Course on Phase Equilibrium Thermodynamics
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Lecture No 39
Ideal solutions(Contd.)

Well, we were we were discussing ideal solutions and in ideal solutions we had I had already discussed the P-x-y diagrams which is shown here and then I had also discussed the Txy diagram and these diagrams they are particularly useful for describing the process of rectification which is distillation a number of times which we use very frequently in chemical engineering in order to separate 2 particular components with small differences in boiling point when the difference is very large then it is simply vaporized.

We start vaporizing the mixture and then condense it then in that case we can get a good enough separation but when the boiling point differences are not very large we need to repeat this process of boiling and condensation a large number of times.

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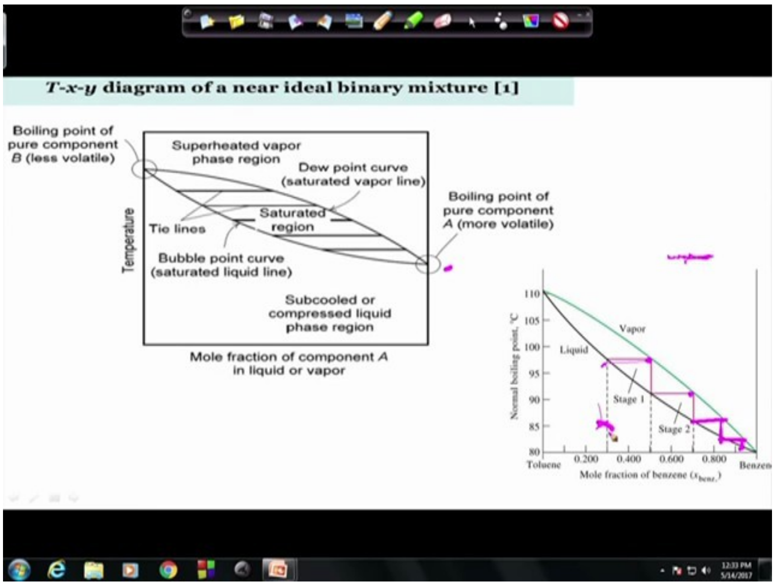

T-x-y diagram of a near ideal binary mixture [1]

Let us see how this particular process works. Say suppose we have started with a liquid of composition, we start heating we keep on heating it till we reach the bubble point curve, once reached the bubble point curve when we start vaporizing we will find that the vapor composition is given here we already find that the vapor is richer in more volatile component as the liquid phase. Now we condense the whole vapor, what we do?

We simply cool it we do not do anything and then again we start vaporizing, moment we start vaporizing the first vapor again we find it is richer than the liquid with which we started and it is much more richer than the liquid mixture which we had originally taken. Now suppose we keep on repeating this we simply condense the whole thing and again we vaporize it, right? This is the composition of the vapor we simply condense the vapor and again we start to vaporize it.

So in the process what have we got? In the process we find that we have we and we have come to a liquid solution which is much richer almost which comprises of the pure component of the more volatile component where we had started with a mixture which had much less proportion of the more volatile component. Now in this particular process is the basic principle underlying the process of rectification which we will be learning in great details when you go further into your training of chemical engineering?

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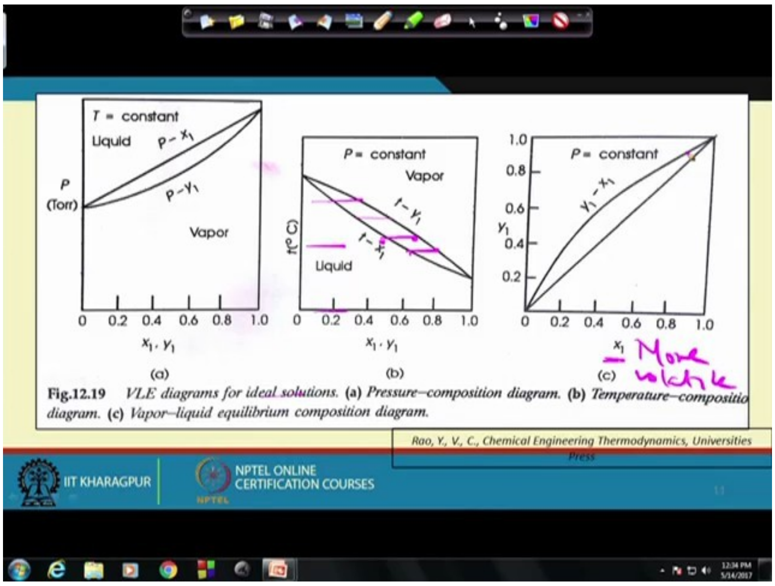

Fig.12.19 *VLE diagrams for ideal solutions.* **(a)** *Pressure–composition diagram.* **(b)** *Temperature–compositio diagram.* **(c)** *Vapor–liquid equilibrium composition diagram.*

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

So by this time what are the things that we have done? We have dealt with Pxy we have dealt with Pxy diagrams we have dealt with Txy diagrams and now from this Txy diagrams we find that locating the Tie lines with we can generate the vapor and the liquid, the liquid and the vapor in equilibrium with one another and this particular compositions they are then plotted in the x1 versus y1 curve. Now here I would like to mention one thing again I would like to remind that what is x1?

x1 refers to the more volatile component, this is something very important that you need to remember throughout you can perform the entire phase diagrams with the less will tell component the only difference is this the curves will be just they will just be reversed that is only difference but by convention we usually perform phase diagrams using the more volatile component for the composition of the more volatile component in the x axis and accordingly we plot either P in the Y axis or T in the Y axis for Y1 in the Y axis. Now under this condition we always find that Y1 is always greater than X1 as expected because we are dealing with a more volatile component, right?

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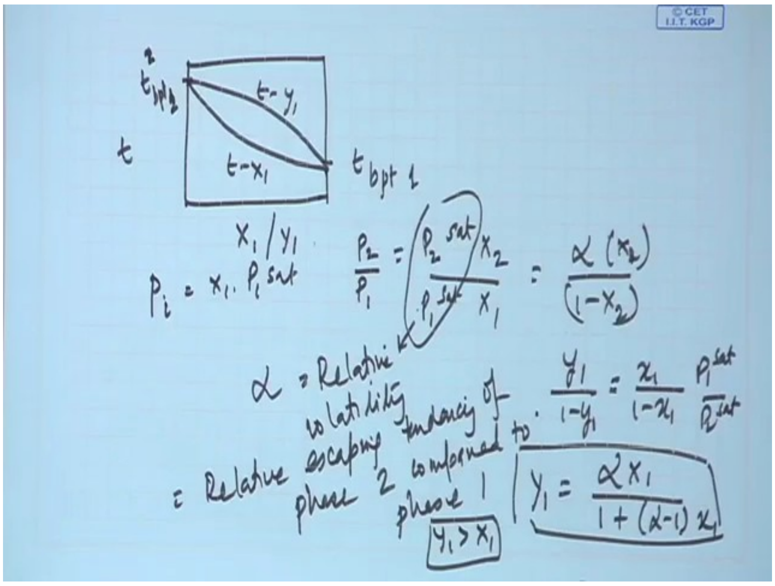

$P_i = x_i \cdot P_i^{sat}$

$\frac{P_2}{P_1} = \frac{P_2^{sat} x_2}{P_1^{sat} x_1} = \frac{\alpha (x_2)}{(1 - x_2)}$

α = Relative volatility

= Relative escaping tendency of phase 2 compared to phase 1

$\frac{y_1}{1-y_1} = \frac{x_1}{1-x_1} \frac{P_1^{sat}}{P_2^{sat}}$

$\boxed{y_1 = \frac{\alpha x_1}{1 + (\alpha - 1) x_1}}$

$\boxed{y_1 > x_1}$

Now in this particular case we can I can just mention in this case Pi this is equals to Xi Pi saturated or in other words for 2 common mixtures I can write down the ratio of their partial pressures as P2 saturated X2 by P1 saturated X1 plot this particular ratio this P2 by P1 this is known as alpha which we define as the relative volatility. What is this relative volatility? It is the relative escaping tendency of this second phase with respect to the first phase, right?

So therefore this is the relative escaping tendency of phase 2 compared to phase1, right? So therefore this is termed as alpha, so therefore we can write this down as alpha into X2 by 1 minus or alpha into X2 by 1 minus X2 we can write it down in this particular term. From where we can find out that Y this is Y, let it be Y2 it does not matter.

From here we find out that Y1 by 1 minus Y1 this is nothing but x1 by 1 minus x1 P1 saturated by P2 saturated, from here what do we get? We get Y1 equals to alpha X1 by 1 plus alpha minus 1 x1 from where we know that y1 will always be greater than x1, right?

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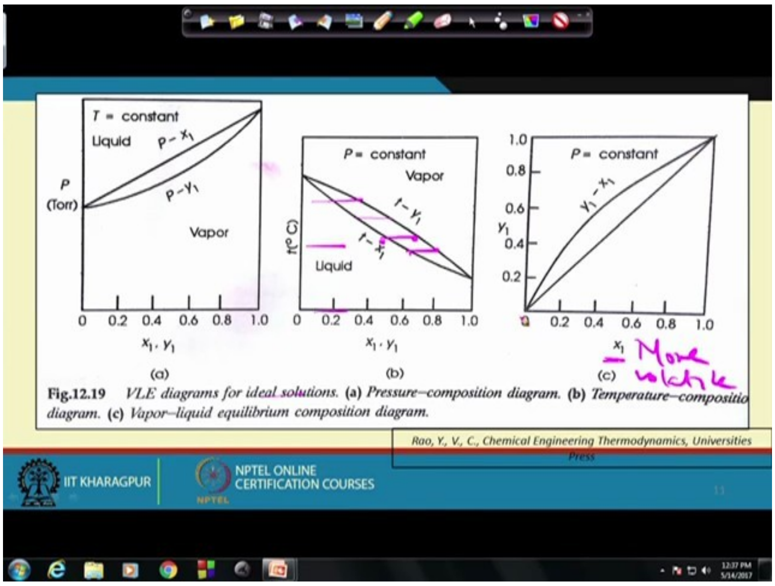

Fig.12.19 *VLE diagrams for ideal solutions.* **(a)** *Pressure–composition diagram.* **(b)** *Temperature–compositio diagram.* **(c)** *Vapor–liquid equilibrium composition diagram.*

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

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And therefore we find that we always get a plot which is which is sort of a hyperbolic curve and for all particular cases except for x1 equals to 0 and x1 equals to 1 y1 will always be greater than x1. Well so till now what are the things that we have done? We have discussed ideal solutions, we have discussed the Lewis Randall rule, we have developed the Raoult's law from the Lewis Randall rule, we have discussed under what conditions ideal solution model can be applicable, we have also discussed under what are the properties of ideal solutions no heat absorption or evolution etc . Increase in randomness of mixing quite naturally otherwise they will not mix spontaneously. Then we have discussed different phase diagrams for binary ideal solutions the vapor and the liquid phases both are both exhibit ideal solution model.

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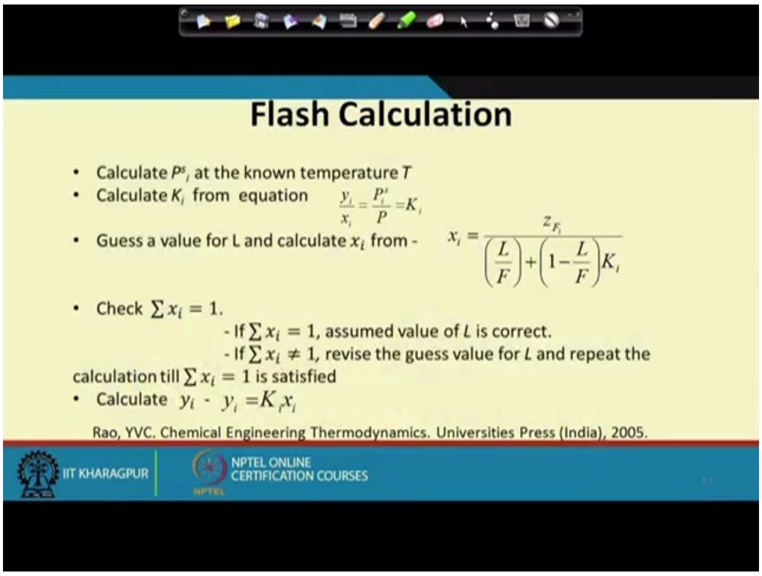

Flash Calculation

- Calculate P^s_i at the known temperature T
- Calculate K_i from equation $\frac{y_i}{x_i} = \frac{P^s_i}{P} = K_i$
- Guess a value for L and calculate x_i from - $x_i = \frac{z_{F_i}}{\left(\frac{L}{F}\right) + \left(1 - \frac{L}{F}\right)K_i}$
- Check $\sum x_i = 1$.
  - If $\sum x_i = 1$, assumed value of L is correct.
  - If $\sum x_i \neq 1$, revise the guess value for L and repeat the calculation till $\sum x_i = 1$ is satisfied
- Calculate y_i - $y_i = K_i x_i$

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

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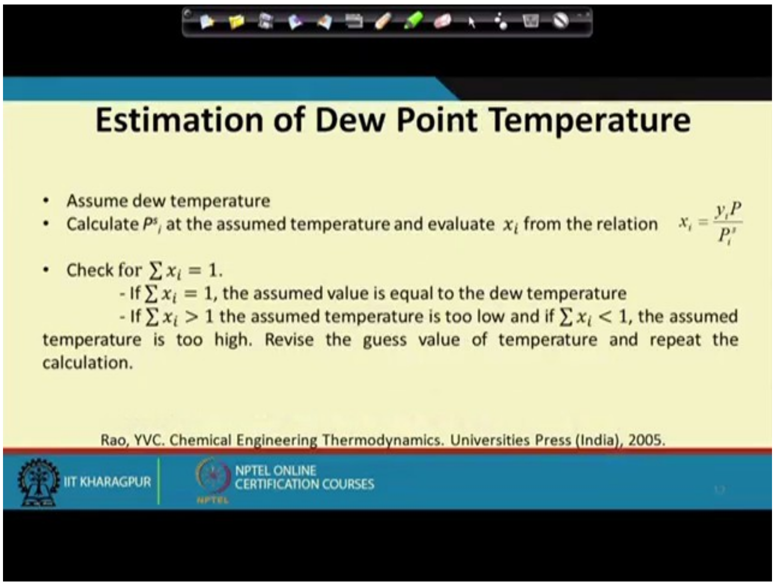

Estimation of Dew Point Temperature

- Assume dew temperature
- Calculate P^s_i at the assumed temperature and evaluate x_i from the relation $x_i = \frac{y_i P}{P^s_i}$
- Check for $\sum x_i = 1$.
  - If $\sum x_i = 1$, the assumed value is equal to the dew temperature
  - If $\sum x_i > 1$ the assumed temperature is too low and if $\sum x_i < 1$, the assumed temperature is too high. Revise the guess value of temperature and repeat the calculation.

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

Well, I had also discussed how to how to construct the Pxy, Txy diagrams and in the next few slides I have just noted down the procedures for finding out the dew point temperature and also the bubble point temperature etc. So these procedures can be followed and different problems can be dealt with.

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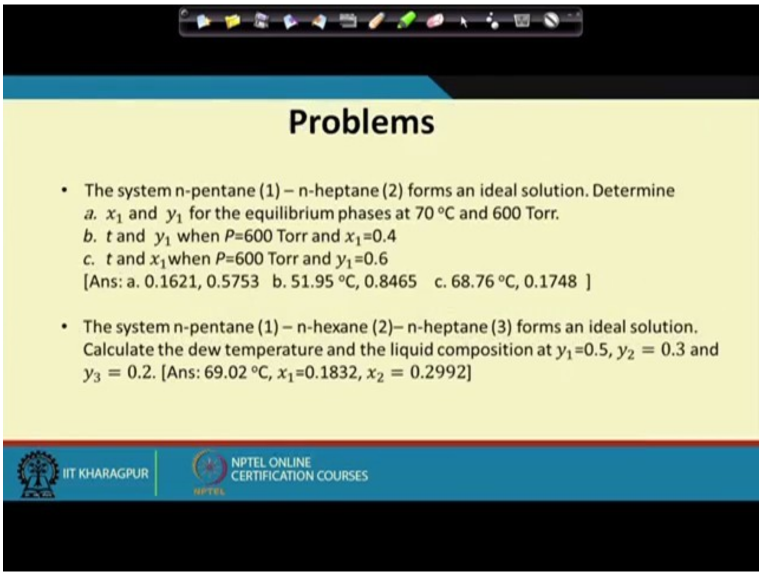

Problems

- The system n-pentane (1) – n-heptane (2) forms an ideal solution. Determine
  a. x_1 and y_1 for the equilibrium phases at 70 °C and 600 Torr.
  b. t and y_1 when P=600 Torr and x_1=0.4
  c. t and x_1 when P=600 Torr and y_1=0.6
  [Ans: a. 0.1621, 0.5753 b. 51.95 °C, 0.8465 c. 68.76 °C, 0.1748]
- The system n-pentane (1) – n-hexane (2)– n-heptane (3) forms an ideal solution. Calculate the dew temperature and the liquid composition at y_1=0.5, $y_2 = 0.3$ and $y_3 = 0.2$. [Ans: 69.02 °C, x_1=0.1832, $x_2 = 0.2992$]

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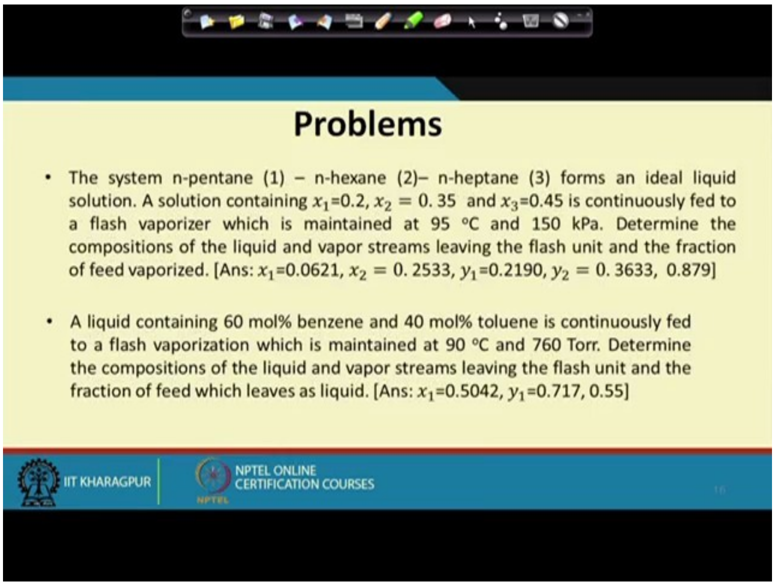

Problems

- The system n-pentane (1) – n-hexane (2)– n-heptane (3) forms an ideal liquid solution. A solution containing x_1=0.2, $x_2 = 0.35$ and x_3=0.45 is continuously fed to a flash vaporizer which is maintained at 95 °C and 150 kPa. Determine the compositions of the liquid and vapor streams leaving the flash unit and the fraction of feed vaporized. [Ans: x_1=0.0621, $x_2 = 0.2533$, y_1=0.2190, $y_2 = 0.3633$, 0.879]
- A liquid containing 60 mol% benzene and 40 mol% toluene is continuously fed to a flash vaporization which is maintained at 90 °C and 760 Torr. Determine the compositions of the liquid and vapor streams leaving the flash unit and the fraction of feed which leaves as liquid. [Ans: x_1=0.5042, y_1=0.717, 0.55]

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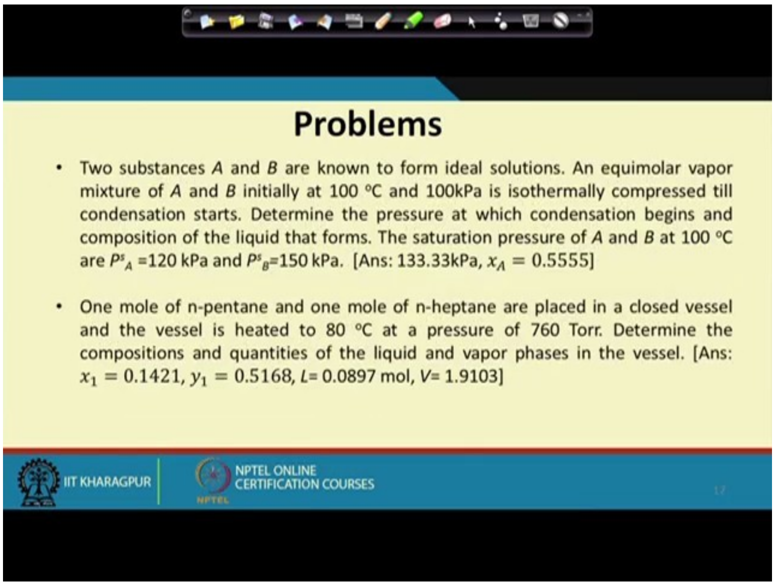

Problems

- Two substances *A* and *B* are known to form ideal solutions. An equimolar vapor mixture of *A* and *B* initially at 100 °C and 100kPa is isothermally compressed till condensation starts. Determine the pressure at which condensation begins and composition of the liquid that forms. The saturation pressure of *A* and *B* at 100 °C are P^s_A =120 kPa and P^s_B=150 kPa. [Ans: 133.33kPa, $x_A = 0.5555$]
- One mole of n-pentane and one mole of n-heptane are placed in a closed vessel and the vessel is heated to 80 °C at a pressure of 760 Torr. Determine the compositions and quantities of the liquid and vapor phases in the vessel. [Ans: $x_1 = 0.1421$, $y_1 = 0.5168$, *L*= 0.0897 mol, *V*= 1.9103]

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The different problems are given at the end of this particular lecture series. So you can try out these problems one or 2 problems I have already done before you. You can try out the other problems and in each problem you will find that the answers are also provided for your benefit. Now there is one particular type of your problem which we have not dealt with till now which I would like to deal these problems is known as Flash calculation problems, what are these?

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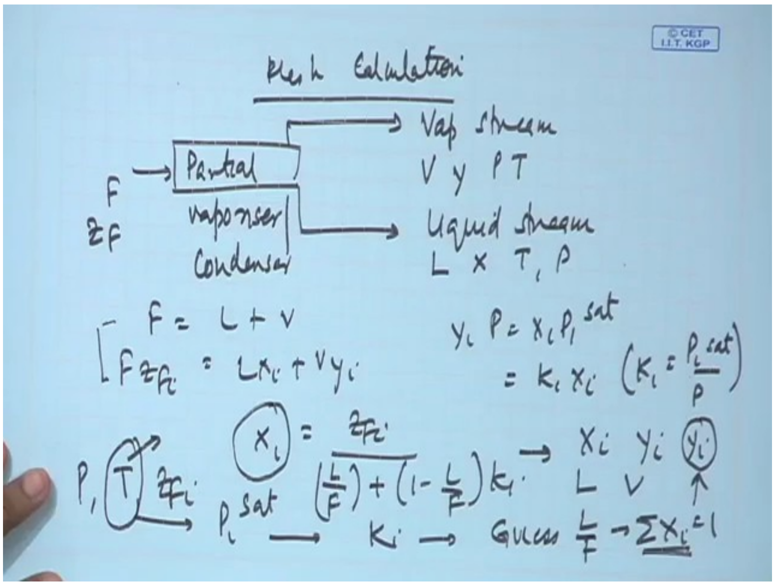

$F = L + V$

$F z_{Fi} = L x_i + V y_i$

$y_i P = x_i P_i^{sat} = K_i x_i \quad \left(K_i = \frac{P_i^{sat}}{P}\right)$

$x_i = \frac{z_{Fi}}{\left(\frac{L}{F}\right) + \left(1 - \frac{L}{F}\right) K_i} \rightarrow x_i \; y_i \; y_i \quad L \; V$

$P, T, z_{Fi} \rightarrow P_i^{sat} \longrightarrow K_i \rightarrow \text{Guess } \frac{L}{F} \rightarrow \sum x_i = 1$

Very frequently we encounter a situation where we find that more or less we introduce any particular feed it can be vapor feed it can be a liquid feed since we have we just to make matters general I would like to mention the feed composition as ZF, right? And then it is introduced into a partial vaporizer or a partial condenser whatever the case may be. From here what do I get? It flashes I get a vapor stream with the amount of vapor formed it's V moles the your composition is given by y and pressure and temperature I also get a liquid stream which again with the total fraction or rather total moles of liquid being L the composition x and temperature and pressure conditions.

So from here what I have done? I have just flashed any particular liquid or a vapor mixture for partial separation into a vapor stream and a liquid stream. For this case from the overall material balance I know this and I also know from the component material balance ZFi equals to Lxi plus Vyi, right? And with this we also know the equations yiP equals to xiPi saturated or in other words this is can be written down as Kixi where Ki is nothing but Pi saturated by P, right?

So therefore I I have these 2 equations and I have got a set of Ki equations as we say it, from there we can find out xi as ZFi we can just calculate these and find out this is equals to L by F plus 1 minus L by F into Ki. So in this particular case usually what are known? We know pressure we know temperature we know they composition of the feed and what are we required to find out? We are required to find out composition in the liquid phase, composition in the vapor phase, amount of liquid formed, amount of vapor formed.

So how do we proceed in this particular case? We know the temperature once we know the temperature we can find out each Pi saturated, agreed? Once we know the Pi saturated we know the pressure then from there should be able to find out Ki, Ki is Pi saturated for P. So for each case you can find out the Ki once can find out the Ki then what we do? We guess either a L by F or a V by F whatever it is. If we guess it we can find out xi.

We can find out xi for all the components i, fine. And then once you have calculated xi for all the components we then check-up Sigma xi equals to 1. If we find it is not equal to one that again we start with a different assumed temperature continue the process till we get xi equals to 1 if we get Sigma xi equals to 1 we know that my guess temperature is correct and I have come or I have reached the correct mole fractions in the liquid phase. Once I have done this then from there what I do? I find out yi for the individual components.

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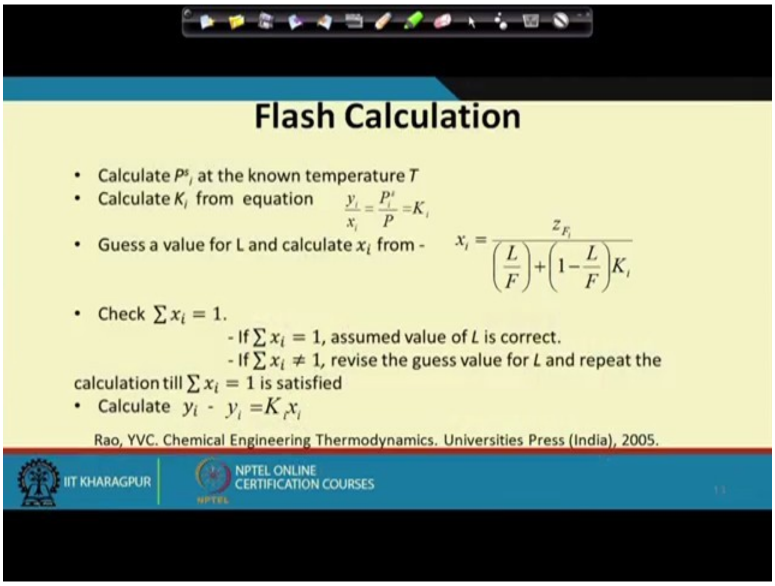

Flash Calculation

- Calculate P^s_i at the known temperature T
- Calculate K_i from equation $\frac{y_i}{x_i} = \frac{P^s_i}{P} = K_i$
- Guess a value for L and calculate x_i from - $x_i = \frac{z_{F_i}}{\left(\frac{L}{F}\right) + \left(1 - \frac{L}{F}\right)K_i}$
- Check $\sum x_i = 1$.
  - If $\sum x_i = 1$, assumed value of L is correct.
  - If $\sum x_i \neq 1$, revise the guess value for L and repeat the calculation till $\sum x_i = 1$ is satisfied
- Calculate y_i - $y_i = K_i x_i$

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

So in this particular procedure it has also been written down here. So accordingly we can perform these particular equations or rather these calculations and we can perform a few Flash calculations in this way there are few problems which have been given at the end of the assignment I guess there is one problem of pentane, hexane and Heptane this is the problem, right? So in this particular problem also suppose we find that these 3 they formed the ideal condition, okay.

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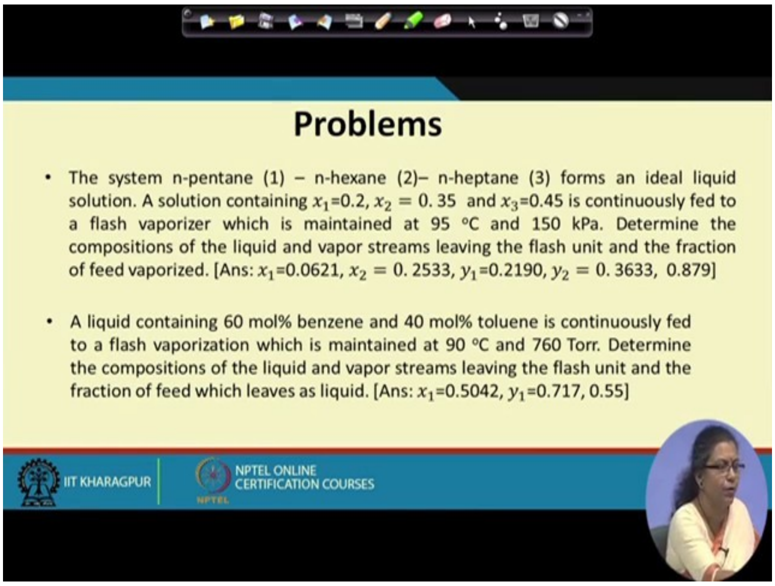

Problems

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- A liquid containing 60 mol% benzene and 40 mol% toluene is continuously fed to a flash vaporization which is maintained at 90 °C and 760 Torr. Determine the compositions of the liquid and vapor streams leaving the flash unit and the fraction of feed which leaves as liquid. [Ans: x_1=0.5042, y_1=0.717, 0.55]

And this is given problem. This particular case the way I have told you the x the compositions are given ZF's are given.

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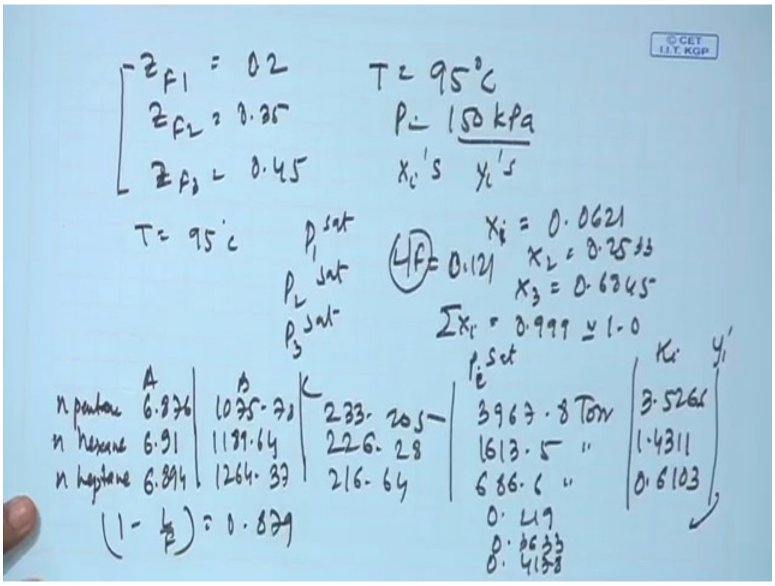

$z_{F1} = 0.2$
$z_{F2} = 0.35$
$z_{F3} = 0.45$

$T = 95°C$
$P = \underline{150\ kPa}$
$x_i's \quad y_i's$

$T = 95°C \quad P_1^{sat} \quad P_2^{sat} \quad P_3^{sat}$

$\psi_F = 0.121$

$x_1 = 0.0621$
$x_2 = 0.2533$
$x_3 = 0.6845$
$\Sigma x_i = 0.999 \simeq 1.0$

	A	B	C	P_i^{sat}	K_i
n pentane	6.876	1075.78	233.205	3967.8 Torr	3.5266
n hexane	6.91	1189.64	226.28	1613.5 "	1.4311
n heptane	6.894	1264.37	216.64	686.6 "	0.6103

y_i
0.219
0.3633
0.4158

$(1 - \psi_F) = 0.879$

So therefore ZF1 this is equals to 0.2 ZF2 equals to 0.35, ZF3 equals to 0.45 we know that they Z's are actually axis here because introduce a ideal rather we introduce a liquid solution here the temperature is given as 95 degree centigrade, the pressure is given as 150kpa.

So what are we required to find out? We are required to find out xi's and yi's, right? So what we do? Again the way I have said T equals to 95 degrees centigrade I calculate the P1 saturated, P2 saturated, P3 saturated in this particular case from the Antoine's constant. The

Antoine constant you can note down the ABC, so for this case n pentane is my component 1 so for this case A is 6.876, B is 1075.78 and C is 233.205.

For n Hexane this is 6.91, 1189.64 and this is 226.28. For n Heptane what do we find? n Heptane this is 6.894, 1264.37, 216.64 so from here we can find out the P1 saturated, we can find the Pi saturated we find that this is 3967.8torq this is 1613.5torq this is 686.6torq. We know the pressure the total pressure it is 150kpa. So therefore we can find out the Ki's here. What are the Ki's? In this case it is 3.5266 and then this is 1.4311, this is 0.6103.

So once we have done it we can find out the Xi's, right? For finding out the Xi's we need to guess L by F, say suppose I start with my first guess of L by F as 0.121 and find out the corresponding Xi, say in this particular case suppose I start with 0.121 my X1 will be equal to 0.0621 and accordingly my X2 will be 0.2533, X3 is going to be 0.6845 more or less my Sigma Xi is 0.999 which I can take as one this particular case. Accordingly I find my Yi the Yi's in this particular case if I write it down here the Yi's will be 0.219, 0.3633 and 0.4178. So therefore the fraction which was vaporized one minus L by F is nothing but equal to 0.879.

A few other problems have also been provided here we can try out the problems. So in this particular class what have I done? I have discussed different problems of concerning ideal solutions for example I have discussed if Px is given how to find out Ty. Ty is given how to find out Tx. If Tx is given how to find out, If Px is given how to find out Ty or if Py is given how to find out Tx and I have also discussed Flash distillation problems there are a few problems which are there in this particular slide the answers are provided you can work them out to have more feel of ideal solutions.

Now suppose we go to next part of our lecture which deals with non-ideal solutions. What you expect what is going to happen for non-ideal solutions? What are the things that we expect in this particle case? Let us see, so in non-ideal solutions let us see what happens.

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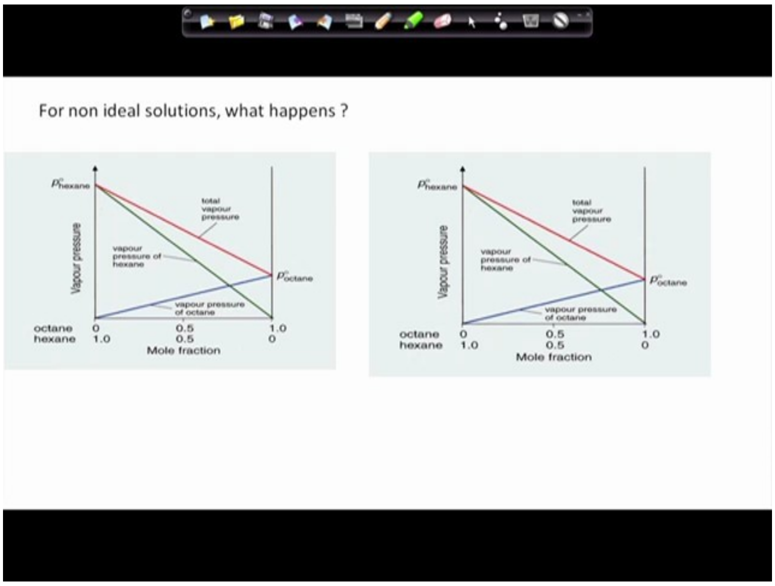

For non ideal solutions, what happens ?

In ideal solutions I have already drawn this particular case. We have, what did we find? We have found that for ideal solutions the partial pressure and the total pressure they vary linearly with mole fraction. Definitely the solution does not behave ideally and along with that what are the other things that we have found?

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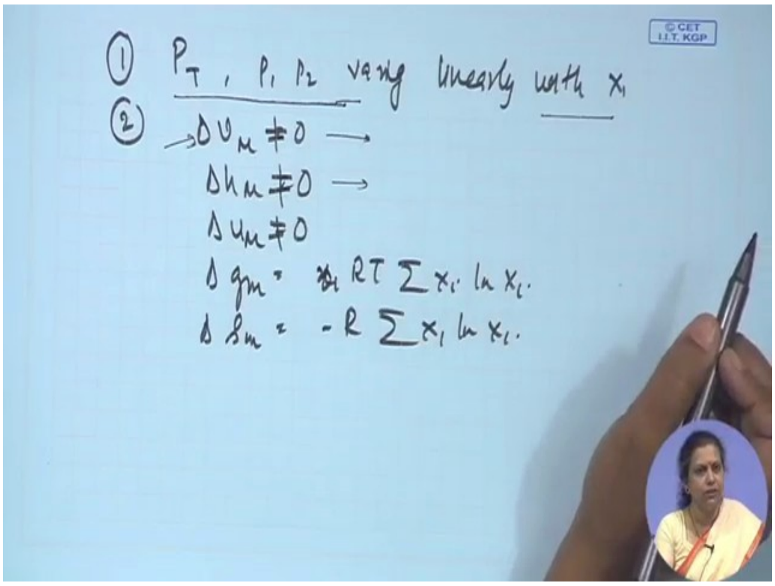

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① P_T , P_1 P_2 vary linearly with x_1

② $\rightarrow \Delta V_M \neq 0 \longrightarrow$

$\Delta h_M \neq 0 \longrightarrow$

$\Delta U_M \neq 0$

$\Delta g_m = \cancel{x_i}\, RT \sum x_i \ln x_i.$

$\Delta s_m = -R \sum x_i \ln x_i.$

We found 3 features of ideal solution, first feature is that partial pressure and total pressures they vary linearly with mole fraction number 1. Number 2 we have observed that Delta vM equals to 0, Delta gm equals to xi, RT sigma xi ln xi and Delta sm was equals to minus R sigma xi ln xi these are the things that we observed. If it is non-ideal then definitely there will be some evolution or absorption of heat and when the 2 components mix then definitely we expect that either there will be contraction of there will be expansion in volume.

So therefore what do we expect? We expect that this might be not equal to 0, this might not be equal to 0 and so if these, one of these are not 0 then this again becomes not equal to 0 etc it continues in this particular way. Now remember one thing non-ideal solution can have only one particular property different for example it can have Delta vM not equal to 0 while the other characteristics they follow the ideal solution model, okay it can happen.

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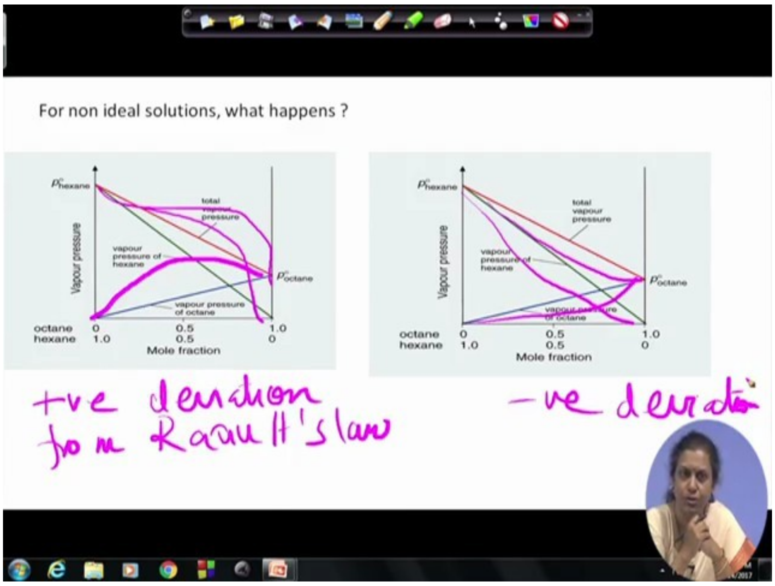

For non ideal solutions, what happens ?

+ve deviation from Raoult's law

-ve deviation

Or it can happen that maybe more than one particular characteristics are not been exhibited by the non-ideal solution. So therefore for non-ideal solution firstly if these things happen then quite naturally your pressure cannot vary linearly with xi it is going to deviate from this and the deviation can be either way. We can find that the pressure is actually higher than the. There can be 2 things one is the pressure can be vapor pressure can be higher than that calculated from the ideal solution model. It can be same for all the cases.

And accordingly since this happens, so naturally the total pressure will also be exhibiting will be also be higher as compared to the total pressure calculated from your ideal solution model. So therefore in this case what do we say? We say that this exhibits positive deviation from Raoult's law. We can also have other things we can say that moment we mix the 2 components what happens? There is a contraction in volume it can happen.

And under that case what do we find? Suppose, see it all depends on the interaction of the molecules repeatedly I have said that when we assume that the interaction between unlike and unlike molecules are the same then we have ideal solutions. Suppose we see that that the interaction between unlike molecules it is greater than the interaction between like molecules then what happens? Then in that case when we mix than the interaction it increases.

When the interaction in the liquid phase increases naturally the tendency to go into the vapor phase that decreases and under that condition what do we have? We have a negative deviation of the Raoult's law, every case you are going to have a negative deviation from Raoult's law. And when we find that the intermolecular interaction between unlike molecules are less as compared to the intermolecular interactions between like molecules then when we mix then what happens?

They are not very comfortable so there is a greater tendency of vapor formation, so as a result the saturated partial the saturated pressure becomes higher as compared to that calculated from the Raoult's law. So therefore we have a positive deviation, so when the unlike interactions are less as compared to the like interactions we have positive deviation from Raoult's law when the unlike interactions are higher as compared to like interactions we have negative deviations from Raoult's law.

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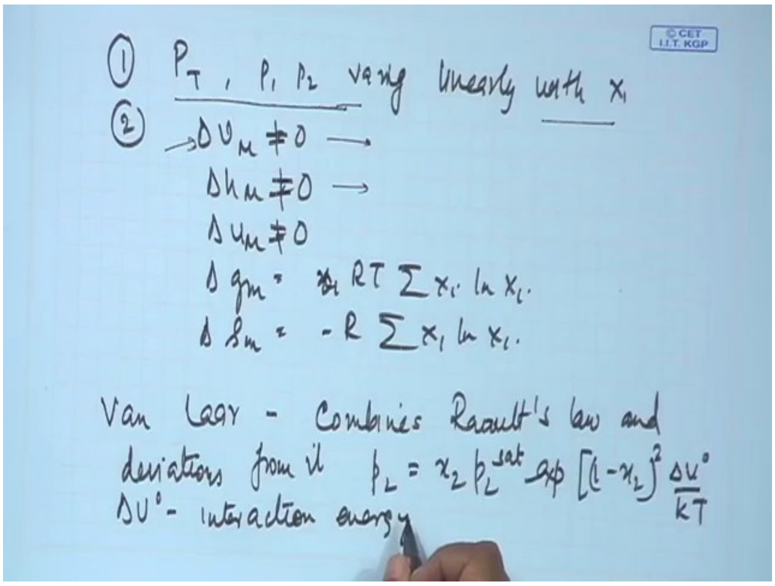

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① P_T, P_1 P_2 varying linearly with x_1

② $\rightarrow \Delta v_M \neq 0 \rightarrow$

$\Delta h_M \neq 0 \rightarrow$

$\Delta u_M \neq 0$

$\Delta g_m = RT \sum x_i \ln x_i.$

$\Delta s_m = -R \sum x_i \ln x_i.$

Van Laar - Combines Raoult's law and deviations from it $p_2 = x_2 p_2^{sat} \exp\left[(1-x_2)^2 \frac{\Delta u^0}{kT}\right]$

Δu^0 - interaction energy

The entire thing can be summarized by a formula which has been provided by Van Laar. Now this particular person as we know that he has worked throughout with solutions and he has proposed a formula which accounts or rather which combine Raoult's law and deviations from it. What is the formula that he has given? It’s quite an interesting formula.

He suggest P2 it is equal to x2P2 saturated which is Raoult's law where the correction factor as exponential one minus x2 whole square Delta u0 by KT, right? Where what is Delta u0 equals to? Delta u0 is the interaction energy which takes into account the differences in nature of the interaction of like and unlike molecules, right?

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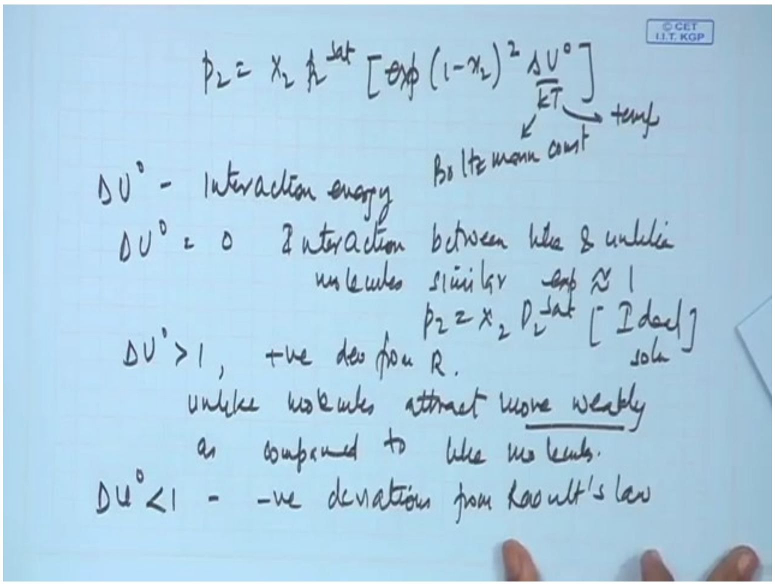

$$p_2 = x_2 p_2^{sat} \left[\exp (1-x_2)^2 \frac{\Delta U^0}{KT} \right]$$

Boltzmann const

temp

ΔU^0 - Interaction energy

$\Delta U^0 = 0$ Interaction between like & unlike molecules similar exp ≈ 1

$p_2 = x_2 p_2^{sat}$ [Ideal soln]

$\Delta U^0 > 1$, +ve dev from R.

unlike molecules attract more weakly as compared to like molecules.

$\Delta U^0 < 1$ - -ve deviation from Raoult's law

So therefore in this particular equation if I write the equation once more here just to define all the properties it is the correction term to Raoult's law is one minus x2 square Delta u0 by KT where K is nothing but the Boltzmann constant, T is the temperature as we all know this is the temperature and this Delta u0 this is the interaction energy this takes into account the differences in nature of interaction between like and unlike molecules.

Now when Delta u0 equals to 0 then naturally we find that interaction between like and unlike molecules similar. So therefore the exponential term it becomes almost equal to one and P2 can be given as x2 P2 saturated which is the case for ideal solution. When we find Delta u0 is greater than one under that condition we get positive deviation from Raoult's law and when does this happen? This positive deviation happens when you are unlike this happens when unlike molecules attract more weakly as compared to like molecules, right?

Under this condition as I have explained. So therefore evaporation is facilitated and vapor pressure is higher than that calculated by Raoult's law and if Delta u0 is less than one then in that case as I have said at unlike molecules attract more strongly and so therefore the total molecular interaction increases and the evaporation of molecules becomes more difficult and we have negative deviations from Raoult's law. So therefore we can have 2 types of deviations from Raoult's law.

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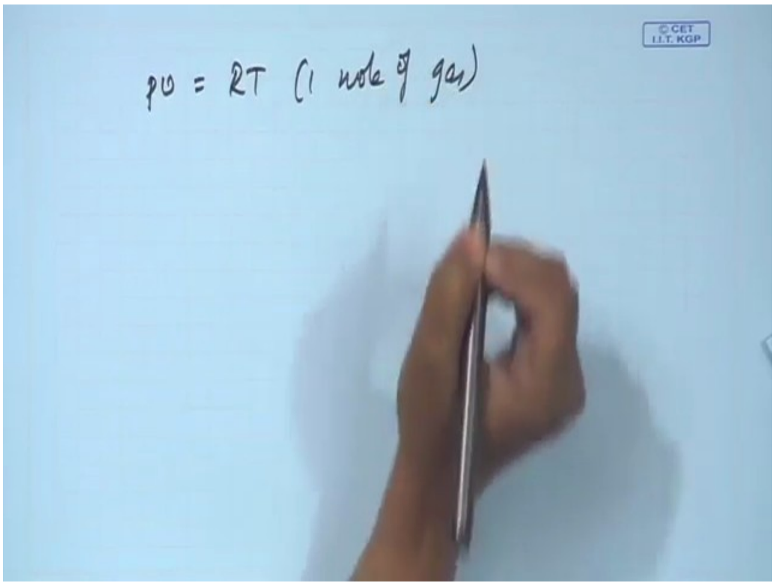

$pv = RT$ (1 mole of gas)

Now what to do under this case? If you have some deviations what are what is the thing? How we are going to account for the deviation? For everything you will notice that we take help of or rather we go to my to the ideal the gas state and try to find something. In the gas state what did we find? We found Pv was equals to RT for one mole of gas definitely most of the gases they were not ideal and as I had mentioned we had introduced a compressibility factor to account for non-ideal behaviour. So in this case also we found that for ideal solutions this is the situation. So therefore when it is not ideal people thought why not introduce a correction factor here such that this correction factor would take into account the deviations from ideality.

And the correction factor which was introduced here that is known as the activity coefficient and this particular correction factor they found that this gamma i can be greater than 0.

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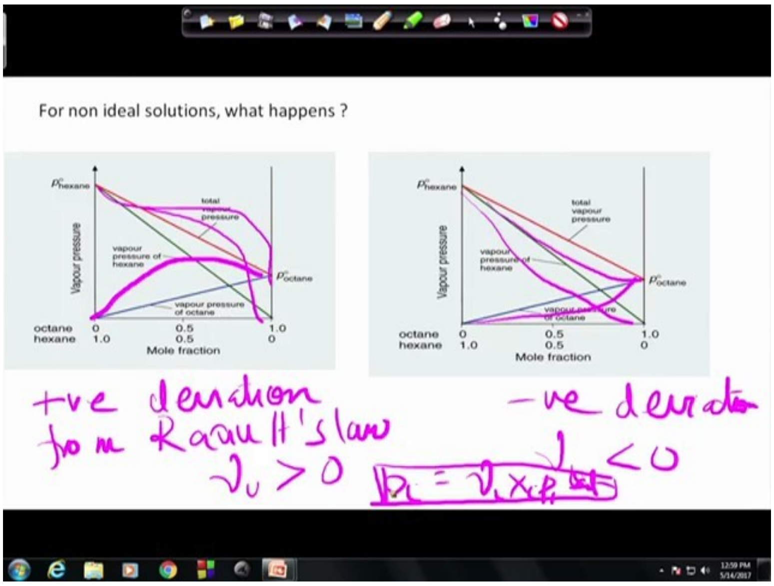

For non ideal solutions, what happens ?

+ve deviation from Raoult's law

$\gamma_i > 0$

-ve deviation

$\gamma_i < 0$

$\boxed{p_i = \gamma_i x_i p_i^{sat}}$

For this particular case gamma i should be greater than 0, here gamma i should be less than 0, right? So therefore what are the things which happened when a solution does not behave ideally? There are 2 things first thing is we find that there is either positive deviation or negative deviation from Raoult's law. So therefore we find that in this particular case the linearity is not followed and this is modified by introducing a gamma i here where we can write down Pi equals to gamma i XiPi saturated.

So therefore the equation for non-ideal case it becomes this. Along with that what happens? Just the way I have written down the there are some volume changes of mixing.

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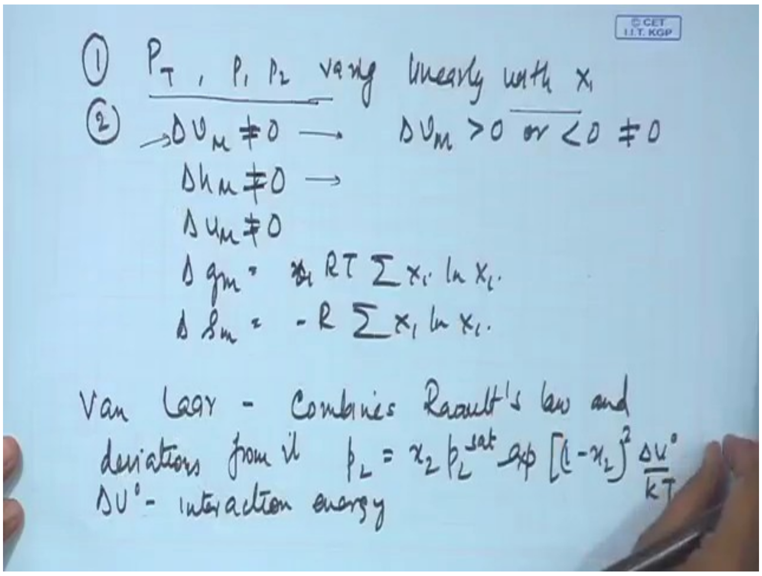

① P_T , P_1 P_2 vary linearly with x_1

② $\rightarrow \Delta v_M \neq 0 \longrightarrow \Delta v_M > 0$ or $< 0 \neq 0$

$\Delta h_M \neq 0 \longrightarrow$

$\Delta u_M \neq 0$

$\Delta g_m = RT \sum x_i \ln x_i$

$\Delta s_m = -R \sum x_i \ln x_i$

Van Laar - Combines Raoult's law and deviations from it $p_2 = x_2 p_2^{sat} \exp\left[(1-x_2)^2 \frac{\Delta u^\circ}{kT}\right]$

Δu° - interaction energy

Definitely under that cases we will not have Delta m equal to 0 we will have some Delta m some something some Delta Delta Vm which may be either greater than 0 or it may be less than 0 but it will not definitely be equal to 0 and this excess property which the solution has just because it is not ideal is known as the excess property of the solution.

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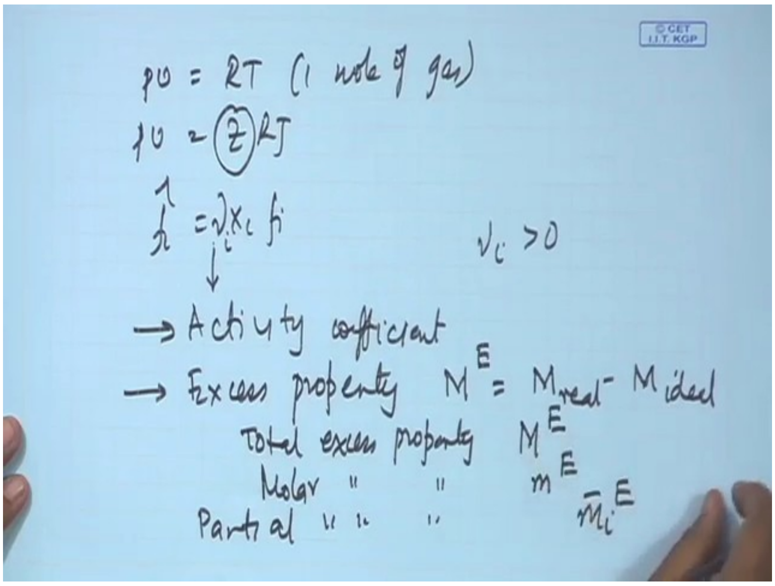

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$pv = RT$ (1 mole of gas)

$pv = \boxed{z} RT$

$\hat{f}_i = \gamma_i x_i f_i \qquad \gamma_i > 0$

→ Activity coefficient

→ Excess property $M^E = M_{real} - M_{ideal}$

Total excess property M^E

Molar " " m^E

Partial " " " $\bar{m}_i^E$

So therefore with advent of non-ideality what are the things that that we have come across we have come across an activity coefficient and we have come across another set of properties which are known as the excess properties something similar to concept as the departure functions or the residual properties which we had described for real gases you will remember under that condition the residual properties was real gas value minus ideal gas value.

In this case the excess property, suppose it is we denote it as M excess it is the M real value minus the M ideal value. So the property in the real solution minus the property in the ideal solution again when we went we have defined the set of property excess properties we have total excess properties which will be given by capital letters with a superscript E we will be having, naturally when we have excess properties all of these are extensive we will be having molar excess properties will be given by a small case letter.

And very sadly we will also be having a partial molar excess property which will be given by this particular set and we also find out that just the way of total properties molar properties in this case also they obey all the equations which are applicable for molar properties and total properties.

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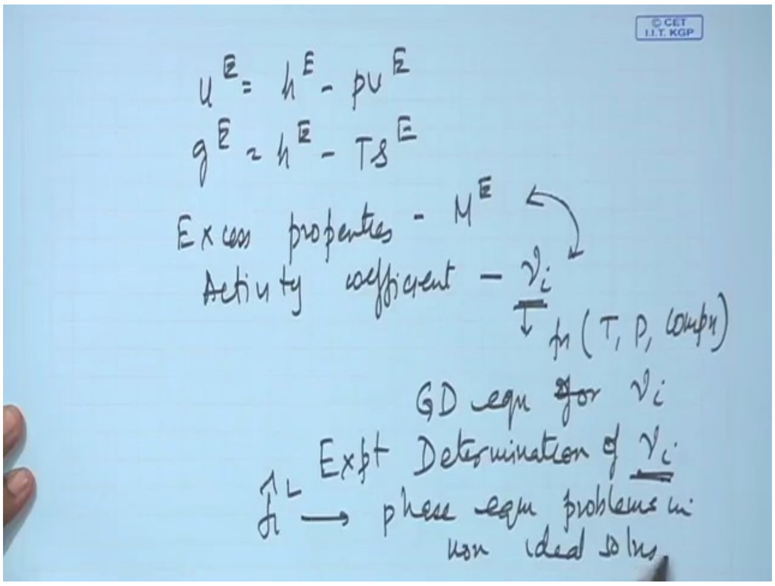

$u^E = h^E - pv^E$

$g^E = h^E - Ts^E$

Excess properties - M^E

Activity coefficient - γ_i

γ_i fn (T, P, compn)

GD eqn for γ_i

Expt Determination of γ_i

$\hat{f}_i^L \longrightarrow$ phase eqm problems in non ideal solns

For example in this particular case also we will have u excess equals to h excess minus pv excess. We will have g excess equals to h excess minus Ts E excess and so on and so forth. So in the next class what we do? We deal with non-ideal solutions and for dealing with non-ideal solutions we will be dealing with excess properties and we will be dealing with activity coefficients and we need to remember that the activity coefficients has come up because the solution is not ideal. The excess properties have come up because the solution is not ideal. So therefore there should be some relationships between the excess properties and the activity coefficient.

So in the next class we will be trying to establish relationships between activity coefficient and excess property and since we have defined a new property gamma i we would like to find out how gamma i it varies with temperature, pressure and composition. We would be deriving an equivalent Gibbs Duhem equation for gamma i and then we would like to find out, how we can determine gamma i from known experimental parameters because finally the prediction of gamma i would help us to calculate the fugacity in the liquid phase from where we can proceed for further phase equilibrium problems in non ideal solutions. So we enter into the domain of non-ideal solutions in the next class and it will make your journey of thermodynamics slightly more difficult but I hope you will be enjoying it with that, thank you very much.