Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
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Lecture No 46
Tutorial

Hello everybody, so today before I proceed further I would like to go for a recap of whatever we have done for solutions both ideal and nonideal we will try to solve a few problems and then we will go for some other new topics.

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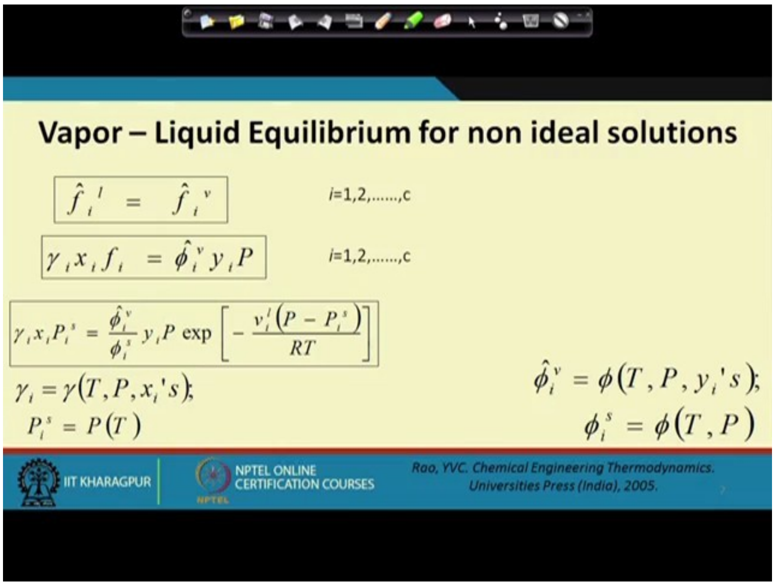

Vapor – Liquid Equilibrium for non ideal solutions

$$\boxed{\hat{f}_i^{\,l} = \hat{f}_i^{\,v}} \qquad i=1,2,\ldots\ldots,c$$

$$\boxed{\gamma_i x_i f_i = \hat{\phi}_i^{\,v} y_i P} \qquad i=1,2,\ldots\ldots,c$$

$$\boxed{\gamma_i x_i P_i^s = \frac{\hat{\phi}_i^{\,v}}{\phi_i^s} y_i P \exp\left[-\frac{v_i^l\left(P-P_i^s\right)}{RT}\right]}$$

$$\gamma_i = \gamma\left(T,P,x_i's\right); \qquad \hat{\phi}_i^{\,v} = \phi\left(T,P,y_i's\right);$$

$$P_i^s = P\left(T\right) \qquad \phi_i^s = \phi\left(T,P\right)$$

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Rao, YVC. Chemical Engineering Thermodynamics. Universities Press (India), 2005.

Now as a recap let us see what are the equations or rather what are things that we have already studied?

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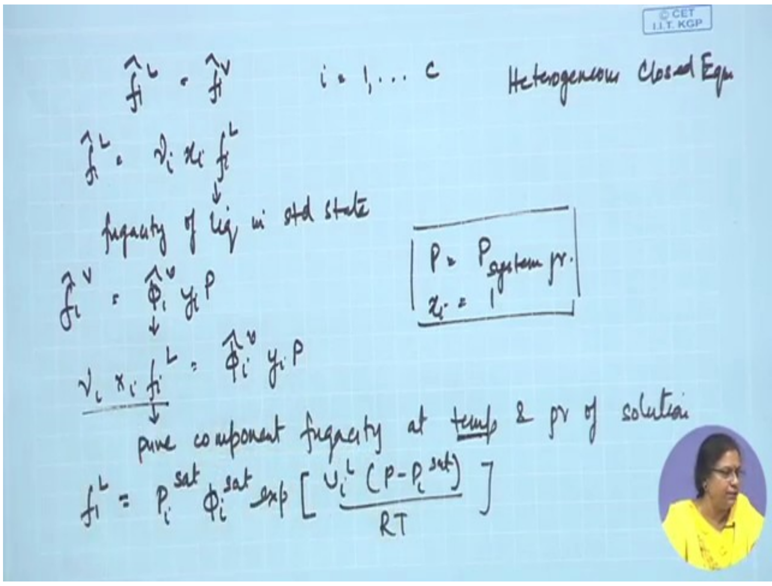

$\hat{f}_i^L = \hat{f}_i^V$ i = 1, ... C Heterogeneous Closed Eqm

$\hat{f}_i^L = \gamma_i x_i f_i^L$

fugacity of liq in std state

$\hat{f}_i^V = \hat{\phi}_i^V y_i P$

$\boxed{\begin{array}{l} P = P_{\text{system pr.}} \\ x_i = 1 \end{array}}$

$\gamma_i x_i f_i^L = \hat{\phi}_i^V y_i P$

pure component fugacity at temp & pr of solution

$f_i^L = P_i^{sat} \phi_i^{sat} \exp\left[\frac{v_i^L (P-P_i^{sat})}{RT}\right]$

The first thing is for phase equilibrium the basic equation is the fugacity's of any component i is same in the vapor phase and the liquid phase, okay. So this is applicable for any component i where i can be component 1 to component C. So for the time being we are considering a heterogeneous closed system, okay. If you recall when we were when I had first started considering equilibrium initially we had considered homogeneous closed systems, then we had considered your homogeneous open systems and then we had considered heterogeneous closed system where each heterogeneous closed systems comprises of 2 homogeneous open systems.

In this case also there are 2 homogeneous open systems one is the liquid phase the other is the vapor phase each phase comprising of C number of components the component number is denoted by i. For each particular component we have one such equation. So therefore we have C number of such equations. Now what is fiL equals to? If you recall this is equal to gamma i Xi into Fi. What is this fi? This is the fugacity fiL Fugacity of liquid in standard state.

What is fiV equals to? This is equal to phi i v the partial rather the partial fugacity of component i in the vapor phase into yiP. So therefore this is basically the correction for non-ideality in the vapor phase and this is the correction for non-ideality in the liquid phase. Now if we equate these two, what do we get? On equating these 2 we get gamma i Xi fiL equals to phi i v yi into P, agreed? Where we know gamma i as you know its activity coefficient Xi is a mole fraction of component i in the liquid state yi is a mole fraction of component i in the vapor phase P is the total pressure and fiL as I have already mentioned its fugacity of liquid in the standard state.

Now we can select any particular standard state but for most of this of the situations just for convenience what do we select? We select pure component liquid at the system pressure and at the system temperature. Now from thermodynamics the only requirement is maintenance of the same temperature of the solution and the pure state. We could have selected any other pressure or any other composition but since it is convenient we select the standard state P equals to P system pressure and xi equals to 1, so this is the pressure and composition under which we select a rather we define fiL.

So naturally what this becomes? This becomes the pure component fugacity at temperature and pressure of solution, this is by convention we take this and out of this is mandatory and this we could have taken something else and is important to remember that very frequently it can happen that this particular state it is fictitious because the component which we are selecting may not exist in the liquid state at the system temperature and pressure but it hardly matters whether it is real or fictitious.

And we have already found out how we can estimate pure component fugacities of both the vapor and the liquid. So therefore what is this equal to? If you remember this is the saturated vapor pressure of the component and this has to be corrected by 2 factors, one arises due to non-ideality in the vapor phase and the other arises due to completion of the liquid phase from the saturated pressure to the pressure of interest this particular factor it is known as the poynting correction factor. Its P is very close to Pi saturated then naturally this term it disappears off, fine.

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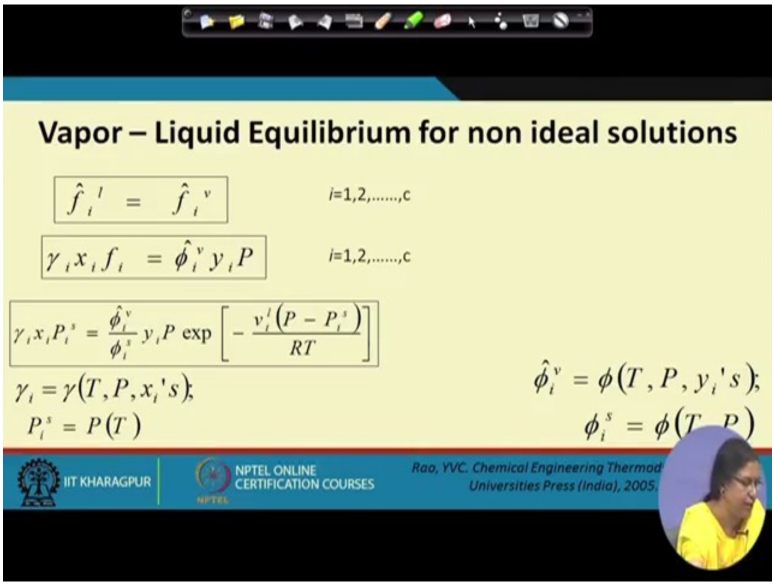

Vapor – Liquid Equilibrium for non ideal solutions

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$$\boxed{\gamma_i x_i f_i = \hat{\phi}_i^{\,v} y_i P}$$ i=1,2,.......,c

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$\gamma_i = \gamma(T,P,x_i's);$ $\hat{\phi}_i^{\,v} = \phi(T,P,y_i's);$

$P_i^s = P(T)$ $\phi_i^s = \phi(T,P)$

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Rao, YVC. Chemical Engineering Thermod
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So therefore now if we substitute this fiL in this particular equation and equate it with this, then finally what do we get? Finally we get an equation as has been mentioned, this is the equation that we are finally going to get, right?

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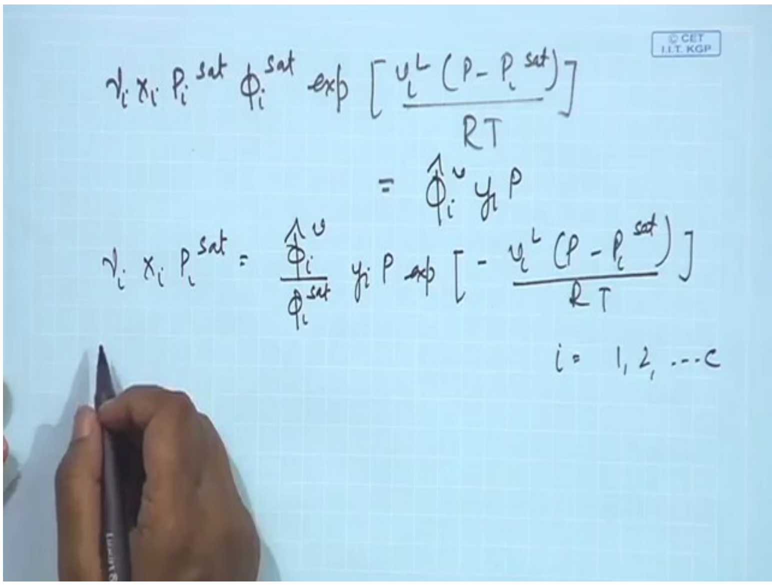

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$$\gamma_i x_i P_i^{sat} \phi_i^{sat} \exp\left[\frac{v_i^L(P-P_i^{sat})}{RT}\right] = \hat{\phi}_i^{\,v} y_i P$$

$$\gamma_i x_i P_i^{sat} = \frac{\hat{\phi}_i^{\,v}}{\phi_i^{sat}} y_i P \exp\left[-\frac{v_i^L(P-P_i^{sat})}{RT}\right]$$

$i = 1, 2, \ldots c$

So therefore if I just write down the equation for your convenience we find the equation is gamma i Xi Pi saturated phi i saturated exponential viL P minus Pi saturated by RT this is equal to Phi i v yi into P, right? Or in other words we can also write it down as gamma i Xi Pi saturated this is the fugacity coefficient of component i in the vapor mixture, fugacity component of component i under the set pure component i under the saturated conditions into yiP exponential minus viL P total pressure minus Pi saturated by RT, please remember this is applicable for each component i.

Well, this particular equation this is the thermodynamically most rigorous equation and this forms the basis for vapor liquid equilibrium and in this particular equation we find gamma i.

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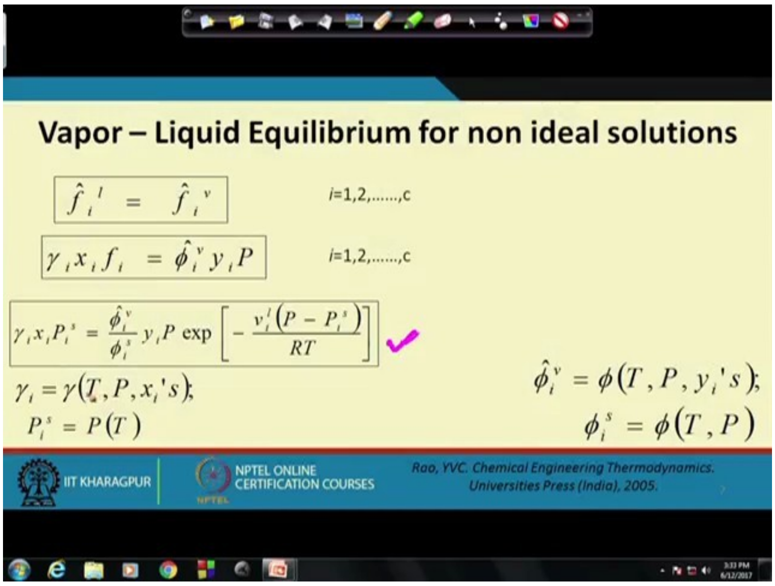

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$$\gamma_i = \gamma\left(T, P, x_i's\right); \qquad \hat{\phi}_i^{v} = \phi\left(T, P, y_i's\right);$$

$$P_i^{s} = P\left(T\right) \qquad \phi_i^{s} = \phi\left(T, P\right)$$

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What is gamma i? Gamma i is a function of temperature, pressure and mole fractions, we know phi i v is a function of temperature, pressure, mole fraction in the vapor phase, naturally the saturated fugacity coefficient is a function of temperature and pressure is a function of temperature because P saturated is a function of temperature and we know P just the same thing as been written down here. So therefore this is the basic equation using which we are going to solve different vapor liquid problems.

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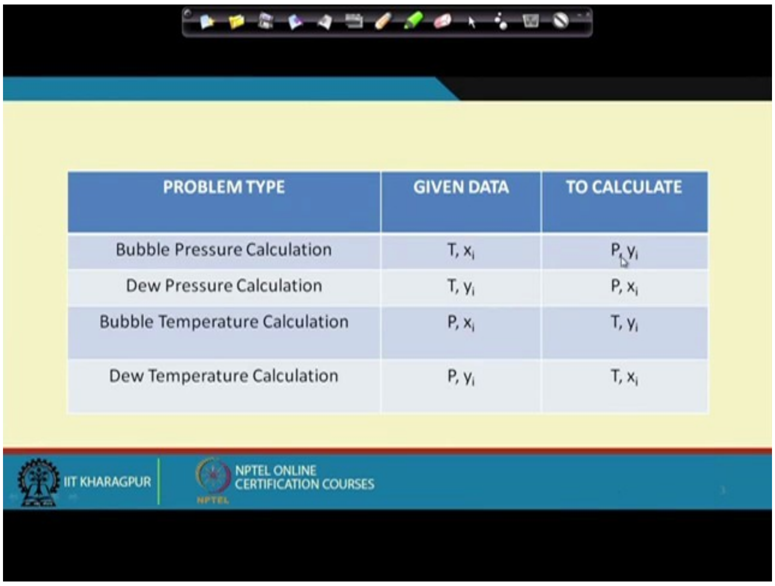

PROBLEM TYPE	GIVEN DATA	TO CALCULATE
Bubble Pressure Calculation	T, x_i	P, y_i
Dew Pressure Calculation	T, y_i	P, x_i
Bubble Temperature Calculation	P, x_i	T, y_i
Dew Temperature Calculation	P, y_i	T, x_i

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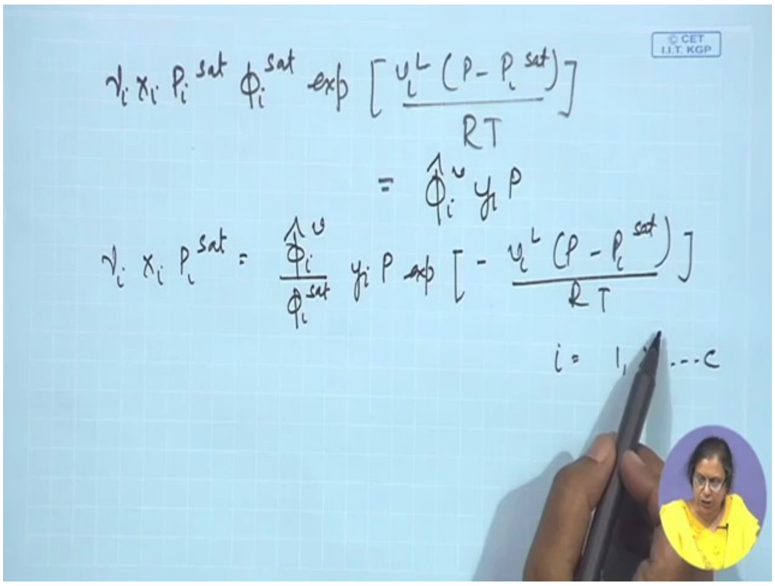

$$\gamma_i x_i P_i^{sat} \phi_i^{sat} \exp\left[\frac{v_i^L (P - P_i^{sat})}{RT}\right] = \hat{\phi}_i^v y_i P$$

$$\gamma_i x_i P_i^{sat} = \frac{\hat{\phi}_i^v}{\phi_i^{sat}} y_i P \exp\left[-\frac{v_i^L (P - P_i^{sat})}{RT}\right]$$

$$i = 1, 2, \ldots c$$

Now for the different vapor liquid problems, for we can encounter different sort of vapor liquid problems and the problems which we encounter we have already discussed day they can be bubble pressure calculation, dew pressure calculation, bubble temperature calculation, dew temperature calculation no matter whatever the problem be this is the basic equation which we are going to write.

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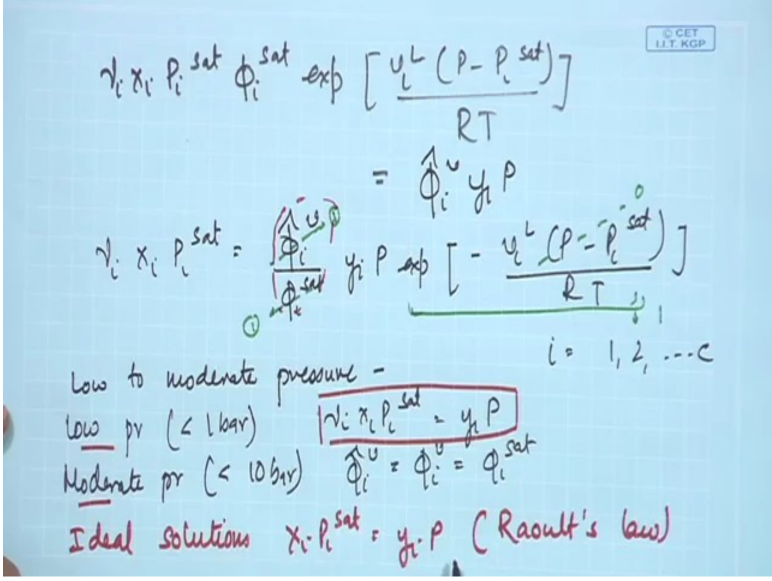

$$\gamma_i x_i P_i^{sat} \phi_i^{sat} \exp\left[\frac{v_i^L(P-P_i^{sat})}{RT}\right] = \hat{\phi}_i^v y_i P$$

$$\gamma_i x_i P_i^{sat} = \frac{\overset{1}{\hat{\phi}_i^v}}{\underset{1}{\phi_i^{sat}}} y_i P \underbrace{\exp\left[-\frac{v_i^L(\overset{0}{P-P_i^{sat}})}{RT}\right]}_{1}$$

$i = 1, 2, \ldots c$

Low to moderate pressure -

Low pr (< 1 bar) $\boxed{\gamma_i x_i P_i^{sat} = y_i P}$

Moderate pr (< 10 bar) $\hat{\phi}_i^v = \phi_i^v = \phi_i^{sat}$

Ideal solutions $x_i P_i^{sat} = y_i P$ (Raoult's law)

Now for most of the cases we find that we deal with low to moderate pressures, what happens at low to moderate pressure let us see? Does this equation reduce to something simple you already know what happens suppose we are dealing with low pressure, say less than 1 bar. What do, what's the first thing that you expect is going to happen?

First thing which is going to happen is that the vapor phase starts behaving ideally, when the vapor phase starts behaving ideally, naturally this becomes equal to one and this also becomes equal to one, when we are dealing with low pressure naturally P will be close to Pi saturated. So this becomes 0 as a result of which this whole term this becomes equal to one. So therefore what happens for low pressure?

Low pressure we find gamma i Xi Pi saturated you are already aware this is equals to yiP. For moderate pressures say less than 10bar suppose what happens under this condition? Definitely under this condition this does not disappear this does not disappear but although we cannot assume the vapor phase to behave as ideal gas we can always assume that the vapor mixture behaves as an ideal mixture or in other words it obeys the Amagat's law of additive volumes accordingly what do we have under this condition? Under this condition we can have phi i v is equal to phi i v which is equal to phi i saturated this we can safely assume.

So when we can safely assume this naturally what happens this whole term it becomes equal to one and again we find that for moderate pressure also P will not be very far removed from Pi saturated as a result of which this term also becomes 0 and exponential term becomes equal to one. So we find that for both low pressures and for low to moderate pressures this particular equation holds and when we are dealing with ideal solutions I need not repeat it once more it's very you know it very well that XiPi saturated becomes equals to yiP which is nothing but the famous Raoult's law with which we have been dealing for quite some time, right?

So therefore now depending upon the situation, it's a very complex or rather if you are dealing at high pressure we should be dealing with this equation. If you're dealing with low to moderate pressure we should be dealing with this equation. If you're dealing with ideal solution we should be dealing with this particular equation.

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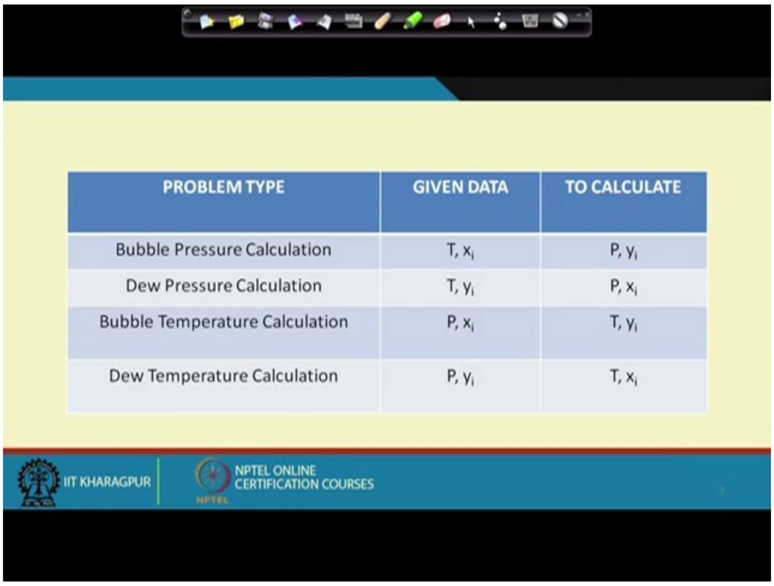

PROBLEM TYPE	GIVEN DATA	TO CALCULATE
Bubble Pressure Calculation	T, x_i	P, y_i
Dew Pressure Calculation	T, y_i	P, x_i
Bubble Temperature Calculation	P, x_i	T, y_i
Dew Temperature Calculation	P, y_i	T, x_i

No matter which condition we are dealing with does not matter the problem types are as I have mentioned they can be bubble pressure, dew pressure calculation, bubble temperature dew temperature calculations.

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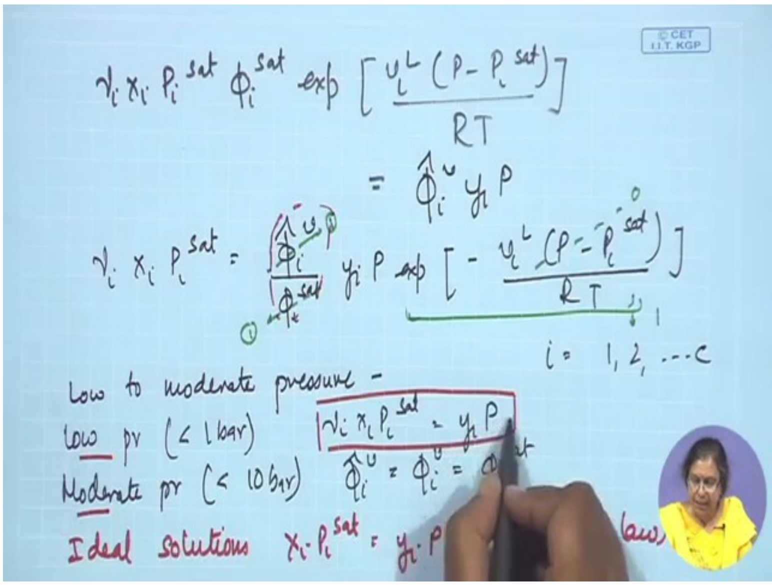

$$\gamma_i x_i P_i^{sat} \phi_i^{sat} \exp\left[\frac{v_i^L (P - P_i^{sat})}{RT}\right] = \hat{\phi}_i^v y_i P$$

$$\gamma_i x_i P_i^{sat} = \underbrace{\frac{\hat{\phi}_i^v}{\phi_i^{sat}}}_{①} y_i P \underbrace{\exp\left[-\frac{v_i^L (P - P_i^{sat})}{RT}\right]}_{1}$$

$i = 1, 2, \ldots c$

Low to moderate pressure -

Low pr (< 1 bar) $\boxed{\gamma_i x_i P_i^{sat} = y_i P}$

Moderate pr (< 10 bar) $\hat{\phi}_i^v = \phi_i^v = \phi_i^{sat}$

Ideal solutions $x_i P_i^{sat} = y_i P$ law)

Whatever be the situations we will be having i such equations or i such equations along with those i sorry not i’s C equations C number of this or C number of this equations.

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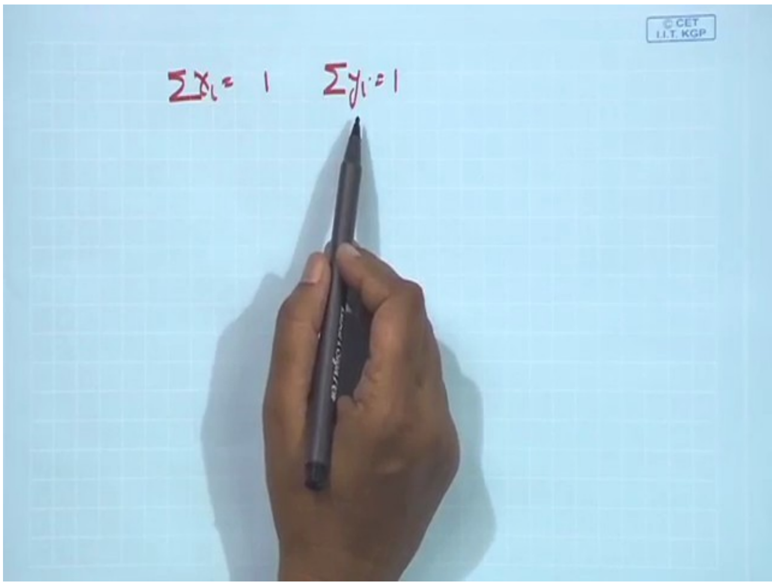

$$\sum x_i = 1 \quad \sum y_i = 1$$

Along with that we are going to have two additional constraints which also you are well aware Sigma xi equals to 1, Sigma yi equals to 1 or very often when we have to take up some trial and error cases then whether we have guess or guess values are correct or not we understand by these particular checks.

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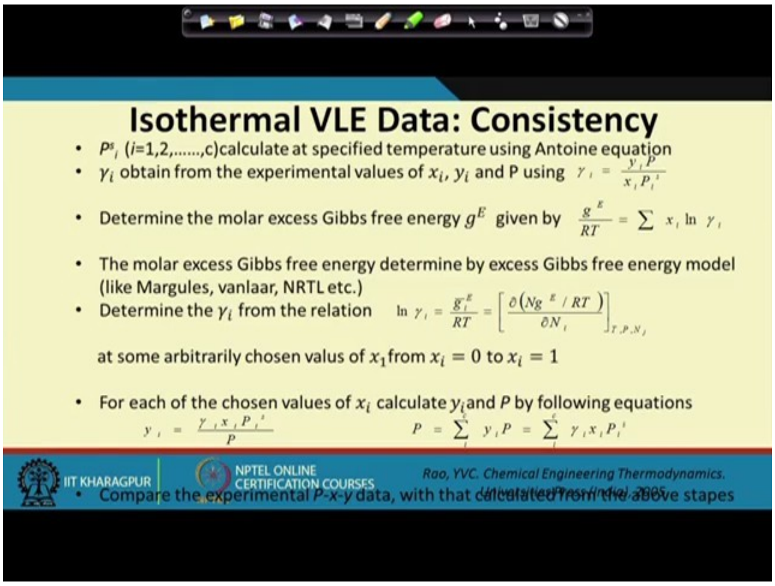

Isothermal VLE Data: Consistency

- P^s_i (i=1,2,……,c)calculate at specified temperature using Antoine equation
- γ_i obtain from the experimental values of x_i, y_i and P using $\gamma_i = \frac{y_i P}{x_i P_i^s}$
- Determine the molar excess Gibbs free energy g^E given by $\frac{g^E}{RT} = \sum x_i \ln \gamma_i$
- The molar excess Gibbs free energy determine by excess Gibbs free energy model (like Margules, vanlaar, NRTL etc.)
- Determine the γ_i from the relation $\ln \gamma_i = \frac{\bar{g}_i^E}{RT} = \left[\frac{\partial (Ng^E / RT)}{\partial N_i}\right]_{T,P,N_j}$

  at some arbitrarily chosen valus of x_1 from $x_i = 0$ to $x_i = 1$

- For each of the chosen values of x_i calculate y_i and P by following equations

  $y_i = \frac{\gamma_i x_i P_i^s}{P}$ $\qquad P = \sum_i^c y_i P = \sum_i^c \gamma_i x_i P_i^s$

- Compare the experimental P-x-y data, with that calculated from the above stapes

Now let us take up each problem maybe the first time let us take up isothermal data and let us see how we can find out or rather how we can calculate.

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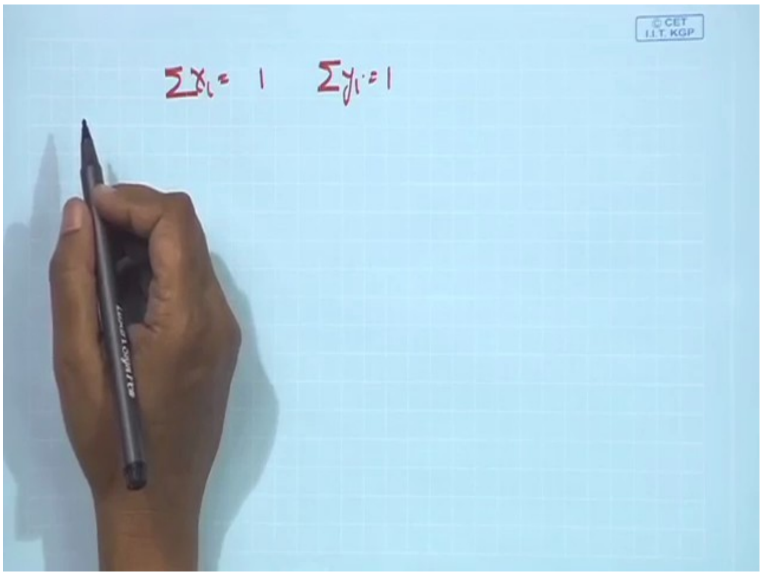

$\sum x_i = 1 \qquad \sum y_i = 1$

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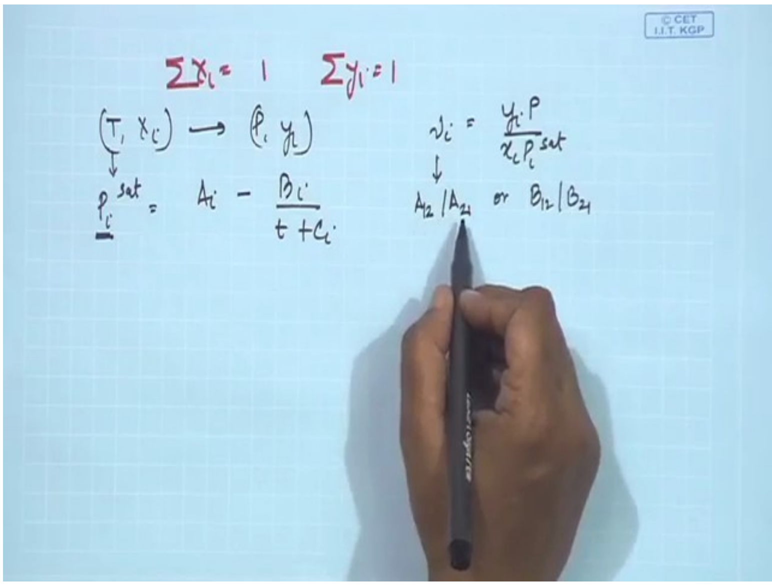

For suppose you’re the first type which I have told you say T and xi are given. Suppose the first type remember whatever be the type and if supposed to find P and yi, whatever be it we will be dealing with the or rather we will be dealing with the same type of equations just we will be rearranging them according to the condition.

For example suppose Y and Xi are given, what are we supposed to do? If T is given we can find out Pi saturated for each component i it will nothing be but equal to Ai minus Bi by t plus Ci, so therefore we can find out t. Sorry we can find out Pi saturated for each component. Once we can find out Pi saturated we know Xi and suppose we have some fragmentary data on yi and P then in that case with those at least if you have data even on one particular point also Pxy, yy data at constant T then we are in a position to find out gamma i.

What is gamma i? It is nothing but yi P by xiPi saturated for that component i. Moment we have found out gamma i, now we need to select the excess Gibbs free energy models. For this particular class although I have discussed the large number of models, for this particular class we will be confining our attention either to 2 suffix Margules equation or 3 suffix Margules equation or van laar equation. You need not memorize the equations the basic equations will be provided to you but derivations from the equations you are supposed to do it on your own.

So therefore once we know gamma i then for one particular value then from here we are in a position to find out. We are going to select either the van laar or the 3 suffix Margules equation accordingly we will be in a position to find out either A12 or A21 or B12 or B21 remember one thing that these are these are refer to the constants of the 3 suffix and the van laar equations of state. Once we know this we know that we have already assumed that they are independent of temperature and pressure so that we can use the same constants to find out gamma i for other Xi values. Accordingly we can generate the whole set of PXY data from the fragmentary set of data.

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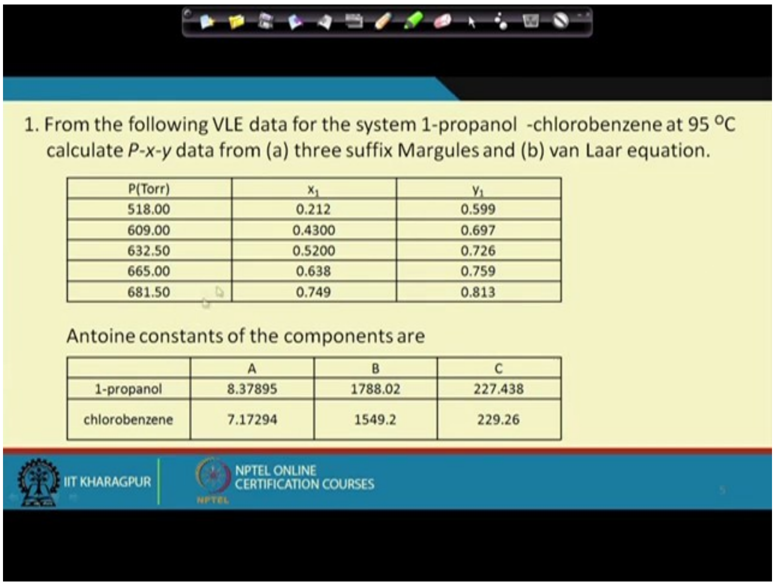

1. From the following VLE data for the system 1-propanol -chlorobenzene at 95 °C calculate *P*-*x*-*y* data from (a) three suffix Margules and (b) van Laar equation.

P(Torr)	x_1	y_1
518.00	0.212	0.599
609.00	0.4300	0.697
632.50	0.5200	0.726
665.00	0.638	0.759
681.50	0.749	0.813

Antoine constants of the components are

	A	B	C
1-propanol	8.37895	1788.02	227.438
chlorobenzene	7.17294	1549.2	229.26

Now let us take up a few examples just to verify just to ratify what I have been discussing so far. This is one of the problems which I have, in this problem what do we find? there is a propanol and chlorobenzene, temperature is given 95 degrees centigrade we are required to find out Pxy data from just as I have mentioned 3 suffix Margules and the van laar equation. What are the data which are given then in this particular case?

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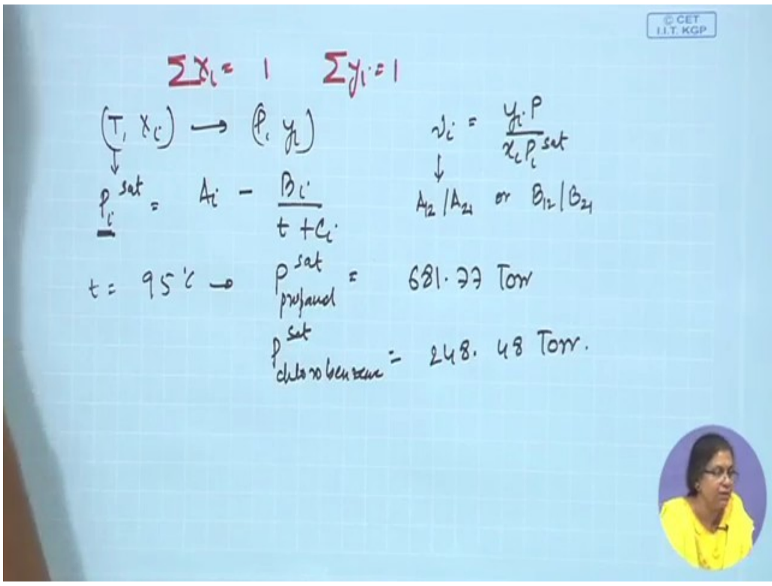

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$$\Sigma x_i = 1 \qquad \Sigma y_i = 1$$

$$(T, x_i) \longrightarrow (P, y_i) \qquad \gamma_i = \frac{y_i \cdot P}{x_i P_i^{sat}}$$

$$\downarrow \qquad\qquad\qquad \downarrow$$

$$P_i^{sat} = A_i - \frac{B_i}{t + C_i} \qquad A_{12}/A_{21} \text{ or } B_{12}/B_{21}$$

$$t = 95°C \rightarrow P^{sat}_{propanol} = 681.77 \text{ Torr}$$

$$P^{sat}_{chlorobenzene} = 248.48 \text{ Torr.}$$

T equals to 95 degrees centigrade we already know, right? And then once we know this it's a binary mixture, we are in a position to find out the saturated pressure of propanol the saturated pressure of chlorobenzene if you calculate this you will be finding that the saturated pressures are 681.77 Torr you can check it up just see that units etc are consistent otherwise there is no place where you can make a mistake, right?

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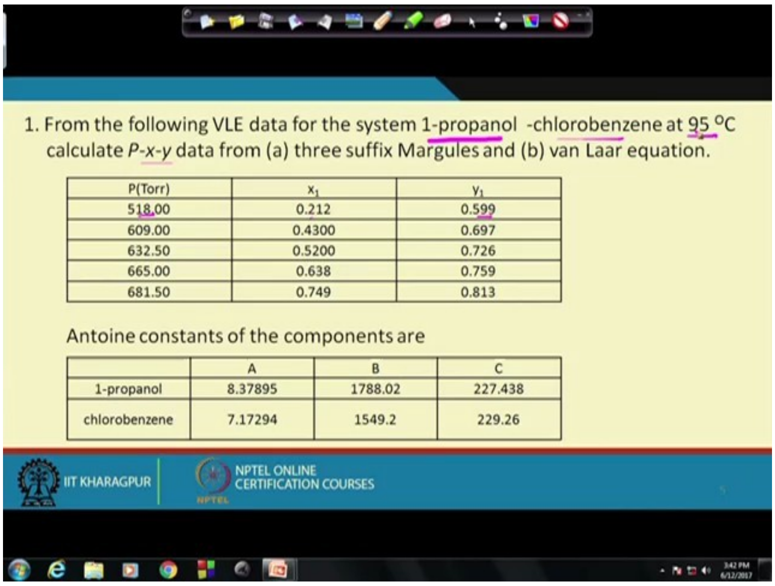

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So you have got this, once you have got this then for the first set of data you know x1, you know y1, you know P you know T.

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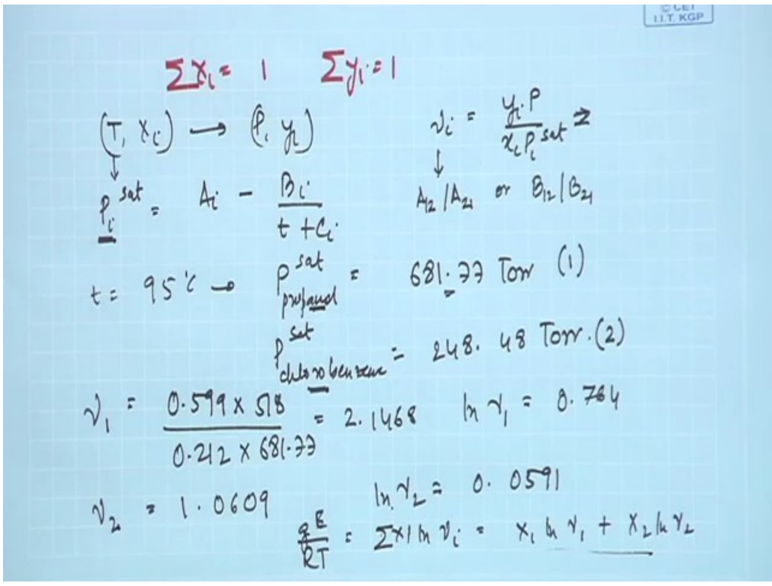

$\Sigma x_i = 1 \quad \Sigma y_i = 1$

$(T, x_i) \rightarrow (P, y_i)$

$\gamma_i = \frac{y_i P}{x_i P_i^{sat}}$

$\downarrow$

A_{12}/A_{21} or B_{12}/B_{21}

$P_i^{sat} = A_i - \frac{B_i}{t + C_i}$

$t = 95°C \rightarrow P^{sat}_{propanol} = 681.77$ Torr (1)

$P^{sat}_{chlorobenzene} = 248.48$ Torr. (2)

$\gamma_1 = \frac{0.599 \times 518}{0.212 \times 681.77} = 2.1468 \quad \ln \gamma_1 = 0.764$

$\gamma_2 = 1.0609 \quad \ln \gamma_2 = 0.0591$

$\frac{g^E}{RT} = \Sigma x_i \ln \gamma_i = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$

So therefore you are in a position to find out gamma1, right? Just the way using this particular equation here only I can, okay I will write it down here one thing I would like to mention that for my case I have assumed propanol to be component1 chlorobenzene to be component 2. Usually you will find lot of problems we just specify that use this as component 1 use this is component 2 if it is not specified we already know that we usually plot all the phase diagrams with the more sorry the more volatile phase as component 1 and the less volatile phase as component 2.

So therefore in this particular case we can since this is got a higher saturated vapor pressure we take this as component 1 we take this as component 2. So now we can find out gamma1 we know y1 is nothing but equals to 0.599 P we have already know it's 518 if you just observe this you can find and we know X1 is equals to0.212 and we know the saturated vapor pressure as this 681.77, right? So if you calculate you find this is 2.1468 and accordingly your ln gamma1 this become 0.764.

Same way we can we can calculate it for gamma2 just substitute the proper values you find gamma 2 is going to be 1.0609 and ln gamma2 is going to be 0.0591. Now you have you have got ln gamma1 and gamma 2 once you have got this then you can find out the excess Gibbs free energy of the mixture from experimental data, what is this? This is nothing but equals to Sigma Xi ln gamma i. For a binary mixture it is X1 ln gamma 1 plus X2 ln gamma2. So you're in a position to find because you know gamma 1 gamma 2 X1 X2 you can find this out. So with this your entire experimental data is more or less ready with which you are supposed to work, right?

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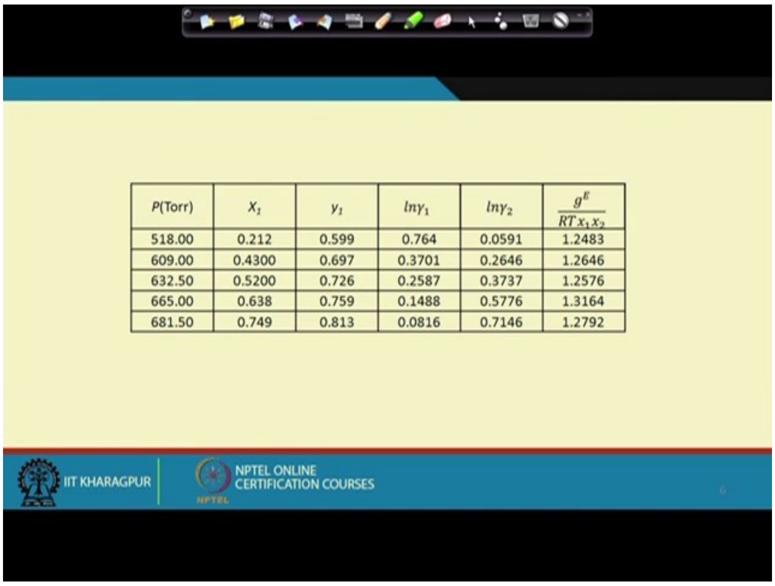

P(Torr)	X_1	y_1	$ln\gamma_1$	$ln\gamma_2$	$\frac{g^E}{RTx_1x_2}$
518.00	0.212	0.599	0.764	0.0591	1.2483
609.00	0.4300	0.697	0.3701	0.2646	1.2646
632.50	0.5200	0.726	0.2587	0.3737	1.2576
665.00	0.638	0.759	0.1488	0.5776	1.3164
681.50	0.749	0.813	0.0816	0.7146	1.2792

So once you have got this more or less your entire till gE by RT the entire thing is ready for you, agreed? Now once this part is ready, now here we have already mentioned that you are you are supposed to use the van laar equation as well as the 3 suffix Margules equation. So therefore from the experimental data we have already found out gamma1 X1 this part was applied. We were in a position to find out gamma 1 gamma 2 then ln gamma1 ln gamma 2 and then till gE by RT we could find out.

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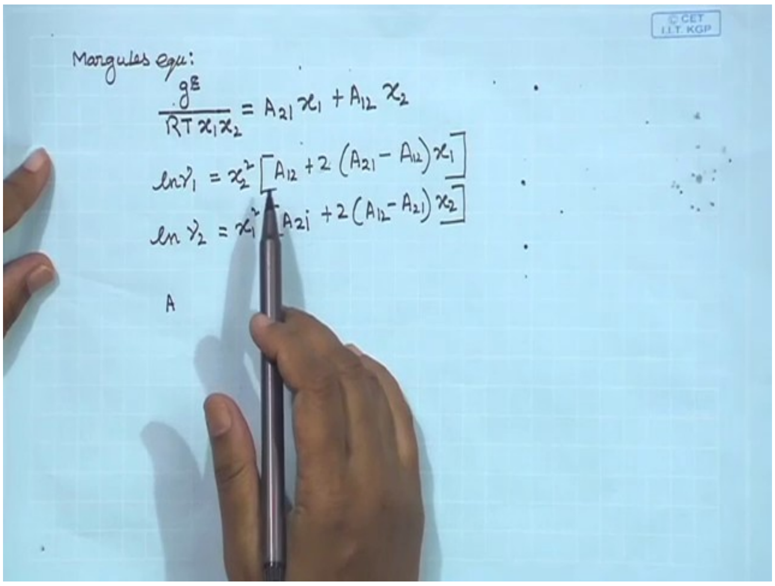

Margules eqn:

$$\frac{g^E}{RT x_1 x_2} = A_{21} x_1 + A_{12} x_2$$

$$\ln\gamma_1 = x_2^2 \left[A_{12} + 2(A_{21} - A_{12}) x_1\right]$$

$$\ln\gamma_2 = x_1^2 \left[A_{21} + 2(A_{12} - A_{21}) x_2\right]$$

A

Now suppose initially we take up the 3 suffix Margules equation, now all of us know the 3 suffix Margules equation is given by this particular formula. So from here what do we find out? We find out that for 3 suffix Margules equation if we plot this particular term gE by RT x1x2 is a function of x1 it should give you are linear plot and from the linear plot from the intercept at x1 equals to 0 what do we get? A12 and then x1 equals to 1 what do we get? A21.

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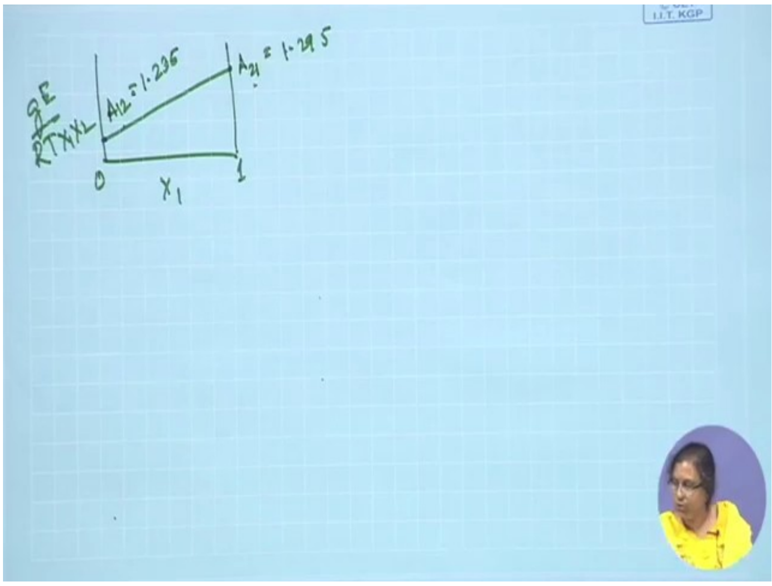

So therefore once we have found out gE by RT we know x1 we know x2 we are in a position to find this out. Once we are in a position to find this out, so therefore we can always plot gE by RT X1X2 as a function of X1 this will go till 0 to 1, right? And then from the intercepts you can find out that at X1 equals to 0 your A12 in this case it is going to be 1.231, A21 is going to be 1.295 in this case.

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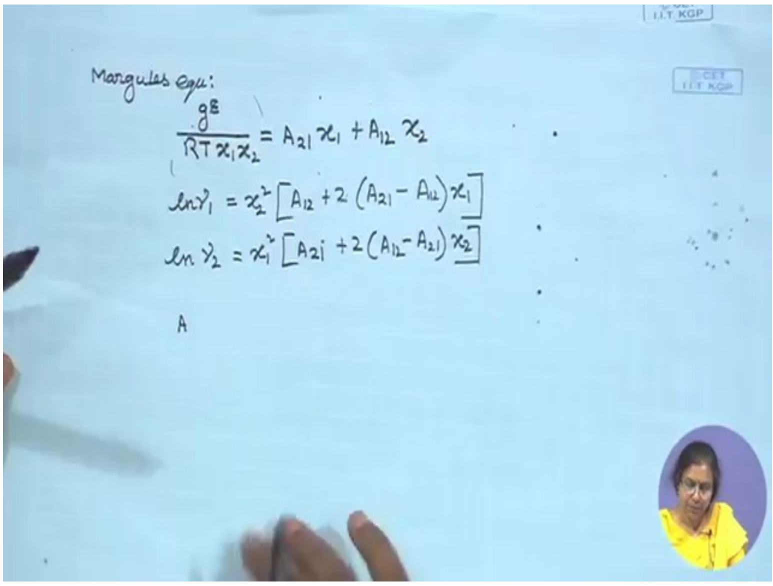

Margules equ:

$$\frac{g^E}{RTx_1x_2} = A_{21}x_1 + A_{12}x_2$$

$$\ln\gamma_1 = x_2^2\left[A_{12} + 2(A_{21} - A_{12})x_1\right]$$

$$\ln\gamma_2 = x_1^2\left[A_{21} + 2(A_{12} - A_{21})x_2\right]$$

A

Moment you have found out A1 A2, now you can use again this particular equation you know A12, A21 for each particular x1x2 you are now in a position to find out ln gamma1 ln gamma

2. Once you found out ln gamma1 ln gamma 2 from these you can find out gamma1 and gamma 2. Moment you have found out gamma1 gamma 2 then using the data of x1 and P or x1P1 saturated you will be in a position to find out y1 and P and this is precisely what we have done.

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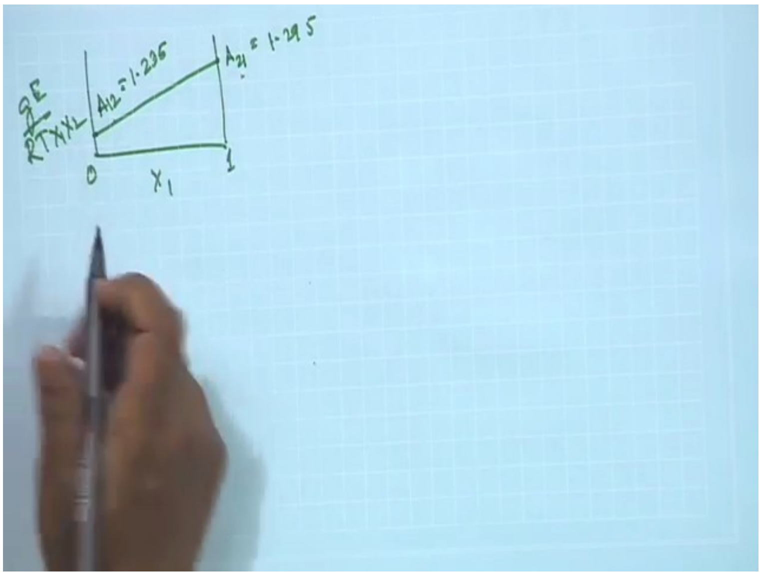

If you find it out say let us take up the first data, right? For the first data we already know A12 A21.

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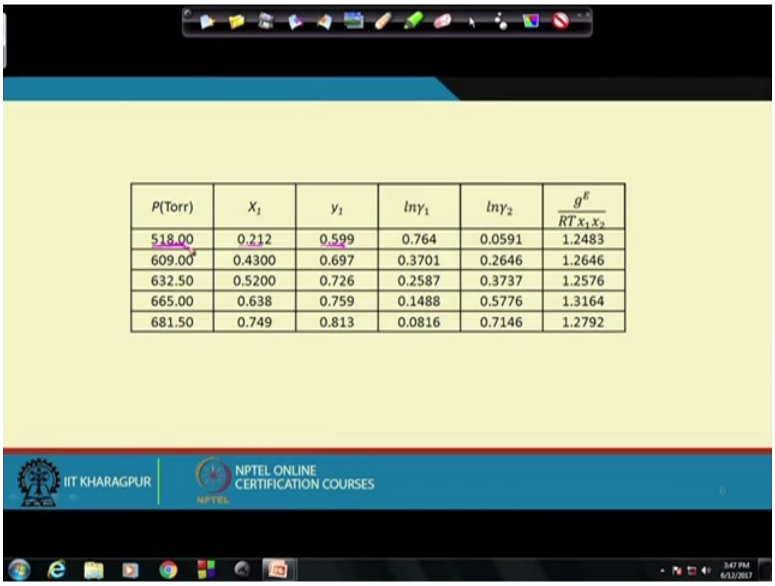

P(Torr)	x_1	y_1	$\ln\gamma_1$	$\ln\gamma_2$	$\frac{g^E}{RTx_1x_2}$
518.00	0.212	0.599	0.764	0.0591	1.2483
609.00	0.4300	0.697	0.3701	0.2646	1.2646
632.50	0.5200	0.726	0.2587	0.3737	1.2576
665.00	0.638	0.759	0.1488	0.5776	1.3164
681.50	0.749	0.813	0.0816	0.7146	1.2792

The first data if you observe here, the first data is x1 equals to 0.212 y1 is given P is given, right?

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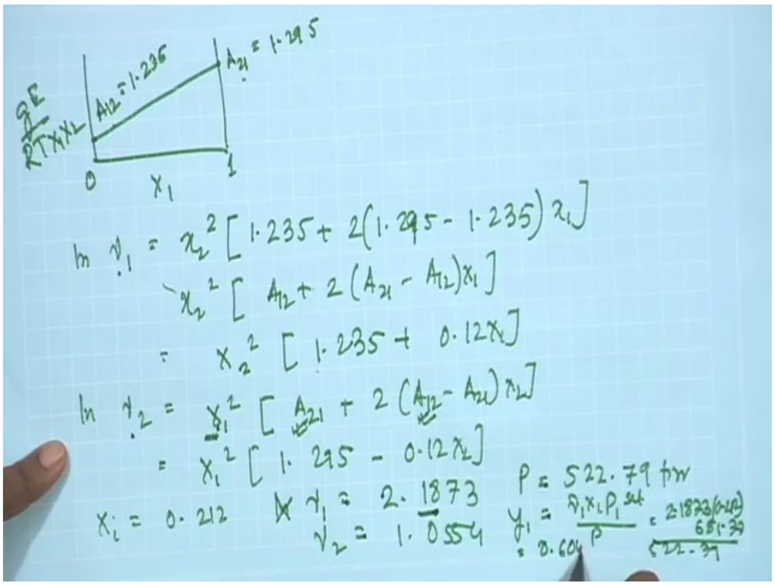

$\ln\gamma_1 = x_2^2[1.235 + 2(1.295 - 1.235)x_1]$

$x_2^2[A_{12} + 2(A_{21} - A_{12})x_1]$

$= x_2^2[1.235 + 0.12x_1]$

$\ln\gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2]$

$= x_1^2[1.295 - 0.12x_2]$

$x_1 = 0.212$ $\gamma_1 = 2.1873$ $\gamma_2 = 1.0554$

$P = 522.79$ torr

$y_1 = \frac{\gamma_1 x_1 P_1^{sat}}{P} = \frac{2.1873(0.212)\,651.39}{522.79}$

$= 0.604$

So for this particular data we find ln gamma1 using that particular equation we get it is going to be x2 square into 1.235 plus2 into 1.295 minus1.235, isn't it? into x1, agreed because if you remember x2 square is nothing but A12 plus 2 into A21 minus A12 into x1. So therefore on further simplification we find this is 1.235 plus 0.12X1, agreed?

Same way you can substitute for ln gamma 2, you get this is going to be just like the since it is already written I would like to mention this is A21 plus A12 minus A21 into X2 which is nothing but X1 square into 1.295 minus 0.12 X2, agreed? So for so therefore from these 2 equations you if you know X1 A21 and A12 we have already found out, you can find out ln gamma 2 for different X1s. We can also find out ln gamma 1 for different X1s.

So for X1 equals to 0.212 you can find out ln gamma1 would have been equal to, you can just substitute them instead of X1 you can put 0.212 and then finally you find out gamma 1 as 2.1873 gamma 2 as 1.0554, what is P equals to? P will be equal to 522.79 Torr and what will y be equal to y1 will be equal to it is gamma1 X1 P1 saturated by P. Substitute all the values gamma 1 is equal to 2.1873, let me substitute 2.1873. What is X1? 0.212, what is P1 saturated? That also we have already calculated it is 681.77.

What is the total pressure? It's already written down there it is 522.79, so what is y1 that you get, 0.6047 agreed?

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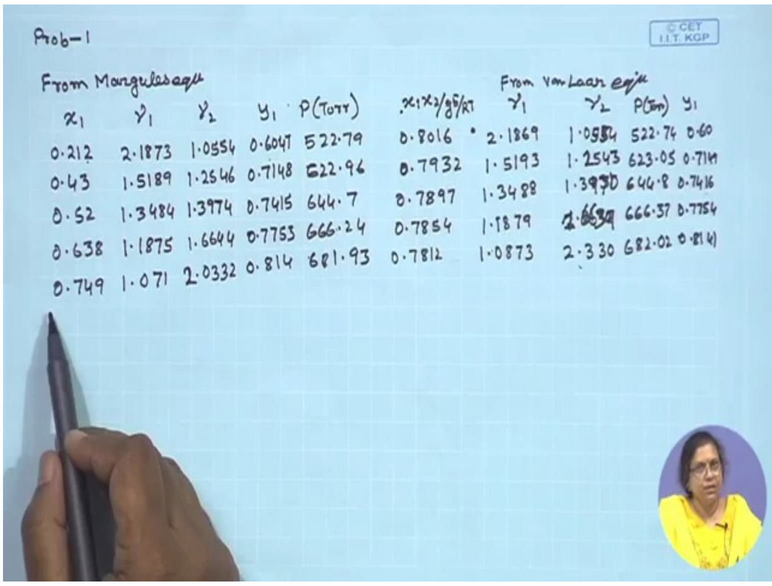

Prob-1

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From Margules eqn						From van Laar eqn			
x_1	γ_1	γ_2	y_1	P(Torr)	$x_1x_2/g^E/RT$	γ_1	γ_2	P(Torr)	y_1
0.212	2.1873	1.0554	0.6047	522.79	0.8016	2.1869	1.0554	522.74	0.60
0.43	1.5189	1.2546	0.7148	622.96	0.7932	1.5193	1.2543	623.05	0.714
0.52	1.3484	1.3974	0.7415	644.7	0.7897	1.3488	1.3930	644.8	0.7416
0.638	1.1875	1.6644	0.7753	666.24	0.7854	1.1879	1.6639	666.37	0.7754
0.749	1.071	2.0332	0.814	681.93	0.7812	1.0873	2.330	682.02	0.8141

So therefore for the first case you are in a position to find out your X you are in a position to find out all the values. You are in a position I have done it here and it is provided here, so therefore you gamma 1 gamma 2 y1P everything has been there using 3 suffix Margules equation; instead of 0.212 you can repeat the calculations with 0.43. Same way you are going to proceed you are going to find out you know A12 A21, so you are in a position to find out ln gamma1 ln gamma 2 from ln gamma 1 gamma 2 you can find out gamma 1 and gamma 2. Once you notice can find out P you can find out y1, so if you repeat this calculations this is the final Pxy data that you will be in a position to generate using 3 suffix Margules equation.

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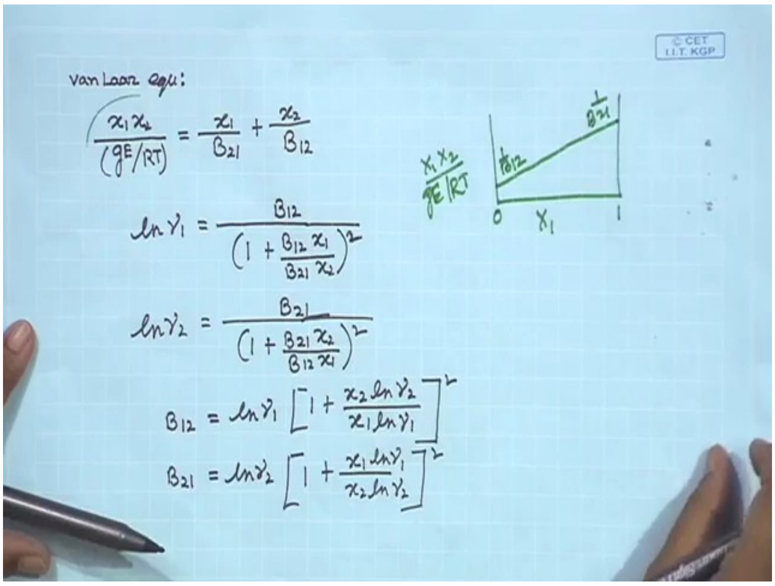


Van Laar equ:

$$\frac{x_1 x_2}{(g^E/RT)} = \frac{x_1}{B_{21}} + \frac{x_2}{B_{12}}$$

$$\ln\gamma_1 = \frac{B_{12}}{\left(1 + \frac{B_{12} x_1}{B_{21} x_2}\right)^2}$$

$$\ln\gamma_2 = \frac{B_{21}}{\left(1 + \frac{B_{21} x_2}{B_{12} x_1}\right)^2}$$

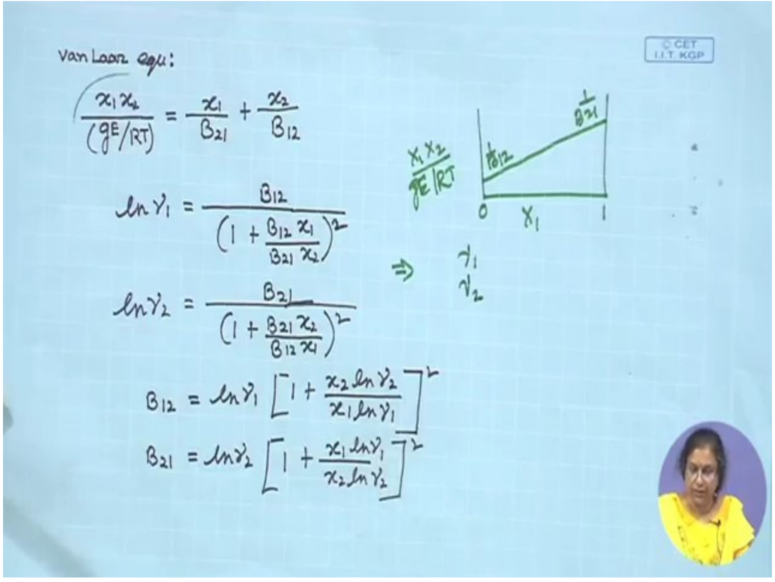
$$B_{12} = \ln\gamma_1 \left[1 + \frac{x_2 \ln\gamma_2}{x_1 \ln\gamma_1}\right]^2$$

$$B_{21} = \ln\gamma_2 \left[1 + \frac{x_1 \ln\gamma_1}{x_2 \ln\gamma_2}\right]^2$$

Now suppose I tell you to repeat the same way van laar equation, the procedure is completely same just the equations are different. For van la equation if you remember, this is the equation which we have, right? So in this equation if you're going to plot this particular term with x1 again in this case we are going to get a straight line here, okay.

And so if you're plotting here what do we get? Suppose we are plotting X1 X2 by gE by RT as a function of X1 ranging from 0 to 1 this case also we will be getting a straight line where this part the at X1 equals to 0 you get 1 by B12 from here you can see and here you get 1 by B21, right? From which from the reciprocal values you're in a position to find out the actual B12 B21.

(Refer Slide Time: 26:18)


Van Laar equ:

$$\frac{x_1 x_2}{(g^E/RT)} = \frac{x_1}{B_{21}} + \frac{x_2}{B_{12}}$$

$$\ln \gamma_1 = \frac{B_{12}}{\left(1 + \frac{B_{12} x_1}{B_{21} x_2}\right)^2}$$

$$\ln \gamma_2 = \frac{B_{21}}{\left(1 + \frac{B_{21} x_2}{B_{12} x_1}\right)^2}$$

$$B_{12} = \ln \gamma_1 \left[1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right]^2$$

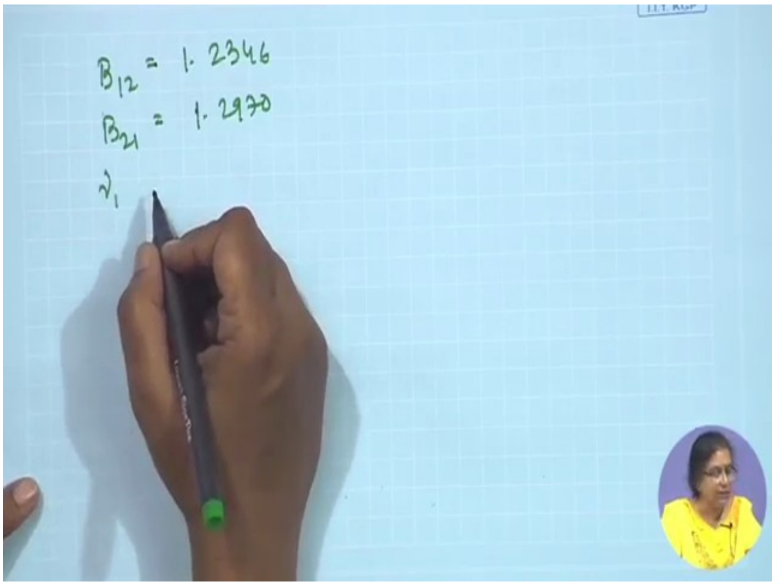
$$B_{21} = \ln \gamma_2 \left[1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right]^2$$

$\Rightarrow \gamma_1$

γ_2

So in this particular case if you’re repeating it, you are going to see that for your case B12 will be equal to 1.2346, B21 will be equal to 1.2970. Now once you once you know this then you are again in a position to find out gamma 1 for the for the different cases ln gamma 1 values are given, ln gamma 2 values are given so once these 2 are given you know B12, you know x1 x2 you can find out these. Once you can find out gamma 1 and gamma 2 you will be in a position to find out sorry from the ln values you’re in a position to find out gamma1 and gamma 2.

(Refer Slide Time: 26:25)

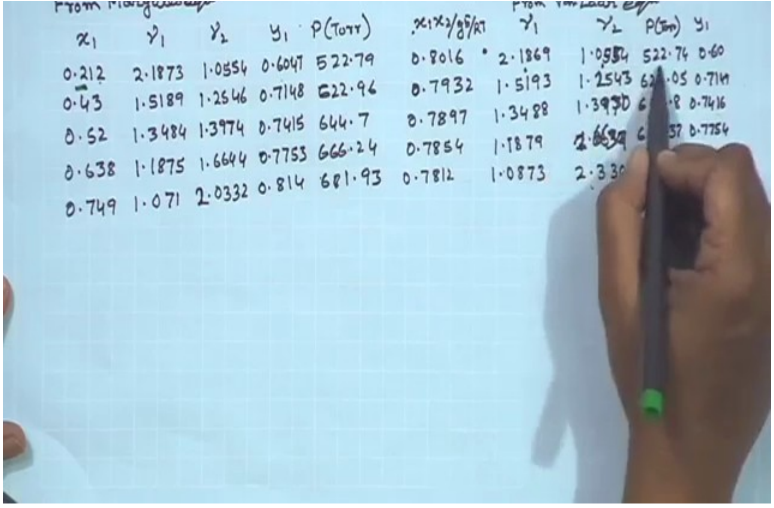

$B_{12} = 1.2346$

$B_{21} = 1.2970$

γ_1

Moment you know gamma 1 and gamma 2 then you can use it to find out y1 and P. Say for example suppose we start with X1 it’s the same X1 value the first value 0.212, right? From here if you do you find out gamma1 is going to be using the van laar equation it is going to be 2.1869, gamma 2 is going to be 1.0554. From here you can find out P, what is P going to be? It is 2.1869 into 0.212 into 681.77 plus your 1.0554 into 1 minus 0.212 which is 0.788, 248.48 which gives you the P as 522.74

Torr. (Refer Slide Time: 27:43)



x_1	γ_1	γ_2	y_1	P(Torr)	$x_1x_2/g^E/RT$	γ_1	γ_2	P(Torr)	y_1
0.212	2.1873	1.0554	0.6047	522.79	0.8016	2.1869	1.0554	522.74	0.60
0.43	1.5189	1.2546	0.7148	622.96	0.7932	1.5193	1.2543	62[illegible].05	0.714
0.52	1.3484	1.3974	0.7415	644.7	0.7897	1.3488	1.3930	6[illegible].8	0.7416
0.638	1.1875	1.6644	0.7753	666.24	0.7854	1.1879	1.6639	6[illegible]57	0.7754
0.749	1.071	2.0332	0.814	681.93	0.7812	1.0873	2.33[illegible]		

e

What is y1 equals to then? y1 if you calculate you will find out that this is going to be 0.6047. So therefore just the way I have I have I have done the calculations for the first case 0.212 this is the situation I have found out gamma1 gamma 2, P Torr and y1, right? So therefore I can repeat it for the other x1 and generate the Pxy data using the van laar equation.

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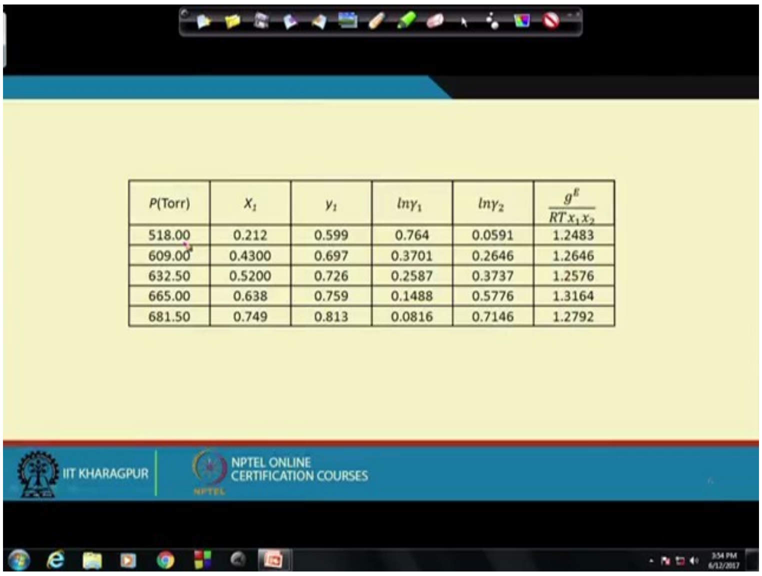

P(Torr)	X_1	y_1	$ln\gamma_1$	$ln\gamma_2$	$\frac{g^E}{RTx_1x_2}$
518.00	0.212	0.599	0.764	0.0591	1.2483
609.00	0.4300	0.697	0.3701	0.2646	1.2646
632.50	0.5200	0.726	0.2587	0.3737	1.2576
665.00	0.638	0.759	0.1488	0.5776	1.3164
681.50	0.749	0.813	0.0816	0.7146	1.2792

So therefore in this particular way what have we done? We have generated the Pxy data for using the 2 suffix sorry 3 suffix Margules equation.

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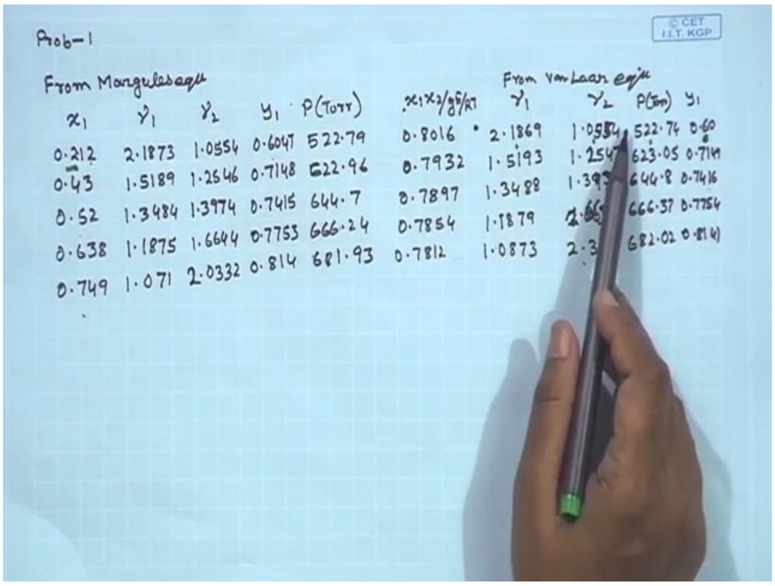

Prob-1

From Margules eqn					From van Laar eqn				
x_1	γ_1	γ_2	y_1	P(Torr)	$x_1x_2/g^E/RT$	γ_1	γ_2	P(Torr)	y_1
0.212	2.1873	1.0554	0.6047	522.79	0.8016	2.1869	1.0554	522.74	0.60
0.43	1.5189	1.2546	0.7148	622.96	0.7932	1.5193	1.2547	623.05	0.714
0.52	1.3484	1.3974	0.7415	644.7	0.7897	1.3488	1.39	644.8	0.7416
0.638	1.1875	1.6644	0.7753	666.24	0.7854	1.1879	1.66	666.37	0.7754
0.749	1.071	2.0332	0.814	681.93	0.7812	1.0873	2.3	682.02	0.8141

We have generated the data from the van laar equation and now if you compare these particular data with the original data you can understand for yourself which one is much more accurate. Well, this was when you are dealing with isothermal VLE data. Now in chemical process industries we find that distillation operation are usually carried out under isobaric conditions. So it's often much more convenient to deal with isobaric data than with isothermal data.

We will be dealing with this in the next class. We'll be taking up a specific problem and see how we are just going to rearrange the equations which we which we have rather discussed in this class in order to obtain isobaric VLE data, thank you very much.