

Course on Phase Equilibrium Thermodynamics
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Lecture 19
Property Estimation(Contd.)

Well, so apart from what we have already done we were trying to find out the departure functions from the PVT behavior of gases. Now apart from PVT Behavior we can also use the compressibility factor chart for finding out the departure functions for that we need to just reorient the equation which we have derived we just need to write them in terms z and T_r P_r etc, how to do this?

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

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

$$v = \frac{zRT}{P} \quad \left(\frac{\partial v}{\partial T} \right)_P = \frac{zR}{P} + \frac{RT}{P} \left(\frac{\partial z}{\partial T} \right)_P = \frac{R}{P} \left[z + T \left(\frac{\partial z}{\partial T} \right)_P \right]$$

$$\left[\frac{\partial (\Delta h^*)}{\partial P} \right]_T = \frac{zRT}{P} - T \frac{R}{P} \left[z + T \left(\frac{\partial z}{\partial T} \right)_P \right]$$

$$= \frac{zRT}{P} - \frac{zRT}{P} - \frac{RT^2}{P} \left(\frac{\partial z}{\partial T} \right)_P$$

$$\Delta h^* = -RT \int_0^P \left(\frac{\partial z}{\partial T} \right)_P \frac{dP}{P} = -RT T_c \int_0^{P_r} \left(\frac{\partial z}{\partial T} \right)_{T_c} \frac{dP_r}{P_r} = RT T_c^2 \int_0^{P_r} \left(\frac{\partial z}{\partial T_r} \right)_{T_c} \frac{dP_r}{P_r}$$

Let us see v is nothing but equal to zRT by P . Δv ΔT at constant P then we can write it down as zR by P plus RT by P Δz ΔT at constant P or in other words we can write it down as R by $P z$ plus T Δz ΔT at constant P , isn't it? So in that case Δ of $\Delta h^* \Delta P$ at constant T , what is this? This is nothing but if we simply substitute this equation here then what do we get? Instead of v we are going to write zRT by P and then minus T the expression for Δv ΔT at constant P .

What does it reduce to? zRT by P minus $T R$ by $P z$ plus $T \Delta z \Delta T$ at constant P , agreed? Or in other words this reduces to zRT by P minus this term is also zRt by P minus RT square by $P \Delta z$

del T at constant P or in other words this can be also written down as delta h star on integration you will get this is nothing but equal to minus R integral minus RT square integral 0 to P del z del T at constant P dp by P, isn't it?

And so therefore this equation we can also write it down in terms of reduced parameters like minus R Tr square Tc square for T integral 0 to Pr del z del Tr Tc dPr Pc by Pr Pc, isn't it? And then what do we find finally? We find that we have expressed delta h star in terms of minus R Tr square Tc integral 0 to Pr del z del Tr at constant Pr d Pr by Pr, agreed? So therefore from this we find we are we could express delta h star in terms of TR and PR.

And so therefore if we know z in terms of TrPr we can substitute it and we can find out Delta h star, for finding or using z we recollect that they have already shown you the use of compressibility factor charts which express z as a function of Tr and Pr. Just in the way they have expressed delta h star we should be in a position to express delta s star as well, how to express?

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

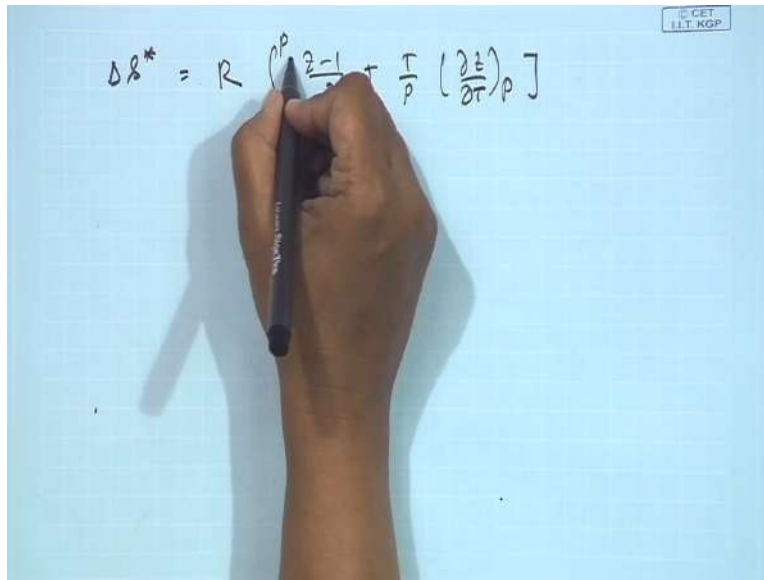
$$\Delta h^*|_{T,P} = - \int_{P=0}^P \left(\frac{\partial v}{\partial T} \right)_P dP - \int_{P=0}^P \frac{R}{P} dP$$

$$v = \frac{RT}{P} \quad \left(\frac{\partial v}{\partial T} \right)_P = \frac{R}{P} + \frac{RT}{P^2} \left(\frac{\partial z}{\partial T} \right)_P = \frac{R}{P} \left[z + T \left(\frac{\partial z}{\partial T} \right)_P \right]$$

$$\left[\frac{\partial (\Delta h^*)}{\partial P} \right]_T = \frac{RT}{P} \left[z + T \left(\frac{\partial z}{\partial T} \right)_P \right] - \frac{RT^2}{P^2} \left(\frac{\partial z}{\partial T} \right)_P$$

$$\Delta h^* = -RT \int_0^P \left(\frac{\partial z}{\partial T} \right)_P dP + \int_{T_c}^{T_r} \left(\frac{\partial z}{\partial T} \right)_{P_r} \frac{dT}{T} + \int_{P_r}^{P_c} \left(\frac{\partial z}{\partial P} \right)_{T_r} \frac{dP}{P}$$

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$$\Delta S^* = R \int_0^P \left[\frac{z-1}{T} + \frac{T}{P} \left(\frac{\partial z}{\partial T} \right)_P \right] dp$$

In the same way we are going to substitute this expression here and we are going to work it out, this gives minus R integral 0 to P, z minus 1 by P plus T by P del z del T at constant P dp, isn't it? And this also we can write it down as R integral 0 to P z minus 1 plus Tr del z Del TR constant P whole thing dP by P.

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

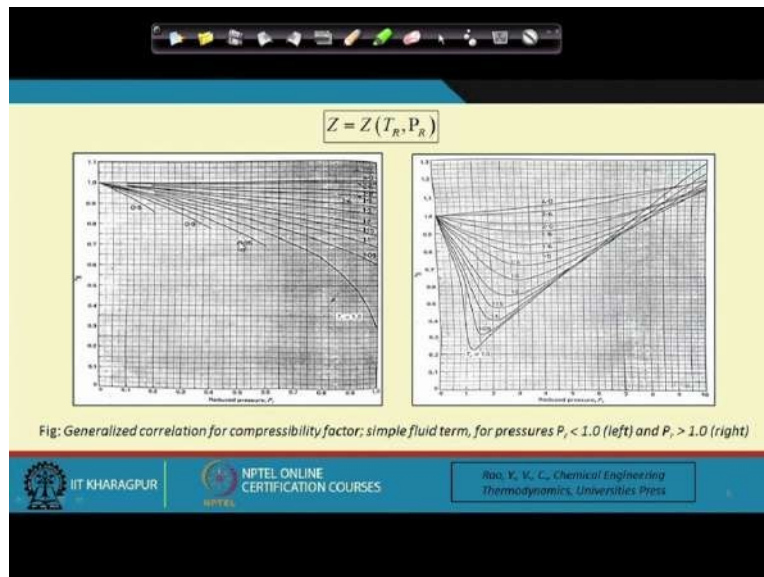
$$v = \frac{ZRT}{P} \quad \left(\frac{\partial v}{\partial T} \right)_P = \frac{ZR}{P} + \frac{RT}{P} \left(\frac{\partial Z}{\partial T} \right)_P = \frac{R}{P} \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_P \right]$$

$$\left[\frac{\partial (\Delta h^*)}{\partial P} \right]_T = \frac{ZRT}{P} - T \frac{R}{P} \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_P \right]$$

$$= \frac{ZRT}{P} - \frac{ZRT}{P} - \frac{RT^2}{P} \left(\frac{\partial Z}{\partial T} \right)_P$$

$$\Delta h^* = -RT \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} = -RT \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} = -RT \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP}{P}$$

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So we can also find out Δs^* and Δh^* in terms of Z , T_r , P_r we can use this compressibility factor charts to find Z then we can integrate Z as a function of T_r and P_r . Z is the function of T_r at constant P_r and we can very well do this but there is something more interesting if you observe the equations that I have written down.

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Handwritten equations on a blue grid background:

$$\frac{\Delta S^*}{R} = R \int_0^P \left[\frac{z-1}{P} + \frac{T}{P} \left(\frac{\partial z}{\partial T} \right)_P \right] dP$$

$$\frac{\Delta S^*}{R} = R \int_0^{P_r} \left[(z-1) + T_r \left(\frac{\partial z}{\partial T_r} \right)_{P_r} \right] \frac{dP_r}{P_r}$$

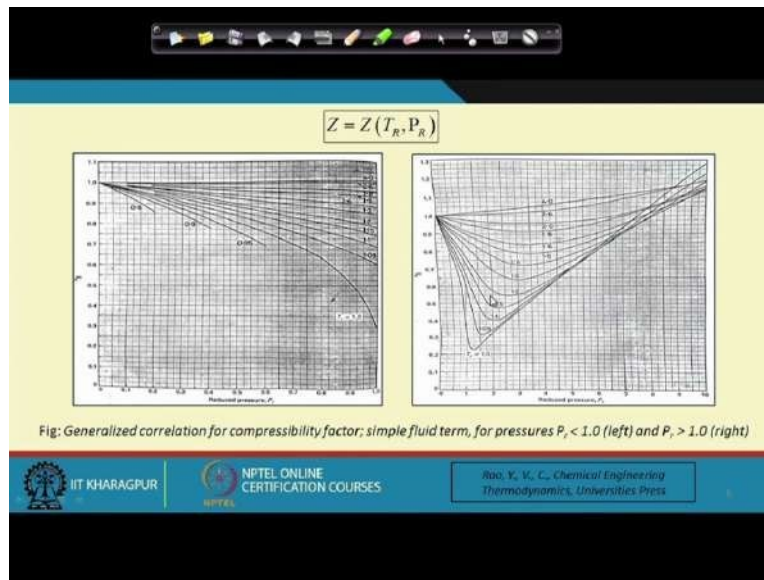
$$\frac{\Delta H^*}{RT_c} = R T_r^2 P_c \int_0^{P_r} \left(\frac{\partial z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

Obey the law of corresponding states

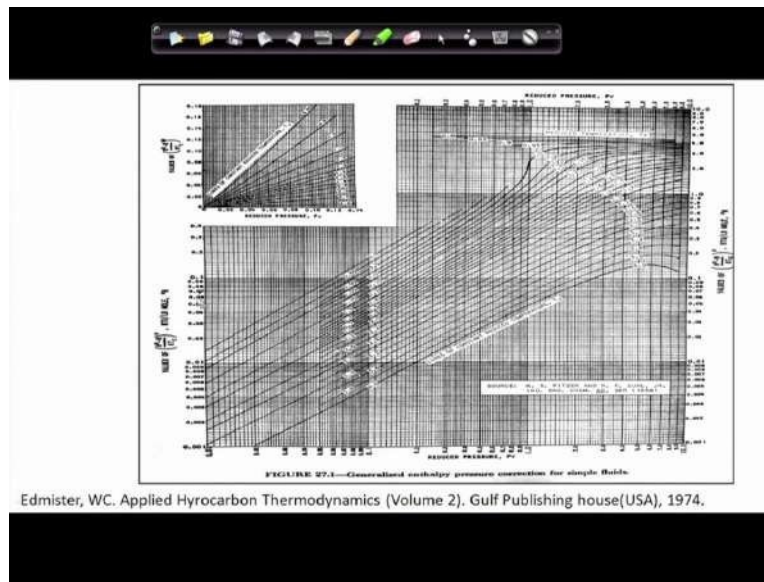
The equation for Delta s star and the equation of delta h star I will rewrite it just for your convenience. This is integral 0 to Pr del z del Tr at constant Pr dPr by Pr observe this equation carefully, what do you find? You find that suppose you can express this equation as delta s star or else delta s star by R then what do you find?

You will find the right-hand side it just express in terms of reduced volumes. So what does it show? It shows that this parameter Delta s star by R this definitely obeys the law of corresponding states. In the same way if you can express this equation of delta h star in this way you find again the right-hand side it contains only the reduced parameters and z and nothing else, what does it imply?

It implies that these 2 terms Δs^* by R and Δh^* by RT_c they definitely obey the law of corresponding states. So therefore we need not refer to the compressibility factor charts that I have shown in here. We should be able to generate identical curves using Δh^* by RT_c as a function of P_r and T_r .



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We should be able to generate Δs^* by R curve as a function of unique functions of T_r and P_r and this has been done by a large number of researchers so long and the curves they are of this particular form. These curves they have been generated by Edmister and they are used very frequently in the hydrocarbon industries in order to estimate the reduced enthalpy departure function as a function of reduced pressure and a function of reduced parameter, okay.

And in the same way graphs have also been generated for the entropy departure function. Now it is important for us to remember that just like the compressibility factor chart which we have discussed we had found out that the 2 parameter law of corresponding states it is not very accurate and we often resort to the 3 parameter law of corresponding states. For the 3 parameter law what do we need to do?

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$$Z = Z^0 + \omega Z^1$$

$$\Delta h^* |_{T, P} = -R \frac{T_c^2}{T_c} \int_0^{P_r} \left(\frac{\partial Z^0}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} + \omega R \frac{T_c^2}{T_c} \int_0^{P_r} \left(\frac{\partial Z^1}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

$$\frac{\Delta h^*}{RT_c} |_{T, P} = \left(\frac{\Delta h^*}{RT_c} \right)^0 + \omega \frac{(h^0 - h^1)}{RT_c}$$

$$\frac{\Delta h^*^0}{RT_c} = T_c^2 \int_0^{P_r} \left(\frac{\partial Z^0}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

$$\left(\frac{\Delta h^*}{RT_c} \right)^1 = T_c^2 \int_0^{P_r} \left(\frac{\partial Z^1}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

We simply express z as a function of z^0 , this is for simple compound for simple molecules and then we incorporate a correction using a third parameter which is the acentric factor. So therefore if we wish to incorporate this and express Δh^* by RT_c in terms of the 3 parameter law of corresponding states that also we can do in this particular case, for that what we need to know?

We just need to substitute instead of z we need to substitute z^0 plus Ωz^1 and find out the relevant equation, what is the equation let us see? The equation becomes minus this becomes minus RT square by T_c integral 0 to P_r del z^0 del T_r at constant P_r dP_r by P_r we are simply substituting that and elaborating the equation by T_c integral 0 to P_r del z^1 del T_r at constant P_r dP_r by P_r or in other words we find that we are in a position to write the enthalpy departure function in terms of something like Δh^* by RT_c as Δh^*^0 by RT_c plus ω , plus this was already minus ω .

So therefore plus ω into this particular term which is h^0 minus h^1 by RT_c where this term it can be written down as ωT_r square integral 0 to P_r del z^1 del T_r at constant P_r , dP_r by P_r , right? So therefore we find from here the 2 parameter expression it is nothing but T_r , so I will just write down Δh^* by RT_c 0 this is nothing but TR square integral 0 to PR del z^0 del T_r at constant P_r dP_r by P_r and Δh^* by RT_c 1 this is equal to TR square integral 0 to

PR del z_1 del Tr at constant Pr d equal, I am confusing the small and all of these are small alphabets dPr by Pr.

So therefore just like we have discussed for the case of your the compressibility factor in this case also we find that for greater accuracy we need to incorporate not only the 2 parameter but also that 3 parameter law of corresponding states. Now similar exercise can also be performed for the entropy correction or the entropy departure function as well.

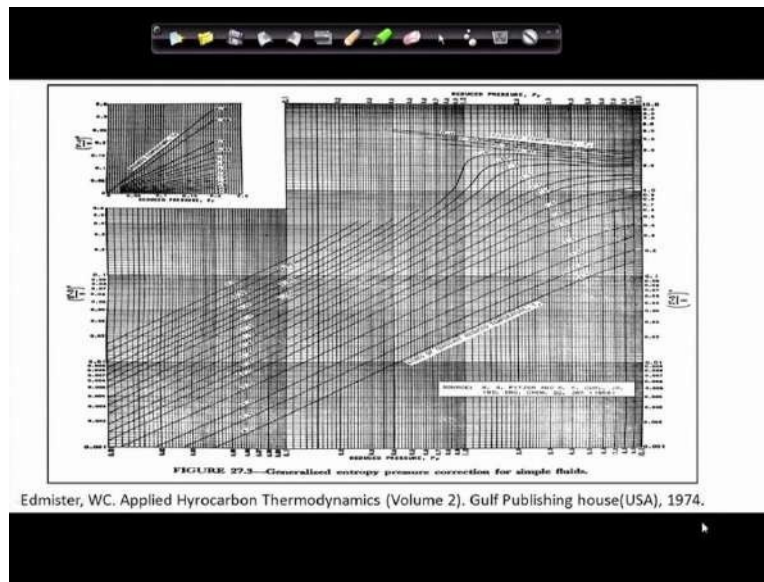
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$$\frac{\Delta s^*}{R} = \int_0^{Pr} \left[z^0 - 1 + Tr \left(\frac{\partial z^0}{\partial Tr} \right)_{Pr} \right] \frac{dTr}{Tr} \frac{\Delta s^0}{R} + \omega \int_0^{Pr} \left[z^1 + Tr \left(\frac{\partial z^1}{\partial Tr} \right)_{Pr} \right] \frac{dTr}{Tr}$$

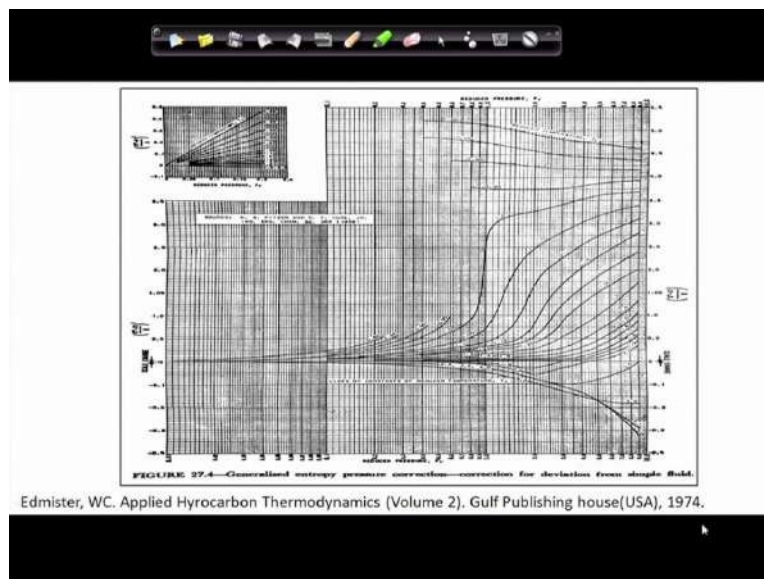
($\frac{\Delta s^*}{R}$)¹

In that case also if we proceed in this particular way, we will find that Delta s star by R it can be expressed as 0 to Pr z_0 minus 1 plus Tr del z_0 del Tr at constant Pr this whole thing dPr by Pr plus omega integral 0 to Pr z_1 plus Tr del z_1 del Tr at constant Pr whole thing dPr by Pr where this particular path this whole part is nothing it is nothing but delta s star1 by R and this part it can be written down at delta s star0 by R.

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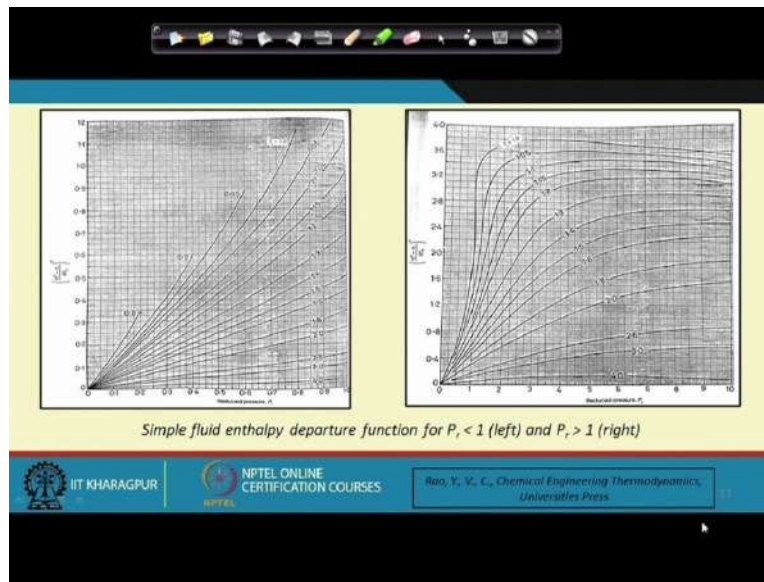


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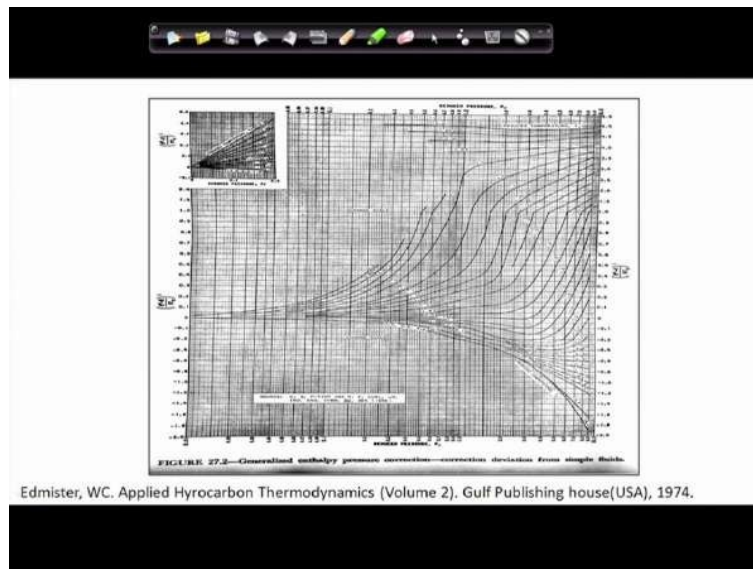


Now several charts have been proposed as I have already discussed there are charts by Edmister and one can refer to those charts by going to the book of Edmister we find that there are enthalpy departure functions, there are entropy departure functions for 2 parameter as well as the 3 parameter law and the 3 parameter corresponding states and usually we prefer the 3 parameter because 2 parameter module it was anyhow not very accurate for predicting compressibility factor. So naturally it fails much more for the case of enthalpy and entropy departure functions as well, right?

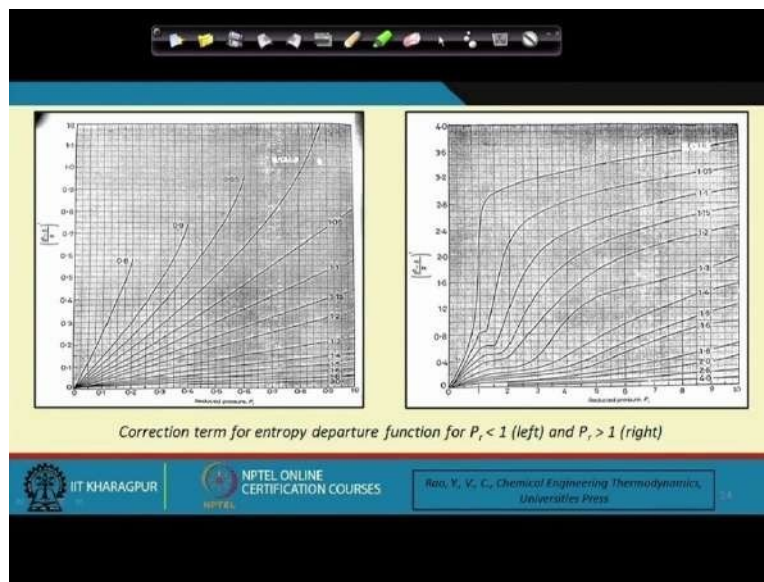
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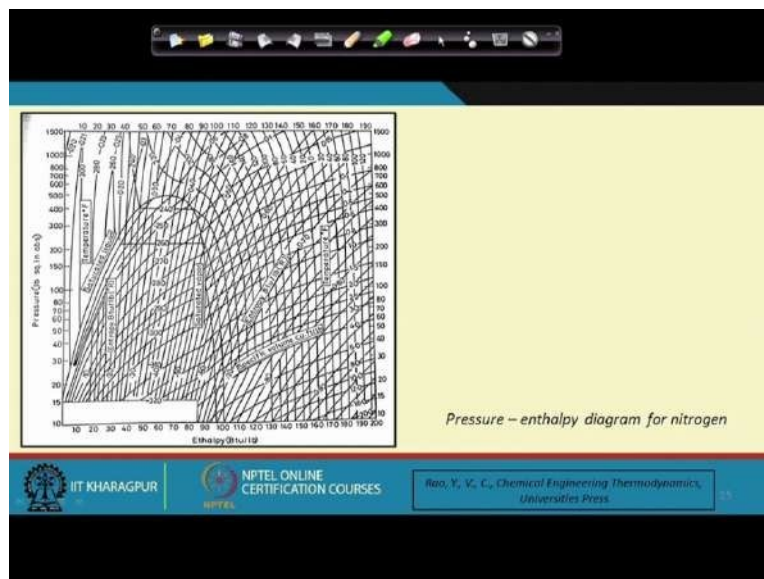
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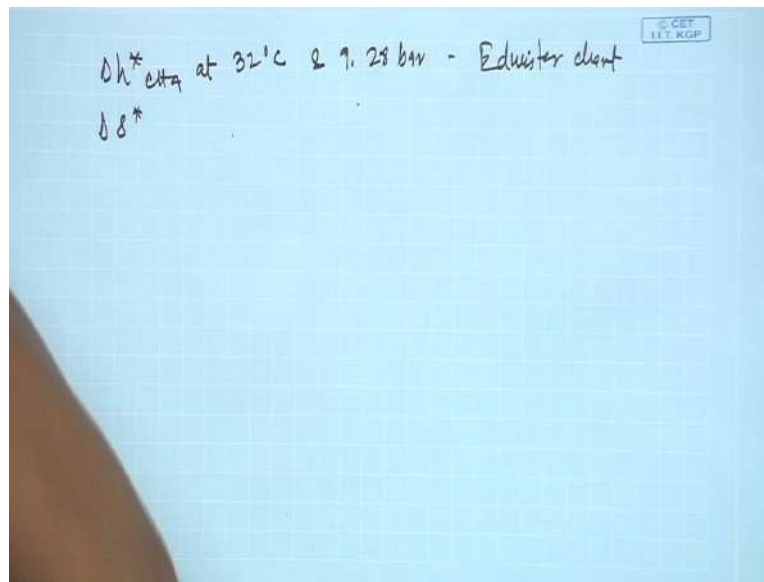


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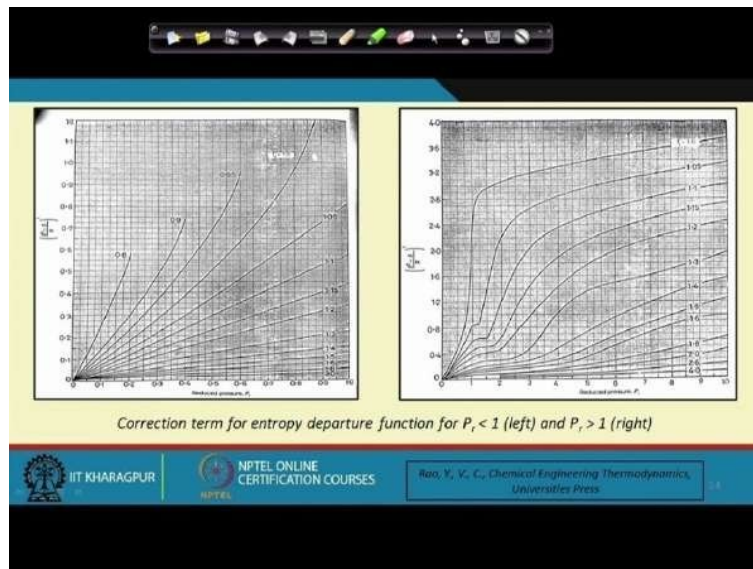


So these are the 2 types of charts which are available, the initial charts which I had shown they are for Edmister they are primarily used for the hydrocarbon industries there are also certain other charts which have been proposed by Lee and Kesler these charts can also be used, you can very well see that they have the 2 parameter and the 3 parameter enthalpy as well as entropy departure functions you can see they have been expressed for lower values of reduced pressure and higher values of reduced pressure one can very well use them and they can find it out, okay.

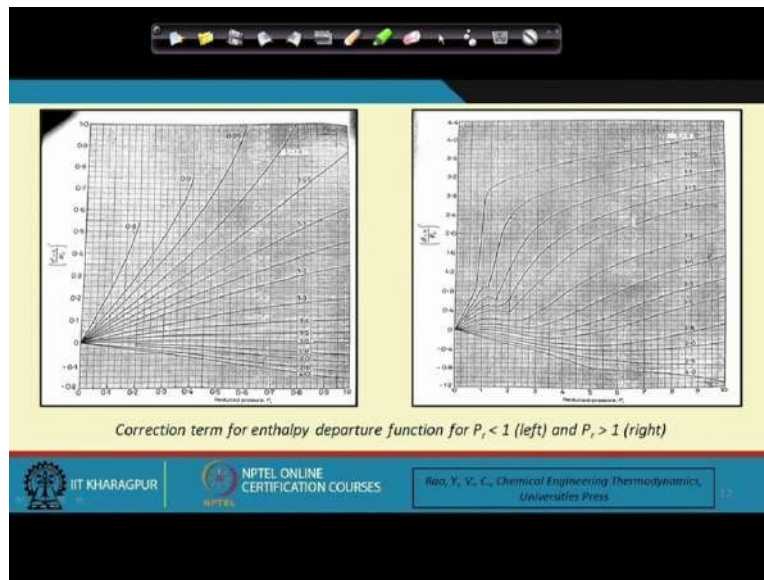
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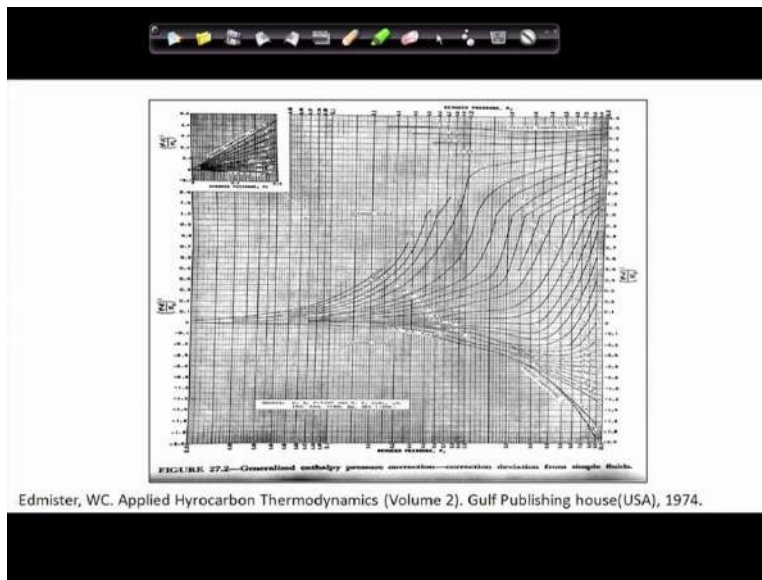


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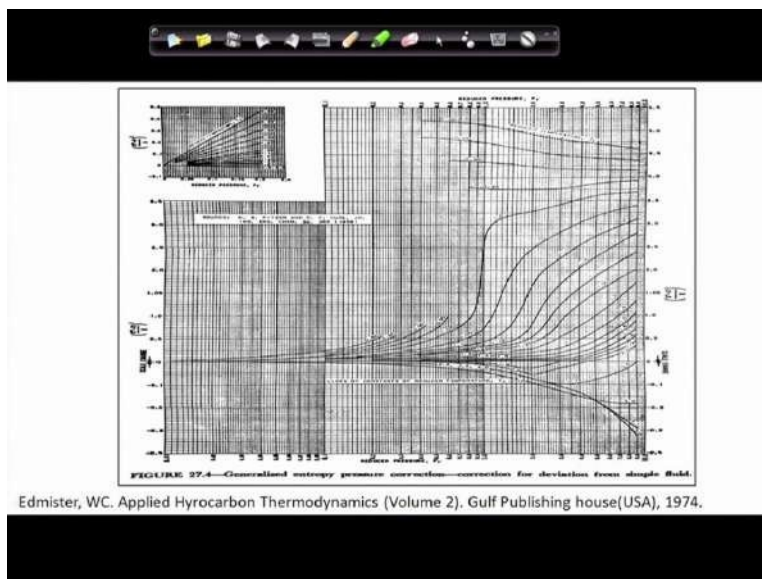


We can do a one or 2 problems regarding this so that you can get a better feel of it, for example suppose I tell you that we would we are interested to find out Δh^* and Δs^* for methane say, okay. For methane at 32 degrees centigrade and say 9.28 bar and I tell you to use Edmister chart for this, so what are you going to do for this? You are required to find out the enthalpy and entropy departure functions for methane at 32 degrees centigrade and 9.28 bar, right?

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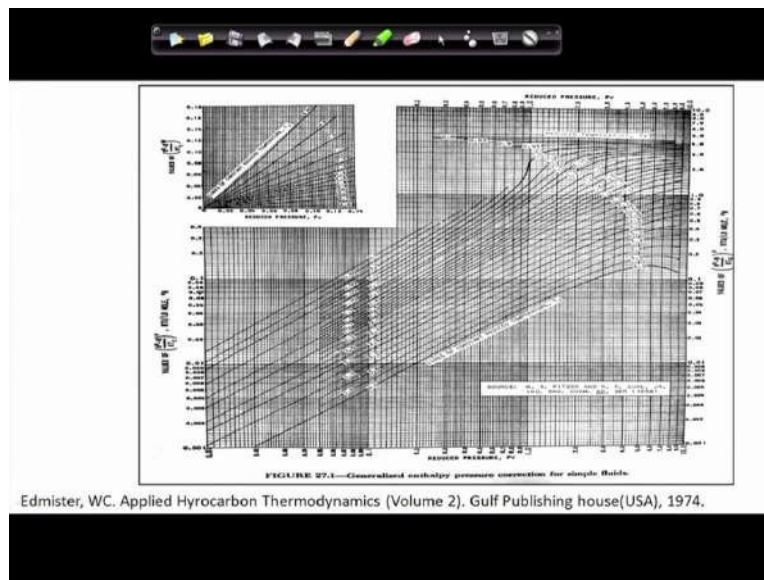
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So let us go to the Edmister's chart for this, the Edmister's chart are this, right? Now for methane the first thing that you need to do, you need to find out T_c and P_c and ω , right? What is T_c in this case? You can find it from any standard table or etc, P_c is going to be 46.41 bar and ω this is going to be 0.011, once you know this you are in a position to find out T_r , remember this T_r and P_r they should be these are in terms of Kelvin. So therefore this also has to be converted to Kelvin.

Now there is one thing which I would like to tell the problems you often tend to make mistakes just because you do not consider the right units, it is very important when you're working with pressure, suppose you are using Antoine's equation very frequently they are given in torr so therefore the pressure which you're going to use has to be in torr. When you're working with temperature see at what in which unit they are given, so these things are very important if you want to arrive at correct answers for not only for thermodynamics for anything for that matter.

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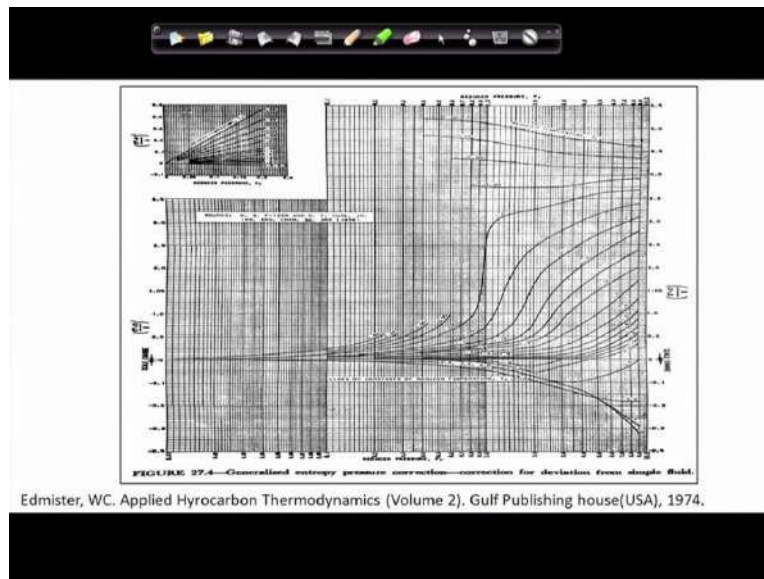


So therefore this becomes 305.15 by 190.7 which is nothing but 1.6 in the same way you can find out P_r it is going to be 9.28 by 46.41 which is equals to 0.2. So therefore you need to find at P_r equals to 0.2 and T_r equals to 1.6 let us go to the enthalpy charts you find out for this particular situation you are going to get from here if you can locate your P_r equals to 0.2 it's here, here somewhere and P_r is equals to 0.2 and T_r equals to 1.6 this is the line.

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Δh^*_{eth} at 32°C & 9.28 bar - Edmister chart
 Δs^* $T_c = 190.7 \text{ K}$
 $P_c = 46.41 \text{ bar}$
 $\omega = 0.011$
 $T_r = \frac{305.15}{190.7} = 1.6$ $P_r = \frac{9.28}{46.41} = 0.2$
 $\frac{\Delta h^*}{RT_c} = 0.085$ $\frac{\Delta h^*}{RT_c} = 0.01$ $\frac{\Delta s^*}{R} = 0.032$
 $\frac{\Delta s^*}{R} = 0.032$ $\frac{\Delta s^*}{R} = 0$ $\Delta s^* = -0.135 \frac{\text{kJ}}{\text{mole K}}$
 $\frac{\Delta h^*}{RT_c} = 0.085 + 0.01(0.011) = 8.571 \times 10^{-2}$

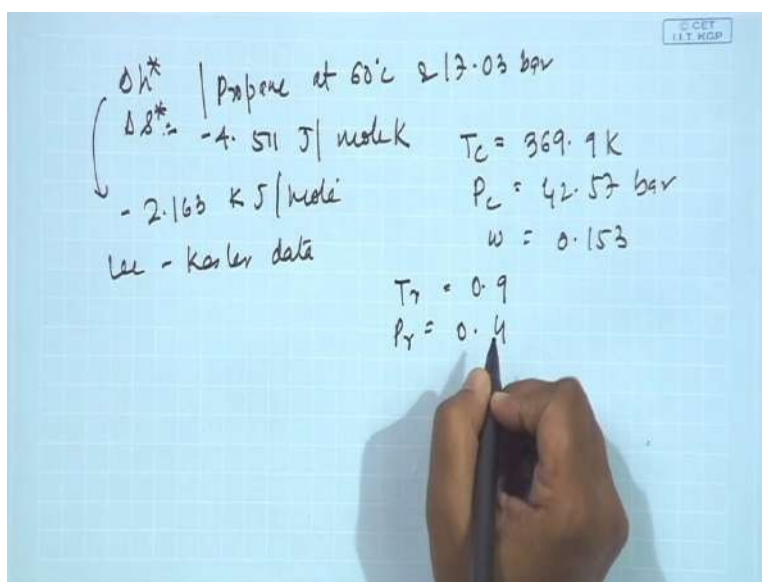
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So if you follow this line and to come to 0.2 you find out that your Δh^* by RT_c this whole thing becomes 0.085, check it up for yourself and find out then if you go to the next curve then you're in a position to find out Δh^* by RT_c find it out you are going to get this is 0.01 similar fashion if you find out Δs^* by R , read it out it's going to be 0.032 Δs^* by R this is going to be equal to 0. You can use these particular graphs and you can find them out.

Now once this is available you can find out Δh^* by RT_c it is just going to be this plus ω of this, so if you calculate it as 0.085 plus 0.01 into 0.011 then from there you find the value is going to be 8.511 into 10 to the power minus 2 and from here what is the value of Δh^* then which you are required to find out? This is nothing but minus 0.135 kilo joules per mole, right? So therefore in the same way if you proceed with Δs^* by R you have got. So therefore we find out that Δs^* by R this is just this value plus ω of 0. So naturally this reduces to 0.032 only which gives you Δs^* as minus 0.266 used per mole Kelvin, right?

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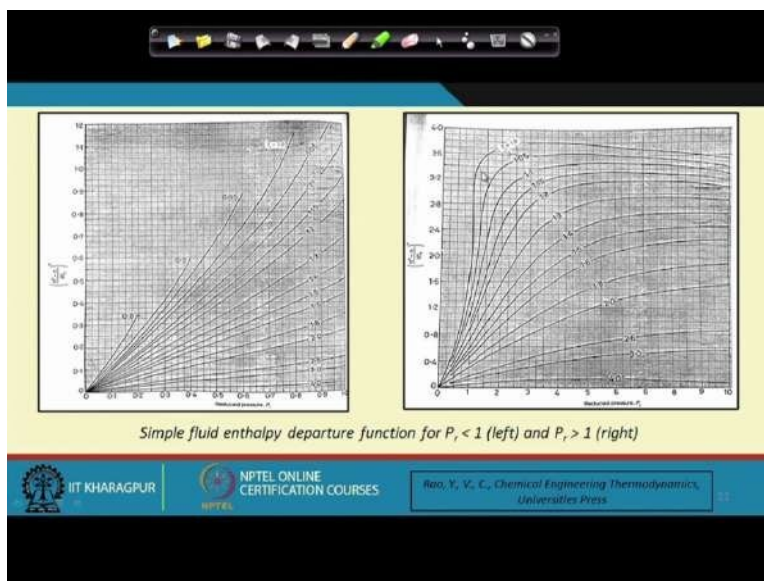
So therefore in this particular way you can take up a few other problems and you can find it out for example suppose take up the problem for propane, instead of methane suppose I tell you to take up the problem on, find out Δh^* and Δs^* for propane at 60 degrees centigrade and 17.03 bar you can use the Edmister's chart for doing this I will just give you the answers you compare and you just see whether you could do it or not.

Δs^* will be minus 4.511 joules per mole Kelvin and the value of Δh^* is going to be minus 2.163 kilo joules per mole, just try it out and see what you're getting. In the same way for using Lee Kesler chart also, suppose I tell you that for the same propane you do it using the Lee Kesler chart. For the using the Lee Kesler data naturally we have to go to the correct graph

for this. These are the graphs for Lee Kasler data, now here also you need to know the value of TC and PC.

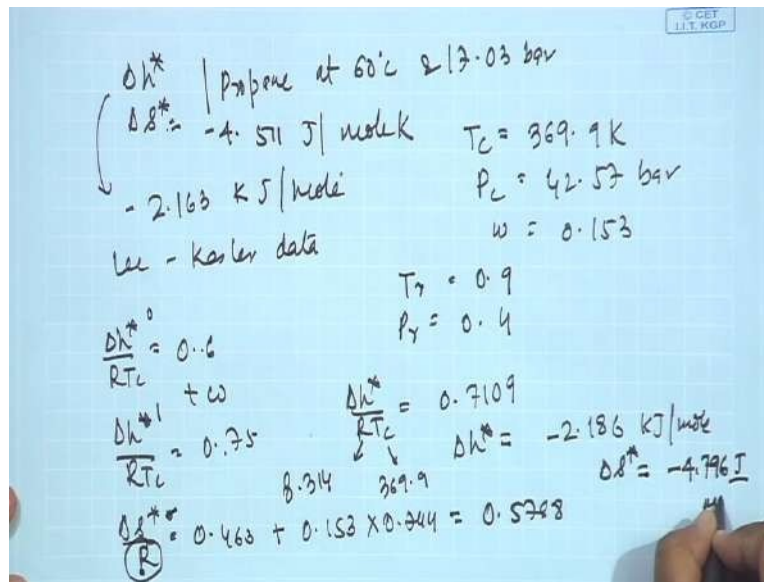
So T_c in this particular case for propane it is 369.9 Kelvin, P_c this is equal to 42.57 bar and ω it is 0.153 provided these are given then you're in a position to find out your ϕ yeah, you're in a position to find out T_r here, T_r is 0.9, P_r this is equals to 0.4.

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So from these particular graphs you will find that for P_r equals to 0.4 and T_r equals to 0.9 you cannot use this graph we have to use this particular graph, right? No, you can use this graph, sorry. So for this T_r equals to 0.9 and P_r equals to 0.4 if you read it out you find that that the value in this particular case it's almost equal to 0.6 it more accurately 0.59 you can take it as 0.6.

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So therefore you will find that Delta h star 0 by RT see in this particular case it 0.6. Again if you go to the next curve you will find that Delta h star 1 by RTc if you read it here again for 0.4 and for 0.9 you find it is about 0.75, right?

So therefore from here you will be in a position to calculate Delta h star by RTc it is just this plus omega of this. So therefore this becomes 0.7109 or 071 you can take, from where we can calculate Delta h star to be minus 2.186 kilo joules per mole, R in this particular case you said dealing with joules this is going to be 8.314 and the value of TC it is 369.9 which I have already mentioned same way if you would wish to calculate Delta s star we can do it as well.

Here also you need to go from 0.4 to 0.9 and you can see the value is about 0.463, isn't it? So therefore Delta s star by R0 this is 0.463 and if you're going to calculate Delta s star1 again from 0.4 to 0.9 it is about 0, his particular value it is about 0.744 something yeah,0.744. So therefore 0.463 plus your 0.153 into 0.744 that gives you Delta s star by R and which is nothing but 0.5768 multiply it with a value of R which is 8.314 and finally you get the value at Delta s star equals to minus 4.796 joules per mole Kelvin. So in this particular way you you can try a large number of problems and you can get yourself conversant with the usage of these charts.

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$$z = \frac{Pv}{RT} = 1 + \frac{BP}{RT} = 1 + \frac{BPr}{RT_c} \left(\frac{T_r}{T_r} \right) \Rightarrow \text{At low to moderate } pr.$$

$$v = \frac{RT}{P} \left(1 + \frac{BP}{RT} \right) = \frac{RT}{P} + B$$

$$\left(\frac{du}{dT} \right)_P = \left(\frac{dB}{dT} \right) + \frac{R}{P}$$

$$\begin{cases} dh^* = (B - T \frac{dB}{dT}) P \\ ds^* = -P \left(\frac{dB}{dT} \right) \end{cases} \quad B = \frac{RT_c}{P_c} (B^0 + \omega B^1)$$

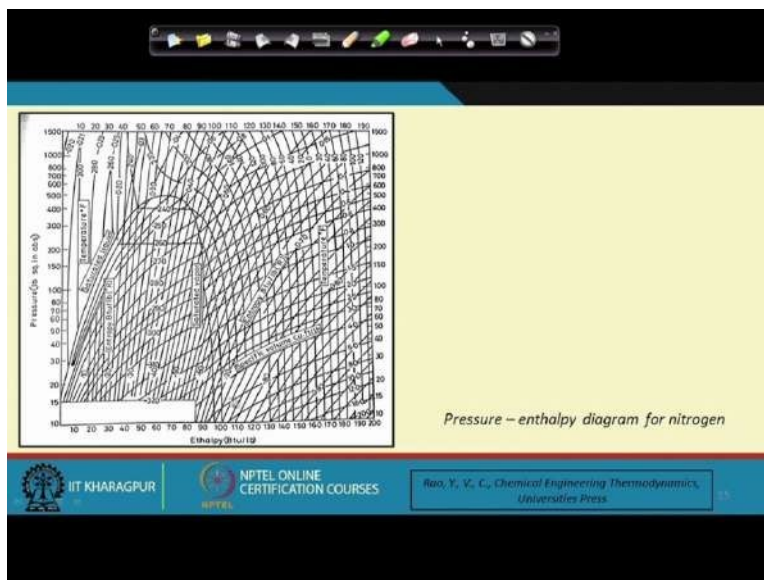
Now before I end it is also important to just have a brief discussion on the prediction of departure functions will be virial equations of state, what is the virial equation of state we know? This is z equals to Pv by RT for low to moderate pressures we truncate it after the first term this can also be written down as BPr by RT_c P_r by T_r , remember one thing this is applicable for low to moderate pressure this is something important.

So then what is v equals to? This is RT by P into 1 plus BP by RT which is nothing but RT by P plus B , accordingly what is $\frac{dv}{dT}$ at constant P this is nothing but $\frac{dB}{dT}$ plus R by P accordingly what is Δh^* that we get from here? The value of Δh^* and the value of Δs^* what are these values that we get from here? These particular values are this is, just substitute and find out B minus T , $\frac{dB}{dT}$ into P and Δs^* this is equals to minus $P \frac{dB}{dT}$, right?

So therefore and here also you can express B in terms of B^0 and ωB^1 , you can also express B in terms of $\frac{RT_c}{P_c} B^0$ plus $\omega \frac{RT_c}{P_c} B^1$ and you can use the 2 and the 3 parameter law what this class it is just sufficient to know that Δh^* and Δs^* they can be defined in this particular way. Now therefore these are the ways by which you can find out the properties using the PvT Behavior of gases or the cubic equations you can use the compressibility factor chart you can use the virial equation of state these were the ways by which you can do it using the PvT Behaviors.

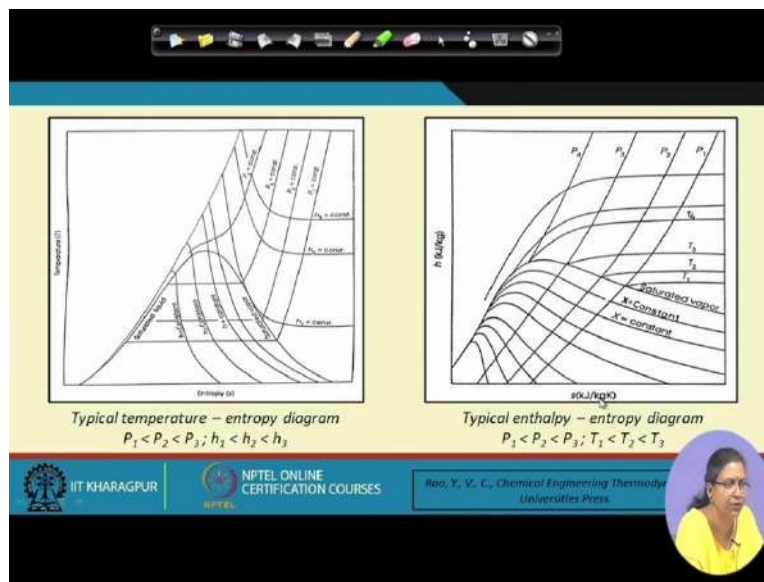
Apart from the generalized equations of state or the generalized compressibility factor charts we also have some particular figures some particular tables in order to find out or predict the thermodynamic properties one such common table is the steam table which you are already aware of. There are certain other charts also available for finding out the properties particularly enthalpy and entropy instead of going through the details calculations that we have said.

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A few of these are the pressure enthalpy diagram which is shown here, these Particular diagram is shown for nitrogen and here if you observe we will find that the entropy curves are given the pressure and enthalpy I have given and we also have the specific volume data and the temperature data. So therefore it contains large number of data and we have been in a position to find out the enthalpy and entropy we can have such particular charts for other gases as well.

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Well, there are also the common the typical temperature entropy diagram and also the enthalpy entropy diagram which is very easy and regarding this enthalpy entropy diagram this is known as the mollier chart this is very convenient because from here we can find out enthalpy we can find out entropy and since it contains constant pressure lines, constant temperature lines as well as constant quality lines in the 2 phase region. So therefore this gives us a large amount of information and this is a very popular chart which is used for predicting the properties of gases. So with this we end the estimation of the properties of pure component gases or mixture of gases where the mixture behaves as a pure component, right?

After this we are going to study the properties of mixtures and we are also going to extend our discussions to homogeneous open systems and heterogeneous closed systems. So with this we close our discussion on homogeneous closed systems we have discussed the estimation of properties and the concept of thermodynamic potential and the concept of chemical potential we are going to use this further in our discussion on phase equilibrium thermodynamics, thank you very much.