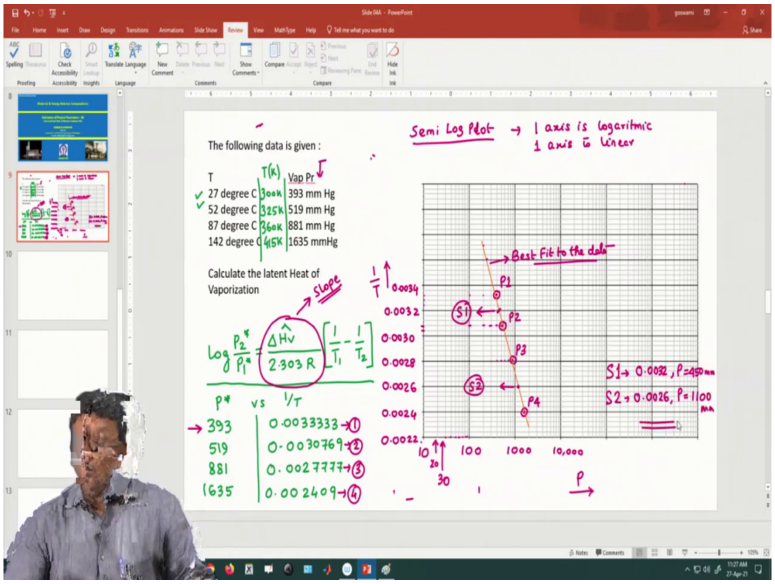
Material and Energy Balance Computations
Prof. Rabibrata Mukherjee
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Lecture –50
Estimation of Physical Parameters - V

So, welcome back today we are essentially approaching the last lecture of tenth week and it is also going to be the last lecture on estimation of physical parameters and in the previous class we talked about Clausius Clapeyron equation. And then how we can calculate the latent heat of vapourization from the reduced values of temperature and pressure and associated equations and then we also talked about the vapour pressure charts or the C ox charts.

And in while teaching Cox chart I highlighted that essentially you see that there is a semi log graph paper. So, what I am going to do today is I am going to first show you how to use the semi log graph paper which is actually a direct consequence you can say of the Clausius Clapeyron equation. So, if there are certain data's you can use that. And next if time permits, I am also going to teach you a very interesting concept which is known as the reference substance plot the turing plots. So, let us see how we can go about it.

(Refer Slide Time: 01:18)



The following data is given :

T	T(K)	Vap Pr
✓ 27 degree C	300K	393 mm Hg
✓ 52 degree C	325K	519 mm Hg
87 degree C	360K	881 mm Hg
142 degree C	415K	1635 mmHg

Calculate the latent Heat of Vaporization

$$\log\frac{P_2^*}{P_1^*} = \boxed{\frac{\Delta\hat{H}_v}{2.303\,R}}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] \xrightarrow{} \text{Slope}$$

P^* vs	$1/T$
→ 393	0.0033333 → ①
519	0.0030769 → ②
881	0.0027777 → ③
1635	0.002409 → ④

Semi Log Plot → 1 axis is logaritmic
1 axis is linear

S1 → 0.0032, P=450 mm
S2 → 0.0026, P=1100 mm

Suppose you have this following data set given that say at 4 different temperatures the vapour pressure of a liquid is given. So, temperature is given in degree centigrade and essentially, we know that we have the Clausius Clapeyron equation which has this functional form which is known to all of us. So, the; first thing to note that we need the absolute temperature values.

So, which are easy to actually make so, this corresponds to so, we can convert this is 300K this is 325K this is 360K and this is 415K. So essentially you now have this data T in Kelvin and correspondingly. So, you can generate a revised data set the data set that you actually need is P* versus (1/T), so, which you can calculate. So, it is the P values are already given and if you just take a calculator and calculate these values, they turn out to be 0.003333.

Please do not truncate very early because then you will have some numerical error or truncation error 0.003730769 this one turns out to be 0.0027777 and this one turns out to be 0.002409. So, we have this data set. So, essentially had you had just two points then what you would have done? You would have simply gone to this equation plugged in the values of 519 by 393 is equal to {(1 /300) – (1/325)} you have to have done that and have calculated.

But now once you have multiple data. So, you cannot just say that I will pick up two points out of those because I just like them. So, you have to take all of them, and we essentially know what we need to do. We actually have to plot a graph and take the best fit data. Now of course if you look at the functionality it is of the form of log P is equal to 1/T. So, 1/T is linear, but the other variable pressure is in logarithmic form.

So, one approach can be you painfully calculate the logarithm big values of log ten values of all these numbers and generate a fresh data log P versus 1 by T but there is something interesting and that is the semi log plots are already available. So, what exactly is a semi log plot? So, semi log plot is one of the axes, is logarithmic and one axis is linear. So, you can see that this is logarithmic, and this is linear and be very careful to start using the semi log plot.

Because it must start from this end and not this and many people you turn it and make a mistake because 1 and 2 the gap is going to be high. So, how to choose that this is one and this is no T 1. So, this is one and this goes to ten then it goes to 100 it goes like that. So, the accessor like T 1 ten 100 or 0.1, 1, 10 it will be like that. So here for the pressure values vary between let us say 393 to 1635.

So, we can start very easily from 100 or maybe just for your understanding I will start from ten. So, this is 100 this is thousand this is going to be 10000 and it goes like this. So, this point is 10 this point is 20 in case some of you do not know I will elaborate it. So, this is going to be 20 this is going to be 30, 40, 50, 60 and so on and this here it will be its logarithmic axis. So, it is actually P you just write P over here and here you take 1 by T along this axis and let us create a little bit of space for us.

So, it goes like this. So, it is 10, 20, 30 and please remember if you have one of the axes logarithmic you can never have an origin which starts from 0,0 it is not possible to pinpoint because log of 0 is undefined. So, you cannot have a value of log 0. So, you cannot you can have very low numbers, but you can never have an axis that starts from 0 and what about T? So, we see that it varies from 0.0024 to 0.0033.

So, we can maybe start from 0.002 to 0.0024, 0.0026, 28, 0030, 00324 and so on. So, this is the numbering system here 1 by T is linear there is no problem along the y axis along the x axis we have P and which is in a logarithmic axis. So, please remember this is 10 this is going to be 100 not 20 this is going to be 100 this is going to be 10000 this is going to be 10000 it goes like this. And then the next graduation is going to be 20.

In for this particular cycle and it goes all the way up to 30, 40, 50, 60, 70, 80, 90 and then 100 and the next one here is not 110 it is 200. So, this is the basic learning. So, now let us try to look at the points on the graph. So, what are the values we have we have 393 versus 0.003333. So, 0.0032 is over here. So, this is going to be 324, 328, 332. So, this is going to be very close to this particular line and there here the values are 393.

So, this point is 100 this is 200 this is 300 this is 400 so 393 will be somewhere over here. So, for your understanding let me mark the points as 1, 2, 3 and 4 which you can revisit at a later time. So, this is your point 1 this is not the way you there is no need for you to mark in the actual graph with 0.1 or whatever this is for your understanding I am doing it. The next point is 519 and 0.003076. So, this is 0.0030. So, this is going to be 0.304 this line 304, 308.

So, this is very close to 0.308 30769 and the value is 519. So, along this line we start over here this is 100, 200, 300, 400, 500. So, somewhere over here is our point 2, then the third point is 881 and it is 0.002777 or 0.0028. So, here we have 0.0028 and 200, 300, 400, 500, 600, 700, 800 its almost 900, 881 this is a best you can see with your eyes probably doing a real graph paper with pen and pencil you will have better resolution but on an online mode this is probably the best what you can do.

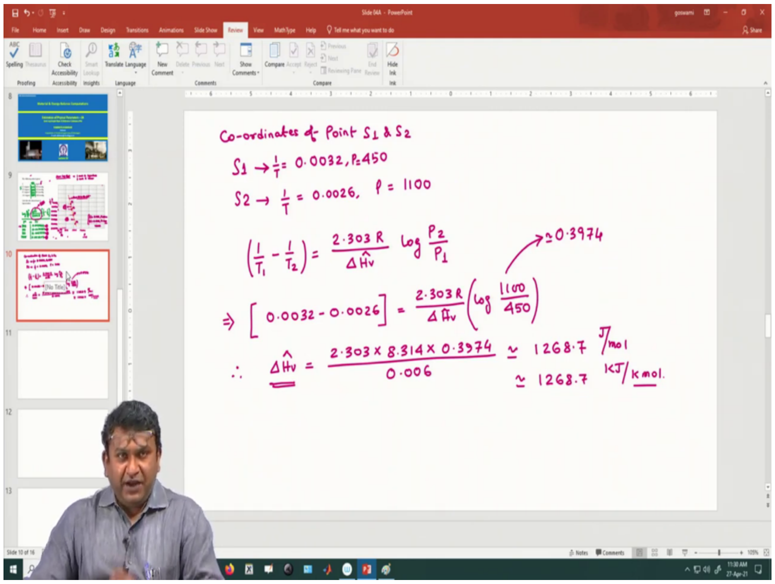
So, this is P 3 and then the4th one the value is 0.0024. So, it is almost on this line and the value is 1635. So, you cross 1000 but this is 2000. So, you have to do some sort of interpolation 1635 will be somewhere over here. So, it goes like this and then what you need to do is you need to draw a best fit line unfortunately I do not have access to a pen and a pencil. So, let me try to draw it digitally and if you draw it digitally you get a line like this the best fit line.

This is something that is you are not going to run a regression analysis or anything for this you will be simply using this line with even with your scale you will be drawing this line. So, this is the best fit to the data you have already obtained the best fit to the data which is all fine. So, here is the best fit to the data ok and let me see. So, again some problem with the pin colour is not changing it is just showing the height ok anyway we will manage with this. So, this is the best fit to the data. So, now from here what do you do?

So, you have found out the best fit and in order to calculate the delta H V what we realize that we need to calculate the slope. So, let us first find out the slope of this line. So, how do you find out the slope of this line? For finding out the slope of the line we identify 2 points. Let us say this is one point. So, we mark it as S1 and let us say this is the second point where it intersects 0.0026. So, this turns out to be S2 and from these values what you actually do you find out the coordinates of S1.

So, S 1 turns out to be 0.0032 and the pressure is 100, 200, 300, 400 maybe 450millimeter mercury and point S2 this thing is 0.0026 and the pressure we find is maybe something of the order of 1100 or something like that or may yeah. So, I hope this is clear to all of you. So, we essentially dig out 2 points. So, these are 2 important points. So, let me write down on the next page.

(Refer Slide Time: 13:04)



Co-ordinates of Point S_1 & S_2

$S1 \rightarrow \frac{1}{T} = 0.0032, P = 450$

$S2 \rightarrow \frac{1}{T} = 0.0026, \quad P = 1100$

$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \frac{2.303 R}{\Delta \hat{H}_v} \log \frac{P_2}{P_1}$$

$$\Rightarrow \left[0.0032 - 0.0026\right] = \frac{2.303 R}{\Delta \hat{H}_v}\left(\log \frac{1100}{450}\right) \quad \simeq 0.3974$$

$$\therefore \underline{\Delta \hat{H}_v} = \frac{2.303 \times 8.314 \times 0.3974}{0.006} \simeq 1268.7 \ J/mol$$

$$\simeq 1268.7 \ KJ/\underline{Kmol}.$$

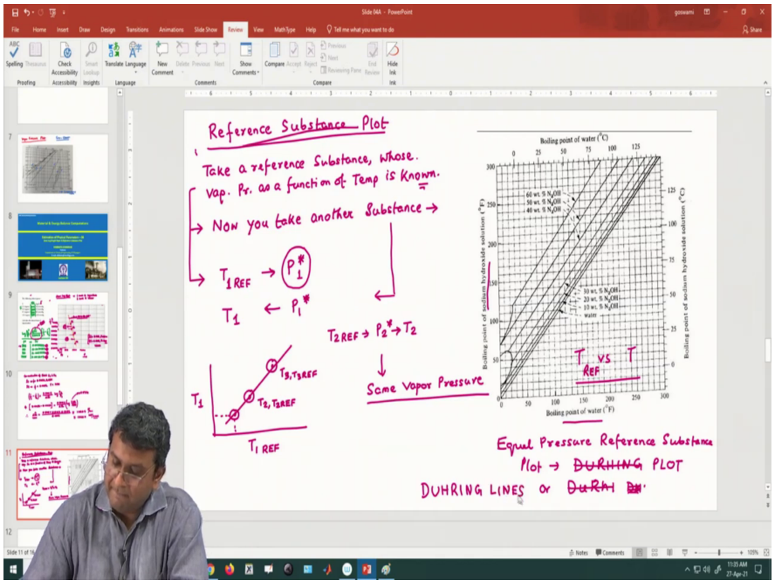
So, coordinates of point S 1 and S 2 these are important points and many people I find that unfortunately they do not or cannot calculate the slope of the base fit. So, P is equal to 450. So, 1 by T is equal to this and P is equal to 450. Similarly, S2 we have 1/T = 0.0026 and P equal to this 1100. So, now what we have now what we have is essentially we now understand that the equation has a functional form because see here T is in the y axis.

So, we typically calculate the slope as y equal to mx + c. So, what we you find here is that we can write the equation as (1/T1 – 1/T2) is equal to 2.303 R divided by ΔH_V into log of P2/P1. So, this turns out to be 0.0032 - 0.0026 equal to 2.303 R divided by H_V into log of 1100 divided by 450 which is very close to 2.5 and if you calculate this value turns out to be something like 0.3974 or something approximately equal to you can just check it.

So, from here you straight away get the value of H_V equal to 2.303 calculate the plug in the value of R in joule per kilo mole per Kelvin and into divided into 0.3974 divided by 0.006 and which turns out to be 1268.7 joule per mole or kilo joule per kilo mole. So, this is how you can calculate the latent heat of vapourization from the vapour pressure data that is provided and if there are multiple data.

You use a semi log graph paper and I have tried to teach you how to draw this semi log graph papers. So, this is one of the things that I wanted to teach you the next important thing very interesting thing of course is what is known as the reference substance plot.

(Refer Slide Time: 16:31)



Reference Substance Plot

Take a reference Substance, whose. Vap. Pr. as a function of Temp is Known.

→ Now you take another Substance →

→ $T_{1\,REF} \rightarrow \boxed{P_1^*}$

$T_1 \leftarrow P_1^*$

$T_{2\,REF} \rightarrow P_2^* \rightarrow T_2$

↓

Same Vapor Pressure

T_{REF} vs T

Equal Pressure Reference Substance Plot → ~~DURHING~~ PLOT

DUHRING LINES or ~~DURAH~~ ~~DH~~

So, this is actually related to the Cox chart we had discussed in the previous class see for drawing this type of a Cox chart you actually need lot of data for vapour pressure as a function of temperature and which might be difficult in many cases to generate. So, one very interesting approach is to find out or take a reference substance whose vapour pressure as a function of temperature is known right. So, let us say it is for example water.

So, whose vapour pressure as a function of temperature is known now you take another substance whose you are measuring the vapour pressure. Now let us say at a given for this reference substance I am unfortunately unable to use a inks of multiple color for this particular class due to some technical problem. So, let us say for T1 reference the vapour pressure is P star 1 this is for the reference substance.

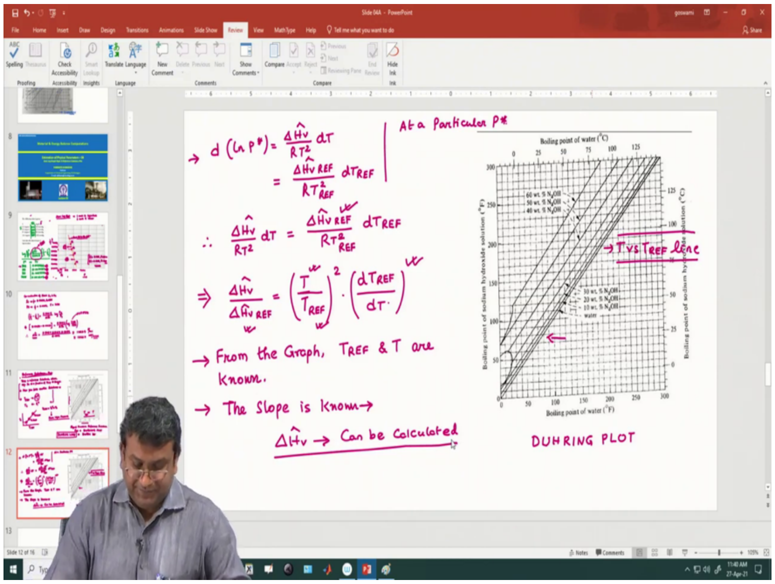
Now the second substance for example shows the same vapour pressure P1* at a temperature another temperature T 1. So, I repeat the T 1 reference at T 1 reference the vapour pressure of the reference substance is P 1 star and the second substance or the substance which you are trying to draw this plot for has the same vapour pressure at a temperature T 1. So, what you eventually do is you actually plot a graph between T 1 and T 1 reference.

So, you now have a value of T 1 reference versus T 1 is known. So, you plot this similarly let us say there is another data set let us say T 2 reference for which the vapour pressure is P 2 star and for which the temperature is T 2. So, you get another point which one is T 2 and T 2 reference a third point let us say T 3 and P 3 reference and now you join this plot. So, essentially you have a T reference versus T plot the one is the reference substance one is the other substance something like this for example this is for sodium hydroxide.

These are different concentrations you see here is the boiling point of water forget about whether it is at Fahrenheit or it does not really matter and here you have the boiling point of the solution. So, all you have is a T versus T plot or rather to be more precise is T reference versus T plot. Now this is this type of lines are called essentially. So, how do you get this T versus T point you get this point for the same vapour pressure I hope this concept is clear to all of you the vapour pressures are same.

So, this is called this type of a graph is called the equal pressure reference substance plot or which is also called ‘Duhring plot’. So, agreeing to existence of such a plot you now see how beautifully this can be used.

(Refer Slide Time: 21:42)



$$\rightarrow d(\ln P^*) = \frac{\Delta\hat{H}_v}{RT^2}\,dT$$

$$= \frac{\Delta\hat{H}_{v\,REF}}{RT_{REF}^2}\,dT_{REF}$$

At a Particular P*

$$\therefore \frac{\Delta\hat{H}_v}{RT^2}\,dT = \frac{\Delta\hat{H}_{v\,REF}}{RT_{REF}^2}\,dT_{REF}$$

$$\Rightarrow \frac{\Delta\hat{H}_v}{\Delta\hat{H}_{v\,REF}} = \left(\frac{T}{T_{REF}}\right)^2 \cdot \left(\frac{dT_{REF}}{dT}\right)$$

→ From the Graph, TREF & T are known.

→ The Slope is known →

$\Delta\hat{H}_v \rightarrow$ Can be Calculated

DUHRING PLOT

So, we now have a during plot let me now write it down. So, what we have we have from the Clausius Clapeyron equation in the differential form we have del n P star is equal to delta H V by RT square into dT and this is for the one substance and since the P star is same. So, at a particular P star or this is at a particular P star we also have this is equal to delta h v ref divided by RT ref square dT ref check if it is clear to all of you we have from the Clausius Clapeyron differential form of the Clausius Clapeyron equation.

This equation to be valid you can integrate it also there is no problem. Now we have a vapour pressure let us say for one reference temperature we have a vapour pressure for the other material the vapour pressure is same. So, therefore dL n P star is equal to delta H V ref divided by T ref square into dT ref it is also equal to delta H V by RT square dT because both of them have the equal vapour pressure.

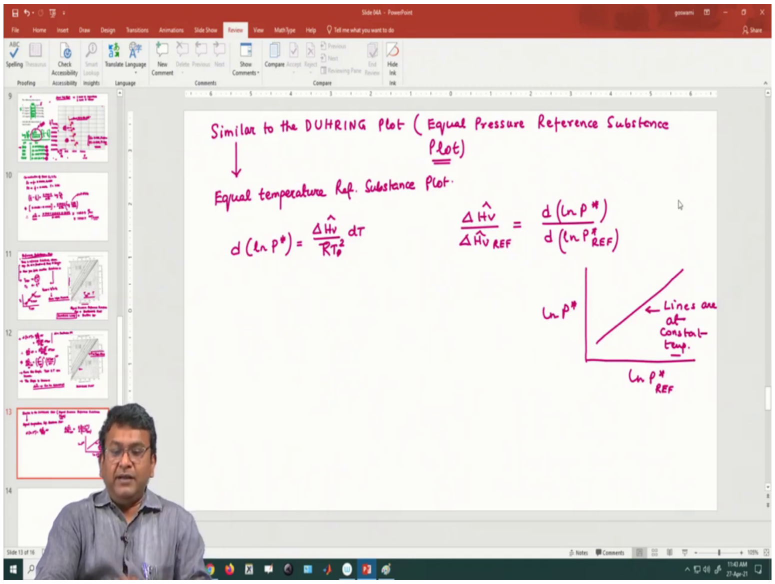
So, therefore what we get by comparing these 2 equations we actually get something very interesting do not get confused if you have any doubt I will clarify it during the online session. So, this is what you get why because both of them are exhibiting the same vapour pressure. So, take a minute to convince yourself what we are talking about we are essentially talking about a system where the vapour the reference substance at a particular temperature exhibits a vapour pressure and the other substance whose latent heat of vapourization you would like to find out also exhibits the same vapour pressure at that point.

And therefore you can equate these 2 and once you equate these 2 now please do understand this one is known what we have is delta H V by delta H V ref is equal to R, R gets cancelled its T by T ref whole square into dT ref by dT now you see from the graph from the graph T ref and T are known the slope what is dT ref by dT? dT ref by dT is nothing but the slope of each of these lines because this lines is now a T versus T ref line.

So, these lines are now T versus T ref line and dT by dT ref by dT is nothing but the slope and in the previous problem I have shown you how to calculate the slope. So, the slope you can find out. So, this comes out from the graph this is known this is known and this is known slope is known and therefore you can calculate delta H V cap can be calculated. So, this is the way you can use the reference substance plot also to generate the latent heat of vapourization.

Of course, for generating the latent heat of vapourization the reference substance plot you have to do some experiments but then with limited number of experiments you can actually use the reference substance plot for calculating latent heat of vapourization. So, now we are seeing that there are quite large number of ways for calculating the latent heat of vapourization.

(Refer Slide Time: 26:46)



Similar to the DUHRING Plot (Equal Pressure Reference Substance Plot)

$\downarrow$

Equal temperature Ref. Substance Plot.

$$d(\ln P^*) = \frac{\Delta \hat{H}_v}{RT_b^2}\,dT$$

$$\frac{\Delta \hat{H}_v}{\Delta \hat{H}_{v\,REF}} = \frac{d(\ln P^*)}{d(\ln P^*_{REF})}$$

Similarly, one can also have similar to the during plot which are equal pressure reference substance plot these are equal pressure reference substance plot similarly one can also have equal temperature reference you can also have equal temperature reference substance plot and. So, essentially what comes out from there what comes out from there is you can just write it r T square d T. So, what we have that temperatures are now equal. So, dT divided by RT RT square R equal R is anyway equal.

So, what we get very easily is delta H V cap divided by delta H V ref is equal to dL n P divided by your dL n P star divided by dL n P reference star. So, again you need to essentially have a plot of L n P star the reference versus L n P star which is for the P star I am using for the vapour pressure nothing else many books it will it will be written as L n P only that which is perfectly fine. So, you have some lines which are at constant temperatures with the lines are at constant temperatures and therefore from that.

So here also this slope of this line will be known and from there you can find it out. So, this of course as you can understand this particular approach this constant equal temperature reference substance plots have this issue of this logarithmic pressure values. So, a more popular option is essentially to use the duhring plots which are the equal pressure reference substance plot because here the T versus T variation is in a linear scale.

So, with that we sort of come to the end of this module as well as today's lecture hope you have now understood and there will be some problems in the assignment which are related to reference substance plot. And in case there are certain questions ah. So, these look very simple but there are certain nitty gritty issues and therefore I would like or request all of you to read the topics or understand the topics very, very carefully.

So, that you develop a thorough understanding and in the process of how to estimate the value of latent heat of vapourization from multiple data using Clausius Clapeyron equation I tried to teach all of you how to use the semi log plot, thank you very much.