# Chemical Engineering Thermodynamics
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**Lecture 52**
**Azeotropes**

Welcome back, so we have been talking last couple of lectures on vapor equilibria and making use of phi gamma approach to obtain phase equilibria, in the last lecture we talked about the difficulty in obtaining particularly when you consider the phi also and gamma also and one has to consider iteratively to obtain phase diagrams and one can also understand phase diagram based on the Gibbs free energy that is what also we covered that.

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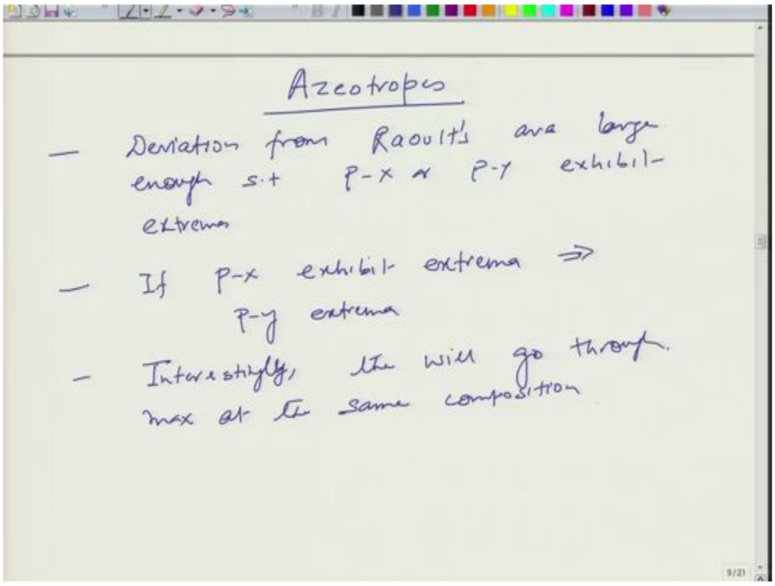
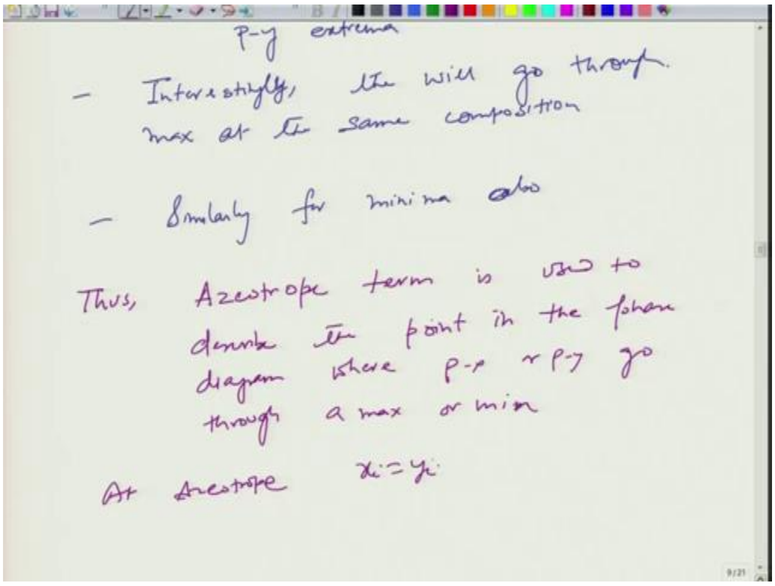


Azeotropes

- Deviation from Raoult's are large enough s.t P-x or P-y exhibit extrema
- If P-x exhibit extrema ⇒ P-y extrema
- Interestingly, the will go through max at the same composition



P-y extrema

- Interestingly, the will go through max at the same composition
- Similarly for minima also

Thus, Azeotrope term is used to denote the point in the phase diagram where P-x or P-y go through a max or min

At Azeotrope $x_i = y_i$

In today’s lecture I will start a case where basically we obtain such a scenario where the composition in the gas phase or in the liquid phase are same, so something we call it Azeotropes, so I will just describe that and a bit of when do we obtain such a scenario, so of course Azeotropes is again for the case when we have this deviation from Raoult’s law but more importantly the deviations are large enough such that px diagram or py diagram shows or exhibits extrema which could be maximum or minimum.

So if such a scenario is the case then essentially it will indicate some kind of Azeotropes or it may have scenario such as Azeotropes. The other thing is that if px exhibits extrema this also means py shows extrema. Now if you have such a scenario then what I am trying to make essential here is that, that in such a scenario interestingly this px or py they will go through maximum at the same composition. Which means basically px and py will intersect or rather coincide, the maximum will coincide leading to the same composition where the maximum is. Now this is the case of maximum but similarly you can have a scenario of a minimum also, so similarly you may have the behaviour obtain from minima also, so the maximum minimum depends on what kind of nature of unlike interactions with respect to like interaction.

So, in such a case where you observe this we call it Azeotropes and Azeotropes term is used to describe the point in the phase diagram where px or py go through maximum or minimum. So in other case at Azeotropes you will have xi is equal to yi, so let us take an example which we have been working on that is a chloroform and normal hexane, so let us try to explain this behaviour of Azeotropes using this example or this mixture which is a binary mixture.

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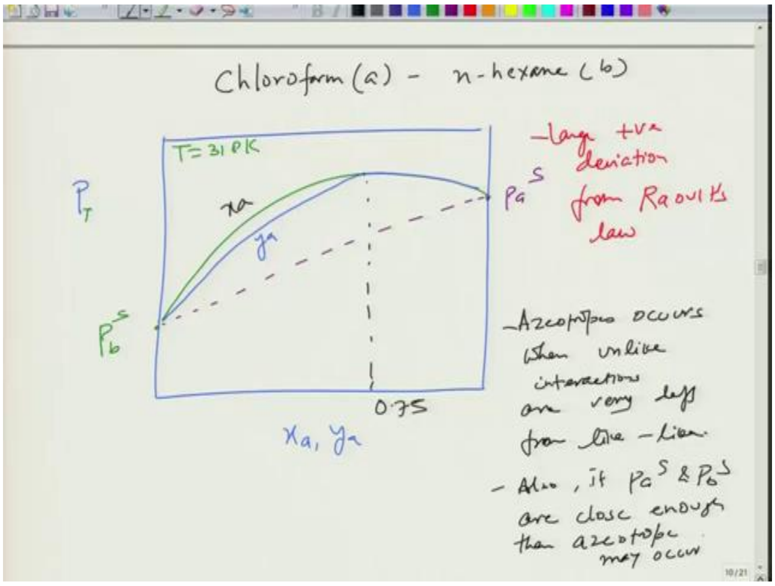
Chloroform (a) - n-hexane (b)

- large +ve deviation from Raoult's law

- Azeotropes occurs when unlike interactions are very less from like-like.

- Also, if $P_a^S$ & $P_b^S$ are close enough than azeotrope may occur

Chloroform let us say it is a and normal hexane let us say it is b, so if you plot it's px diagram, so this is the total P and this is your xa, ya that is the chloroform and this is the saturation pressure of PB at the specific temperature which we let us say we keep it 318 kelvin because of the experimental data available for us and this is the corresponding pa as which is that of the n hexane, so this is the saturation pressure at that particular temperature for chloroform and this is the saturation pressure of n hexane pure hexane at 313.

The Raoult's law behaviour can be represented by this dash line, but in this case for the case of this we obtain the following, the px diagram is something like this, so this is nothing but xa, so I need to have y such that it touches… let us consider that this is your ya, so this is not exactly the experimental data, so I am just drawing it to representing illustrating this particular behaviour where you have a scenario of maxima which is around 0.75 where you observe this clearly the Azeotropes condition.

Now what you look at… what you observe here is that the saturation pressure or for that matter the total pressure this may be t, so this is more than that of the case of either the saturation pressure here or here or in general which is more than at any point is more than that of the Raoult's law behaviour, so essentially it undergoes a Maxima, so if you think about it, it undergoes Maxima and then it goes down. So, this will be the case where unlike interactions are weak, where the particle is not able to retain its surrounding particles, so let us say a may not be able to retain the b and they will vaporise essentially leading to more particle in the vapour phase lead into the higher pressure.

So when you have such a scenario where like interactions are weaker and in that case you observe the total pressure more than that corresponds to the pressure obtain from the Raoult's law behaviour and this means this a positive deviation from the Raoult's law because the pressure is more than that, so this is an example of large positive deviation this we already talked about as far as the deviation is concerned but you observe this kind of behaviour where Azeotropes is there when you have a large deviation this is what we emphasise. So it undergoes Maxima and then it comes back to the saturation point, so that is one aspect which leads to the Azeotropes.

So it also means that based on this because of the large deviation it also means that the Azeotropes occurs when unlike interactions are very different from like-like and this is something which is evident. Now the other thing is that you will also notice that when the difference between this pb and pa are small then also we may have this Azeotropes that means if they are very close by, the saturation pressure for the pure competence are close by then also it can lead to such a scenario. If also…if pas and pbs close enough then Azeotropes may occur, so usually if there is a large difference then you may not see this kind of Azeotropes behaviour, it is not very common to have Azeotropic mixture when the saturation pressure or the difference between the saturation pressure of pure component is large, so that usually we do not see that because in order to get this maxima the deviation has to be extremely large which usually is not seen, so that is why it is not so common.

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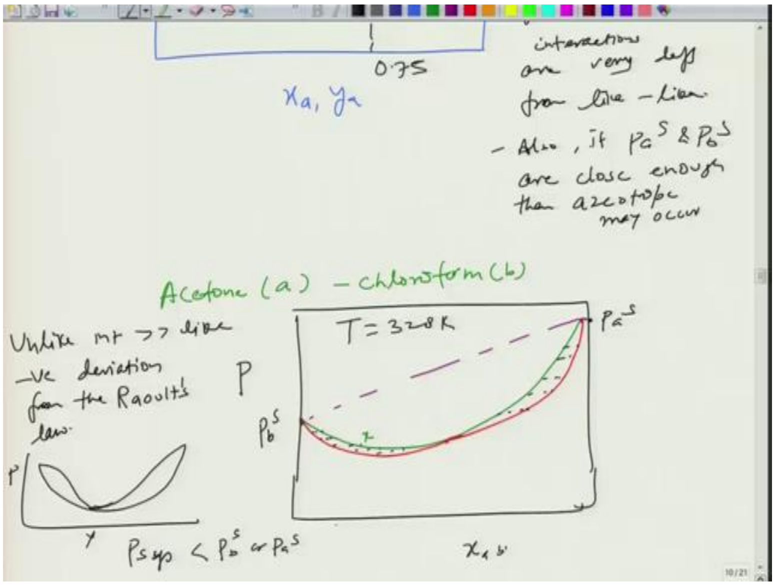


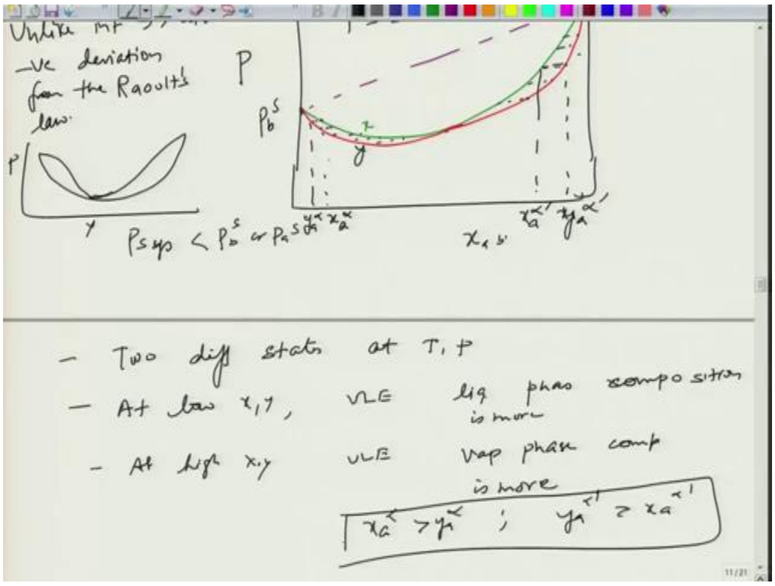
interactions are very diff from like-like

- Also, if $P_a^S$ & $P_b^S$ are close enough than azeotrope may occur

Acetone (a) - chloroform (b)

Unlike int >> like -ve deviation from the Raoult's law.

$P_{sys} < P_b^s$ or $P_a^S$



Unlike int ...
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$P_{sys} < P_b^s$ or $P_a^s$

- Two diff states at T, P
- At low x, y, VLE liq phase composition is more
- At high x, y VLE vap phase comp is more

$$\boxed{x_a^\alpha > y_a^\alpha \; ; \; y_a^{\alpha'} > x_a^{\alpha'}}$$

Now let us take another example, so the one which you talked about is the large positive deviation, so you could also find a case where you may have a negative deviation, so that is something which would be the case of let us say acetone a and chloroform, so this is where unlike interactions are extremely strong because of the molecule nature of acetone and chloroform, so they like each other so much that it does not allow the vaporisation to occur, so usually the pressure in the vapour phase is going to get reduced.

So we can draw a typical diagram of pressure as a function of x and here again we are using a and b, so this is your let us say pbs this is your pbs, so essentially the Raoult's law will be simply this dash line that will be from the Raoult's law but in the case of this, the following results come here, this is the typical let us say x data. For the case of y you may have something like this and here of course you have the tie lines would be something like this where you have this tie lines and then you have this another tie line.

So you can clearly see at a given pressure there is a possibility that you have 2 different regions one at a lower concentration, other at a different concentration having different equilibrium phases with different composition, so that clearly is possible, so this is again at a constant temperature which is from the experimental data it is 328 Kelvin. So this is the case where you have unlike interaction is much greater than like interaction leading to negative deviation from the Raoult's law. So you will always see something like this in the minima if you can draw like this you can also have this kind of thing, something like this, so with the minima as p versus x for example where of course p system is less than pbs or pas.

Now as I said there are 2 different states we observe here at T, P, so if you consider at lower temperature you have, so let us say at lower composition we have VLE where this is x and this is y where basically the liquid phase x composition is more and at higher xy you can still have VLE but here this is other way round, here the vapor phase composition, so if you are considering x is more and you can clearly see, so this is so this could be phase x of…so this is the y here so y of a alpha and if you compare the same thing here or here rather.

So this is your…if this is dash here let us say and this is your xa alpha dash and this would be your xa alpha and this is your ya alpha, so clearly says that xa alpha is greater than ya alpha and ya alpha dash is greater than xa alpha dash, so this is something which you would see in such a scenario. So that is graphically you can observe also, now you have observed this negative deviation, you have observed this positive deviation for such a case but positive deviation is more common in Azeotropes mixtures. Now we mention about pxy in terms of Azeotropes mixtures but you can also translate the same thing on txy also, so temperature and xy plot, so what you want to say is just opposite of that.

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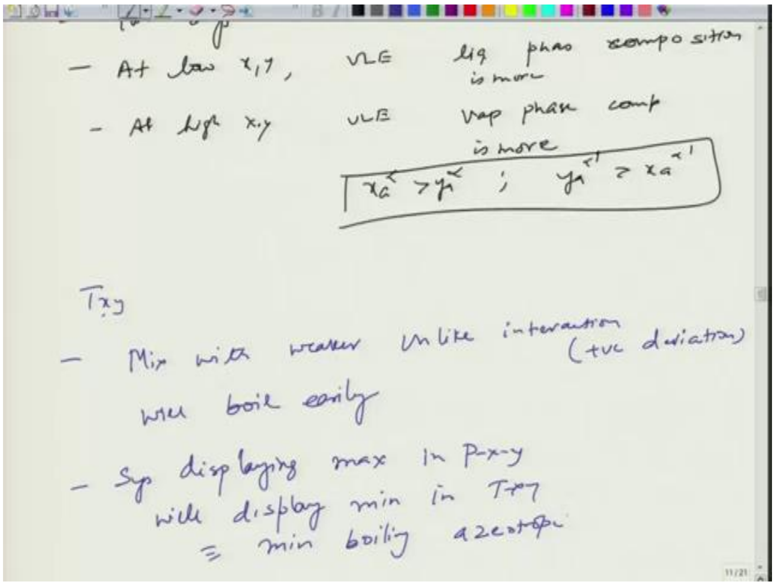

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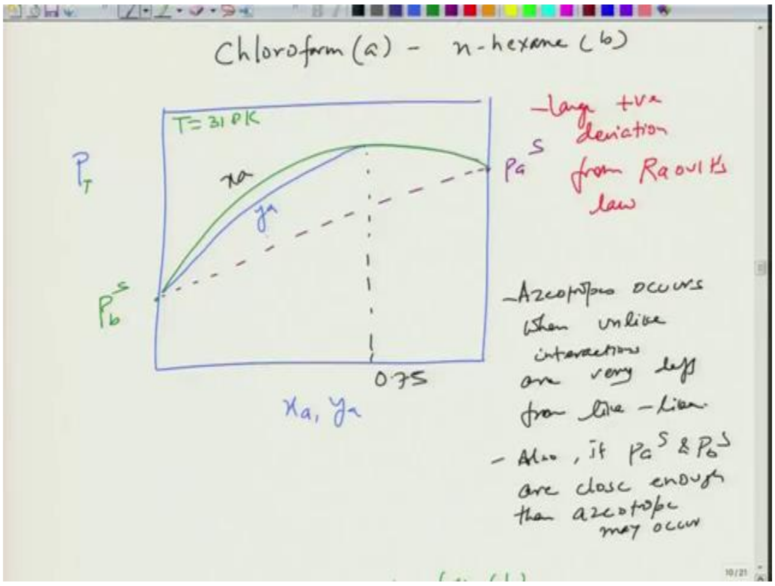
- At high x, y VLE vap phase comp is more

$$\boxed{x_a^{\alpha} > y_a^{\alpha} \; ; \; y_a^{\alpha'} > x_a^{\alpha'}}$$

Txy

- Mix with weaker unlike interaction (+ve deviation) will boil easily
- Sys displaying max in P-x-y will display min in T-x-y
  ≡ min boiling azeotrope



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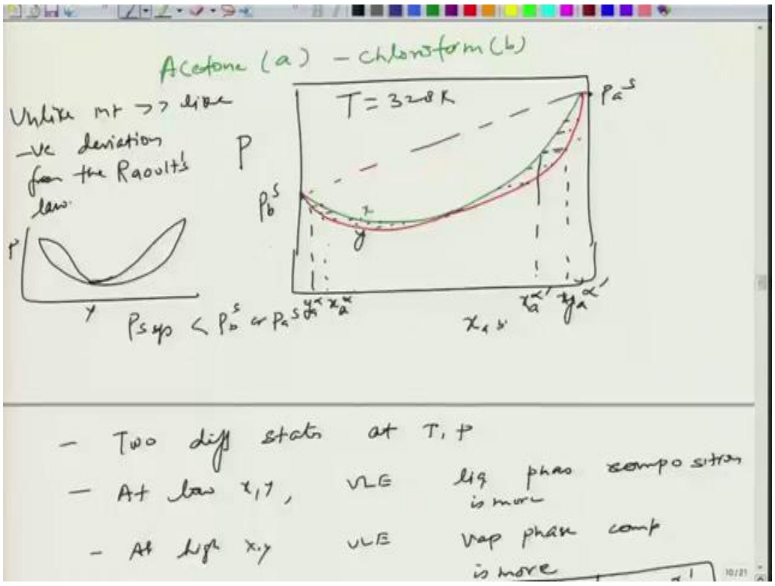

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So mixture with weaker unlike interaction, so in such case of force the vaporisation is weak, in such case of course that also means that the boiling is going to be much easier, so for this of course this is your positive deviation as far as the… Which we talked about using the pxy data, so this mixture will boil easily, so that means that the one which were on pxy we observed maximum, on the contrary for the txy for the same mixture we will observe minimum here, so the system displaying maximum in pxy will display minimum in txy and sometimes we also say this as minimum boiling Azeotropes. So let us try to draw for the 2 cases one is your acetone chloroform, so this is a positive one and this is negative one, so we can draw for both of them on the txy plot.

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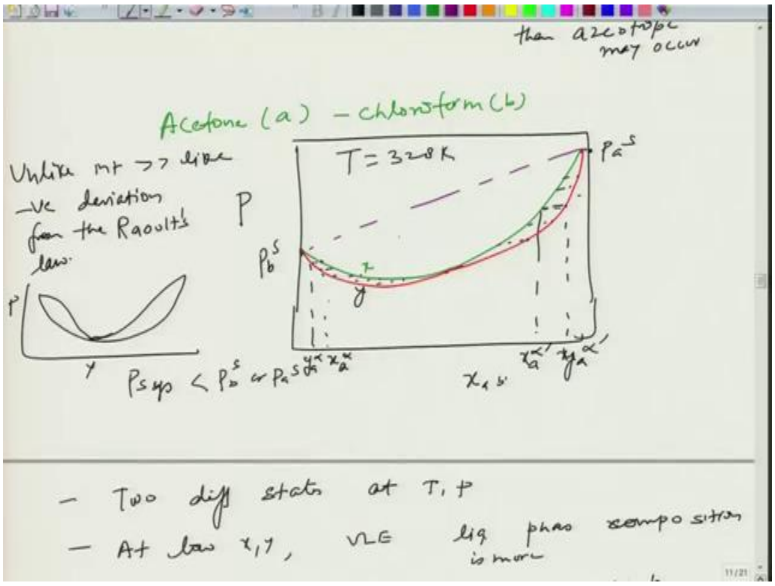

than azeotrope may occur

Acetone (a) – chloroform (b)

Unlike int >> like

–ve deviation from the Raoult's law.

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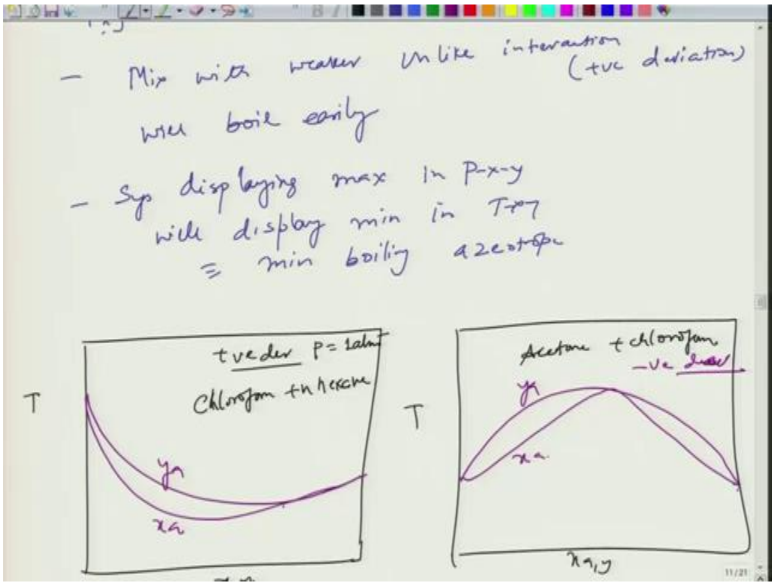

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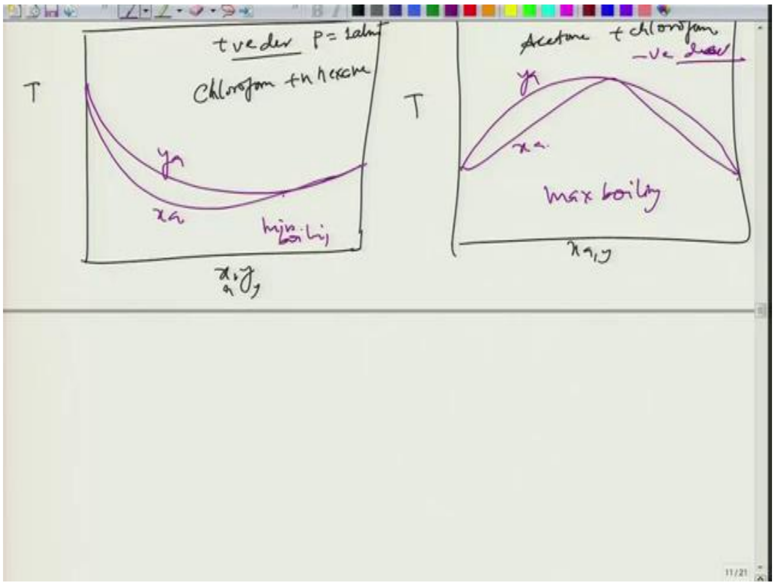

So this is the positive deviation, so let us look at it here you have something like this this be y of a and this will be your x of a. This should be little lower but this is one here, so this is your Azeotropes and the other cases your Ta versus xay okay this is xi yi, this is the case of chloroform and n hexane, this will be the case to acetone and chloroform, so this is something like this is your y of a this is your x of a negative deviation.

Now you can clearly see for the case of acetone chloroform this was negative from Raoult’s law but there was minimum for the case of pxy and the same if you plot it on txy is going to be maximum Azeotropes here. So this will be maximum boiling Azeotropes and this will be your minimum boiling Azeotropes because the temperature is lower than pure cases whereas the temperature is higher in this pure case, so this is your maximum boiling because this is more than the pure cases, this is your minimum boiling.

So that tells you about the concept of Azeotropes, now Azeotropes becomes a problem if you want to separate the mixtures using distillation column or using the boiling point clearly because of this constraint that the composition reaches up straight way basically both the phases have the same composition becomes difficult to segregate so it creates a problem as far as the distillation column is concern if you want to use fractional distillation column.

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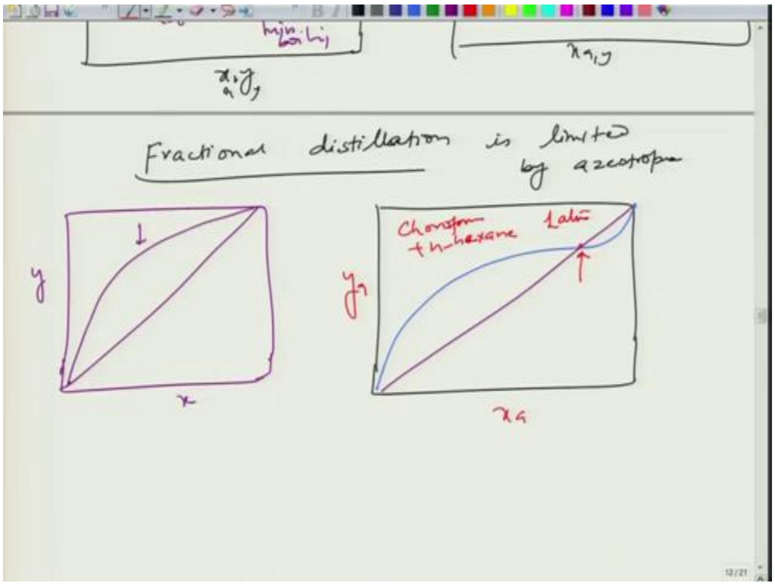
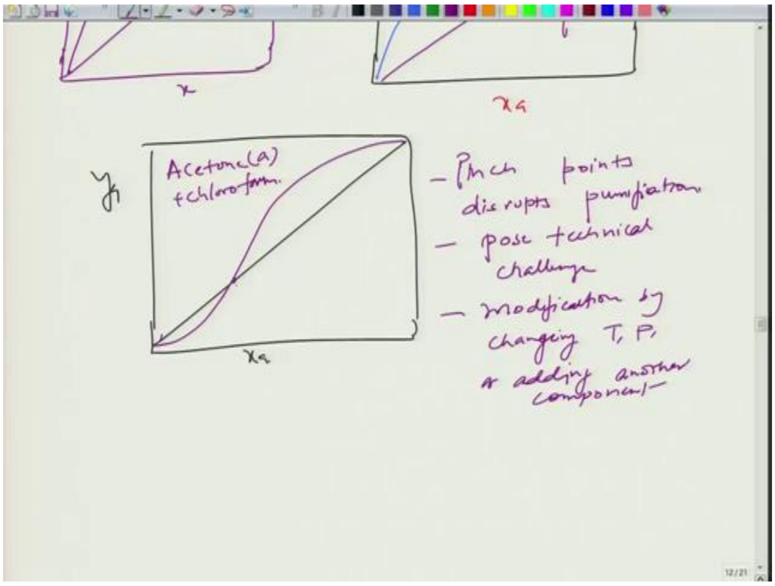


Fractional distillation is limited by azeotrope



- Pinch points disrupts purification
- pose technical challenge
- modification by changing T, P, or adding another component

So let me just give you an idea of that and then we can move to some kind of example. So fractional distillation column is limited by Azeotropes. So take an example of again a chloroform and hexane. So what we want in typically if you consider let us say case of any mixture, so we prefer to plot is y and x, now if you have this…if the actual mixture is away from this for example this could be something like this then this will be the actual mixture this is your basically tells you the equal composition, so if it is far from here, then, in principal you can make use of fractional distillation very well but in the case of Azeotropes the following is observed that so you may have something like this for the case of chloroform and n hexane.

So you have the following situation and this is the case of course because of the fact that this is xy plot ya and xa so this is the point where the Azeotropic point is there and this limits the efficiency of that, that means if you are going from this point to this you cannot go beyond that, so that means no further separation is possible once you reach this point using the simple fraction distillation. So this is the case of chloroform and n hexane and this is one atmosphere. The other case was also for this acetone so if you just plot of acetone for the sake of completion then this is what we are going to get again ya, xa and here you have something like this. Again the same issue of this point here and sometime we call this as a pinch point.

So that means the pinch point, so this is let me just complete here this is acetone and chloroform where acetone is a and now here the chloroform is a. Now this pinch point disrupts purifications, so if I am using fractional distillation then you cannot use it beyond 4 on this point and hence this poses post technical challenge. Then that means how do you further separate if you have encounter such a state, so one can do that by…one can modify this phase diagram by of course change in the temperature pressure and as well as adding some component, so you can get rid of pinch point by…Modification by changing temperature and pressure or adding another component.

So this is something which would…this is commonly done but of course you can understand the issue of a particularly this Azeotropes point and how does that effects the separations as such. The more important thing is Azeotropes occurs because of the intermolecular nature between the different species, it has to be a large deviation from Raoult's law and depending on the unlike interactions strength related to like interaction you may get a positive deviation or you may get negative deviation that means you may get something call maximum boiling point as we discuss or minimum boiling point and that was 2 examples we considered.

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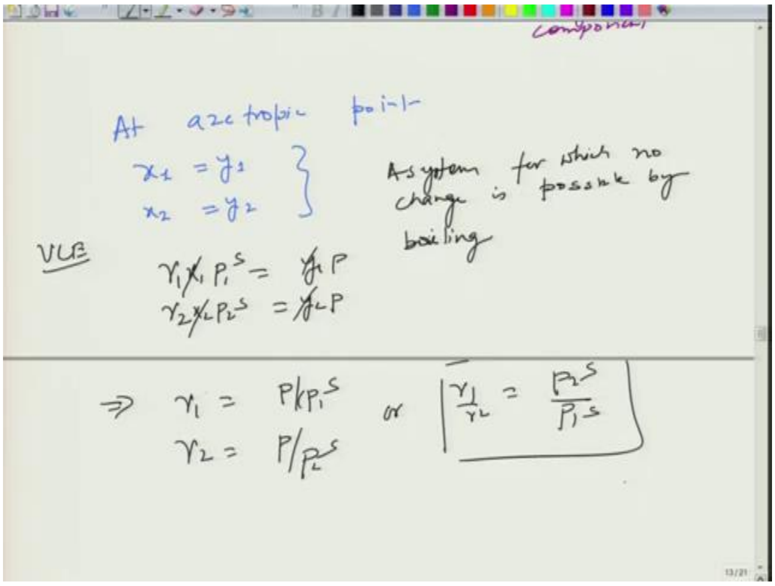


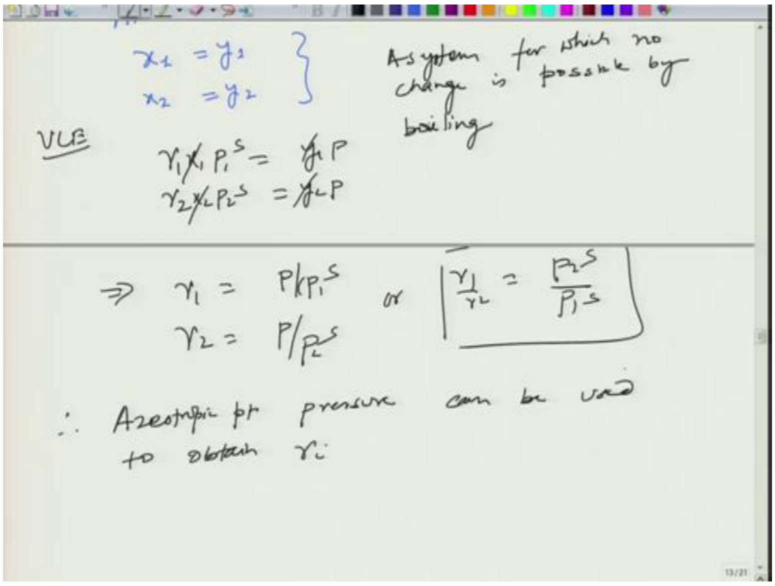
At azeotropic point

$$\left.\begin{array}{l} x_1 = y_1 \\ x_2 = y_2 \end{array}\right\}$$ A system for which no change is possible by boiling

VLE

$$\gamma_1 \cancel{x_1} P_1^S = \cancel{y_1} P$$
$$\gamma_2 \cancel{x_2} P_2^S = \cancel{y_2} P$$

$$\Rightarrow \gamma_1 = P/P_1^S \qquad \text{or} \qquad \boxed{\frac{\gamma_1}{\gamma_2} = \frac{P_2^S}{P_1^S}}$$
$$\gamma_2 = P/P_2^S$$



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$$\gamma_2 = P/P_2^S$$

∴ Azeotropic pt pressure can be used to obtain $\gamma_i$

So in Azeotropic point as we must have understood by now that Azeotropic point x1 if they are let us say binary component should be equal to y1 which also means that it implies that x2 is y2, so this condition also indicates that you cannot change the system by just boiling, so a system for which no change is possible by boiling. Now here this point another thing which you can do is you can also use this Azeotropic point to find couple of things such as for example activity coefficient, so let me just write down further Azeotropes compositions so assuming that you have a system now where you have observed this Azeotropes point.

So given this if you apply the VLE criteria which still will remain true is that gamma 1 x1 and P1 sat is y1 P assuming that your phi 1 sat and phi are 1 and as well as the pointing correction can be considered as one so if you consider this for this one component is this in relation and the second is x2 p2s is y2p, so this can be cancelled because it is Azeotropic which means that gamma 1 is nothing but the ratio of system pressure and the saturation pressure of the component 1.

Similarly, gamma 2 is the ratio of system pressure and saturation pressure of the pure component too or in other word gamma 1 by gamma 2 is nothing but p2s by p1s. So this is something which we can also use if you want to find out let us say the gamma is here or the activity coefficient so essentially if you can use Azeotropic point to obtain so you would have the total pressure of the system at which this Azeotropes occurs and of course if you have the handle of information of the saturation pressure of the pure component then you can find out the activity or the gamma, so that means Azeotropic point pressure can be used to obtain gamma i so that is come thing which we can do that.

$$At\ azeotrope\ point \quad x_1 = y_1;\ \ x_2 = y_2$$

$$VLE:\ \ \gamma_1 x_1 P_1^S = y_1 P \qquad \gamma_2 x_2 P_2^s = y_2 P$$

$$or,\ \ \gamma_1 = \frac{P}{P_1^S} \qquad \gamma_2 = \frac{P}{P_2^S}$$

$$or, \qquad \frac{\gamma_1}{\gamma_2} = \frac{P_2^s}{P_1^s}$$

So I think because top here and this probably as given the sound foundation for us to take one example and particularly asking a very pertaining question that if somebody ask this that how we can prove that at Azeotropic condition which means that there is maxima, the composition needs to be same, so something which we can try to prove, so these 2 things which we have to do which is to work on the examples, making use of this Azeotropic conditions and the second is to prove that x1 is equal to y1 or xi is equal to yi for Azeotropic conditions, so this is something which we will take it up in the next class so I will see you in the next class.