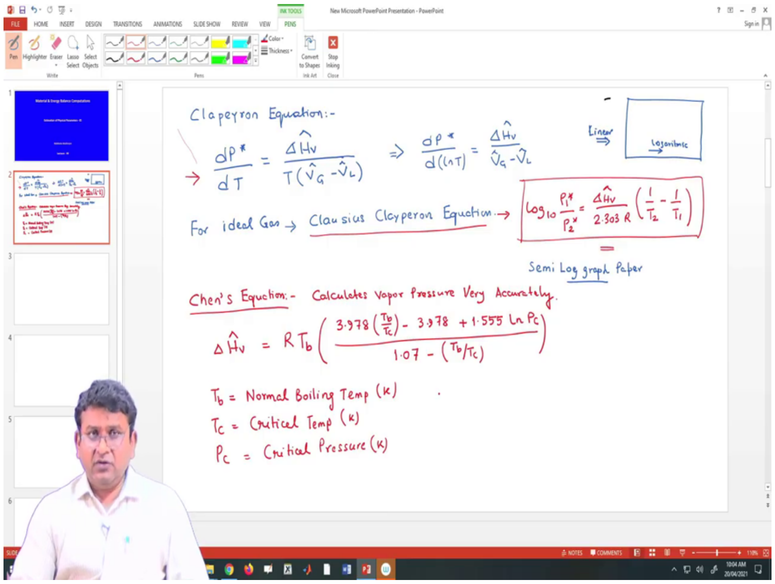
Material and Energy Balance Computations
Prof. Rabibrata Mukherjee
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Lecture –49
Estimation of Physical Parameters - IV

So, welcome back to our 49th lecture of material and energy balance computations. So, last 4 classes we had pretty exhaustive discussion on some tutorial problems and particularly I have taught you how to handle the steam table. I hope all of you have practiced problems which have been given in the assignments and some text book problems may be taken from the book I have prescribed. We were before taking up the tutorials we were essentially discussing another very very important aspect and which is the estimation of physical parameters.

(Refer Slide Time: 00:55)



Clapeyron Equation:-

$$\rightarrow \frac{dP^*}{dT} = \frac{\Delta \hat{H}_v}{T(\hat{V}_G - \hat{V}_L)} \Rightarrow \frac{dP^*}{d(\ln T)} = \frac{\Delta \hat{H}_v}{\hat{V}_G - \hat{V}_L}$$

For ideal Gas → Clausius Clayperon Equation →

$$\boxed{\log_{10} \frac{P_1^*}{P_2^*} = \frac{\Delta \hat{H}_v}{2.303\, R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

Semi Log graph Paper

Chen's Equation:- Calculates Vapor Pressure Very Accurately.

$$\Delta \hat{H}_v = R T_b \left(\frac{3.978 \left(\frac{T_b}{T_c}\right) - 3.978 + 1.555 \ln P_c}{1.07 - (T_b/T_c)} \right)$$

T_b = Normal Boiling Temp (K)
T_c = Critical Temp (K)
P_c = Critical Pressure (K)

And the last topic that we discussed is essentially how to find out the latent heat of vapourization and which we are good that you have a thermodynamic equation in the form of Clapeyron equation and which is of this particular form which we discussed. And then for an ideal gas you can simplify it to Clausius Clapeyron equation, and you get exact thermodynamic relation of ΔH_V as a function of vapour pressure at two different temperatures. So, if just two temperatures and the corresponding vapour pressures are given then of course you can estimate.

We have also discussed what exactly is vapour pressure but there can be several questions that

that can come. So, number one is in order to effectively use the Clausius Clapeyron equation you need to have the vapour pressure data. So, we will discuss today how this vapour pressure data can be available or in which form it can be available because see as I have told you that physical estimation of physical parameters itself is an important thing.

So, you can again you are back to the same point that you can use this equation very effectively provided your vapour pressure data is available. So, we are going to talk about that another situation that you need to understand is there can be a situation where at let us say five different temperature the five vapour pressure values are given. So, how do you do that I mean you certainly all of you know that the best way to do is essentially plot the data and get a best fit out of it.

But if you look at the nature of the functionality you essentially have a log linear dependence what I mean by log linear dependence? Here what are the two variables? Vapour pressure and temperature are the two variables. And if you look at the equation what you find that temperature or (1/T) is variable which is in the linear form, but pressure is in the logarithmic form. So, of course one approach can be to draw a graph, you can essentially still plot 1/T versus log P and then convert it into a linear plot and find out the slope from which you can find out the ΔH_V data but that is something that is not normally done and what is specifically done in cases like this is to use a special type of a graph paper called the semi log graph paper.

So, one typically uses the semi log graph paper for this type of calculations which can be done very effectively. As the name suggests what happens is in a semi log plot you essentially have one axis is logarithmic and the other axis is linear. So, what I will do not in today's class but in the next lecture I will actually take up a problem and demonstrate how to use the semi log plot. Because this is again from my own teaching experience for from a for a long time, I have figured out that many students fumble to use the log-log plot and the semi-log plot effectively.

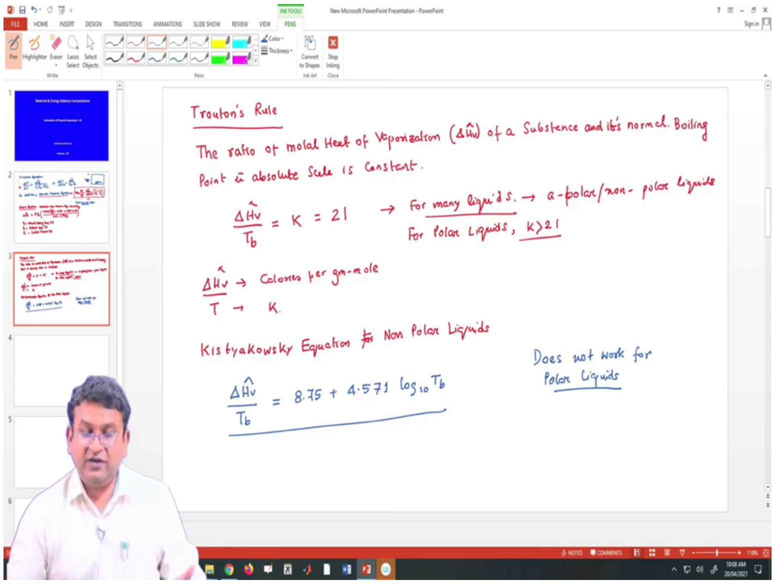
So, this is actually a good opportunity for you to learn handling how the semi log plot is can be used and Clausius Clapeyron equation is sort of a very good example for using or problems associated with Clausius Clapeyron equations are very good examples where one can use the semi log plot. So, that I will take up in the next class but let us go ahead with some more discussion on the latent heat of vapourization.

How one can find out this latent heat of vapourization. There are certain other empirical relations which can also be used for finding out. So, one of them is the chains equation these are stuff that I am going to teach nothing exotic, but it is important that you know about the existence of such relations very accurately. So, here is the relation you can refer to any textbook and you will get the relation these are empirical relations. So, please do not ask from where these constants have come people did lot of equation a lot of experiments did some fit this and that and obtained this, but these are very useful equations where T b is the normal boiling point in Kelvin.

T_c is the critical point I hope all of you remember about critical point we discussed about critical point in the context of phase diagram. And so, this is actually the critical not exactly critical point I would say this is the critical temperature this is also normal boiling temperature sorry about the mesh and P_c is the critical pressure. So, it is important that you know that some relation like this exists.

I will not say that for the examination that you have to write after the you have taken this particular course you do not really need to remember these constants or values it is more important that you know you have done a course on this on the calculations and you have done something on the estimation of physical parameters and you know something called change equation exists.

(Refer Slide Time: 07:42)



Trouton's Rule

The ratio of molal Heat of Vaporization ($\Delta\hat{H}_v$) of a Substance and it's normal. Boiling Point in absolute Scale is Constant.

$$\frac{\Delta\hat{H}_v}{T_b} = K = 21$$ → For many liquids. → a-polar/non-polar liquids

For Polar Liquids, $K > 21$

$\Delta\hat{H}_v$ → Calories per gm-mole

T → K.

Kistyakowsky Equation for Non Polar Liquids

$$\frac{\Delta\hat{H}_v}{T_b} = 8.75 + 4.571 \log_{10} T_b$$

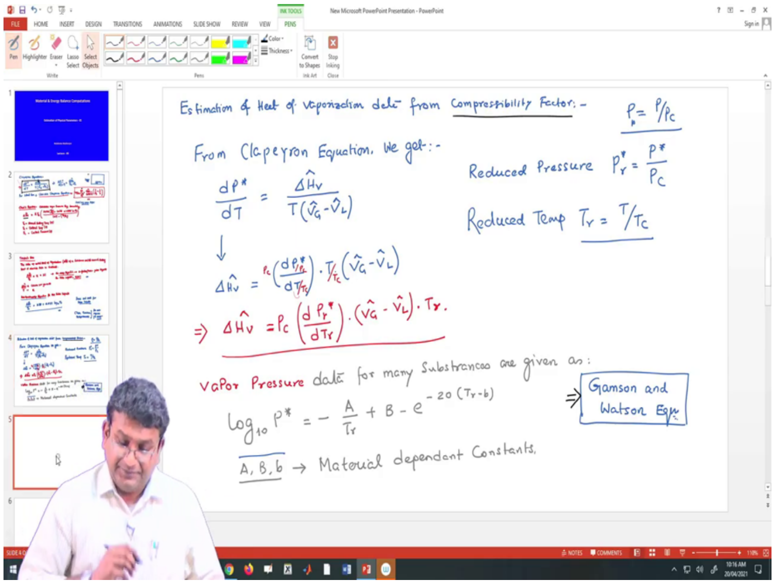
Does not work for Polar Liquids

The next one is what is known as the Trouton's rule and this suggests the ratio of molal heat of vapourization at its normal boiling point not at and its normal boiling point in absolute temperature or in absolute scale is constant and for many liquids this constant. So, this is essentially what it says its normal boiling point. So, it is at one atmospheric pressure and for many liquids the value is 21 of course this works well for apolar or nonpolar liquids and for polar liquids the ratio k is much greater than 21.

You need to remember that ΔH_V in this particular case must be expressed in calories per gram mole and T in Kelvin. So, this is what is Trouton rule. There is another equation which is called the Kistyakawsky equation for non polar liquids again as you can see it is valid for non polar liquids which gives ΔH_V to T_b not equal to 21 but it sort of improves on the constant predicted from Trouton's rule and therefore it is much more accurate T b this is what is known as the Kistyakawsky equation for non polar liquids.

This does not work for polar liquids. So, these are easy stuff of course this equation, look jumbo but these are much easier compared to what we have discussed. So, far you just know the normal boiling point and you can sort of estimate the delta h v.

(Refer Slide Time: 11:21)



Estimation of Heat of vaporization data from Compressibility Factor:-

$P_r = P/P_c$

From Clapeyron Equation, we get:-

$$\frac{dP^*}{dT} = \frac{\Delta \hat{H}_v}{T(\hat{V}_G - \hat{V}_L)}$$

↓

$$\Delta \hat{H}_v = P_c\left(\frac{d\, P^*/P_c}{d\, T/T_c}\right)\cdot \frac{T}{T_c}\left(\hat{V}_G - \hat{V}_L\right)$$

$$\Rightarrow \underline{\Delta \hat{H}_v = P_c\left(\frac{dP_r^*}{dT_r}\right)\cdot\left(\hat{V}_G - \hat{V}_L\right)\cdot T_r.}$$

Reduced Pressure $P_r^* = \frac{P^*}{P_c}$

Reduced Temp $T_r = T/T_c$

vapor Pressure data for many substances are given as:

$$\log_{10} P^* = -\frac{A}{T_r} + B - e^{-20(T_r - b)}$$

$\Rightarrow$ $\boxed{\text{Gamson and Watson Eqn}}$

A, B, b → Material dependent Constants.

We are if we come back to Clapeyron equation we can actually estimate from compressibility factor that is also something you can do this is a very interesting approach but quite effective I must say. So, from Clapeyron equation now we introduce here the concept of reduced variables or reduced pressure I do not know how many of you know we talk about reduced pressure and reduced temperature.

So, reduced pressure P_r is defined as or reduced vapour pressure which is equal to P^*/P_c under normal circumstances. Here we are talking about vapour pressure therefore we have put P_r^* but reduced pressure normally goes as P/P_c. So, any pressure if you divide it by the critical pressure this is what is known as the reduced pressure and similarly reduced temperature is T/T_c this is what is reduced temperature. So, what you can do is you can convert clapper on equation in terms of the reduced variables.

So, what we get is $dP^*/dT = \Delta H_V/[T(V_G$ cap - V_L cap)]. So, kindly refer to lecture number 44 if you would like to have a detailed idea about Clapeyron equation if you are unable to recollect everything, we discussed therefore I am not going into the details. And this if you essentially what you do is you would like to convert it into reduced variables. So, what turns out is ΔH_V cap=P_c (dP_r^*/dT_r) (V_G cap - V_L cap) T_r.

So, this is essentially the Clapeyron equation in terms of reduced variables. Now in many cases the vapour pressure given as

$\text{Log}_{10}P^* = -(A/T_r) + B - e^{-20(Tr-b)}$ where a and b are material dependent constants and this equation is known as the 'Gamson and Watson equation'. This is a very common form that your vapour pressure is given in terms of the reduced temperature and of course there are certain material dependent constant.

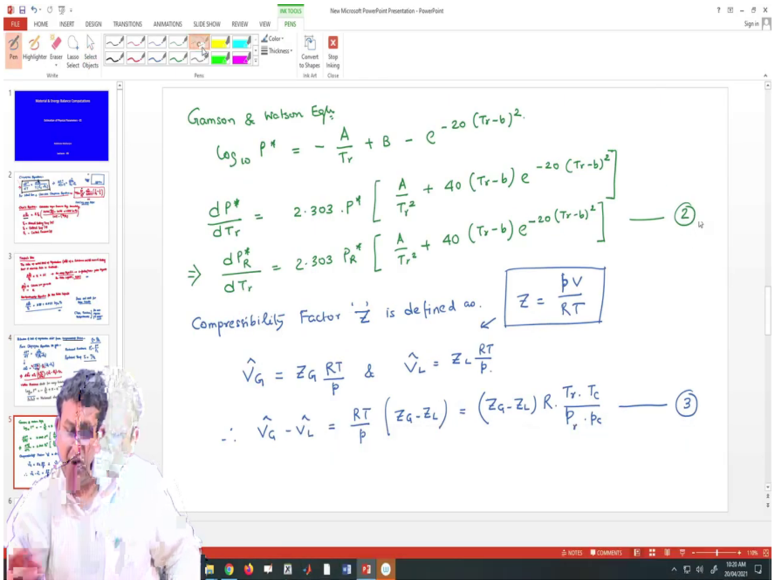
So, this is again we are essentially heading back at now obtaining relations based on which you can find out the vapour pressure. So, there are essentially you can see two approaches let me just quickly revise. So, that you all remember and understand what is going on. One is essentially the thermodynamically valid relation that we talked about is that we have the Clapeyron equation and which for an ideal gas gate gets converted you can have the Clausius Clapeyron equation.

From which you can most accurately measure because this is a thermo dynamic equation you can measure the latent heat of vapourization but for that you need the vapour pressure data as a function of temperature. The other approaches that we quickly talked about is essentially Chain rule and then the Trouton rule and Krityakowsiky equation which are empirical but quite effective because what is the advantage in all these you do not really need the vapour pressure data please do understand this.

So, here the boiling point critical temperature these are enough. So, all of this what we talked about this Chain rule, Trouton Kistyakowski do not require the vapour pressure data. So, this is the advantage but then as you can see these are, they do not work well for polar liquids. So, therefore we essentially have to use the Clapeyron equation or some analog of that in some form of the other. So, what we are now talking is how the compressibility factor can be effectively used.

So, towards that we now understand that there is something called the Gamson and Watson equation which gives vapour pressure as a function of reduced temperature and this is the functional form. So, here essentially you have differentiating logs.

(Refer Slide Time: 19:41)



Gamson & Watson Eqn:

$$\log_{10} P^* = -\frac{A}{T_r} + B - e^{-20(T_r-b)^2}.$$

$$\frac{dP^*}{dT_r} = 2.303 . P^* \left[\frac{A}{T_r^2} + 40(T_r-b)e^{-20(T_r-b)^2} \right]$$

$$\Rightarrow \frac{dP_R^*}{dT_r} = 2.303\, P_R^* \left[\frac{A}{T_r^2} + 40(T_r-b)e^{-20(T_r-b)^2} \right] \text{ --- ②}$$

Compressibility Factor 'Z' is defined as. $\boxed{Z = \frac{pV}{RT}}$

$$\hat{V}_G = Z_G \frac{RT}{p} \quad \& \quad \hat{V}_L = Z_L \frac{RT}{p}.$$

$$\therefore \hat{V}_G - \hat{V}_L = \frac{RT}{p}(Z_G - Z_L) = (Z_G - Z_L) R . \frac{T_r . T_c}{P_r . P_c} \text{ --- ③}$$

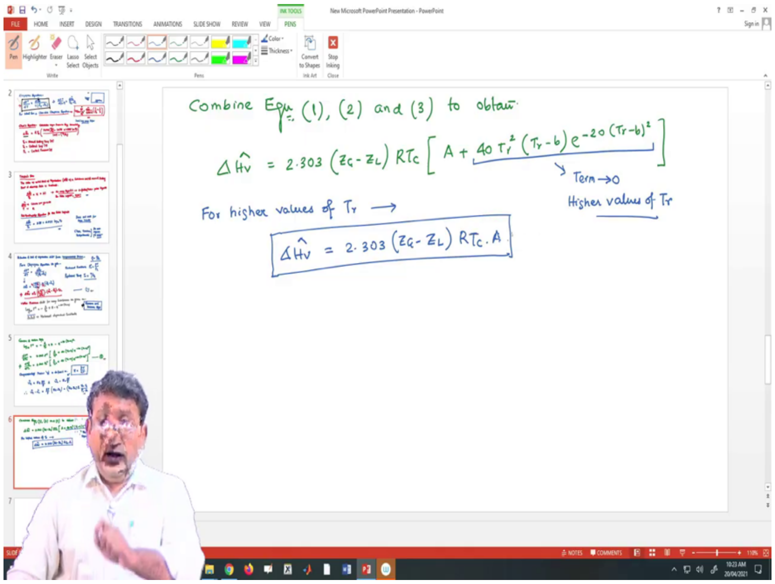
So, it is 1/P will come into P star into within bracket A divided by T r square plus forty into T r - b e to the power -20 T r - b whole square you are all welcome to check the differential.

So, what we do we divided both the sides by critical pressure. So, this gets read converted to dP star of the reduced vapour pressure 2.303 P r star into A divided by T r square + 40 into T r - b e to the power -20 T r - b whole square. So, let us mark this equation as equation 2 this equation as equation 1 and we also know that compressibility factor z is defined as z equal to PV by RT for ideal gas of course it is 1.

So, z equal to PV by RT. So, this is what is compressibility factor and what we have is therefore V G one can get as Z G RT by P and V L. So, from here essentially for liquid and gas V L one can get as Z L RT by P and therefore V G cap - V L cap turns out to be RT by P into Z G - Z L is equal to this now if we would like to take in the form of reduced variables. So, what we get is T r into T c or I can do it if you want or let us leave it you can you can do it I am sure P r into P c let us write the small r as we have been writing.

So, let us term this as equation 3. So, these are the three important equations that are necessary at this point of time this is equation 1, equation 2 and equation 3.

(Refer Slide Time: 24:09)



Combine Eqn. (1), (2) and (3) to obtain:

$$\Delta \hat{H_V} = 2.303\,(Z_G - Z_L)\,RT_c\left[A + \underbrace{40\,T_r^2\,(T_r - b)\,e^{-20\,(T_r - b)^2}}\right]$$

→ Term → 0
Higher values of Tr

For higher values of T_r →

$$\boxed{\Delta \hat{H_V} = 2.303\,(Z_G - Z_L)\,RT_c \cdot A}$$

And if we combine equation 1, 2 and 3 to obtain ΔH_V cap = 2.303 (Z_G - Z_L) RT_cA. now by combining equation 1, 2 and 3,

ΔH_V cap = 2.303 (Z_G - Z_L) RT_c [$A + 40\ T_r^* (T_r - b)\ e^{-20\ (Tr-b)2}$

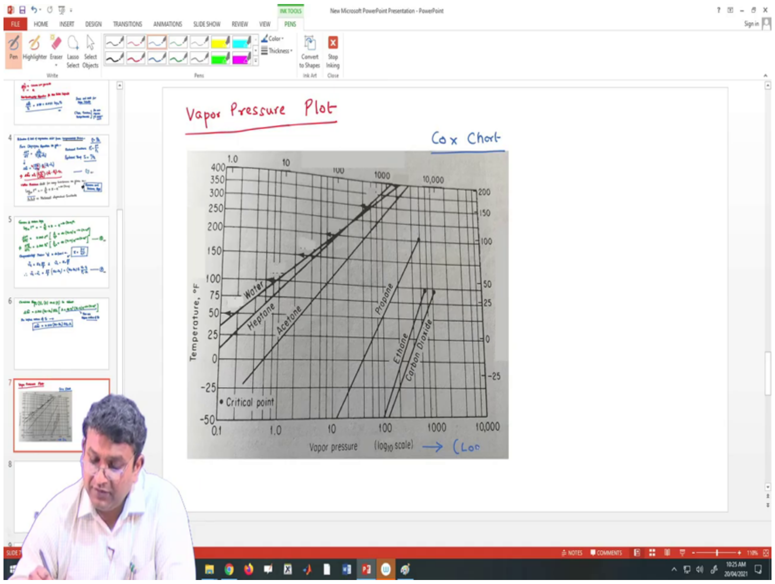
So, you can do this, this is something that I want all of you to do and get this and if you have problem in obtaining this expression please tell me during the online interactive session I will clarify how to get it.

But this is something you should do and for higher values of T_r essentially what happens is since we have e to the power -20 into T r - b to the power whole square, this term will tend to 0. Therefore, the equation significantly simplifies to ΔH_V cap = 2.303 (Z_G - Z_L)RT_c A

So, what is this equation you can again circumvent the vapour pressure.

And once you have the compressibility factors Z_G and Z_L given at a particular temperature and the critical temperature is known and of course the material dependent property a is known you can estimate ΔH_V.

(Refer Slide Time: 26:45)


Vapor Pressure Plot

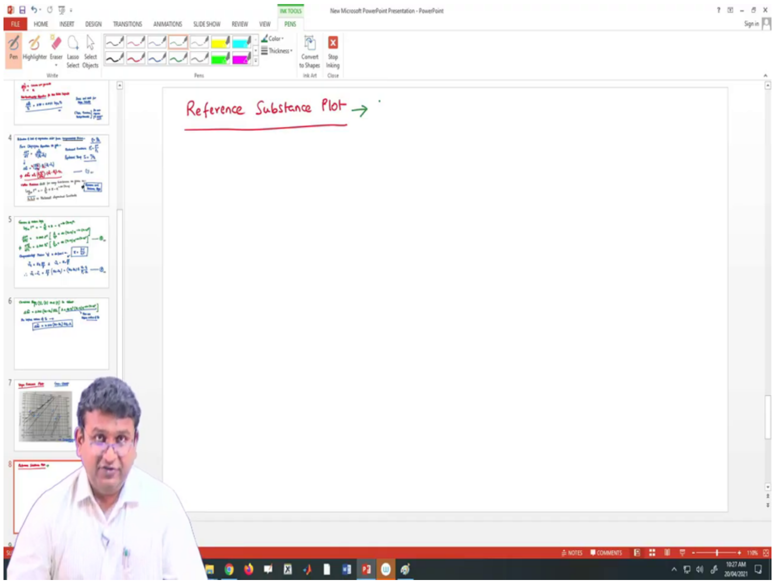
Cox Chart

So, these are some of the interesting approaches you have I am not saying that we need to use all of them at all point of time but these are some interesting approaches now coming back to estimation of vapour pressure vapour pressure is two important a parameter and you cannot really ignore it. So, what you often have is the vapour pressure plot and just give me a second please. So, this vapour pressure plot something like this you essentially have again as I was mentioning as I will take up in the next class you will all learn how to construct it.

So, this is how a vapour pressure plot looks like this is often referred to as the 'Cox chart'. So, it is a very simple plot. So, you have vapour pressure in the x axis but please note the axis is logarithmic and correspondingly for different material. For example, here you have different materials you get a straight line because from the Clausius equation you know that the dependence between the vapour pressure and temperature is logarithmic. So, the relation between (1/T) and ln(vapour pressure) is linear.

So, you get straight line. So, this is how a Cox chart looks like and often you might be I mean if you have access to Cox chart then at different temperature you can find out the vapour pressure. And once you know for example once for a particular material once you have Cox chart available then you can easily estimate because at two different temperatures you can calculate the vapour pressure from the Cox chart and you can very easily estimate the latent heat of vapourization.

(Refer Slide Time: 28:52)



Reference Substance Plot →

The other interesting concept that we are running out of time today, so in the next class what we will do is we will talk about this other interesting con concept which is called the reference substance plot. So, this is a very interesting concept in the sense that estimation. So, for example for generating Cox chart you actually need to do lot of experiment. So, as a function of temperature you need to keep on measuring the vapour pressure to get the points and then eventually join them up to get the slopes.

So, even that is difficult at times to perform. So, many experiments. So, there is a very, very nice way of circumventing this problem by using what is known as the reference substance plot. So, I will not start the topic today. So, in the next class what we will do we will talk first about the reference substance plot followed by we will pick up one small or short problem which will allow you to have an understanding of how to use the semi log plot. So, this for the next class, thank you very much.