Chemical Engineering Thermodynamics
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Lecture 55
Liquid-Liquid Equilibria (continued) and solid-liquid equilibria

Welcome back, we were discussing about liquid-liquid equilibria. So, I will continue with that discussion and then subsequently we will take vapour liquid-liquid equilibria and solid-liquid equilibrium, okay.

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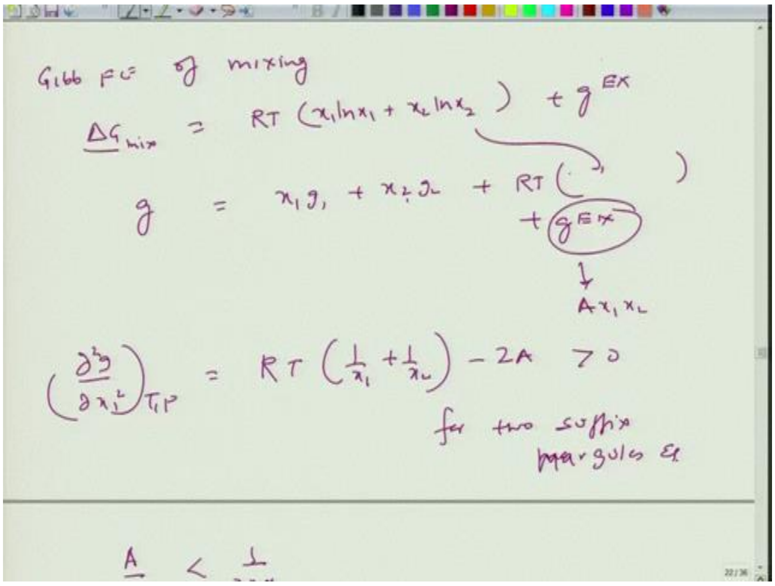


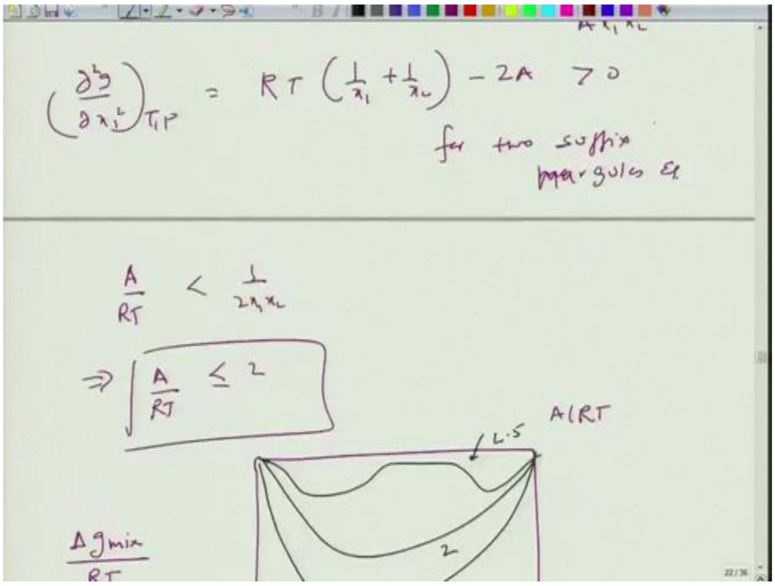
Gibb FE of mixing

$$\Delta G_{mix} = RT(x_1 \ln x_1 + x_2 \ln x_2) + g^{EX}$$

$$g = x_1 g_1 + x_2 g_2 + RT(\cdot\ ) + \boxed{g^{EX}} \rightarrow A x_1 x_2$$

$$\left(\frac{\partial^2 g}{\partial x_1^2}\right)_{T,P} = RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right) - 2A > 0$$

for two suffix margules Eq



$$\left(\frac{\partial^2 g}{\partial x_1^2}\right)_{T,P} = RT\left(\frac{1}{x_1} + \frac{1}{x_2}\right) - 2A > 0$$

for two suffix margules Eq

$$\frac{A}{RT} < \frac{1}{2x_1x_2}$$

$$\Rightarrow \boxed{\frac{A}{RT} \le 2}$$

So we particularly looked at the cases where we can represent the models of delta GX in terms of 2 suffix Margules equation. Now this particular constant A depends on the temperature and this can affect a bit of the phase diagram.

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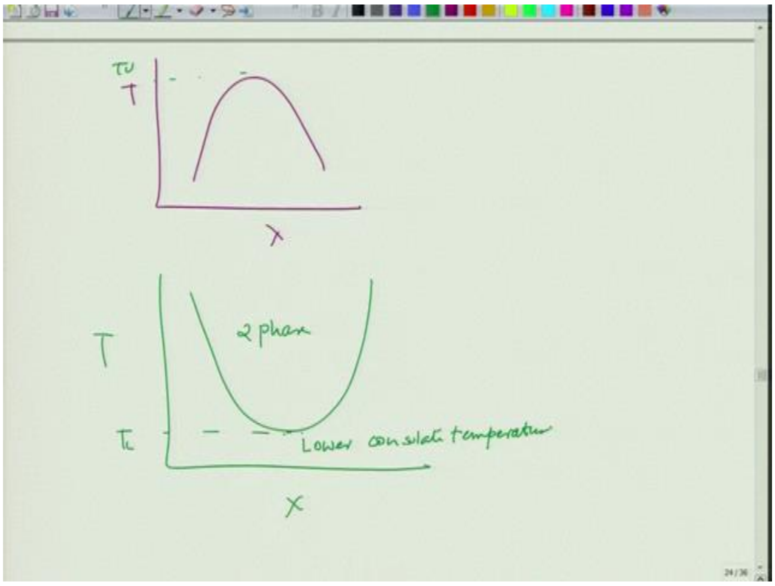

Phase diagram for the case of a liquid-liquid equilibria usually seen such as this right. So this is the usual case. However, because of the nature of the constant A dependency on the temperature, we may observe different kind of scenario. For example, we can also see something like this. So, this is your temperature and X. So, this was your TU upper consulate temperature and this would be your case where we can say this is TL which is a lower consulate temperature. Okay and it is going to be 2-phase here. Okay. But, beside this lower or upper consulate temperature, there could be other possibilities and that will depend again on the interaction behaviour between the different components.

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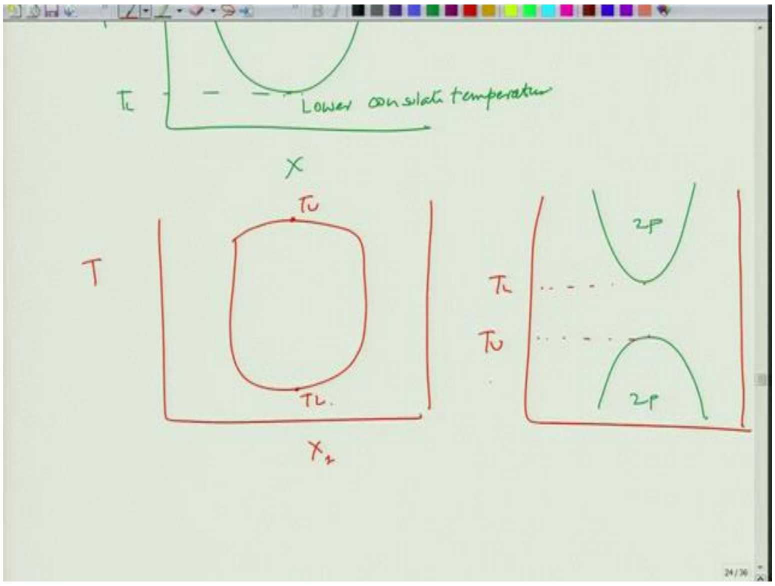

So, you can have something like this also, where it is more like this where you have 2 points here which is T of U and T of L, there could be also something like this. Okay, where this is your 2-phase, this is also 2-phase. In this case, this would be your T of L and this would be your T of U. Okay. So, as I said this all depends on the interaction behaviour between different components which can create significant non-ideality leading to different natures of the phase diagram as I just illustrated.

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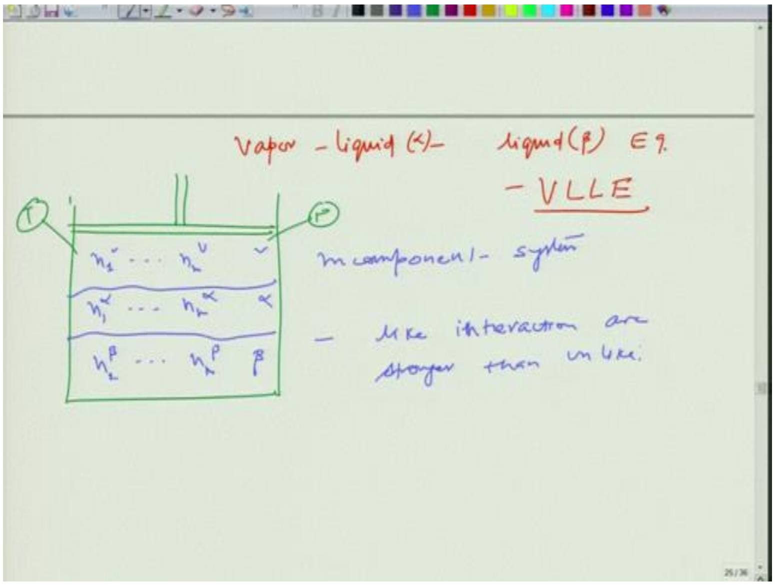
Vapor - liquid (α) - liquid (β) Eq.

- VLLE

m component system

- like interaction are stronger than unlike.

Now, let us take a case of vapour, liquid-liquid okay equilibria. So, this can be written as let say alpha, this is your beta and this is your VLLE okay. So, schematically I can represent this in the following form, I can write I can draw it like this, that this is let say maintain at a certain pressure. Okay, so we have let say piston and there is a pressure controller or pressure measurement you can see the temperature and pressure. Okay, so in such a case where you have vapour-liquid-liquid equilibrium.

So we can assume this to be vapour, this could be another liquid, this is alpha phase, this is vapour phase and this is your beta phase and if it is M components system, you can have something like this, where number of certain moles are present in vapour phase and so forth for other, okay. Similarly, for alpha, okay and this is going to be beta. So, these are the mount of components which are present in different phases. Okay.

Now given this how do you find out typical behaviour that is something which you will illustrate now. This particular scenario where you have VLLE, this usually seen when like interactions are stronger than unlike interaction. Okay.

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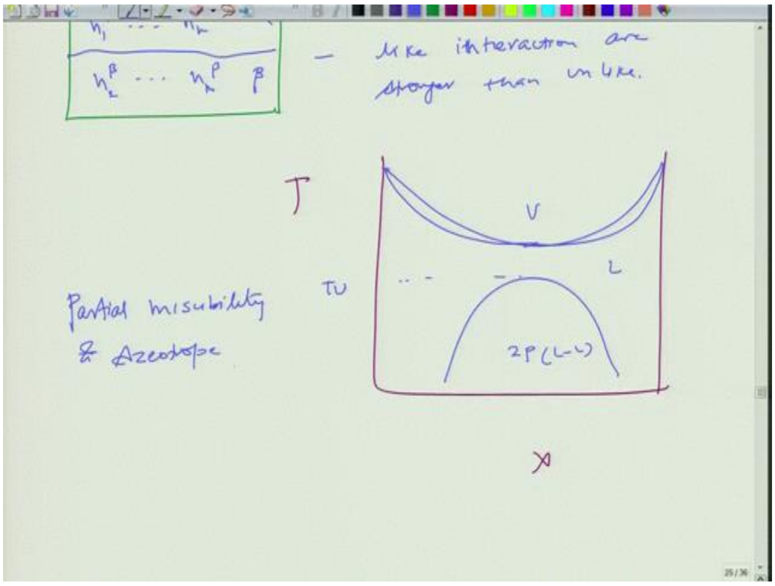

— like interaction are stronger than unlike.

Partial misubility & Azeotope

In such is a case, then you may see something which where, which we know now, would be something closer to or a minimum isotropic bowling condition. So that kind of scenario, you can see that. So, if you plot let say temperature versus X you may get some kind of plot like this, the phase diagram okay and then you have this another one where you have this upper absolute temperature.

So, this is again 2-phase. Okay, this is your vapour and this is single phase, this is liquid. So, this is again, liquid-liquid, so this is liquid-liquid here and this is your TU, okay. So, what you see is a partial miscible scenario, and azeotrope. So, this is a case where you have a like interactions are stronger than unlike. So, you have partial miscibility, which is this range and azeotrope.

Now in such a scenario, how do you calculate compositions? Okay, so we will be making use of the same concept that if you have equilibrium, then of course if you have fugacities of the component in different phases have to be equal. Okay and if it is a VLLE, for example in this case, particularly when this particular TU also merges with this point, you may get scenario of properly VLLE.

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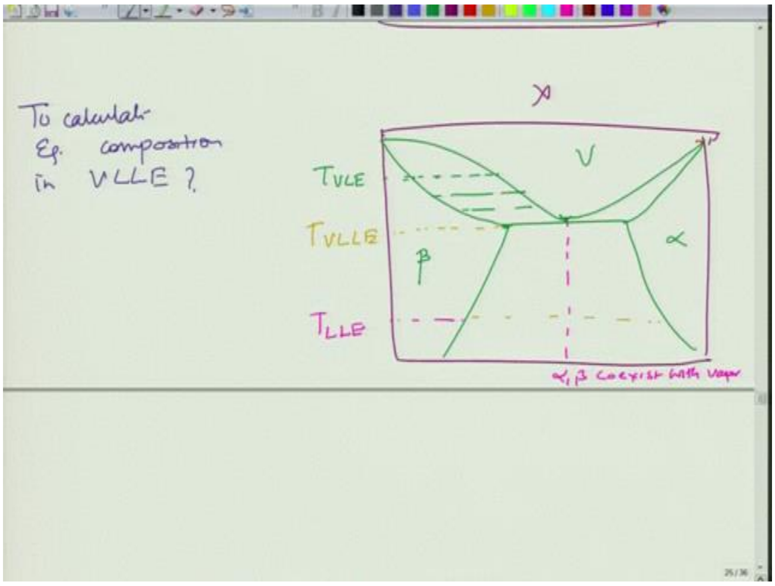
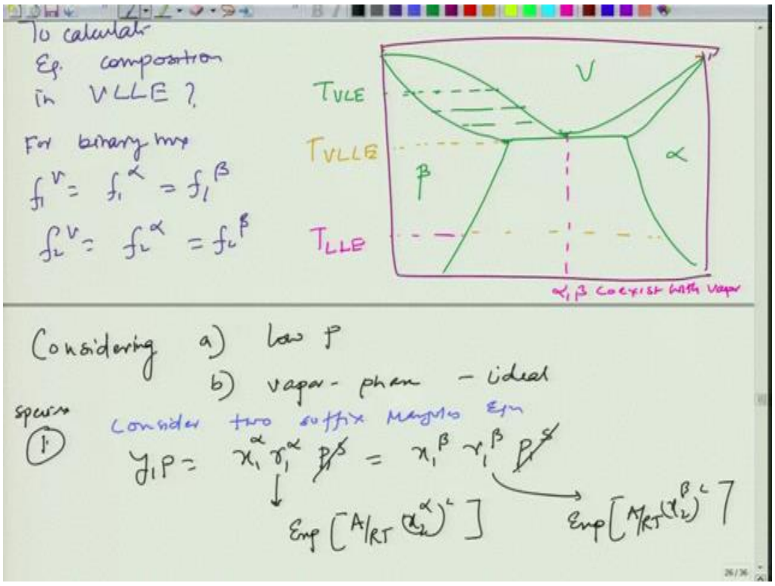


To calculate Eq. composition in VLLE ?



To calculate Eq. composition in VLLE?

For binary mix

$$f_1^V = f_1^\alpha = f_1^\beta$$

$$f_2^V = f_2^\alpha = f_2^\beta$$

Considering a) low P

b) vapor-phase - ideal

species ① consider two suffix Margules Eqn

$$y_1 P = x_1^\alpha \gamma_1^\alpha \cancel{P_1^s} = x_1^\beta \gamma_1^\beta \cancel{P_1^s}$$

$$\gamma_1^\alpha \downarrow \operatorname{Exp}\left[\frac{A}{RT}(x_2^\alpha)^2\right] \qquad \gamma_1^\beta \rightarrow \operatorname{Exp}\left[\frac{A}{RT}(x_2^\beta)^2\right]$$

$$For\ binary\ mixture, \quad f_i^v = f_i^\alpha = f_i^\beta$$

$$f_L^v = f_L^\alpha = f_L^\beta$$

So that would be something like this, so something like this, right. So, in this case, you have beta phase is here, alpha phase is here, V and this is a 2-phase region. So, this is vapour liquid region, okay and hence at any given point here, this are the tie lines right. So, this corresponds to TVLE okay and this part which is there, where your vapour is also at equilibrium with two liquid phases. Okay, you have this as temperature VLLE okay.

And what about this part. So here it is going to be temperature of LLE. Okay, so you have LEE here, you have VLE here and then this particular range which is precisely across a certain composition that would be your vapour liquid-liquid equilibrium. Okay, so for that matter. I can for example find out a specific composition here, which, at which these two liquids and a vapour at coexistence. So this will be where alpha, beta coexist with vapour okay.

And for the binary component, of course, this will be very fixed point, you know because of the degree freedom. Now, for such a scenario, how do you find out the equilibrium compositions? Okay, so will now try to look at the details of the calculations. So again, this is to calculate equilibrium composition in VLLE? Okay, so how do you do that?

Okay, so as I said, you need to consider, let say, if it is a binary component. For binary mixture. Okay, you have f1v is equal to f1 alpha is equal to f1 beta and then you have f2v is equal to f2 alpha is equal to f2 beta, okay. Alright, so the conditions are straightforward as we have done for other cases. So we need to make use of some of the models for G axis and then of course we can take some approximation in the vapour phase. We can consider vapour phase to be ideal, considering this, let say as a low pressure.

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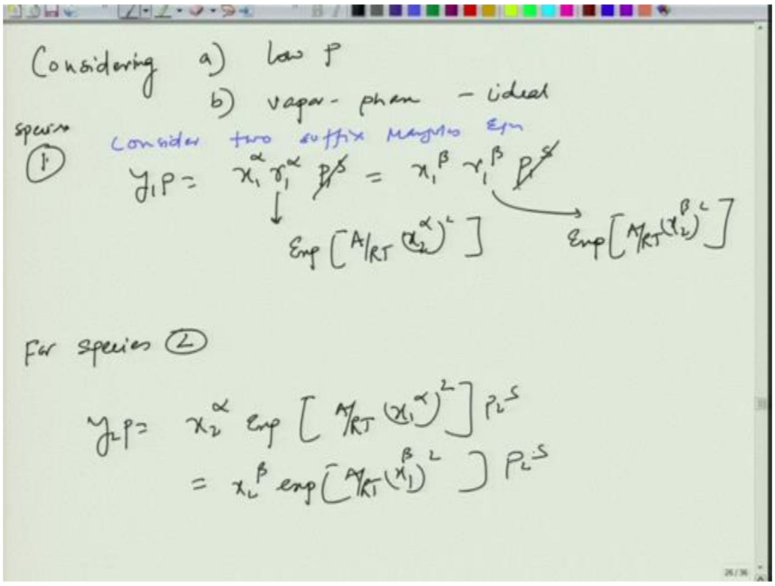

Considering a) low P

b) vapor-phase – ideal

species ①

Consider two suffix Margules Eqn

$$y_1P = x_1^{\alpha}\gamma_1^{\alpha}\cancel{P_1^s} = x_1^{\beta}\gamma_1^{\beta}\cancel{P_1^s}$$

$$\gamma_1^{\alpha} \downarrow \operatorname{Exp}\left[A/RT\,(x_2^{\alpha})^2\right] \qquad \gamma_1^{\beta} \rightarrow \operatorname{Exp}\left[A/RT\,(x_2^{\beta})^2\right]$$

For species ②

$$y_2P = x_2^{\alpha}\exp\left[A/RT\,(x_1^{\alpha})^2\right]P_2^s$$

$$= x_2^{\beta}\exp\left[A/RT\,(x_1^{\beta})^2\right]P_2^s$$

$$y_1P = x_1^{\alpha}\gamma_1^{\alpha}P_1^s = x_1^{\beta}\gamma_1^{\beta}P_1^s$$

$$or, \qquad y_1P = x_1^{\alpha}\exp\left[\frac{A}{RT}(x_2^{\alpha})^2\right]P_1^s = x_1^{\beta}\exp\left[\frac{A}{RT}\left(x_2^{\beta}\right)^2\right]P_1^s$$

$$y_2P = x_2^{\alpha}\exp\left[\frac{A}{RT}(x_1^{\alpha})^2\right]P_2^s = x_2^{\beta}\exp\left[\frac{A}{RT}\left(x_1^{\beta}\right)^2\right]P_2^s$$

So, considering first that it is a low pressure and of course with that we can assume vapour phase to be ideal. Okay, then for species 1, we can write this as the first equation can be written as Y1P. The second equation would be X1, gamma 1 and FI alpha, which can be written as P1 sat. So this can be now if I considering two suffix Margulies equation. Okay, which will represent the liquid gammas, then I can write this as gamma 1 and I can of course FIL alpha can be written as P1 sat okay.

And this would be alpha and this also can be written as X1 beta, okay. So I am ignoring the other components here, when I representing FI of the pure component. So I am just representing by this P1 sat. And here also I can write gamma 1 beta, again FIL beta pure, or F1 pure would be, can be written as FIS or even if you use this a Luis Randall fame work. Then essentially FI pure in the liquid phase will come in to the picture and these two terms, that is alpha, beta, they will cancel out just like this one. Okay.

So, now this gamma can be represented in terms of exponential A by 2, sorry A by, A by RT and then you have this, X2 alpha square right. Similarly, here is going to be exponential A by 2, X2, beta square. Okay, so this is a first equation. Similarly, I can do the same thing for the second species, okay. I can write again Y2P as X2, alpha exponential A by RT X1 alpha square P2S. This equal to X2 beta exponential A by RT X1 beta square P2S, okay. So, this are the two specific equation which I have written here.

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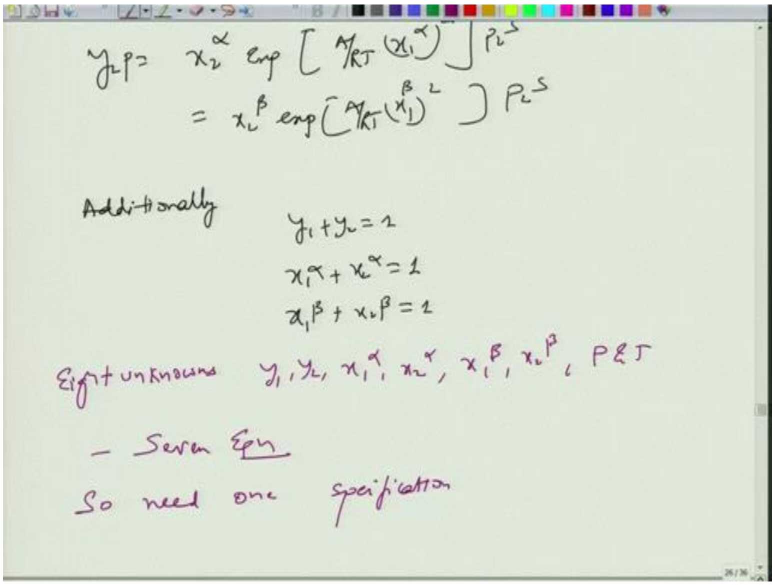

$$y_2 P = x_2^{\alpha} \exp\left[\frac{A}{RT} (x_1^{\alpha}) \right] P_2^S$$

$$= x_2^{\beta} \exp\left[\frac{A}{RT} (x_1^{\beta})^2 \right] P_2^S$$

Additionally

$$y_1 + y_2 = 1$$

$$x_1^{\alpha} + x_2^{\alpha} = 1$$

$$x_1^{\beta} + x_2^{\beta} = 1$$

Eight unknowns $y_1, y_2, x_1^{\alpha}, x_2^{\alpha}, x_1^{\beta}, x_2^{\beta}$, P & T

– Seven Eqn

So need one specification

$$Additionally, \qquad y_1 + y_2 = 1$$

$$x_1^{\alpha} + x_2^{\alpha} = 1$$

$$x_1^{\beta} + x_2^{\beta} = 1$$

Now in addition to that I will be also having additional constraint, additionally Y1 plus Y2 should be equal to 1. X1 alpha plus X2 alpha is equal to 1 and X1 beta plus X2 beta that equal to 1. So, if you look at number of unknowns, we have eight unknowns which are Y1, Y2, X1 alpha, X2 alpha, X1 beta, X2 beta okay and in addition we have P and T. That condition where the equilibrium will occur.

So, if you look at it there are eight unknowns and what about the number of equation? You have essentially two equations are coming from here and two is from here and three is here. That means there are seven equation okay. So from the degree freedom point of view we need to specify. So need one specification okay, to solve this variables. Once you specify then you can, you can try to solve it using some Excel sheet or MATLAB or Mathematica and so forth.

As far as tool is concern, you can take any of this to get this solution. Okay, so that was the case of the vapour liquid-liquid equilibria. Now, let me move to specifically solid liquid-liquid equilibrium. Okay, the fundamental does not change much. Okay, but the way we are going to handle the solid liquid will be little different.

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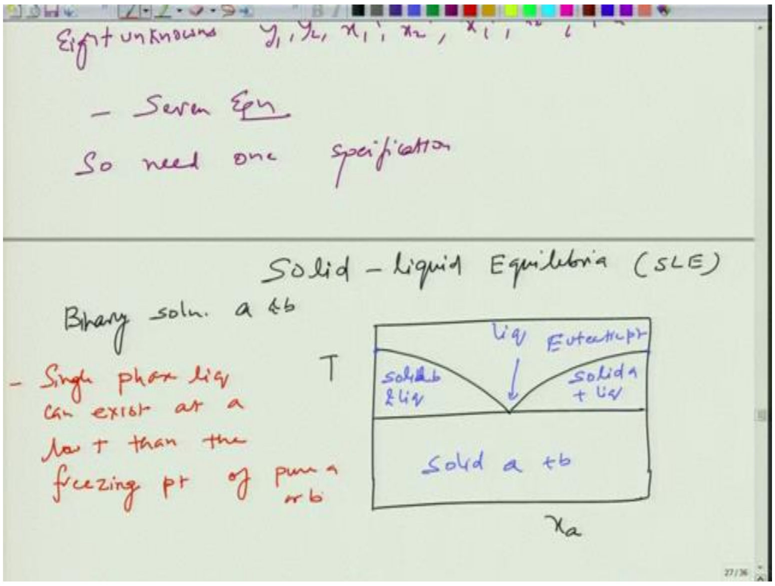

Eight unknowns y_1, y_2, x_1, x_2, x_1

- Seven Eqn

So need one specification

Solid – liquid Equilibria (SLE)

Binary soln. a &b

- Single phase liq can exist at a low T than the freezing pt of pure a or b

So, let me first bring little bit of clarity of what are the different things you see in a solid liquid equilibria. So, you can say equilibria SLE. So, let us consider again binary solution okay. So here it would be A and B right. So you have let say a typical solid liquid-liquid equilibria would be like this. Okay for component solid A and B. So this would be something like T as a function of composition of A and this will be your solid, okay. So you, what you have here is a liquid completely, here is a solid B and liquid equilibria, here is a solid A and liquid. So solid A and plus B okay.

So, what you notice is that if this is a basically the case where at a given point here. So you have this pure melting or freezing point is here right for the pure cases so and. So we do not expect for the pure case to be seen at liquid phase at lower than this temperature. But when you mix this what we observe is that, there is a possibility of a single phase or rather, we observe a single liquid phase below the freezing point of the pure component temperature or below the freezing point of the pure components.

So this is the kind of a lowest temperature at which the liquid can exist in such a kind of a mixtures for the case of a solid liquid equilibria and this lowest temperature or this point is often called eutectic point okay. So the couple of thing which we observe here can be summarised that single phase liquid. So this would be the mixture, that means mixtures of A and B can exist at a lower T than the freezing point of pure a or b, right.

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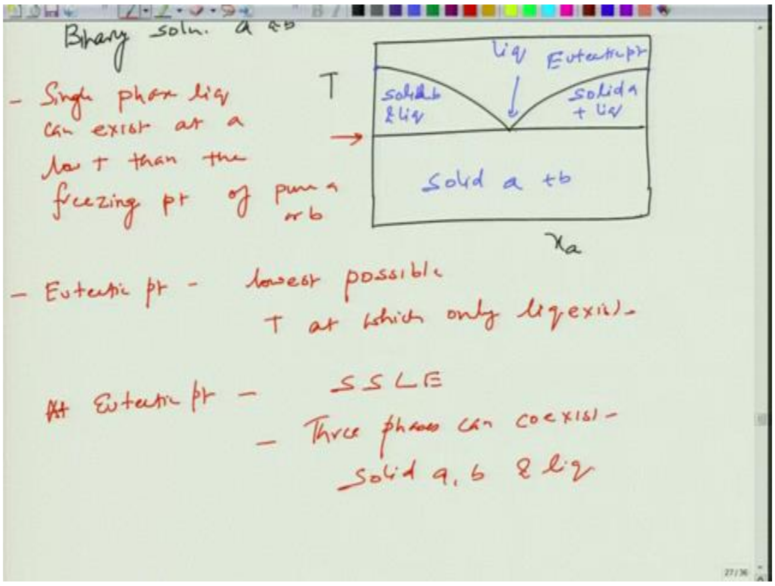

Binary soln. a & b

- Single phase liq can exist at a low T than the freezing pt of pure a or b

- Eutectic pt - lowest possible T at which only liq exist.

At Eutectic pt - SSLE

- Three phases can coexist - solid a, b & liq

And the other thing is the eutectic point is at lowest temperature. So we are defining eutectic point okay. Thus, at lowest possible, possible T at which only liquid exist okay, at T here. So this essentially is a eutectic point. So this line shows you that or this point here, you have a scenario where you have a solid-solid and liquid equilibria okay. So at eutectic point you have solid-solid liquid equilibria. That means three phases can coexist. Okay, that would be solid a, b and liquid okay. Now based on the binary solution and considering the degree of freedom analysis. So eutectic point for a given binary mixtures is going to be fixed, right.

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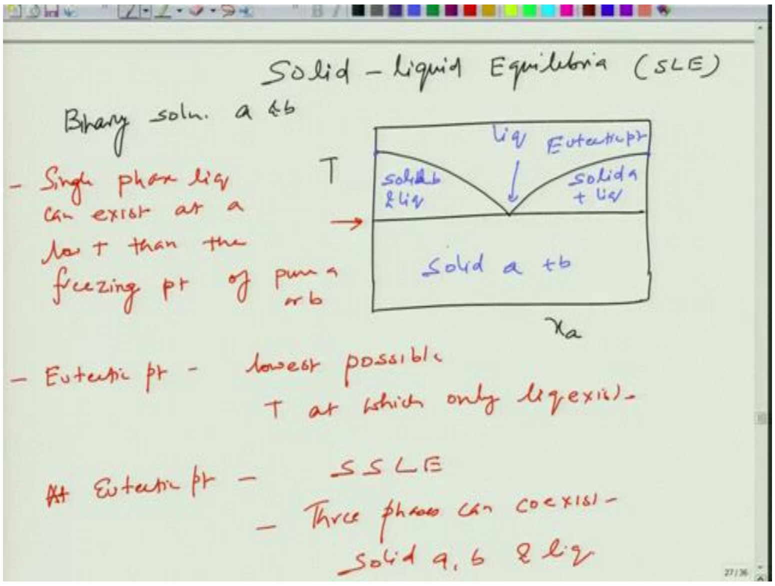

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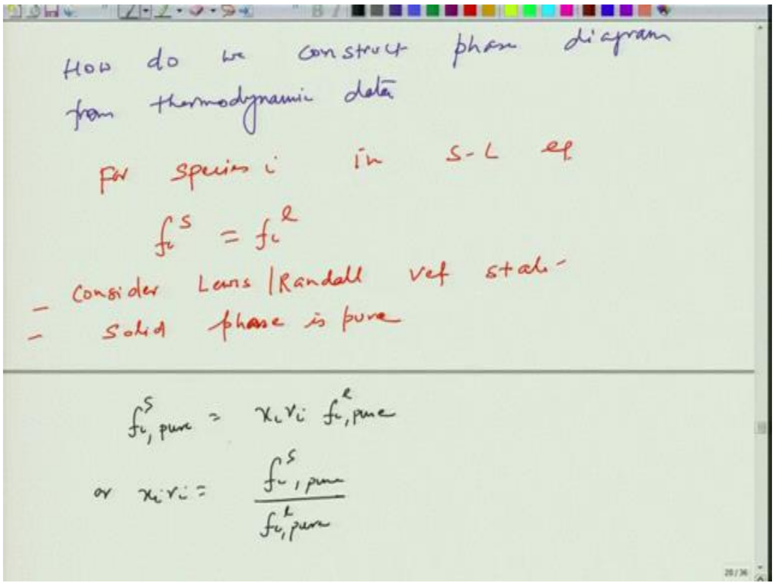

How do we construct phase diagram from thermodynamic data

For species i in S-L eq

$$f_i^s = f_i^l$$

- Consider Lewis|Randall ref state
- Solid phase is pure

$$f_{i,pure}^s = x_i \gamma_i f_{i,pure}^l$$

$$\text{or} \quad x_i \gamma_i = \frac{f_{i,pure}^s}{f_{i,pure}^l}$$

$$for\ species\ i\ in\ S - L\ eq:$$

$$f_i^s = f_i^l$$

$$f_{i,pure}^s = x_i \gamma_i f_{i,pure}^l$$

$$x_i \gamma_i = \frac{f_{i,pure}^s}{f_{i,pure}^l}$$

Okay, so this is something which is for the simple solid-solid liquid equilibria. But more complicated phase diagrams are also available. Okay and you can look at many textbooks have a more complicated cases where you can have two eutectic point in a given mixtures. Okay and since something which we are not covering but of course, this is something which you can look at in different textbook, you find that it is there. So at this point, what would you like to focus is that how do you, or how do we construct phase diagram of such a system from thermodynamic data?

So that is an important question because. For example, how do you generate this data if some properties are known to you. So the properties could be your let say delta H of fusion or fusion or heat of enthalpy change at the solid to liquid phase transition. So in other word, we are simply asking that how do you track this solid to liquid equilibria for a given species. So since it is the equilibria for spaces i in solid liquid equilibria. I can write this as FIS is equal to FIL right. So that is something which I can do that easily.

Now you consider, let say we consider the case or the references Lewis Rendell reference state. Okay, so that is one we can consider. Second, we can consider is a solid phase is pure okay. So which means that this component here which is in the mixture can be represented as FIS pure and this one can be written as XI, gamma I, FIL pure right. So I can write now this as XI, gamma I is FI solid pure divided by FIL liquid pure. So that is based on the Rendell, Lewis Rendell reference state, okay.

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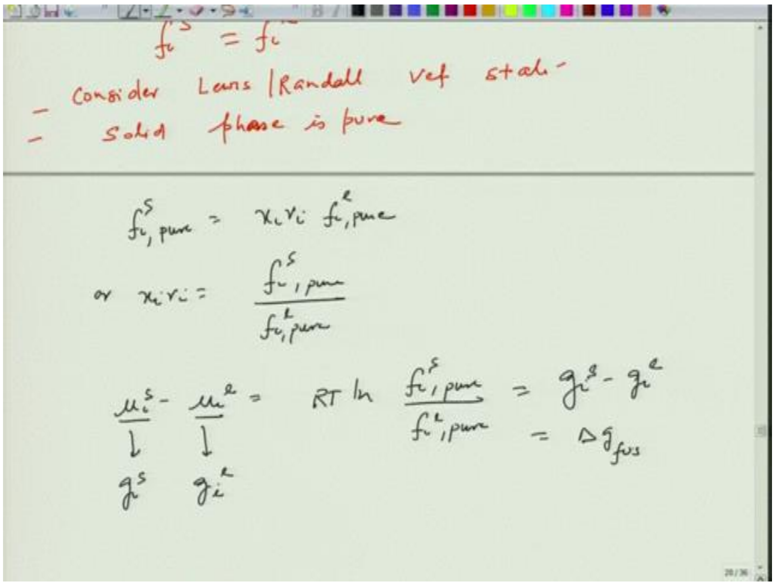

$f_i^s = f_i^l$

- Consider Lewis|Randall ref state
- solid phase is pure

$f^s_{i,pure} = x_i \gamma_i f^l_{i,pure}$

or $x_i \gamma_i = \frac{f^s_{i,pure}}{f^l_{i,pure}}$

$\underset{g_i^s}{\underset{\downarrow}{\underline{\mu_i^s}}} - \underset{g_i^l}{\underset{\downarrow}{\underline{\mu_i^l}}} = RT \ln \frac{f^s_{i,pure}}{f^l_{i,pure}} = g_i^s - g_i^l = \Delta g_{fus}$

$$\mu_i^s - \mu_i^l = RTln\frac{f_{i,pure}^s}{f_{i,pure}^l} = g_i^s - g_i^l = \Delta g_{fis}$$

But recall that this ratio also connect us to the change in the chemical potentials from the liquid pure case to the solid pure case at a given temperature and pressure. So I can write based on the chemical potential definition that this can be written as RT LN, FIS pure by FIL pure okay. And this is nothing but GIS that is a Molar Gibbs Free Energy of the pure component in the solid phase and this mu IL is nothing but Molar Gibbs Free Energy of component i in a liquid phase. Which means I can write this as GIS minus GIL and this is nothing but delta G of fusion, okay.

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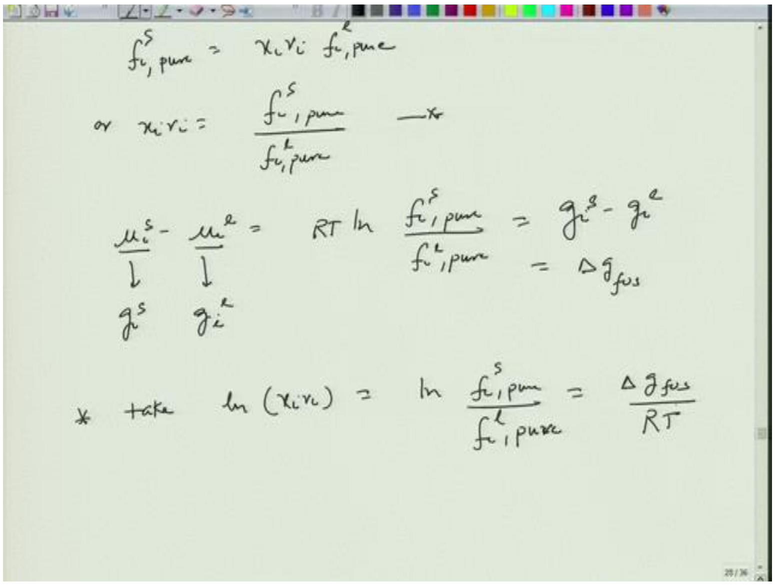

$$f^s_{i,pure} = x_i \gamma_i f^l_{i,pure}$$

or $x_i\gamma_i = \frac{f^s_{i,pure}}{f^l_{i,pure}}$ —*

$$\underset{g^s}{\underset{\downarrow}{\mu_i^s}} - \underset{g_i^l}{\underset{\downarrow}{\mu_i^l}} = RT \ln \frac{f^s_{i,pure}}{f^l_{i,pure}} = g_i^s - g_i^l = \Delta g_{fus}$$

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

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

Now, if I take this, so expression and this and take logarithmic for both the side or log in the both the side. Than I can write this as XI gamma I, this is LN of FIS pure divided by FIL pure okay. Which means I cannot use this expression here and I can write this as delta GF fusion divided by RT.

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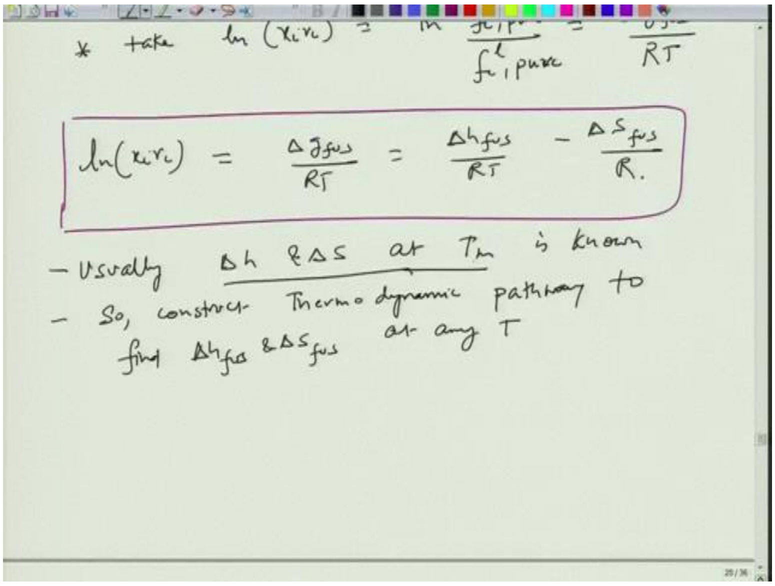
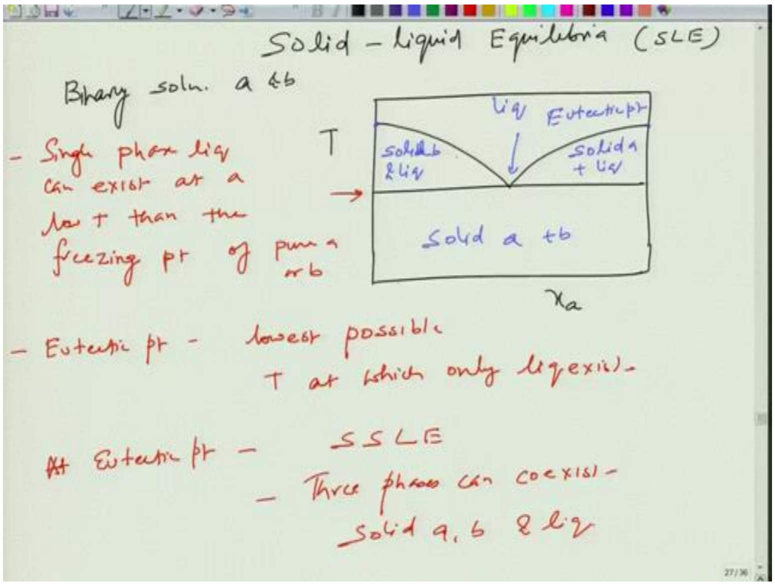


$$* \text{ take } \ln(x_i\gamma_i) = \ln \frac{}{f^l_{i,pure}} = \frac{}{RT}$$

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

- 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

$$\ln(x_i\gamma_i) = \frac{\Delta g_{fis}}{RT} = \frac{\Delta h_{fis}}{RT} - \frac{\Delta S_{fis}}{R}$$



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At Eutectic pt - SSLE
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So I have never a very interesting relation, which relates this XI gamma I to delta G fusion by RT which I can write as delta H fusion by RT minus delta S fusion by R okay. So I can relate this composition of a component I okay and the activity coefficient here to the free energy change okay, along the fusion line and which can be connected to the enthalpy and the entropy part.

Now this is a relation which we got okay, so we can use this relation. Often what we know is delta H and delta S at melting condition is known okay. So, but our interest is to find out this T okay, across the functions. So that means the T has to be variable also, it is not just TN but TN can be used as a reference also. So what we have to do is to construct a thermodynamic pathway to find delta H fusion and delta S fusion and this is at any temperature.

So using this as a reference because this is the point which we know, which will assume that this information is given to you. If you want to find out delta H fusion and delta S fusion at any other temperature. Then we have to create a thermodynamic pathway okay, which should be a reversible. And if you do that then we will be able to find out this information of the composition at a different temperature okay.

So there two ways to do that either we assume the certain model for gamma I or we can assume this, that is this is something is a ideal solution and hence a gamma is equal to 1 and that is something which we can look at in the next class. So I will stop here and essentially I will take this in the next class where we are going to construct a thermodynamic pathway to find out the delta H fusion and delta S fusion at a different temperature and then subsequently we will use it in this equation to find the composition versus temperature plot for solid liquid equilibria. Okay, so with that, I will close today and I will see you in the next class.