^{P} \left(\frac{\partial v}{\partial T}\right)_P dp - \int_{P=0}^{P} R\frac{dp}{P}$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \qquad P =$$

I will just write it down for solving it, this is given as integral P equals to 0 to P, v minus T del v del T at constant P dp or in other words very sorry this is Delta h star equals to, right? Or in other words we can also write it down as integral P equals to 0 P vdp minus T integral P equals to 0 to P del v del T at constant P dp.

In the same way we can also write down Delta s star as minus integral P equals to 0 to P, del v del T at constant P dp minus integral P equals to 0 to P, R dp by P and R R ln p, right? So therefore apparently if you look at these expressions what do you find? If you have the PVT behavior of the gases it becomes very easy, we have already discussed the PvT Behavior of the gases, right?

So therefore from those particular expressions if you can substitute rather if you can express v in terms of p then you should be able to find out this integral and if you can compute del v del T at constant P and then you can express it as a function of P you should be in a position to find out this particular integral this is quite easy, right? But if you go back and if you observe the cubic equations of state that we have discussed say for example the Van der waals equation of state, in what way have did we express the Van der waals equation of state?

The Van der waals equation of state usually we write it down as RT by v minus b minus a by v square. Same way we usually for the Peng-Robinson and the Redlich Kwong equation of state also if you go back to our discussion you will find that all these equations are written in terms of P equals to some function of v and T or in other words for all these equations we find they are for these equations temperature and volume are taken as the independent variables and for all these equations they express P in terms of T and v.

So therefore it is not very straightforward to find out the dependence of v on P from these particular equations it will be much more useful if we can write down this equations in terms of not dp but dv, let us see how to do it?

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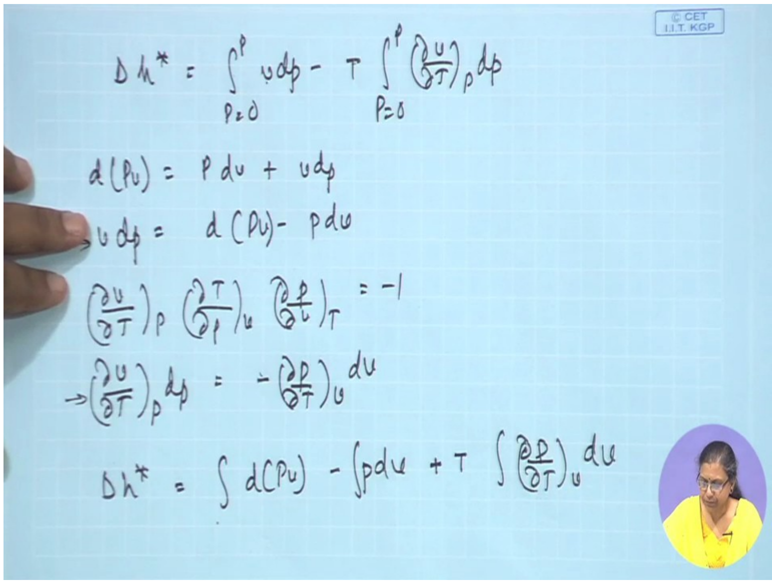

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$$\Delta h^* = \int_{P=0}^{P} v\,dp - T\int_{P=0}^{P} \left(\frac{\partial v}{\partial T}\right)_P dp$$

$$d(Pv) = P\,dv + v\,dp$$

$$\rightarrow v\,dp = d(Pv) - P\,dv$$

$$\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_v \left(\frac{\partial P}{\partial v}\right)_T = -1$$

$$\rightarrow \left(\frac{\partial v}{\partial T}\right)_P dp = -\left(\frac{\partial P}{\partial T}\right)_v dv$$

$$\Delta h^* = \int d(Pv) - \int P\,dv + T\int \left(\frac{\partial P}{\partial T}\right)_v dv$$

It is not very difficult, what do we know? We already know that from these equations well, I will write down Delta h star once more so that it becomes easy for me to follow and I also have this in front of me, right? What do we know already? We know that dPv this can be written down as Pdv plus vdp, right? So therefore instead of vdp we can write it down as dPv minus Pdv, agreed? Now also we know from the cyclic rule that del v del T at constant P, del T del P at constant v, del P del v at constant T this is equals to minus 1, agreed?

So therefore we can express it as del v del T at constant P dp this is equal to minus del P del T at constant v dv. So therefore we can substitute this equation this expression and this expression in the expression of Delta h star, what does the expression become? Delta h star therefore it becomes instead of vdp we can write it down as dPv we will put the limits later on minus pdv, right? Instead of this we have these 2 terms minus (minus) becomes plus in this case plus T we have del P del T at constant v dv.

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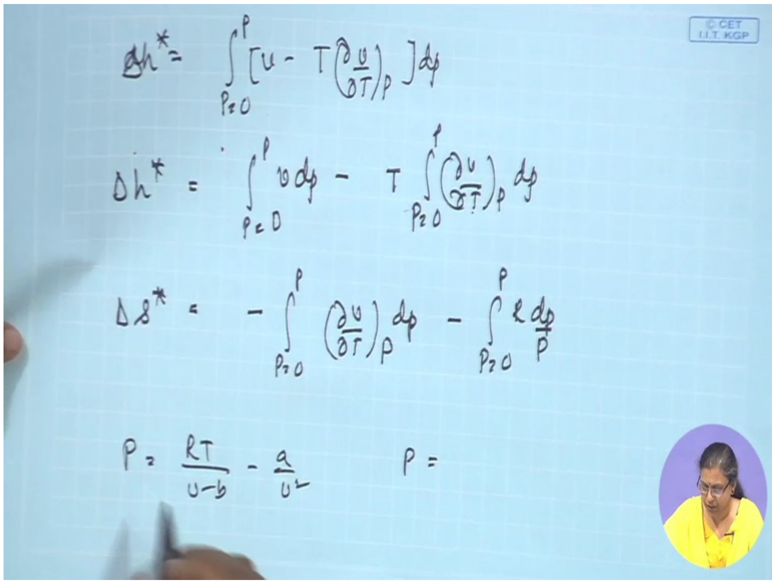

$$\Delta h^* = \int_{P=0}^{P} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right] dp$$

$$\Delta h^* = \int_{P=0}^{P} v\,dp - T\int_{P=0}^{P} \left(\frac{\partial v}{\partial T}\right)_P dp$$

$$\Delta s^* = -\int_{P=0}^{P} \left(\frac{\partial v}{\partial T}\right)_P dp - \int_{P=0}^{P} R\,\frac{dp}{P}$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \qquad P =$$

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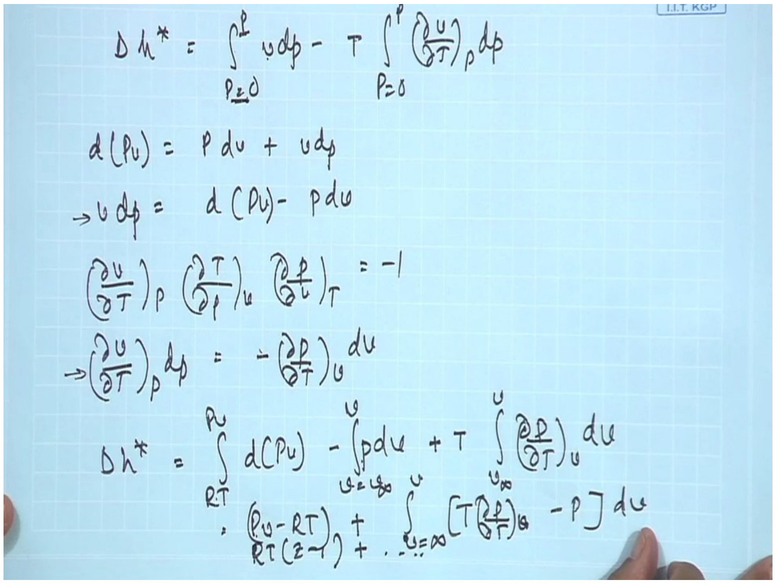

$$\Delta h^* = \int_{P=0}^{P} v\,dp - T\int_{P=0}^{P} \left(\frac{\partial v}{\partial T}\right)_P dp$$

$$d(Pv) = P\,dv + v\,dp$$

$$\rightarrow v\,dp = d(Pv) - p\,dv$$

$$\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial p}{\partial v}\right)_T = -1$$

$$\rightarrow \left(\frac{\partial v}{\partial T}\right)_P dp = -\left(\frac{\partial p}{\partial T}\right)_v dv$$

$$\Delta h^* = \int_{RT}^{Pv} d(Pv) - \int_{v=v_\infty}^{v} p\,dv + T\int_{v_\infty}^{v} \left(\frac{\partial p}{\partial T}\right)_v dv$$

$$= (Pv - RT) + \int_{v=\infty}^{v} \left[T\left(\frac{\partial p}{\partial T}\right)_v - P\right] dv$$

$$RT(z-1) + \ldots$$

So therefore if you have an equation of this particular form P equals to so and so you can very easily find out del P del T at constant V you can find out pdv etc and you can compute this out, only part remaining are the fitting of the limits of the integral. Initial limits were from P equals to 0 at very low pressure to a pressure of interest.

Now what is Pv at P equals to 0? At P equals to 0 the gas behaves as an ideal gas, so for that case Pv becomes equal to RT you need to remember that we are all dealing with only molar quantities. So therefore this becomes RT to Pv this becomes at very low volume it's v infinity to the volume of interest this is also from very low volume to the volume of interest.

So if you solve it what do you get? It becomes Pv minus RT plus it is going to become plus v equals to v infinity to v, T del P del T at constant v minus P dv, agreed? And this particular term Pv minus RT, Pv is nothing but equal to, for ordinary gases this is going to be z RT minus RT. so this can also be written down as RT into z minus 1 plus the term which we have written down, isn't it? So therefore from this particular equation we find in a very simple form once if you know the equation of state we are in a position to find out Delta h star from this equation.

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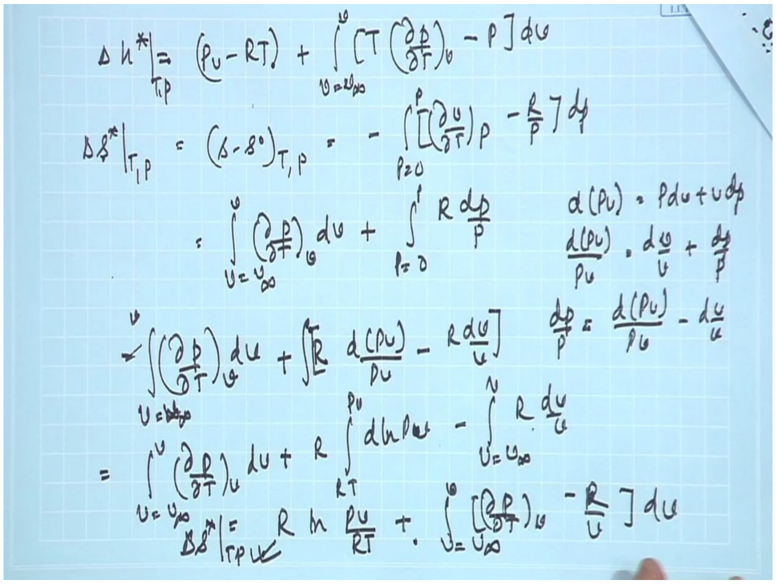

$$\Delta h^*\Big|_{T,P} = (Pv - RT) + \int_{v=v_\infty}^{v} \left[T\left(\frac{\partial p}{\partial T}\right)_v - P\right] dv$$

$$\Delta s^*\Big|_{T,P} = (s - s^0)_{T,P} = -\int_{P=0}^{P} \left[\left(\frac{\partial v}{\partial T}\right)_P - \frac{R}{P}\right] dp$$

$$= \int_{v=v_\infty}^{v} \left(\frac{\partial P}{\partial T}\right)_v dv + \int_{P=0}^{P} R\frac{dp}{P}$$

$$d(Pv) = Pdv + vdp$$

$$\frac{d(Pv)}{Pv} = \frac{dv}{v} + \frac{dp}{P}$$

$$\frac{dp}{P} = \frac{d(Pv)}{Pv} - \frac{dv}{v}$$

$$= \int_{v=v_\infty}^{v} \left(\frac{\partial p}{\partial T}\right)_v dv + \int \left[R\frac{d(Pv)}{Pv} - R\frac{dv}{v}\right]$$

$$= \int_{v=v_\infty}^{v} \left(\frac{\partial P}{\partial T}\right)_v dv + R\int_{RT}^{Pv} d\ln Pv - \int_{v=v_\infty}^{v} R\frac{dv}{v}$$

$$\Delta s^*\Big|_{T,P,v} = R\ln\frac{Pv}{RT} + \int_{v=v_\infty}^{v} \left[\left(\frac{\partial P}{\partial T}\right)_v - \frac{R}{v}\right] dv$$

So therefore we find that delta h star it can be expressed as I just write it down once more for your convenience integral v equals to v infinity that is a volume of the ideal gas to v T del p del T at constant v minus P dv. Similarly suppose we start working with delta s star at any particular temperature and pressure it is nothing but equal to s minus s0 at that temperature and pressure, what is the expression?

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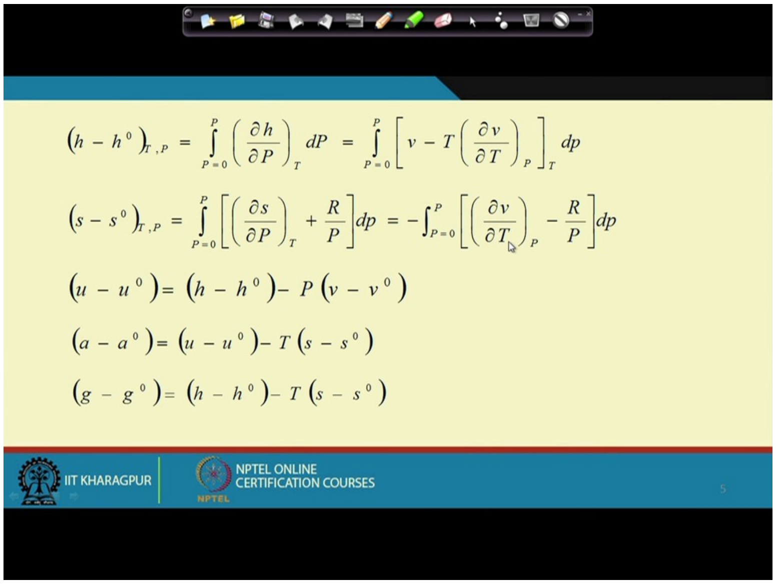

$$\left(h - h^{0}\right)_{T,P} = \int_{P=0}^{P} \left(\frac{\partial h}{\partial P}\right)_{T} dP = \int_{P=0}^{P} \left[v - T\left(\frac{\partial v}{\partial T}\right)_{P}\right]_{T} dp$$

$$\left(s - s^{0}\right)_{T,P} = \int_{P=0}^{P} \left[\left(\frac{\partial s}{\partial P}\right)_{T} + \frac{R}{P}\right] dp = -\int_{P=0}^{P} \left[\left(\frac{\partial v}{\partial T}\right)_{P} - \frac{R}{P}\right] dp$$

$$\left(u - u^{0}\right) = \left(h - h^{0}\right) - P\left(v - v^{0}\right)$$

$$\left(a - a^{0}\right) = \left(u - u^{0}\right) - T\left(s - s^{0}\right)$$

$$\left(g - g^{0}\right) = \left(h - h^{0}\right) - T\left(s - s^{0}\right)$$

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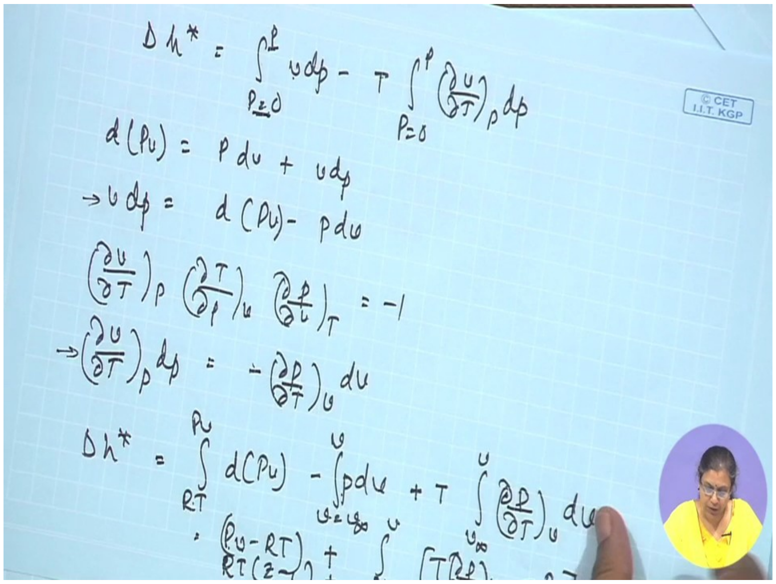

$$\Delta h^{*} = \int_{P=0}^{P} v\,dp - T\int_{P=0}^{P} \left(\frac{\partial v}{\partial T}\right)_{p} dp$$

$$d(Pv) = P\,dv + v\,dp$$

$$\rightarrow v\,dp = d(Pv) - p\,dv$$

$$\left(\frac{\partial v}{\partial T}\right)_{p} \left(\frac{\partial T}{\partial p}\right)_{v} \left(\frac{\partial p}{\partial v}\right)_{T} = -1$$

$$\rightarrow \left(\frac{\partial v}{\partial T}\right)_{p} dp = -\left(\frac{\partial p}{\partial T}\right)_{v} dv$$

$$\Delta h^{*} = \int_{RT}^{Pv} d(Pv) - \int_{v=v_{\infty}}^{v} p\,dv + T\int_{v_{\infty}}^{v} \left(\frac{\partial p}{\partial T}\right)_{v} dv$$

$$= \left(Pv - RT\right) + \int^{v}$$

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That I have already shown the expression here, so therefore using that particular expression this is minus P equals to 0 to P del v del T at constant P minus R by P dp we will just replace del v del T just as the way we have done with del P del v, so therefore what does it become? It becomes integral v equals to v infinity to v, del P del T at constant v dv plus integral P equals to 0 to p R dp by P, what is R dp by p let us see?

I mean let us find out we have already said dPv this is equals to Pdv plus vdp, right? Now dPv by Pv this is equal to dv by v plus dp by p, isn't it? We are dividing everything with Pv, so therefore from here what do we get? What is dp by P equals to? dPv by Pv minus dv by v, isn't it? So therefore instead of dp by P we can substitute in this particular way.

Therefore this becomes del P del T dv from v equals at constant v definitely, v equals to v infinity to v plus R dPv by Pv minus R dv by v, integral of this whole thing. So therefore this becomes integral from v infinity to v del P del T at constant v dv plus R, here the integration should range from RT to Pv d ln Pv minus integral v equals to v infinity to v, R dv by v.

So from there what do we get? This is basically this becomes R ln Pv by RT plus integral v equals to v infinity to v del P del T at constant v minus R by V whole thing over dv. so therefore using this equation we can find out delta s star at any temperature pressure conditions using this equation you can find out delta h star at any temperature pressure conditions. So therefore if we know which equation it is going to be valid you can very well do it and you can find out these 2 things?

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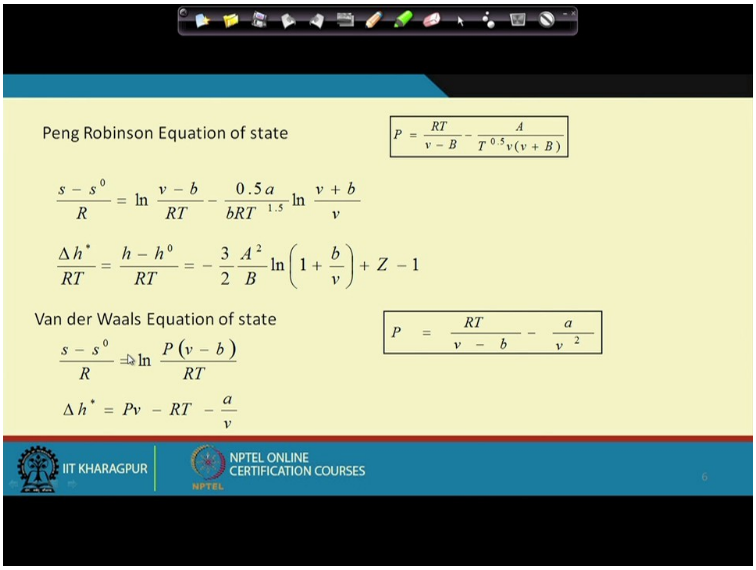

Peng Robinson Equation of state

$$\boxed{P = \frac{RT}{v - B} - \frac{A}{T^{0.5} v(v + B)}}$$

$$\frac{s - s^0}{R} = \ln \frac{v - b}{RT} - \frac{0.5a}{bRT^{1.5}} \ln \frac{v + b}{v}$$

$$\frac{\Delta h^*}{RT} = \frac{h - h^0}{RT} = -\frac{3}{2}\frac{A^2}{B} \ln\left(1 + \frac{b}{v}\right) + Z - 1$$

Van der Waals Equation of state

$$\boxed{P = \frac{RT}{v - b} - \frac{a}{v^2}}$$

$$\frac{s - s^0}{R} = \ln \frac{P(v - b)}{RT}$$

$$\Delta h^* = Pv - RT - \frac{a}{v}$$

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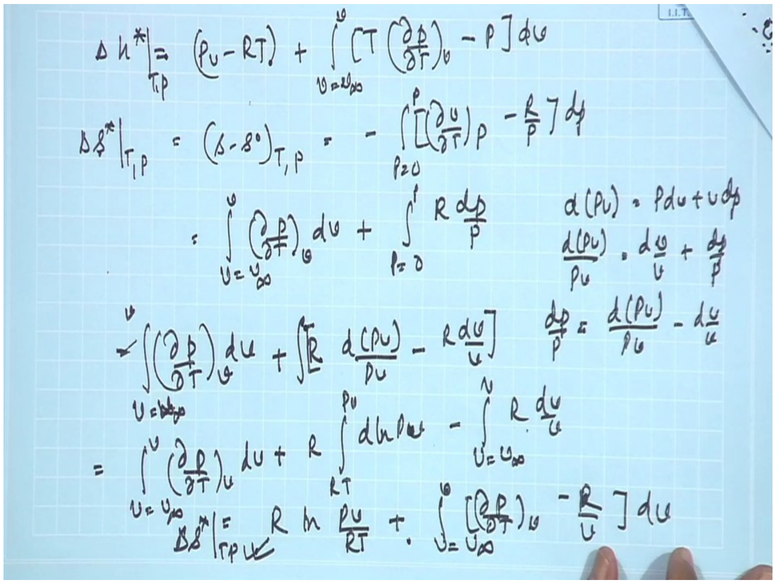

$$\Delta h^*\Big|_{T,P} = (Pv - RT) + \int_{v=v_\infty}^{v} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

$$\Delta s^*\Big|_{T,P} = (s - s^\circ)_{T,P} = -\int_{P=0}^{P} \left[\left(\frac{\partial v}{\partial T}\right)_P - \frac{R}{P}\right] dP$$

$$= \int_{v=v_\infty}^{v} \left(\frac{\partial P}{\partial T}\right)_v dv + \int_{P=0}^{P} R\frac{dP}{P}$$

$$d(Pv) = Pdv + vdP$$

$$\frac{d(Pv)}{Pv} = \frac{dv}{v} + \frac{dP}{P}$$

$$\int_{v=v_\infty}^{v} \left(\frac{\partial P}{\partial T}\right)_v dv + \int \left[R\frac{d(Pv)}{Pv} - R\frac{dv}{v}\right]$$

$$\frac{dP}{P} = \frac{d(Pv)}{Pv} - \frac{dv}{v}$$

$$= \int_{v=v_\infty}^{v} \left(\frac{\partial P}{\partial T}\right)_v dv + R\int_{RT}^{Pv} d\ln Pv - \int_{v=v_\infty}^{v} R\frac{dv}{v}$$

$$\Delta s^*\Big|_{T,P} = R\ln\frac{Pv}{RT} + \int_{v=v_\infty}^{v} \left[\left(\frac{\partial P}{\partial T}\right)_v - \frac{R}{v}\right] dv$$

For the Van der waals equation of state as I have shown in this particular presentation the Van der waals equation of state if you calculate you are going to find out the values as shown, please do the calculation they are pretty simple you just need to evaluate the differentials and perform the integrations correctly. If you do it you are going to find out that for the Van der waals equation of state we are going to find out this.

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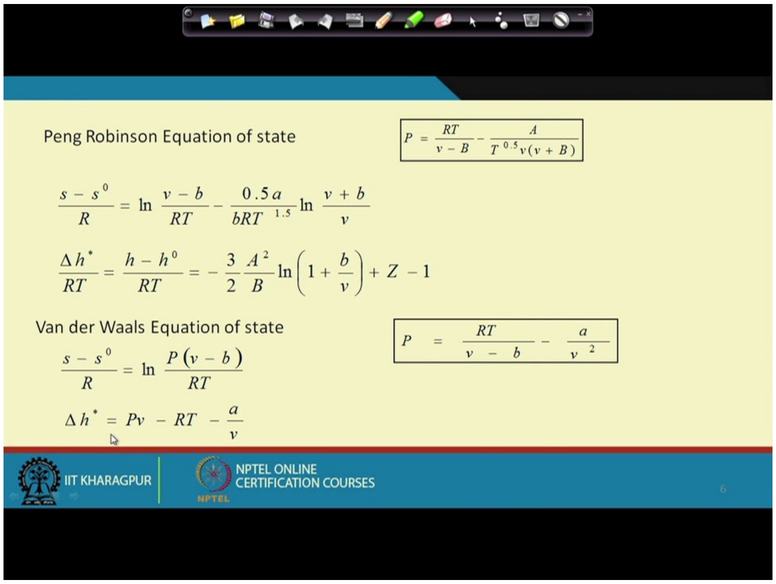

Peng Robinson Equation of state

$$\boxed{P = \frac{RT}{v - B} - \frac{A}{T^{0.5} v(v + B)}}$$

$$\frac{s - s^0}{R} = \ln \frac{v - b}{RT} - \frac{0.5a}{bRT^{1.5}} \ln \frac{v + b}{v}$$

$$\frac{\Delta h^*}{RT} = \frac{h - h^0}{RT} = -\frac{3}{2}\frac{A^2}{B} \ln\left(1 + \frac{b}{v}\right) + Z - 1$$

Van der Waals Equation of state

$$\boxed{P = \frac{RT}{v - b} - \frac{a}{v^2}}$$

$$\frac{s - s^0}{R} = \ln \frac{P(v - b)}{RT}$$

$$\Delta h^* = Pv - RT - \frac{a}{v}$$

Usually we find in the hydrocarbon industries people use the Peng-Robinson equation of state. So if you perform the calculations with the Peng-Robinson equation of state, the equation is already provided for you then in that case you are going to arrive at the expressions which have been provided here.

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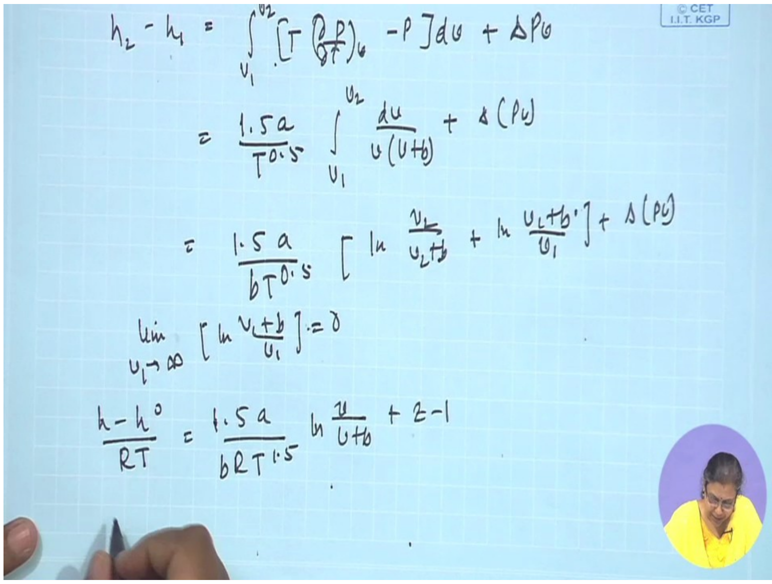

$$h_2 - h_1 = \int_{v_1}^{v_2} \left[T \left(\frac{\partial P}{\partial T}\right)_v - P\right] dv + \Delta P v$$

$$= \frac{1.5a}{T^{0.5}} \int_{v_1}^{v_2} \frac{dv}{v(v+b)} + \Delta(Pv)$$

$$= \frac{1.5a}{bT^{0.5}} \left[\ln \frac{v_2}{v_2+b} + \ln \frac{v_1+b}{v_1}\right] + \Delta(Pv)$$

$$\lim_{v_1 \to \infty} \left[\ln \frac{v_1+b}{v_1}\right] = 0$$

$$\frac{h-h^0}{RT} = \frac{1.5a}{bRT^{1.5}} \ln \frac{v}{v+b} + z - 1$$

I will just do it for you in very briefly, so that you can just check up whether you have got the same thing or not. Say for any particular property h2 minus h1 this is v1 minus v2, T del P del T at constant v minus P dv I have also already written it down for you plus delta Pv, right? Now from the Redlich Kwong equation of state if you perform these particular integrations you will find this is equal to 1.5 a by T to the power of 0.5 integral v1 to v2 dv by v into v plus v plus delta Pv, okay.

If you integrate it correctly this equation then we find this gives you as 1.5a by b T to the power 0.5 ln v2 by v2 plus b plus ln v1 plus b by v1 plus delta Pv. Now suppose the state 2 is the state of interest then state one is the ideal gas state. So therefore in the ideal gas state we know v1 tends to 0 ln v1 plus b by v1 this is naturally b equal to 0.

So with this we find out h minus h0 by RT this is given as the expression which I have already written down 1.5a by b RT to the power 1.5 ln v by v plus b plus z minus 1 and if you make certain substitutions then more or less I think this is the equation that you are going to get.

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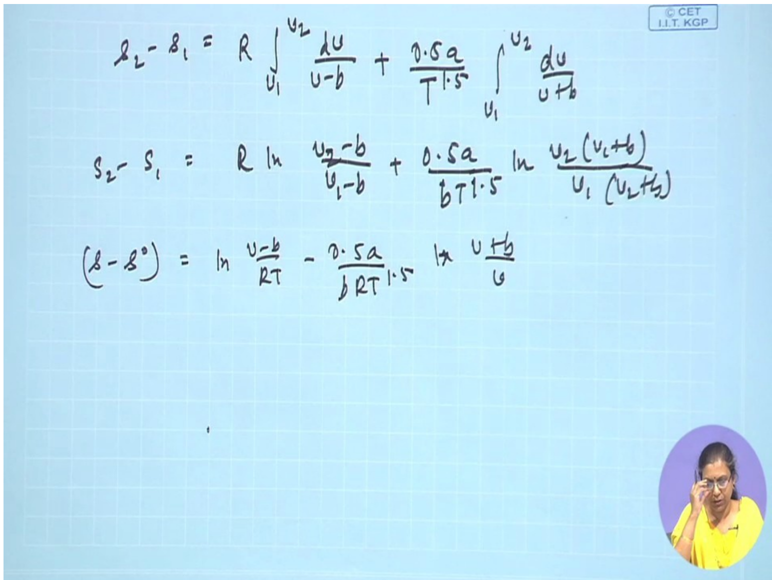

$$s_2 - s_1 = R\int_{v_1}^{v_2}\frac{dv}{v-b} + \frac{0.5a}{T^{1.5}}\int_{v_1}^{v_2}\frac{dv}{v+b}$$

$$s_2 - s_1 = R\ln\frac{v_2-b}{v_1-b} + \frac{0.5a}{bT^{1.5}}\ln\frac{v_2(v_1+b)}{v_1(v_2+b)}$$

$$(s-s^{0}) = \ln\frac{v-b}{RT} - \frac{0.5a}{bRT^{1.5}}\ln\frac{v+b}{v}$$

In a similar form if you proceed with the calculations of delta s star then also you are going to find out that s2 minus s1, this is s2 minus s1 this is nothing but R integral v1 to v2, dv by v minus b plus 0.5 a by T to the power 1.5 integral v1 to v2 dv by v plus b. If you integrate it and then you find s2 minus s1 is R ln v2 by v, I am calculating this out because this is quite commonly used in hydrocarbon industries and since this is slightly involved, so therefore this is T to the power 1.5 ln v2 into v1 plus b by v1 into v2 plus b, right?

If you rearrange it then we find that once you rearrange it and you arrange it properly then finally you get s minus s0 this will be equal to ln v minus b by RT minus 0.5a by b RT to the power of 1.5 ln v plus b by v, right? So therefore in this particular way you can also try out the Redlich Kwong equation of state you find that from these equation from the PvT behavior of the gases if you know that they are obeying any particular equation of state, all the equations are pressure explicit. So using these you will be in a position to find this out.

What are the other ways of estimating enthalpy, entropy departure functions or other departure functions? Because these equations that we have derived were although very accurate an exact but they are very tedious and time-consuming as engineers we would like to have certain faster methods which may not be so accurate but they would help us a quick to obtain a quick estimation of the property. So we are going to discuss that in the next class.