Chemical Engineering Thermodynamics
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Lecture-57
Solid-Liquid Equilibrium examples and properties

Welcome back, last couple of lectures; I have been talking about basically liquid vapor liquid equilibria followed by solid liquid equilibria. And then subsequently, we looked into the way the approaches for using which we can develop the phase equilibria.

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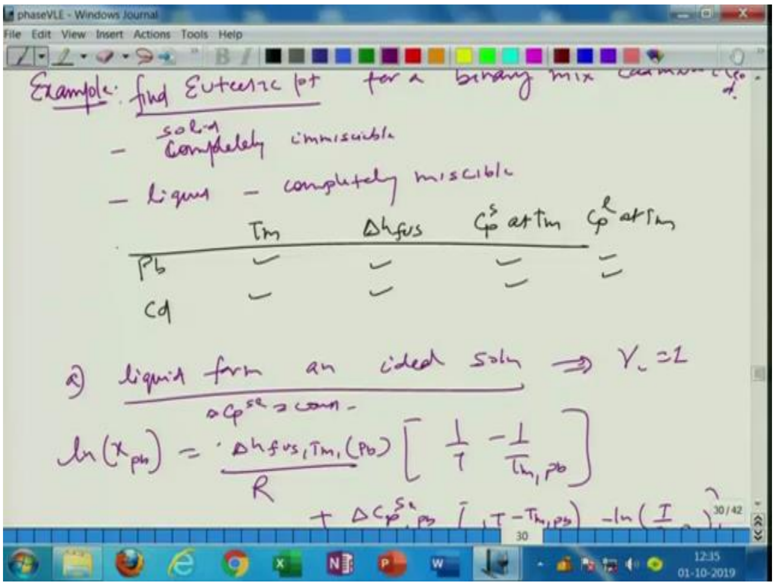

Example: find Eutectic pt for a binary mix

- solid completely immiscible
- liquid - completely miscible

	T_m	Δh_{fus}	C_p^s at T_m	C_p^l at T_m
Pb	✓	✓	✓	✓
Cd	✓	✓	✓	✓

a) liquid form an ideal soln $\Rightarrow \gamma_i = 1$

$\Delta C_p^{sl} = $ const.

$$\ln(x_{Pb}) = \frac{\Delta h_{fus,T_m,(Pb)}}{R}\left[\frac{1}{T} - \frac{1}{T_{m,Pb}}\right]$$

$$+ \Delta C_{p,Pb}^{sl} \left[\left(T - T_{m,Pb} \right) - \ln\left(\frac{T}{\ldots} \right) \right]$$

So something which we have taken these examples of eutectic mixtures and also come up with an expression for which we can get temperature verses compositions that was our last lecture.

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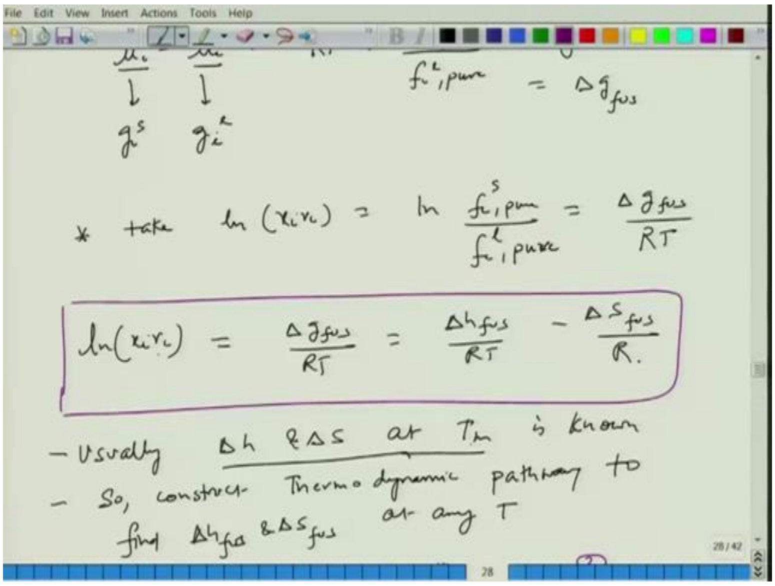

g^s g_i^L

$f^L_{i,pure} = \Delta g_{fus}$

* take $\ln(x_i \gamma_i) = \ln \frac{f^s_{i,pure}}{f^L_{i,pure}} = \frac{\Delta g_{fus}}{RT}$

$$\boxed{\ln(x_i \gamma_i) = \frac{\Delta g_{fus}}{RT} = \frac{\Delta h_{fus}}{RT} - \frac{\Delta s_{fus}}{R}.}$$

- Usually $\underline{\Delta h \ \& \ \Delta s \text{ at } T_m}$ is known
- So, construct Thermodynamic pathway to find Δh_{fus} & Δs_{fus} at any T

So this is what we did in the last lecture where we developed a relation of composition activity with basically the temperature. And then we made use of the fact that we can relate a Delta H and Delta h of fusion at a given temperature to that of the enthalpies and the change in the entropies of the fusion at that T m of melting temperature.

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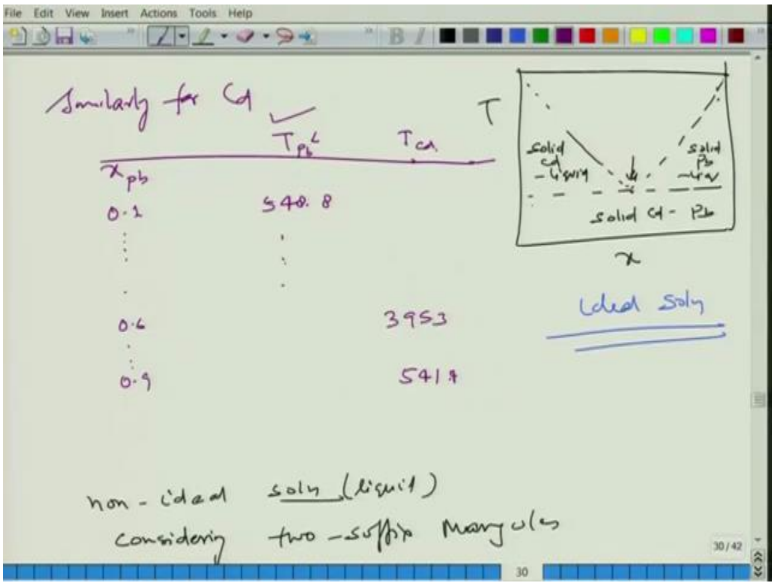
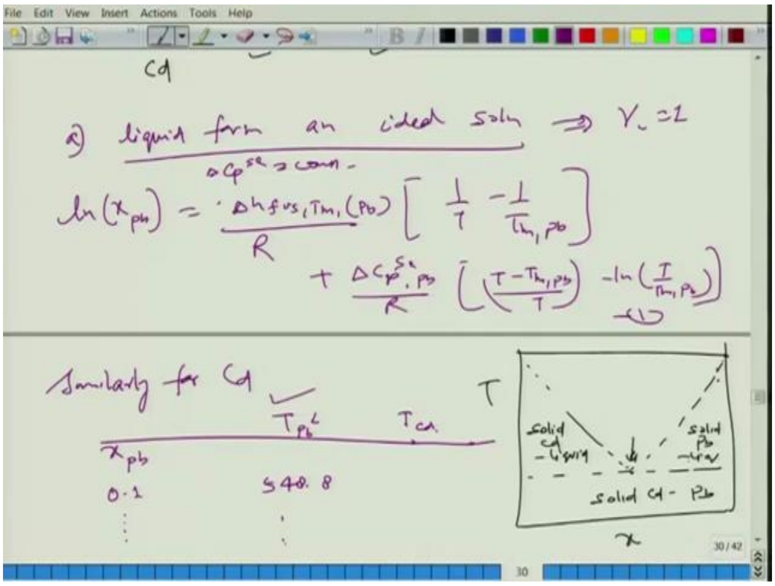


Similarly for Cd

x_{pb}	T_{pb}^L	T_{cd}
0.1	540.8	
⋮	⋮	
0.6		3953
⋮		
0.9		541 [illegible]

Ideal Soln

non-ideal soln (liquid)
considering two-suffix Margules



Cd

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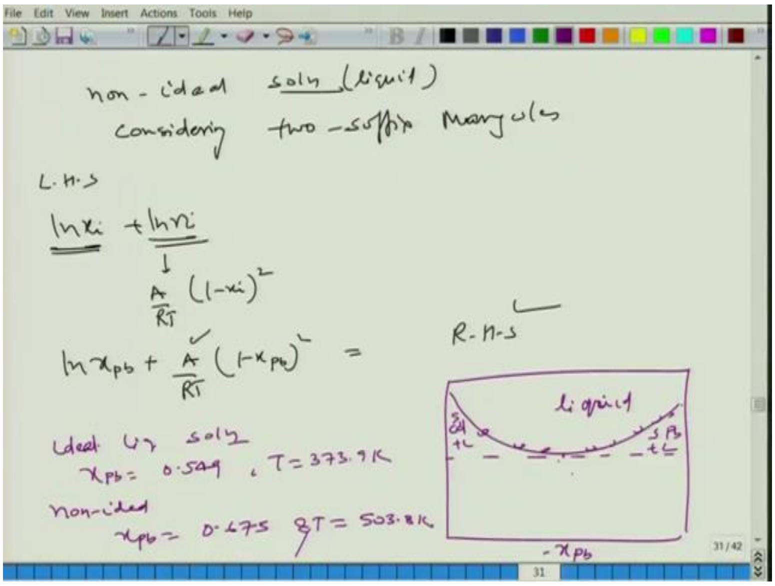
$$\ln(x_{pb}) = \frac{\Delta h_{fus,T_m,(Pb)}}{R}\left[\frac{1}{T} - \frac{1}{T_{m,Pb}}\right] + \frac{\Delta C_{p,Pb}^{sl}}{R}\left[\left(\frac{T-T_{m,Pb}}{T}\right) - \ln\left(\frac{T}{T_{m,Pb}}\right)\right]$$

-(1)

Similarly for Cd

x_{pb}	T_{Pb}^L	T_{Cd}
0.1	540.8	
⋮	⋮	



non-ideal soln (liquid)

considering two-suffix Margules

L.H.S

$\ln x_i + \ln \gamma_i$

$\downarrow$

$\frac{A}{RT}(1-x_i)^2$

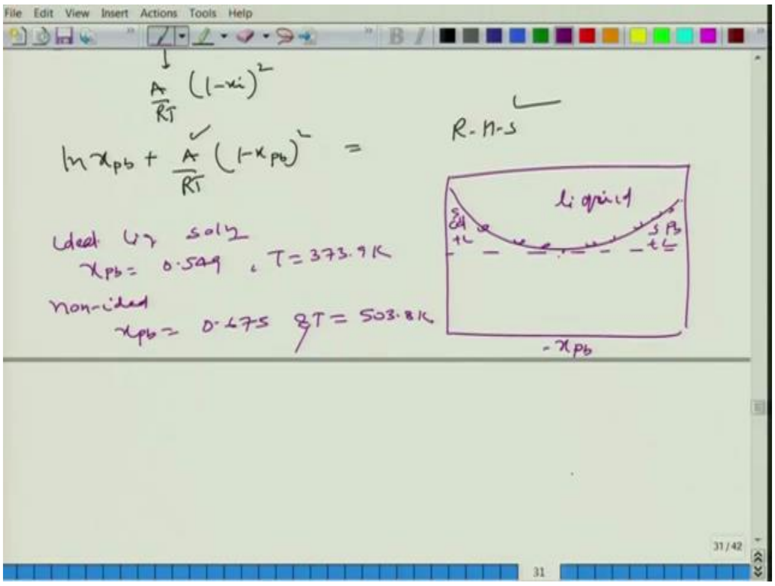
$\ln x_{pb} + \frac{A}{RT}(1-x_{pb})^2 =$ R.H.S

Ideal liq soln

$x_{Pb} = 0.549$, $T = 373.9\text{ K}$

non-ideal

$x_{pb} = 0.475$ & $T = 503.8\text{ K}$



$\downarrow$

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Ideal liq soln

$x_{Pb} = 0.549$, $T = 373.9\text{ K}$

non-ideal

$x_{pb} = 0.475$ & $T = 503.8\text{ K}$

But in many cases, you may see a different kind of application, so here we try to use temperature and the composition where we use this particular lead and cadmium examples to get the eutectic point by drawing or finding out this particular line which is nothing but the solid liquid line and for different composition values okay. And if you can get that you can also obtain eutectic points here. Now, this is something which you are it not elaborated more and something which you can look at it in details in the test book.

But it gives you a flavor that you know how one can use these kind of expressions and little bit of approximation to obtain it. So, if you use ideal solution it turns out to be very simple a simple analysis. But if you use activity models and then things are little more realistic and the values are more realistic as well. And, hence, one need to be little careful about ignoring the fact that the system in such case it would be non-ideal particularly that the liquid phase.

Now there are other cases or other examples, where we can also make use of this and demonstrate it something which you can do it on your own. But let me just take a specific impact or effect of such a kind of fur mixtures particularly for solids which are non-evaporable such as for example salt in liquid what happens to the properties?

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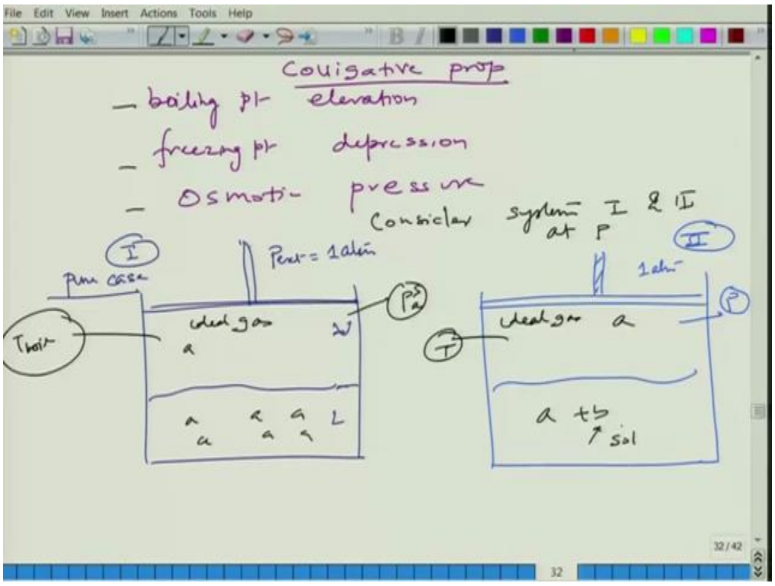

So, if you consider properties such as a boiling point okay freezing point. These are the properties which get affected by the presence of solute in a very small quantity. For example, this we will get elevated and this may get depressed okay. So when you have a presence of a solute and which impacts this kind of a property even and which just does not just depends on the nature of but rather on the concentration and such a kind of property is called colligative properties.

So for such properties we will have something like this where the boiling point gets elevated. That means if we add the concentration of a solute the temperature increases at which the system boils okay. Similarly, if you increase the concentration the freezing point depress you know reduces and that is what we call it a depression point. And third is osmotic pressure something will I will talk about this bit that in such a case, we may see this kind of properties of behavior.

But let me just focus on understanding of this such a system by considering a very simple illustration here. So, let us look at a system okay where you have pure component and this is maintained at let us say atmospheric pressure. That says one atmosphere right, so this is your piston here right. And here you have let us say consider only this for the moment that this is just an example of vapor liquid case, where we are putting some kind of a solute which in a dilute condition.

But let me just first take the case, where we have we say case one which is a pure case okay and the system is at pressure. So this is the system which one is at pressure P, so we are considering cases one case. Or in this case so consider systems let us say it is 1 and 2 which I am going to describe now a bit which will be at pressure P. So this would be your P pressure and this would be your pressure saturation pressure of component a if there is a pure component here.

So these are all component here right and since this is a saturation pressure here and the corresponding temperature would be your T boil. Let us say okay for the pure case I will consider another case, where basically now we have added a big component b which is a solute and we assume that this does not evaporate and in a sense it does not vaporize. So is that could be the case let us say salt. So now you have another system which we say system two and this is again the one atmosphere that is external pressure.

So P external is this, now what we are saying is that the pressure is maintained at at P so we do have a similar situation that we have pressure P. Now here we have a species a plus b, the b is the solute which does not vaporize here. So it remains in the liquid phase and here we have the vapor, vapor will consider like a ideal gas which will be only consisting of a, so this is also a let us say idle gas.

So what we do not know at this point is? Let us say what is the let us say the T the temperature at which this system is at equilibrium. So there will be the corresponding T boil. So we can now try to find out what happens to T boil? When you add a small component of b which remains in the liquid phase that means does not vaporize.

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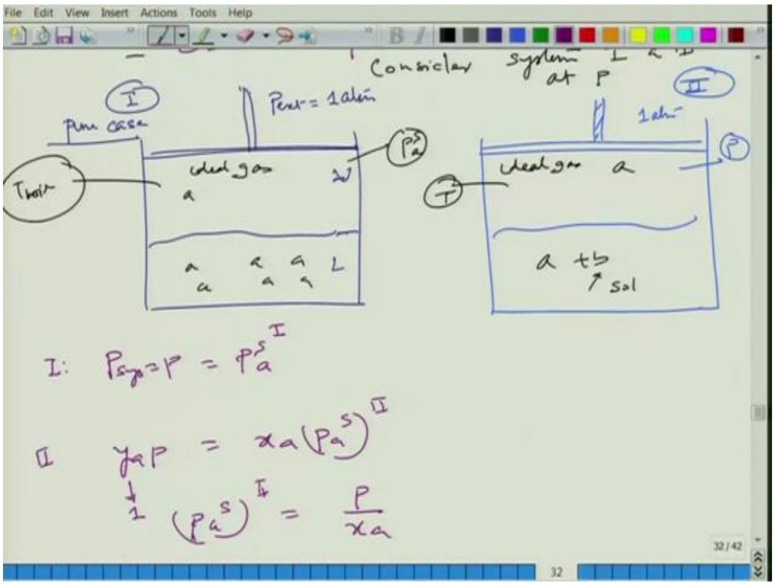
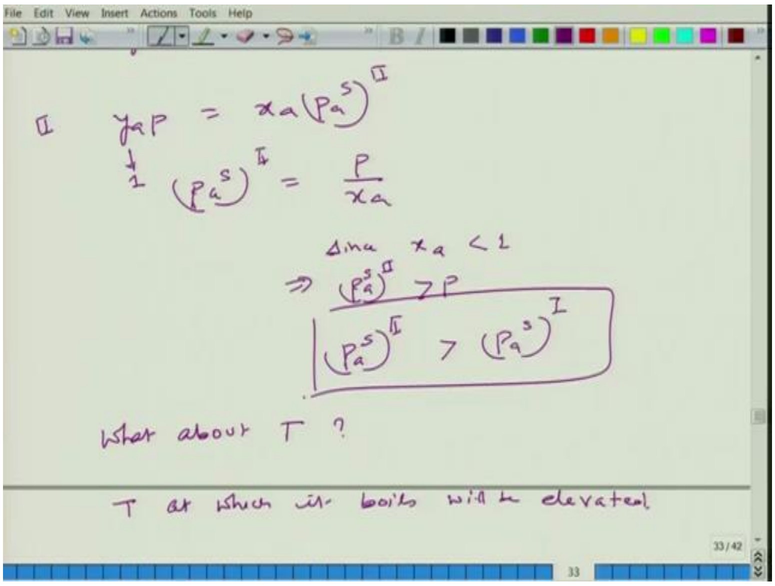


$$I:\ P_{sys} = P = (P_a^s)^{I}$$

$$II\quad y_a P = x_a (P_a^s)^{II}$$

$$y_a \to 1 \qquad (P_a^s)^{II} = \frac{P}{x_a}$$



$$II\quad y_a P = x_a (P_a^s)^{II}$$

$$y_a \to 1 \qquad (P_a^s)^{II} = \frac{P}{x_a}$$

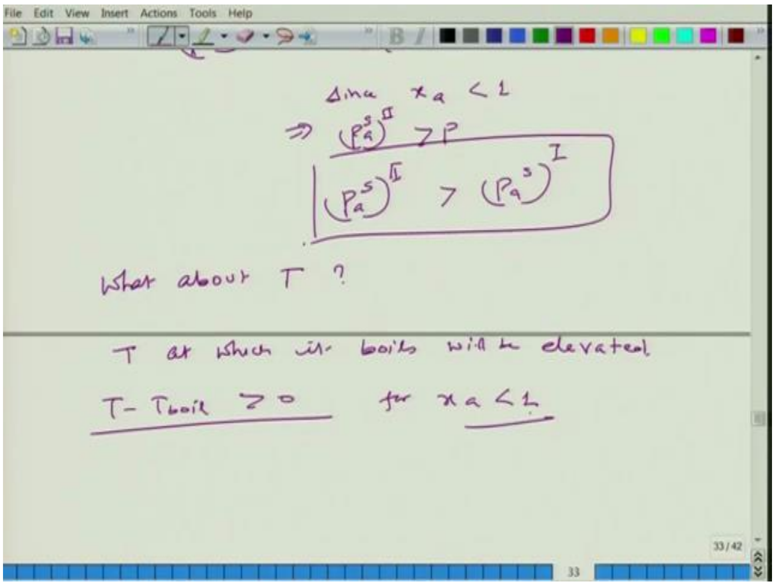
since $x_a < 1$

$$\Rightarrow (P_a^s)^{II} > P$$

$$\boxed{(P_a^s)^{II} > (P_a^s)^{I}}$$

What about T ?

T at which it boils will be elevated



Since $x_a < 1$

$$\Rightarrow (P_a^s)^{II} > P$$

$$\boxed{(P_a^s)^{II} > (P_a^s)^{I}}$$

What about T ?

T at which it boils will be elevated

$T - T_{boil} > 0$ for $x_a < 1$

So here it is now, so let us look at a system one and we apply the basic equilibrium conditions. So, P system or the system of this pressure of the system is nothing but the P, the P of the system is, P is P saturation a okay and so that is one thing which we can clearly right. And for the second case we can use the Raoult's law and considering this idle gas we have this y a P that is for the vapor phase. And then you have this x a and again we are considering very dilute very dilute condition and this way we can remove the rest of the things.

So what remains is the saturation pressure for the system two? So, I would have to say this to be system two for this for the system two and this is system one. Now, why a here being a pure component here in this gas phase would be one. So this would be one, so this P a s of system two that is the corresponding saturation pressure. Here at system two is nothing but this is the system pressure divided by composition.

The saturation pressure of component a is basically it is just a ratio of pressure and the composition. Now this being x a will be less than 1, since x a is less than 1 which means that p a s here would be greater than P right. So this is very clear from here and which essentially means that P a s for the second system the saturation pressure of component a for the second system is greater than such into pressure of component one for the system one.

$$P_{sys} = P = P_a^{sI}$$

$$y_a P = x_a (P_a^s)^{II}$$

$$P_a^{sI} = \frac{P}{x_a} \quad x_a < 1$$

$$P_a^{sII} > P$$

$$P_a^{s^{II}} > P_a^{s^{I}}$$

So it tells you very clearly that upon adding component b the pressure the saturation pressure of a increases for maintaining such an equilibrium. So this is something which is clearly evident. Now you may ask the question that what about the temperature T here, so what about T. We know that as you increase the pressure the corresponding temperature at which is boils will also increase. So hence clearly the temperature for such a system would be higher or compared to that of the pure case.

So in other word we are saying that the T boil that means the T at which it boils will get elevated or will be elevated. So, it is going to be higher than that then the tea boil, so which means T minus T boil should be greater than 0 for x a less than 1. That is what we are trying to make such a case particularly for the binary mixtures or for them in general mixtures but we are considering just a binary mixture here.

$$T - T_{boil} > 0 \;\; for\; x_a < 1$$

So, the question is now how do you come up with an expression which relates this change in the the Delta T boiling to other parameters? So you may do a simple experiment to observe the change in the boiling temperature but can you relate the delta T that is a change the volume temperature to variables such as your activity coefficients. So how do we do that?

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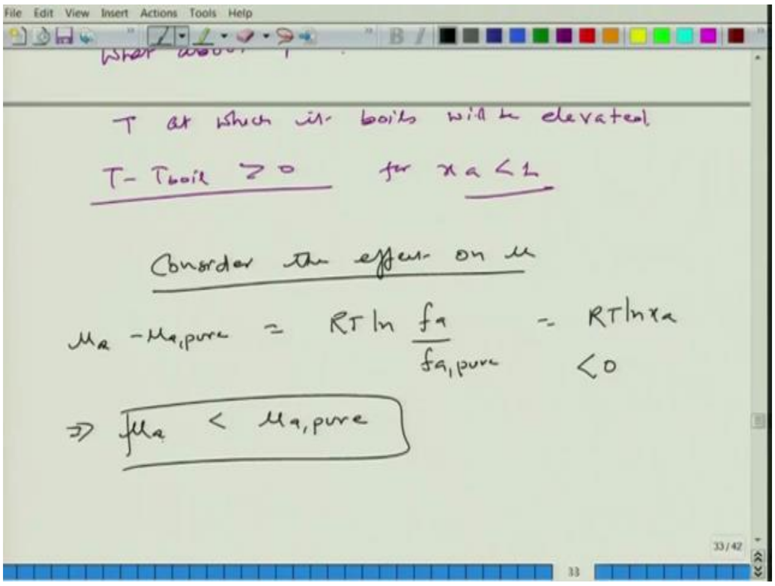


T at which it boils will be elevated

$T - T_{boil} > 0$ for $x_a < 1$

Consider the effect on μ

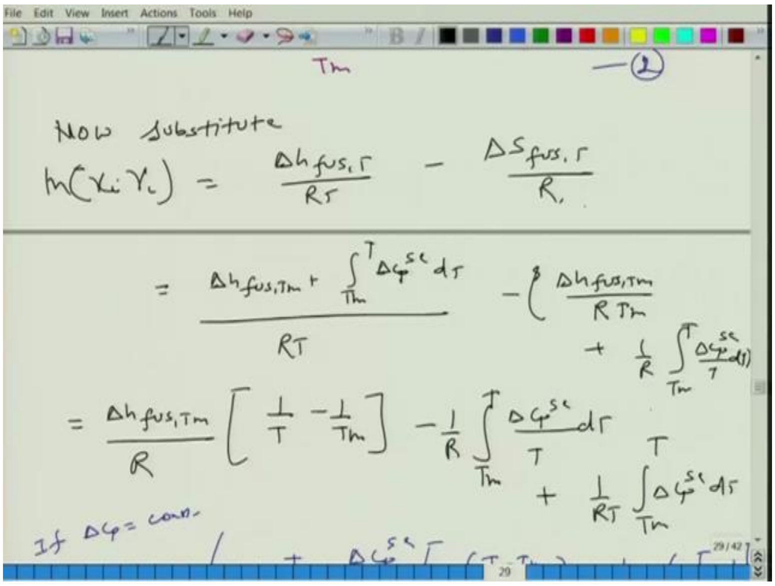
$$\mu_a - \mu_{a,pure} = RT \ln \frac{f_a}{f_{a,pure}} = RT \ln x_a < 0$$

$$\Rightarrow \boxed{\mu_a < \mu_{a,pure}}$$

$$Effect\ on\ \mu$$

$$\mu_a - \mu_{a,pure} = RTln\frac{f_a}{f_{a,pure}} = RTln\ x_a < 0$$

$$\mu_a < \mu_{a,pure}$$



Tm — ②

Now substitute

$$\ln(x_i \gamma_i) = \frac{\Delta h_{fus,T}}{RT} - \frac{\Delta s_{fus,T}}{R}$$

$$= \frac{\Delta h_{fus,Tm} + \int_{Tm}^{T} \Delta c_p^{sc}\, dT}{RT} - \left(\frac{\Delta h_{fus,Tm}}{R\,Tm} + \frac{1}{R}\int_{Tm}^{T} \frac{\Delta c_p^{sc}}{T} d(T) \right.$$

$$= \frac{\Delta h_{fus,Tm}}{R}\left[\frac{1}{T} - \frac{1}{Tm}\right] - \frac{1}{R}\int_{Tm}^{T} \frac{\Delta c_p^{sc}}{T} dT + \frac{1}{RT}\int_{Tm}^{T} \Delta c_p^{sc}\, dT$$

If Δc_p = const.

So, if you can do an experiment you may also be able to figure it. You may also be able to find out the activity and from there you can extract some information's of the model parameters if you want to represent activity and some models representing that particular activity. So in order to get to that point let us consider the case of chemical potential and an impact of this solute on the chemical potential. So consider the an effect on mu okay, so again we are considering a species and b a plus b where b is the solute here.

So if we are saying mu a minus mu a pure okay, so this is your chemical potential difference this we can clearly write based on our earlier understanding as RT Ln, F of a in the mixture divided by F of a of pure. And this can easily be written as RT Ln x a based on our earlier definition. Now this also we can see that this because x a is less than 1 and hence this has to be less than zero which essentially means mu of a is less than mu of a pure, right.

Now what we can make use of at this point that since we are talking about just a chemical potential difference here. The next question which we can ask is can we also relate the composition and activity to this heat of the enthalpy change and the entropy change upon the presence of a small component. So here if you recall we have used this phase transition or in this case effusion lines for the solid-liquid equilibrium be related, we relate this log of Ln of x I gamma I to this particular term.

And later we showed that this can be written as this Delta h fusion Tm r with this. But this particular expression can be written for the current case which we are discussing for also for the vapor-liquid transition okay. Where the Delta h of fusion will be represented or will be replaced by Delta H of vaporization. So I can write the same expression, I can prove it in the same way and write the following expression without going to details, so in the following to way.

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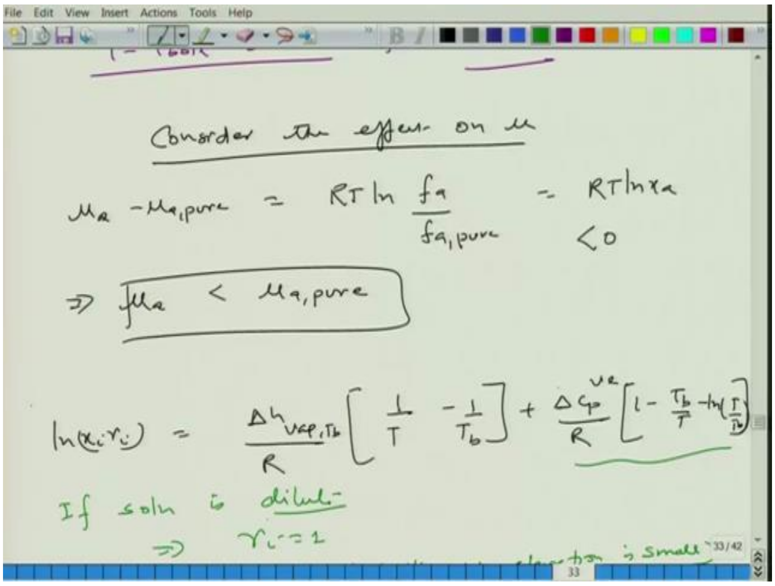

Consider the effect on μ

$$\mu_a - \mu_{a,pure} = RT \ln \frac{f_a}{f_{a,pure}} = RT \ln x_a < 0$$

$$\Rightarrow \boxed{\mu_a < \mu_{a,pure}}$$

$$\ln(x_i \gamma_i) = \frac{\Delta h_{vap,T_b}}{R}\left[\frac{1}{T} - \frac{1}{T_b}\right] + \frac{\Delta c_p^{vl}}{R}\left[1 - \frac{T_b}{T} - \ln\left(\frac{T}{T_b}\right)\right]$$

If soln is dilute

$\Rightarrow \gamma_i = 1$

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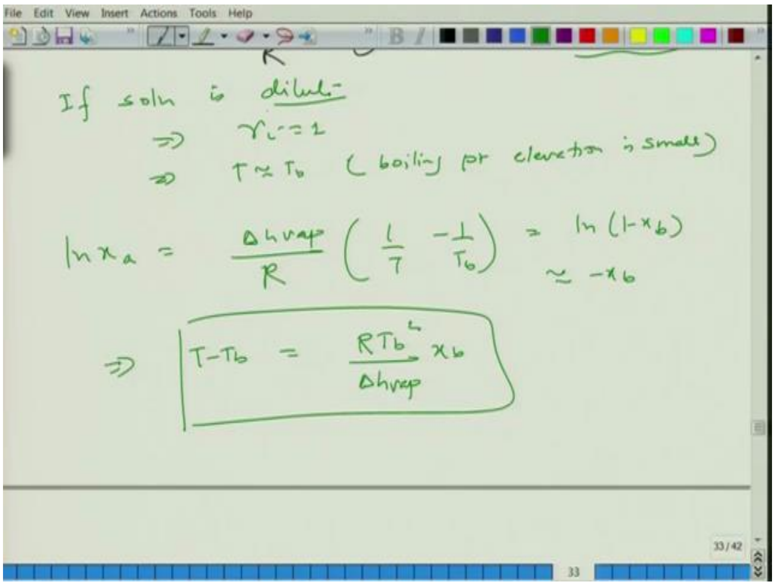

If soln is dilute

$\Rightarrow \gamma_i = 1$

$\Rightarrow T \simeq T_b$ (boiling pt elevation is small)

$$\ln x_a = \frac{\Delta h_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right) = \ln(1 - x_b) \simeq -x_b$$

$$\Rightarrow \boxed{T - T_b = \frac{RT_b^2}{\Delta h_{vap}} x_b}$$

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$$If\ soln\ is\ dilute,\ \ \gamma_i = 1\ or, \qquad T \approx T_b\ (boiling\ point\ elevation\ is\ small)$$

$$\ln x_a = \frac{\Delta h_{vap}}{R}\left[\frac{1}{T} - \frac{1}{T_b}\right] = \ln(1 - x_b) \approx -x_b$$

$$T - T_b = \frac{RT_b^2}{\Delta h_{vap}} x_b$$

$$\gamma_a = \frac{\Delta T \Delta h_{vap}}{RT_b^2 x_b}$$

$$Similarly, for\ freezing\ point\ depression,$$

$$\gamma_a = \frac{\Delta T \Delta h_{fis}}{RT_m^2 x_b}$$

So, Ln x I gamma I is equal to Delta h. So earlier of course our Delta h was Delta h of fusion where we had written 1 by T m right. And this was fusion at T m, so I can actually use the same expression because it will not get changed if I apply to this particular analysis to a vaporization line vapor liquid transition so I can write this as a vapor, a T b and this would become T b. So, I am using the same expression but replacing fusion to vapor line, this is going to be T b okay plus Delta C p is so instead of solid liquid is now vapor liquid by R and then the other terms is there.

So if so, so yeah so now the thing is I can make use of this expression now consists but with an assumption that because we are dealing with a dilute solutions. So if solution is dilute which means we can consider this to be an idle solution, so essentially I can consider gamma to be 1. So which means gamma to be 1 and also for a minutes a very very dilute solution that elevation of the boiling point is going to be very less that means temperature is almost close to the T b and that would be useful for to to neglect this second term.

So this is your boiling point elevation is small and I am neglecting the second term now with the with this assumption what I have is Ln of x let us say a which I am interested to work on and this is nothing but Delta h vapor by R, 1 minus T minus 1 by T, a boiling this corresponds to the pure case. And this I can write it as Ln 1 minus x b because x b is x b is the composition of the solute and this being very small I can approximate this by minus x p because of the fact that is a very dilute and hence I can write this as this.

So, now we have a relation that I can now write this as T minus T b this is can written as RT b square by delta h v vapor x b so this so is the expression which has come if you makes use of this Relation, so if we recall that here in order to get this relation the only assumption which we made was that Delta C p is a constant or here. And now after subsequently after that we have made this approximation and we got this thing.

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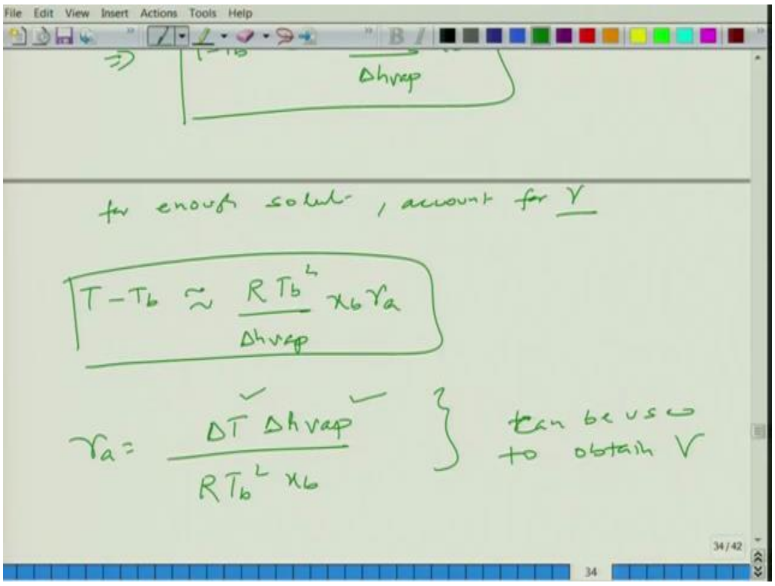

$\Rightarrow$ Δh_{vap}

for enough solute, account for γ

$$\boxed{T - T_b \approx \frac{R T_b^2}{\Delta h_{vap}} x_b \gamma_a}$$

$$\left.\gamma_a = \frac{\Delta T \, \Delta h_{vap}}{R T_b^2 x_b}\right\}$$ can be used to obtain γ

So, if we have enough solute that means more than, so if there is not a dilute for example then of course little the bit we have to rid with this exercise with gamma I cannot be 1. And we can approximate for such a case so for enough solute we have to account for account for gamma. Which means I have to do this exercise again with this an account so T minus T b is approximated to RT b square by Delta h vapor and then we add x a also here, now we multiply x in here also.

So with this we can actually obtain gamma a as simply delta t delta h vapor by RT b square x p. So if you have done an experiment, we can get this information and this information is also available from this information from the experiment and of course T b is available. So you can find out x a for given x b and based on that we can use these to obtain and they used to obtain gamma. And then once you have the gamma you can fade this information of gamma versus a, x and then obtain the appropriate parameters for the activity models which you are interested to use.

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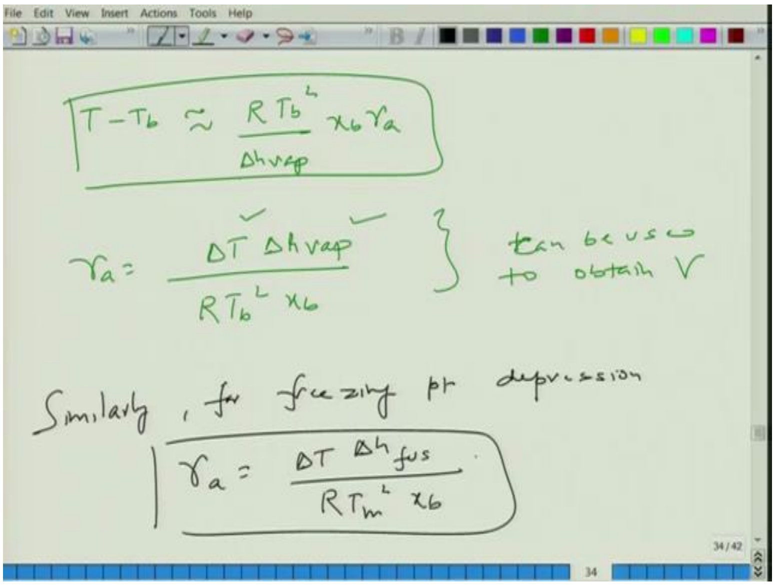

$$\boxed{T - T_b \approx \frac{R T_b^2}{\Delta h_{vap}} x_b \gamma_a}$$

$$\left.\gamma_a = \frac{\Delta T \, \Delta h_{vap}}{R T_b^2 x_b}\right\}$$ can be used to obtain γ

Similarly, for freezing pt depression

$$\boxed{\gamma_a = \frac{\Delta T \, \Delta h_{fus}}{R T_m^2 x_b}}$$

Similar to this boiling point elevation we can do the similar exercise for freezing point depression and I can obtain something like this. So this is at T b right and this is your RT m square x b, so I can get rid of this go for the same nomenclature okay. So, I have this expression which can be used.

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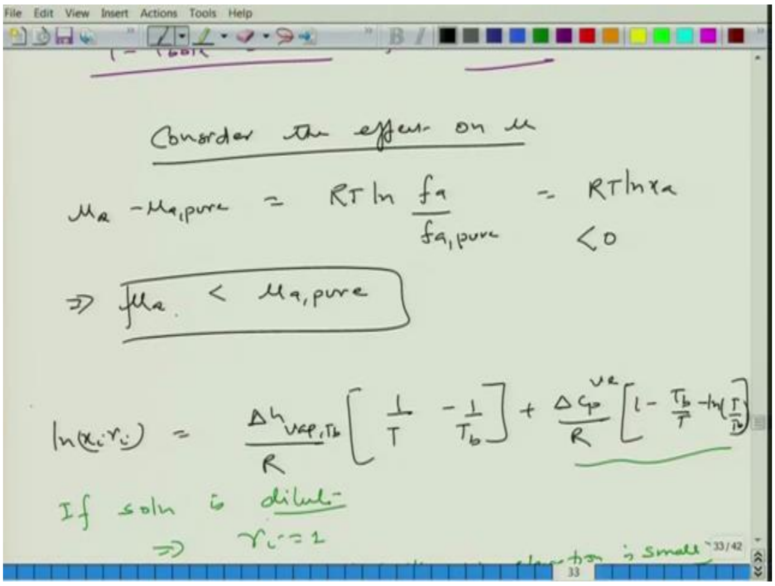

Consider the effect on μ

$\mu_a - \mu_{a,pure} = RT \ln \frac{f_a}{f_{a,pure}} = RT \ln x_a < 0$

$\Rightarrow \boxed{\mu_a < \mu_{a,pure}}$

$\ln(x_i \gamma_i) = \frac{\Delta h_{vap,T_b}}{R}\left[\frac{1}{T} - \frac{1}{T_b}\right] + \frac{\Delta c_p^{vl}}{R}\left[1 - \frac{T_b}{T} - \ln\left(\frac{T}{T_b}\right)\right]$

If soln is dilute

$\Rightarrow \gamma_i = 1$

is small

So if you look at again gamma here it tells you that, sorry if you look at again for the chemical potential which we looked at earlier. The chemical potential of the solution is going to be lower than that of the pure. So let us look at it how it will look like when you draw a chemical potential temperature plot.

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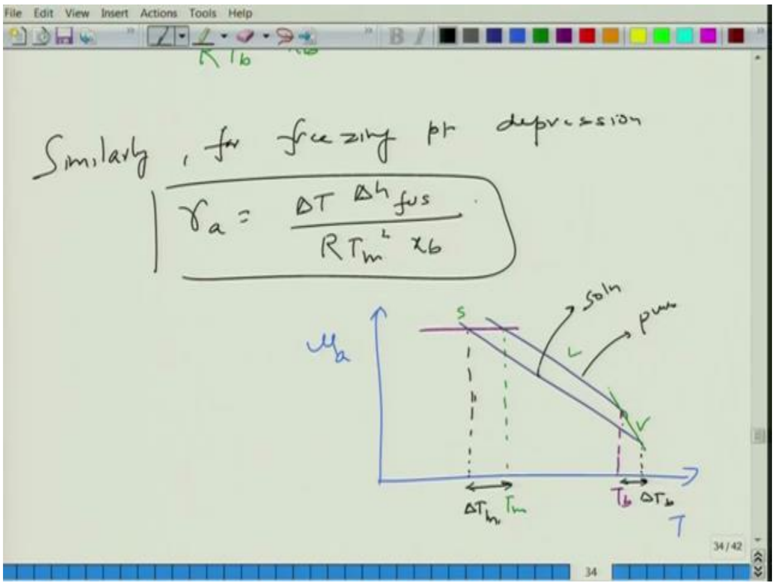

Similarly, for freezing pt depression

$\gamma_a = \frac{\Delta T \, \Delta h_{fus}}{R T_m^2 x_b}$

So this is your chemical potential this is a temperature and now what we have is you have a solid line here okay you have then a liquid line then you have the vapor line. So this is how it looks like this is this is a liquid, this is a solid and this is your vapor. So corresponding the intersection because the chemical position potentials are going to be equal here. The correspondingly this is your T m this is your and this is your so this point will give you the kind of T b right.

Now if there is a solution that means if you added a let us say a component b then essentially this liquid line gets shifted to the low values and what we assuming here is of course in this case, that a vapor and the solid at this point is pure. So what you have is? What you see clearly is that this point here gets have changed to this, so this also gets affected though considering this I have drawn a straight line this becomes a problem.

So this cannot be straight line this vapor line would be something like this okay. So with this you have the intersection is much higher at a much higher temperature, so this would become your, the other so this will become you the increase in the Delta T b that is elevation and this would be your decrease or separation of Delta T m upon the presence of the solution.

So this is your solution, this is your pure liquid. So that is how it looks like when you plot it here the important thing is that we have considered this to be a pure that is why we still use the same thing but only the solution line gets affected because of the presence of the solute.

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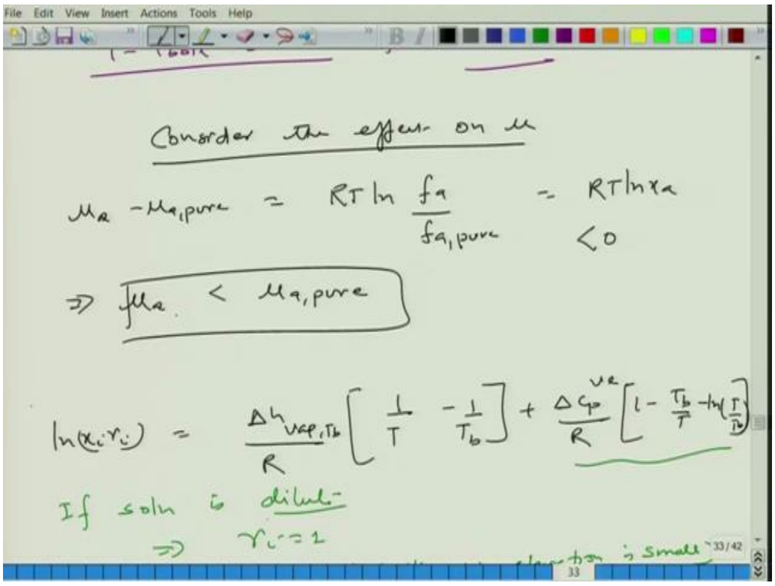


Consider the effect on μ

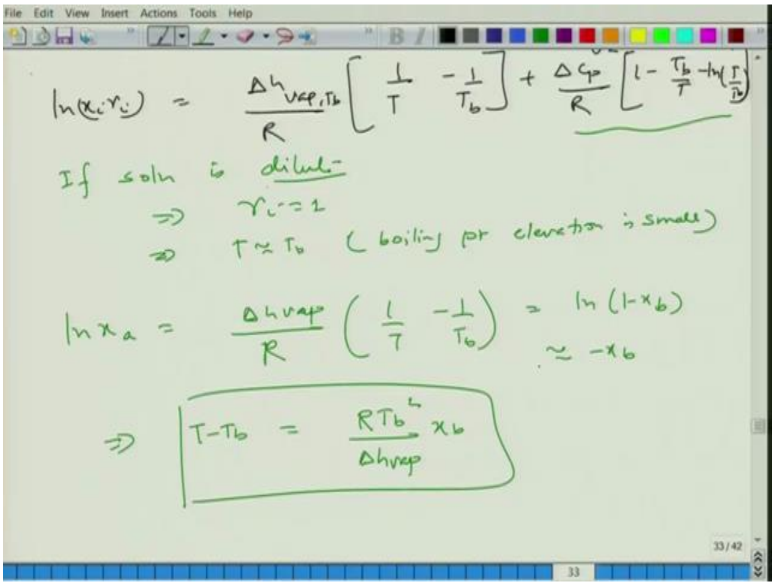
$$\mu_a - \mu_{a,pure} = RT \ln \frac{f_a}{f_{a,pure}} = RT \ln x_a < 0$$

$$\Rightarrow \boxed{\mu_a < \mu_{a,pure}}$$

$$\ln(x_i \gamma_i) = \frac{\Delta h_{vap,T_b}}{R}\left[\frac{1}{T} - \frac{1}{T_b}\right] + \underbrace{\frac{\Delta c_p^{ve}}{R}\left[1 - \frac{T_b}{T} - \ln\left(\frac{T}{T_b}\right)\right]}$$

If soln is dilute

$\Rightarrow \gamma_i = 1$



$$\ln(x_i\gamma_i) = \frac{\Delta h_{vap,T_b}}{R}\left[\frac{1}{T} - \frac{1}{T_b}\right] + \frac{\Delta c_p}{R}\left[1 - \frac{T_b}{T} - \ln\left(\frac{T}{T_b}\right)\right]$$

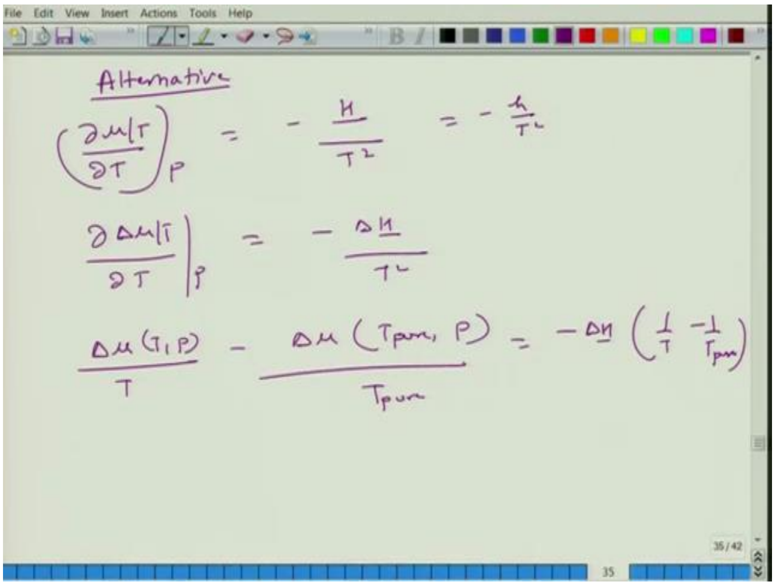
If soln is dilute

$\Rightarrow \gamma_i = 1$

$\Rightarrow T \simeq T_b$ (boiling pt elevation is small)

$$\ln x_a = \frac{\Delta h_{vap}}{R}\left(\frac{1}{T} - \frac{1}{T_b}\right) = \ln(1-x_b) \simeq -x_b$$

$$\Rightarrow \boxed{T - T_b = \frac{R T_b^2}{\Delta h_{vap}} x_b}$$



Alternative

$$\left(\frac{\partial \mu/T}{\partial T}\right)_P = -\frac{H}{T^2} = -\frac{h}{T^2}$$

$$\left.\frac{\partial \Delta\mu/T}{\partial T}\right|_P = -\frac{\Delta H}{T^2}$$

$$\frac{\Delta\mu(T,P)}{T} - \frac{\Delta\mu(T_{pure},P)}{T_{pure}} = -\Delta H\left(\frac{1}{T} - \frac{1}{T_{pure}}\right)$$

$$Alternatively,\ \left(\frac{\partial\left(\frac{\mu}{T}\right)}{\partial T}\right)_P = -\frac{\underline{H}}{T^2} = -\frac{h}{T^2}$$

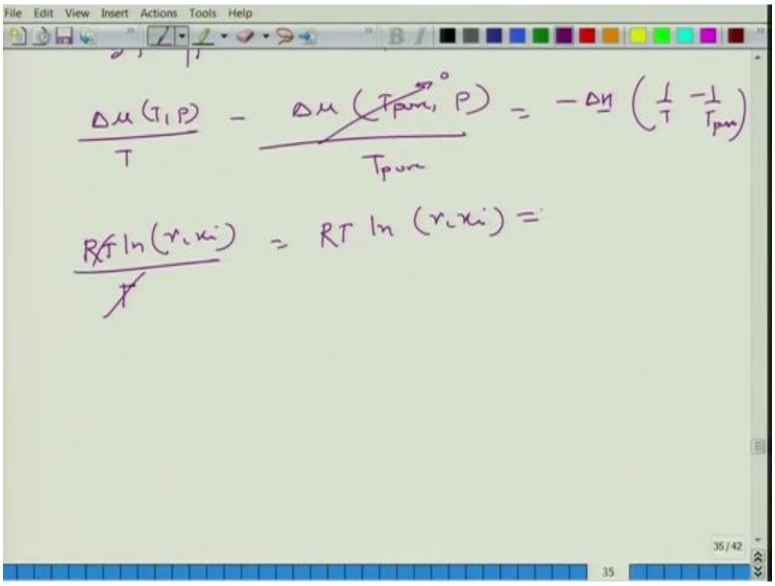
$$\frac{\partial\left(\frac{\Delta\mu}{T}\right)}{\partial T}|_P = -\frac{\Delta\underline{\underline{H}}}{T^2}$$

$$\frac{\Delta\mu(T,P)}{T} - \frac{\Delta\mu(T_{pure},P)}{T_{pure}} = -\Delta\underline{H}\left(\frac{1}{T} - \frac{1}{T_{pure}}\right)$$

$$R\ln(\gamma_i x_i) = \Delta\underline{H}\left(\frac{1}{T} - \frac{1}{T_{pure}}\right)$$

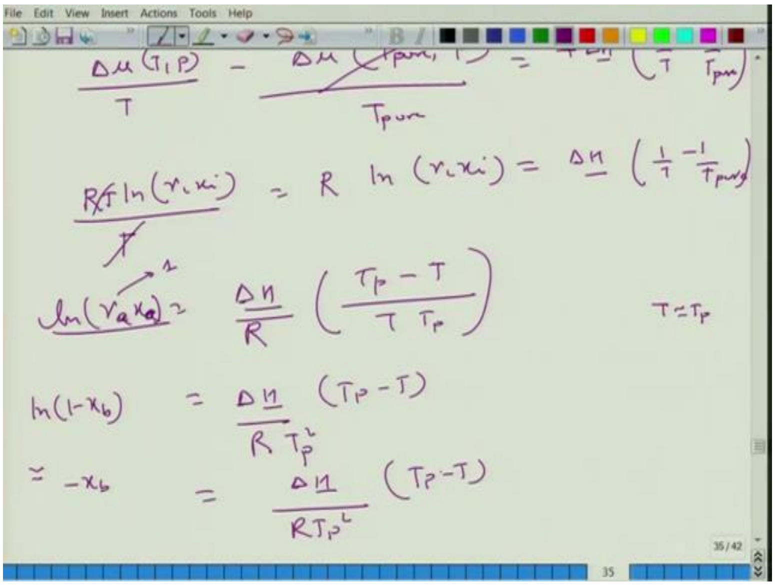
$$\ln(\gamma_a x_a) = \frac{\Delta\underline{\underline{H}}}{R}\frac{T_p - T}{T\,T_p} \approx -x_b = \frac{\Delta\underline{\underline{H}}}{RT_p^2}(T_p - T)$$

$$T - T_{pure} = \frac{RT_{pure}^2 x_b}{\Delta\underline{H}}$$



$$\frac{\Delta\mu(T,P)}{T} - \frac{\cancelto{0}{\Delta\mu(T_{pure}, P)}}{T_{pure}} = -\Delta\underline{H}\left(\frac{1}{T} - \frac{1}{T_{pure}}\right)$$

$$\frac{R\cancel{T}\ln(\gamma_i x_i)}{\cancel{T}} = RT\ln(\gamma_i x_i) =$$



$$\frac{\Delta\mu(T,P)}{T} - \frac{\cancel{\Delta\mu(T_{pure}, P)}}{T_{pure}} = \Delta\underline{H}\left(\frac{}{T} \quad \frac{}{T_{pure}}\right)$$

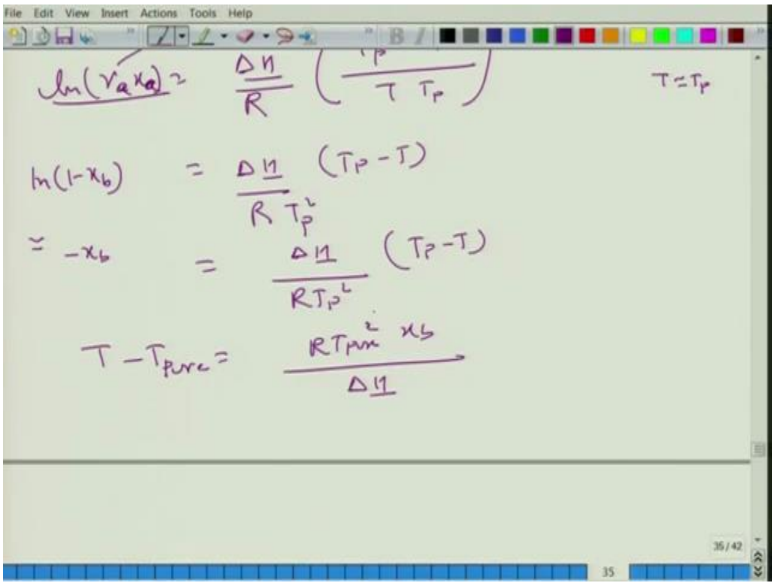
$$\frac{R\cancel{T}\ln(\gamma_i x_i)}{\cancel{T}} = R\ln(\gamma_i x_i) = \Delta\underline{H}\left(\frac{1}{T} - \frac{1}{T_{pure}}\right)$$

$$\underline{\ln(\cancelto{1}{\gamma_a} x_a)} = \frac{\Delta\underline{H}}{R}\left(\frac{T_p - T}{T\,T_p}\right)$$

$T \simeq T_p$

$$\ln(1-x_b) = \frac{\Delta\underline{H}}{R\,T_p^2}(T_p - T)$$

$$\simeq -x_b = \frac{\Delta\underline{H}}{RT_p^2}(T_p - T)$$



$$\ln(\gamma_a x_a) = \frac{\Delta H}{R}\left(\frac{\quad}{T\ T_p}\right) \qquad T \simeq T_p$$

$$\ln(1-x_b) = \frac{\Delta \underline{H}}{R\,T_p^2}(T_p - T)$$

$$\simeq -x_b = \frac{\Delta \underline{H}}{R T_p^2}(T_p - T)$$

$$T - T_{pure} = \frac{R T_{pure}^2\ x_b}{\Delta \underline{H}}$$

Now this particular exercise which we have done we made use of the expression which we derived in the last class but we can actually take an alternative approach and you have to can obtain the same allure expression by just considering the derivative of the mu with respect to temperature and that is connected to you enthalpy. So alternatively, in order to obtain such an expression, we can take a different approach okay, so let us try to do that. It is just for the sake of completion of this whole concepts.

I will consider Del mu by T by Del T and this we know minus H molar enthalpy divided by T Square. So we can do that is minus H also okay and now I can take this I can actually write this also as del Delta mu by T by Del T by at a constant pressure is minus Delta H by T Square. Now if you take this of you integrate the left-hand side from the temperature which is at for the pure case, to the temperature at which actually the system is then I can write this as del mu at temperature and pressure divided by T minus del mu for T pure.

That means the corresponding to the pure phase and that it will be T pure here and this would become minus Delta h one minus T minus T pure. So this will be zero because the delta mu in this such a case would be zero at equilibrium and then what I can do is? I can use this definition of Delta mu because this is with respect to the pure case. So the reference here is where we basically pure if you integrate this is from T pure to T so if you look at this here I can use this Delta mu okay but in this case what we can use is?

We can use this RT Ln gamma I xi, so delta mu would become your RT Ln gamma I xi by T. Here the T gets cancelled, so this is your RT Ln then gamma I xi and that is going to be so this has to be positive right. So this is your delta H bar 1 minus T minus T pure. All right so let me further simplify, log of gamma I X I this must be your Delta H this has to be this right yeah. So Delta H by R and this is your T pure or minus T by T by T pure.

So, I am just using P as pure and I can approximate if it is a very small elevation then I can approximate T as T pure this will be make this as Delta H bar by R T Square or T p square and this becomes T p minus T right. And this again here we can consider gamma to be very diluted hence it is going to be 1 as it was considered earlier and this is for the case of that is a binary mixture this can be written as gamma a x a and then we can say that gamma equal to 1 because of the very dilute solution.

Then this can be written as Ln 1 minus x b and this can be written as approximately minus x b because being a dilute condition. So this you have our T p Square T p minus T, so I can rewrite this as T minus T p or pure is RT pure x b by Delta H bar which is the same expression which we got in the earlier case.

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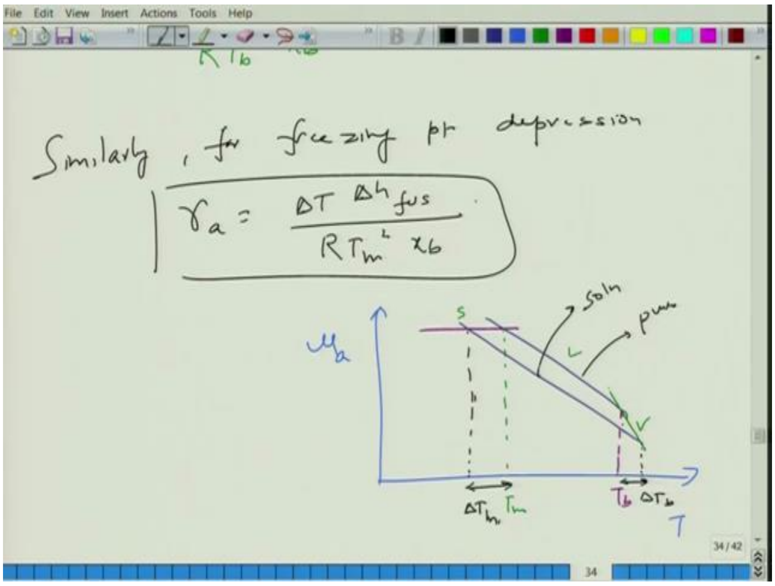
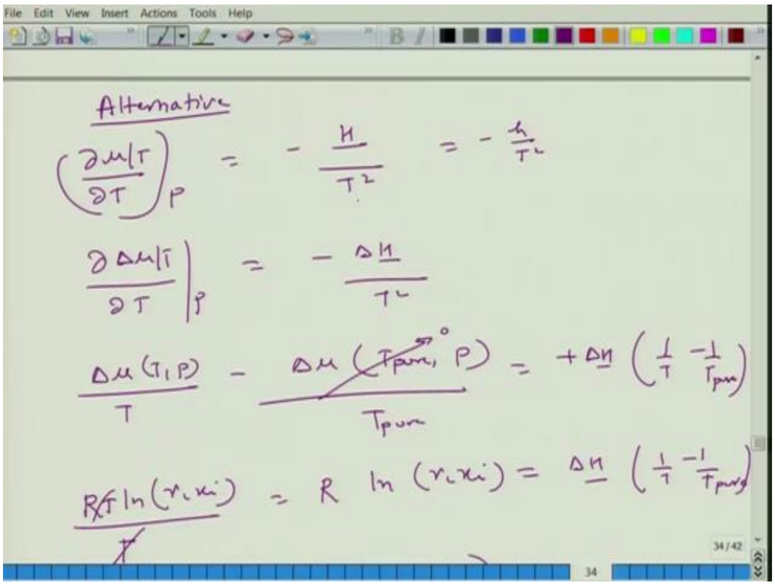


Similarly, for freezing pt depression

$$\boxed{\gamma_a = \frac{\Delta T\, \Delta h_{fus}}{R T_m^2\, x_b}}$$



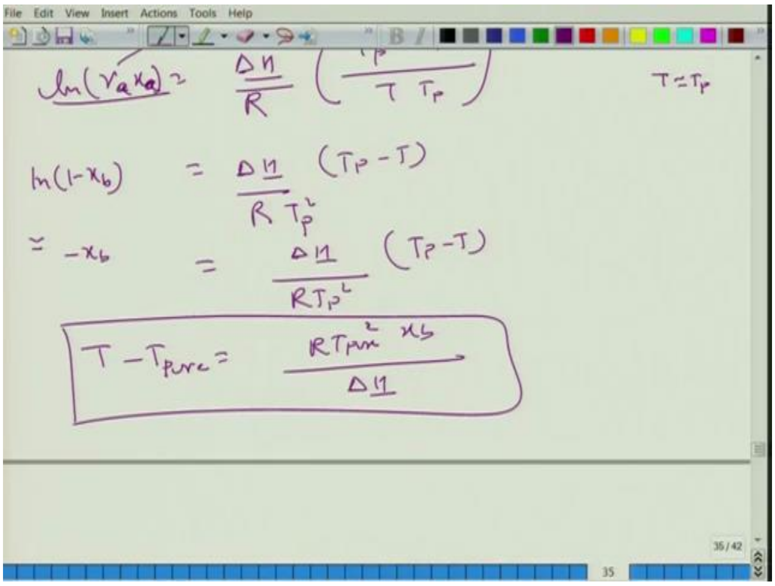
Alternative

$$\left(\frac{\partial \mu/T}{\partial T}\right)_P = -\frac{\underline{H}}{T^2} = -\frac{h}{T^2}$$

$$\left.\frac{\partial \Delta\mu/T}{\partial T}\right|_P = -\frac{\Delta \underline{H}}{T^2}$$

$$\frac{\Delta\mu(T,P)}{T} - \cancelto{0}{\frac{\Delta\mu(T_{pure},P)}{T_{pure}}} = +\Delta\underline{H}\left(\frac{1}{T} - \frac{1}{T_{pure}}\right)$$

$$\frac{R\cancel{T}\ln(\gamma_i x_i)}{\cancel{T}} = R\ln(\gamma_i x_i) = \Delta\underline{H}\left(\frac{1}{T} - \frac{1}{T_{pure}}\right)$$



$$\underline{\ln(\gamma_a x_a)} = \frac{\Delta \underline{H}}{R}\left(\frac{T_p}{T \; T_p}\right) \qquad T \simeq T_p$$

$$\ln(1-x_b) = \frac{\Delta \underline{H}}{R\,T_p^2}(T_p - T)$$

$$\simeq -x_b = \frac{\Delta \underline{H}}{RT_p^2}(T_p - T)$$

$$\boxed{T - T_{pure} = \frac{RT_{pure}^2 x_b}{\Delta \underline{H}}}$$

So essentially you can use the same simple approach also to obtain the same expression to connect this change in the boiling or freezing condition or temperature upon addition of the compositions. So I think you know that is that is the end of today's lecture and I will take a bit more examples and particularly also elaborate atmospheric pressure in the next class okay so I will see you next time.