Advanced Thermodynamics
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Lecture -30
Solid - Liquid Equilibrium

Welcome to the MOOCs course advance thermodynamics the title of this lecture is solid liquid-liquid equilibrium. Till now what we have seen? We have seen our different equilibrium systems like vapor-liquid equilibrium, then a liquid-liquid equilibrium, then vapour-liquid-liquid equilibrium those systems we have seen. We have seen how to construct a phase diagram for different, equilibrium system.

And then also we constructed equilibrium relations in order to obtain the equilibrium composition etcetera those things we have seen and then we have also seen several example problems under each category of VLE, LLE and VLLE. So now what we do? We take the last topic of this course that is solid liquid equilibrium. We will be having two lectures in this particular week. So, first lecture of this week is going to be on solid-liquid equilibrium.

How to construct a phase diagram for this solid liquid equilibrium systems? And then how to construct the equilibrium relation? So that to obtain the equilibrium composition for the case of solid liquid equilibrium as well, that is what we are going to see in this particular lecture and in the next lecture we will be discussing a few problems based on what we are going to discuss in this particular lecture.

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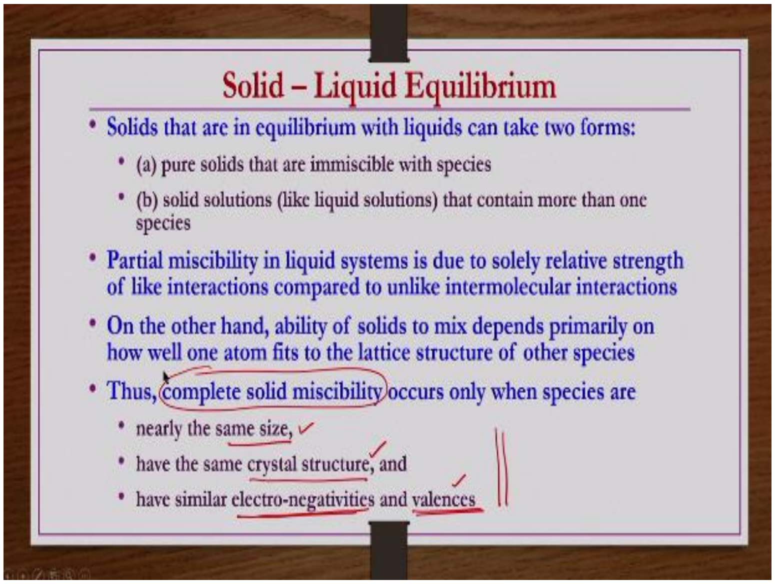

Solid – Liquid Equilibrium

- Solids that are in equilibrium with liquids can take two forms:
  - (a) pure solids that are immiscible with species
  - (b) solid solutions (like liquid solutions) that contain more than one species
- Partial miscibility in liquid systems is due to solely relative strength of like interactions compared to unlike intermolecular interactions
- On the other hand, ability of solids to mix depends primarily on how well one atom fits to the lattice structure of other species
- Thus, complete solid miscibility occurs only when species are
  - nearly the same size,
  - have the same crystal structure, and
  - have similar electro-negativities and valences

Solid-liquid equilibrium; Solids that are in equilibrium with liquids can take two forms, first one is the pure solids that are immiscible with species, then solid solutions like similar to liquid solution that contain more than one species these two forms it is possible, wherever we have solids that are in equilibrium with liquids. What we do, we will be taking individual case like pure solids in equilibrium with liquids then solid solution.

That is partially miscible solid solutions in equilibrium with liquid solutions that is what we are going to take individually. In the case of liquid systems what happens partial miscibility is depends on the related strength of the like and unlike intermolecular interactions. So, if the like interactions are stronger then it is possible that the liquid-liquid system may have a kind of partial miscibility.

So, whereas in the case of solids the ability of solids to mix depends primarily on how well one atom fits to the lattice structure of the other species. So that is the way the solid mixing is taking place. Let us say if component a, solids lattice structure is something like this. Usually it may not be true but let us assume the other one is having like this. So, this lattice structure will not fit onto the component a lattice structure.

So, under such conditions probably it is not possible that is solid solution formation may not take this if the lattice structures are different. Because this lattice structure of you know a, is different from that of b. So, this atom of b is not going to fit comfortably in the lattice structure of this component a. If they are similar, then it is possible this solid solution may take place. So, thus complete miscibility occurs only when species are nearly the same size.

We will take an example also and how the same crystal structure as well and in addition to this one, how the similar electro negativities and then valances as well. So, if you have two solids of similar size say almost same size and then their crystal structure also same. In addition to the size then how the similar electron-negativities and valences it is possible that complete solid miscibility may take place.

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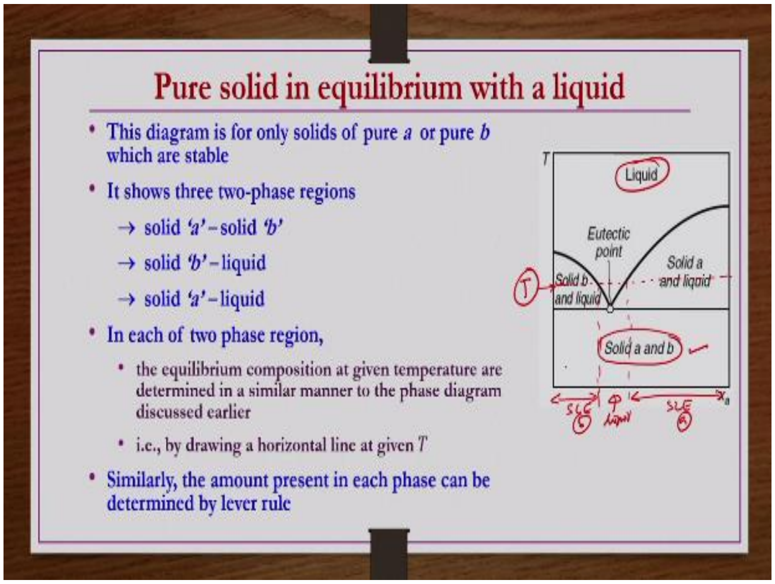

Pure solid in equilibrium with a liquid

- This diagram is for only solids of pure *a* or pure *b* which are stable
- It shows three two-phase regions
  - → solid 'a' – solid 'b'
  - → solid 'b' – liquid
  - → solid 'a' – liquid
- In each of two phase region,
  - the equilibrium composition at given temperature are determined in a similar manner to the phase diagram discussed earlier
  - i.e., by drawing a horizontal line at given T
- Similarly, the amount present in each phase can be determined by lever rule

So now we take a case of pure solid in equilibrium with a liquid. So, what we have? We have a phase diagram of this pure solid in equilibrium with a liquid. So then what we take we take two different solids and then liquid this, solids are pure. So this, solids are dissolving into the liquid phase and then there is a kind of equilibrium. So, in the liquid phase there will be some solid fraction would be there.

So those fractions will be calculated whereas the solids are remaining pure that is liquid are not transferring into the solid phase that is one way transfer is taking place until the equilibrium is established. For that case if you have a T-X_a diagram it looks like this. So here the even the solids are transferring into the liquid. Liquid is not transferring into the solid phases. So this, solids are remaining pure even some fraction of this solids are going into the liquid phases.

So, this diagram is for only solids of pure a or pure b which are stable and then it shows 3 two-phase regions. What are those three two-phase regions? One is this solid a and solid b two-phase region and then solid b and then liquid equilibrium that is SLE. One SLE region here and then solid a, and liquid so, this is another SLE. So liquid is same but in one case this solid is b, and the other case solid is a, and then below certain temperature we have only few solids a and b.

We have only pure solid a and b and then ever certain temperature what we have? Only pure liquid solids are not there. So that is two-phase region solid a and then solid b region. Then solid b and then liquid that SLE region, so this is SLE region and then solid a and then liquid region. These are the three two-phase regions are there. In each of two phase region the equilibrium composition at given temperature are determined.

In a similar manner to the phase diagram discussed earlier in the case of VLE and LLE. How do you find out? That is simply you draw a tie line by drawing a tie line horizontal line at given temperature. Let us say if you wanted to find out the equilibrium composition at this particular certain temperature. So, this temperature if you draw a horizontal line here, so this is the tie line. So as X_a increases, we can say different phases are forming.

So, at the lower X_a regions we have solid b and liquid regions and in further increasing these compositions then we have only liquid regions. So only liquid is there and after that again solid a and then liquid are there, so this is SLE with the solid b and this is SLE with solid a and then in between only liquid is there at this temperature because this temperature we are taking a this temperature.

We have drawn a tie line at this temperature, so this is like this we can find out the corresponding composition you can find out. So similarly, the amount present in each phase can be determined by the lever rule as we have done in the case of VLE problems. We discuss some more details of this phase diagram in the next slide.

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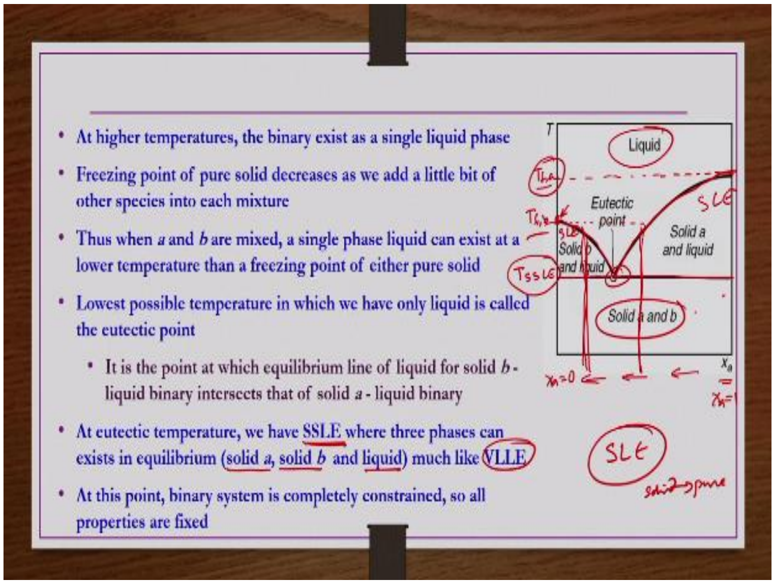

- At higher temperatures, the binary exist as a single liquid phase
- Freezing point of pure solid decreases as we add a little bit of other species into each mixture
- Thus when *a* and *b* are mixed, a single phase liquid can exist at a lower temperature than a freezing point of either pure solid
- Lowest possible temperature in which we have only liquid is called the eutectic point
  - It is the point at which equilibrium line of liquid for solid *b* - liquid binary intersects that of solid *a* - liquid binary
- At eutectic temperature, we have SSLE where three phases can exists in equilibrium (solid *a*, solid *b* and liquid) much like VLLE
- At this point, binary system is completely constrained, so all properties are fixed

So if you have this picture again here, so let us take in the temperature the upper limit of this temperature of this SLV curve with solid a is freezing point of component a and then this temperature is freezing point of component b. So now what happens? So, depending on the composition, let us say if you draw a line here also, so now within this composition region you can have a kind of a liquid that is also possible.

And then eutectic point is the point at which the last liquid drop is remaining below that one there is no liquid actually. Or this is also the point at which SLE curve with solid b and then SLE curve with solid a, these two curves wherever they are intersecting that point is known as the eutectic point and this point this line horizontal line this we can call something like SSLE like VLLE that we have seen.

Now here we have SSLE that is two solids because this point is common to this solid-solid equilibrium as well. This point eutectic point is common point this for SSLE SLE with a and then SLE with b solid for all these things, it is common. So, this we can take as a kind of solid-solid liquid equilibrium kind of thing. So, within the solid liquid equilibrium, we are able to discuss the solid-solid equilibrium as well as the solid-solid liquid equilibrium as well.

In addition to simply solid liquid equilibrium, so these are the things that some more things that we can see here. So, at higher temperature the binary exists as a single liquid phase. Freezing point of pure solid a, let us say if you take purely initially a that decreases as we add a little bit of other species into the mixture so that is means this is initially this is the freezing point of a so that is X_a corresponding to $X_a = 1$.

Corresponding to X_a whatever the temperature is there of this T_{SSE} curve with solid a and then liquid. So that point, that is freezing point of pure component a but now if X_a is decreasing that means you are adding some more foreign species when you are added to this one. So, this freezing point is gradually decreasing. So thus, when a and b are mixed a single, phase liquid can exist at a lower temperature than freezing point of either of pure solids.

So, this is, when $X_a = 0$, so then that is the pure b so the corresponding temperature of here which is the SLE curve for solid b and then liquid. This temperature is nothing but freezing point of b. And then freezing point of a is the top one. So freezing point of b is still lowest one compared to both of these. So below the temperature of this $T_{f,b}$there would be a kind of region where pure liquid can exist so that is this region this is all region.

Lowest possible temperature in which we have only liquid is called this eutectic point this is the point that we have defined already. So, this is the point where lowest possible temperature in which we have only liquid. Eutectic point it is also known as the point at which equilibrium line of liquid for solid b and then liquid binary intersects that of solid a and liquid binary intersects. So that is SLE of a and liquid and then SLE of b and liquid are intersecting at this point.

At eutectic temperature we have SSLE where three phases can exist in equilibrium that is solid phase a, solid phase b and then a liquid phase which is much like VLLE. So, at this point binary system is completely constrained and our properties are fixed. So, this is about the phase diagram of SLE system when solid is pure. So that is transfer is one side only one direction only solids are going into the liquid, but liquid is not going into the solids.

Even when the transfer is taking place that is one, way transfer of the species taking place. So, what we do? We do construction of equilibrium relation so that to estimate the equilibrium composition of this solid liquid equilibrium.

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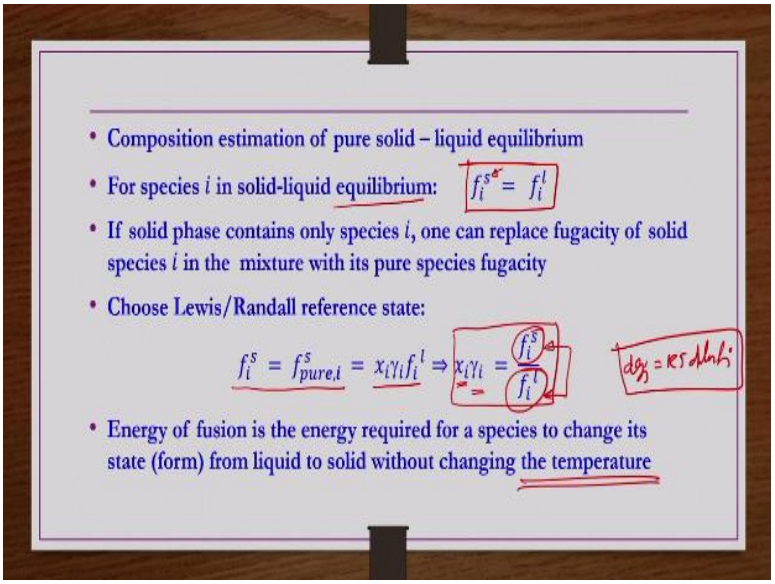

- Composition estimation of pure solid – liquid equilibrium
- For species i in solid-liquid equilibrium: $\boxed{f_i^s = f_i^l}$
- If solid phase contains only species i, one can replace fugacity of solid species i in the mixture with its pure species fugacity
- Choose Lewis/Randall reference state:

$$\underline{f_i^s = f_{pure,i}^s} = \underline{x_i \gamma_i f_i^l} \Rightarrow \boxed{x_i \gamma_i = \frac{f_i^s}{f_i^l}}$$

$$\boxed{dg_i = RT\, d\ln f_i}$$

- Energy of fusion is the energy required for a species to change its state (form) from liquid to solid without changing the temperature

So, for species i in solid liquid equilibrium. So, what we know? At equilibrium, we know the species of component i has to be equal in all the coexisting phases which are at equilibrium. So, $f_i^s = f_i^l$. Now in this case f_i^s is for the pure component because for the solid we are taking pure solid it is not and to this solid liquid is not coming and joining. So only solids are going and then joining the liquid one, way transfer kind of thing.

So, if solid phase contains only species i one can replace fugacity of solid species i in the mixture with its pure species fugacity. So solid is going to the liquid in order to make the transfer of species to take place solid is transferring into the liquid phase that is taking place but this amount of solid may be decreasing this solid phase but that reduced amount of solid is remaining pure. So that is mole fraction of that solid element within the solid phase = 1 always in that case we are taking now.

So, if the solid is pure then fugacity of that pure solid component can be taken as a kind of a pure species fugacity. So here we need to have a kind of a reference state as well. So, let us choose Lewis Randall reference state for the liquid system or the liquid phase. Then f_i^s we are taking as $f_{pure\ i}^s$ and then for the liquid we know $x_i \gamma_i f_i^l$. So, f_i^l we are not writing anything, so let us keep it as it is.

So then x_i γ_i = $\frac{f_i^s}{f_i^l}$, f_i^snothing but the pure component fugacity for the solid and then $f_i^l$is nothing but the, according to Lewis Randall reference state whatever the fugacity of that component is, that is we are taking for the liquid phase, x_i is nothing but the mole fraction of that solid component i in the liquid phase. In the liquid phase how much, solid component is present that is given by x_i.

And then γ_i is nothing but the non-ideality of the liquid phase. So, we do not have, any kind of measurements to do this what is $f_i^l$and f_i^s to do the further calculation. So what we do we get back to the definition dg_i = RT dln f_i this information we make use and then accordingly we write in place of, this one, we take ln both the sides and then we make use of this equation to get relation between x_i γ_i and the Gibbs energy.

So, energy of fusion is the energy required for a species to change its state without changing the temperature has to remain constant.

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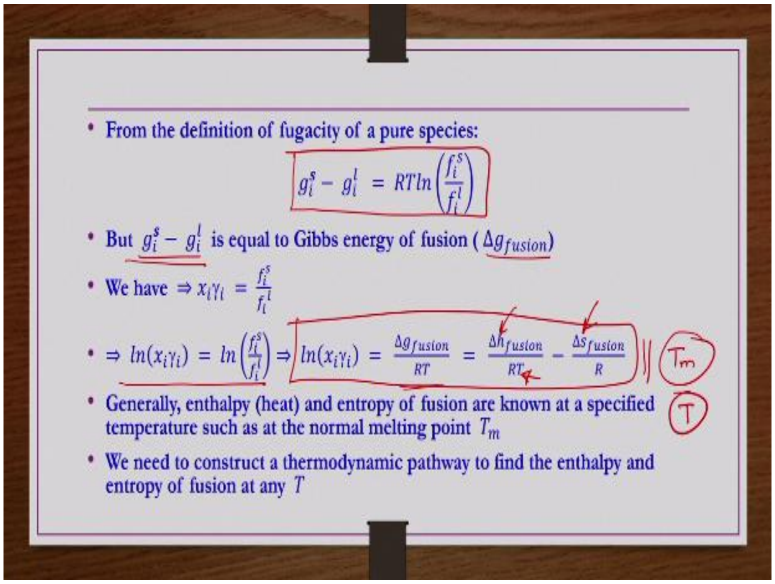

- From the definition of fugacity of a pure species:

$$\boxed{g_i^s - g_i^l = RT\ln\left(\frac{f_i^s}{f_i^l}\right)}$$

- But $g_i^s - g_i^l$ is equal to Gibbs energy of fusion (Δg_{fusion})
- We have $\Rightarrow x_i\gamma_i = \frac{f_i^s}{f_i^l}$
- $\Rightarrow \ln(x_i\gamma_i) = \ln\left(\frac{f_i^s}{f_i^l}\right) \Rightarrow \boxed{\ln(x_i\gamma_i) = \frac{\Delta g_{fusion}}{RT} = \frac{\Delta h_{fusion}}{RT} - \frac{\Delta s_{fusion}}{R}}$
- Generally, enthalpy (heat) and entropy of fusion are known at a specified temperature such as at the normal melting point T_m
- We need to construct a thermodynamic pathway to find the enthalpy and entropy of fusion at any T

So from the definition of fugacity of pure species we know that d gi we can write data as RT d ln f_i so that is g_i^s- g_i^l= RT ln $\frac{f_i^s}{f_i^l}$, whatever d g_i = RT d ln f_i relation that if you apply for this SLE problem for component i then g_i^s- g_i^l = RT ln $\frac{f_i^s}{f_i^l}$. But this g_i^s- g_i^l difference, whatever is there that = the Gibbs energy of fusion that is if you take it as Δg_{fusion}.

Then already we have this $x_i\,\gamma_i = \frac{f_i^s}{f_i^l}$ in the previous slide. So now let us take ln both sides. Then in place of $\ln \frac{f_i^s}{f_i^l}$, you can write $\frac{\Delta g_{fusion}}{RT}$ or $\frac{g_i^s - g_i^l}{RT}$ and g_i^s - g_i^l is nothing but Δg_{fusion} and then Δg_{fusion} we can write Δh_{fusion} - T Δs_{fusion}. So that quantity if you divide by RT then we have $\frac{\Delta h_{fusion}}{RT}$ - $\frac{\Delta s_{fusion}}{R}$.

So then generally enthalpy whatever the enthalpy this Δh_{fusion} and Δs_{fusion}, etc. They are available at some specified temperature something like melting point temperature etc. but these things we wanted to have this calculation this relation that is there at any temperature T. So, in order to have this information at certain temperature T we need to have Δh_{fusion} at those temperatures then only we can do.

Or we have to make a kind of something relation that we get over of this Δh_{fusion} at certain temperature T and then get this x_i composition etc. So how to do that one? So, in order to get that information Δh_{fusion} and Δs_{fusion} is certain temperature T or make a relation between the Δh_{fusion} at different temperatures will be having a thermodynamic pathway. So how that would be looking like.

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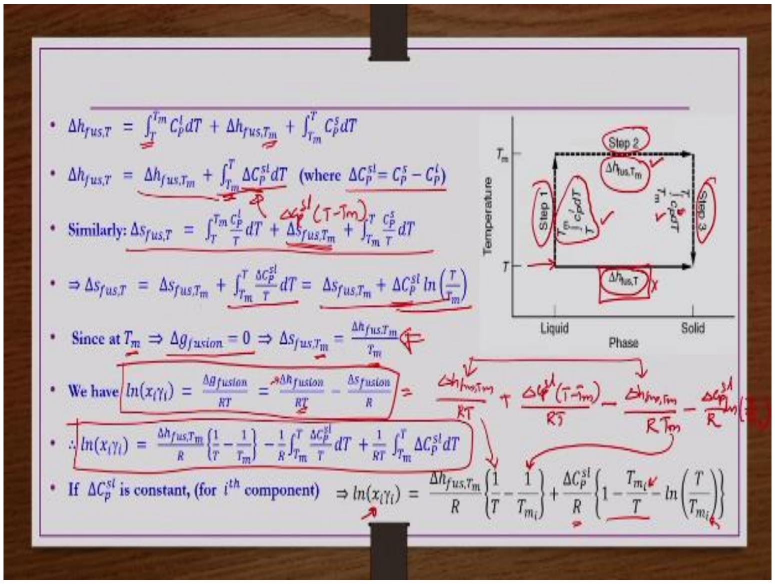

- $\Delta h_{fus,T} = \int_T^{T_m} C_p^l dT + \Delta h_{fus,T_m} + \int_{T_m}^{T} C_p^s dT$
- $\Delta h_{fus,T} = \Delta h_{fus,T_m} + \int_{T_m}^{T} \Delta C_p^{sl} dT$ (where $\Delta C_p^{sl} = C_p^s - C_p^l$)
- Similarly: $\Delta s_{fus,T} = \int_T^{T_m} \frac{C_p^l}{T} dT + \Delta s_{fus,T_m} + \int_{T_m}^{T} \frac{C_p^s}{T} dT$
- $\Rightarrow \Delta s_{fus,T} = \Delta s_{fus,T_m} + \int_{T_m}^{T} \frac{\Delta C_p^{sl}}{T} dT = \Delta s_{fus,T_m} + \Delta C_p^{sl} \ln\left(\frac{T}{T_m}\right)$
- Since at $T_m \Rightarrow \Delta g_{fusion} = 0 \Rightarrow \Delta s_{fus,T_m} = \frac{\Delta h_{fus,T_m}}{T_m}$
- We have $\ln(x_i\gamma_i) = \frac{\Delta g_{fusion}}{RT} = \frac{\Delta h_{fusion}}{RT} - \frac{\Delta s_{fusion}}{R}$
- $\therefore \ln(x_i\gamma_i) = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_m}\right\} - \frac{1}{R}\int_{T_m}^{T} \frac{\Delta C_p^{sl}}{T} dT + \frac{1}{RT}\int_{T_m}^{T} \Delta C_p^{sl} dT$
- If ΔC_p^{sl} is constant, (for i^{th} component) $\Rightarrow \ln(x_i\gamma_i) = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_i}}\right\} + \frac{\Delta C_p^{sl}}{R}\left\{1 - \frac{T_{m_i}}{T} - \ln\left(\frac{T}{T_{m_i}}\right)\right\}$

$\Delta C_p^{sl}(T-T_m)$

$= \frac{\Delta h_{fus,T_m}}{RT} + \frac{\Delta C_p^{sl}(T-T_m)}{RT} - \frac{\Delta h_{fus,T_m}}{RT_m} - \frac{\Delta C_p^{sl}}{R}\ln($

So, let us say a temperature T you wanted to calculate Δh_{fusion}. So, from liquid to solid phase you are going at this temperature T but that is not possible because this information you are not having indeed you wanted to calculate this information. So, but in general for any system C_P information's are known. C_p information's are C_p^s, C_p^l, C_p^v etc. those information's are known.

So now what we do at this liquid stage we increase the temperature T from T to T_m and then whatever the energy is there that you can obtain by $\int_{T_m}^{T} C_p^l dT$ and then integration from T to T_m. Once you have reached at the temperature T_m. At temperature T_m $\Delta h_{fus,T_m}$ are known. So, you do not need to do anything and then from this temperature you reduced temperature, so that you get to the required solid state.

So that energy corresponding energy enthalpy energy that you can get it as $\int_{T_m}^{T} C_p^s dT$. So, this is initially not known. So now this you can obtain by having this thermodynamic path one of step 1, step 2 and step 3 and then all these calculations step 1, step 2, step 3 calculations you can do because $\Delta h_{fus,T_m}$ is known and then C_p information's are in general known.

So, you can add the step 1, step 2, step 3, then you will get $\Delta h_{fus,T}$. So that is the thermodynamic cycle we are developing. So that means $\Delta h_{fus,T}$ is nothing but $\int_{T}^{T_m} C_p^l dT$ + $\Delta h_{fus,T_m}$ that is at melting point + $\int_{T_m}^{T} C_p^s dT$. So that means $\Delta h_{fus,T} = \Delta h_{fus,T_m} + \int_{T_m}^{T} \Delta C_p^{sl} \, dT$ where ΔC_p^{sl} is nothing but C_p^s - C_p^l because this integration limit we are taking from T_m to T.

Whereas for the $\int_{T}^{T_m} C_p^l dT$. So, there is the region - is coming. So now if you take this ΔC_p^{sl} as a constant then this particular term you can write it as, the second term you can write it as $\Delta C_p^{sl}(T - T_m)$. So exactly similar thermodynamic cycle or thermodynamic pathway, you can construct for Δs_{fusion} as well for the entropy at that particular temperature.

So, $\Delta s_{fus,T}$ is nothing but $\int_{T}^{T_m} \frac{C_p^l}{T} dT + \Delta s_{fus,T_m} + \int_{T_m}^{T} \frac{C_p^s}{T} dT$. So here also this $\Delta s_{fus,T_m}$ melting point temperature or in general known for a given system. So that means $\Delta s_{fus,T}$ is nothing but $\Delta s_{fus,T_m} + \int_{T_m}^{T} \frac{\Delta C_p^{sl}}{T} dT$ and then here again ΔC_p^{sl} is nothing but C_p^s - C_p^l.

So again, if you take this ΔC_p^{sl} as constant then integration if you do you will get ln T and then limits when you substitute ln $\frac{T}{T_m}$, you can have. So, but at T_m, $\Delta g_{fusion} = 0$ that means $\Delta s_{fus,T_m} = \frac{\Delta h_{fus,T_m}}{T_m}$. This is what you can have. Why you are doing this one? Because this we wanted to substitute in this relation.

In this relation that we have derived previously so in place of Δh_{fusion}, we have to substitute this part and then in place of Δs_{fusion} you have to substitute this part. So that if you do here $\frac{\Delta h_{fusion}}{RT}$ - $\frac{\Delta h_{fus,T_m}}{RT}$, Because divided by RT is there + $\frac{\Delta C_p^{sl}}{RT}$ $(T - T_m)$ - $\frac{\Delta s_{fus,T_m}}{R}$.

But $\Delta s_{fus,T_m}$ is nothing but $\frac{\Delta h_{fus,T_m}}{T_m}$. So, increase on that one, we can write $\frac{\Delta h_{fus,T_m}}{RT_m}$ and then R is as it is then what is the remaining term? Remaining term is this one so that is - $\frac{\Delta C_p^{sl}}{R}$ and then ln $\frac{T}{T_m}$. So, these terms if you join together Δh_{fusion} terms and then keep the other times separately then you rearrange these terms.

So then you have this particular equation actually after doing integration and subtracting limits, then you have these things and then for ΔC_p^{sl} when it is constant. So when you join these two terms together, so$\frac{\Delta h_{fus,T_m}}{R}$ then $\frac{1}{T}$ from here and then $\frac{1}{T_m}$from here is coming + from the remaining terms $\frac{\Delta C_p^{sl}}{R}$ we are writing. So, $\frac{T-T_m}{T}$ is nothing but 1 - $\frac{T_m}{T}$.

Then from here - ln $\frac{T}{T_{m_i}}$ is there. T_{m_i} separately i, I am adding because this is, equation we are also going to use subsequently. So, for the component i in order to specify it is for component this i have written. So, this is what you did. So now if you know Δh_{fusion} at melting point temperature that is in general known and then if you know C_p^s and then C_p^l for a given system, then you can find out what is the mole fraction of solid component i that is present in the liquid phase that you can calculate. There you can calculate using this equation.

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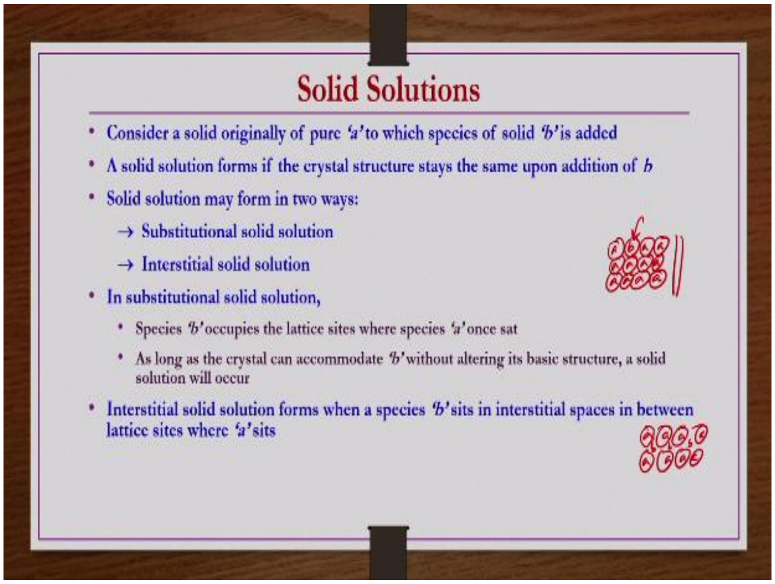

Solid Solutions

- Consider a solid originally of pure *'a'* to which species of solid *'b'* is added
- A solid solution forms if the crystal structure stays the same upon addition of *b*
- Solid solution may form in two ways:
  - → Substitutional solid solution
  - → Interstitial solid solution
- In substitutional solid solution,
  - Species *'b'* occupies the lattice sites where species *'a'* once sat
  - As long as the crystal can accommodate *'b'* without altering its basic structure, a solid solution will occur
- Interstitial solid solution forms when a species *'b'* sits in interstitial spaces in between lattice sites where *'a'* sits

So now what we do? We take a solid solution till now what we have taken? We have taken pure solids in equilibrium with liquid. Now, we take solid solution in equilibrium with certain liquids. So first how the solid solution form that we have to see? Consider a solid originally of pure a to which species of solid b is added. So, it is a solid mixture a and b. A solid solution forms if the crystal structure stays the same upon addition of b.

Solid solution may form in two ways, one of the way is substitutional solid solution form and the second one is the interstitial solid solution form. So in this substitutional solid solution form what happens you have the crystal lattice structure of one component, one atom was sitting in the lattice structure if that has vacated and that lattice structure vacated the point if the other atom b is coming and sitting comfortably without making much changes in the system.

Then we can say that the solid solution is taking place and then that kind of solid solution is known as the Substitutional solid solution. So that is species b occupies lattice sides where species a once sat, so let us say you have lattice structure of component is something like this. For example, I am saying I am drawing for example. So, all these are you know, a atoms are present here like this.

So now let us say this one particular is lattice site is vacated where earlier b were sitting. Now if species a come and then sit here comfortably without making any changes to the lattice structure of this particular system, then we can say solid solution has taken place or the solid solution formation has taken place and then that is taken place by this substitutional solid solution method.

So as long as the crystal can accommodate b without altering its basic structure a solid solution will occur. So, when you make the substitutional arrangement of the species b in the lattice structure of component a if it is not altering the basic structure of component a then solid solution will occur. Interstitial solid solution is the other form that forms when a species b sits in interstitial spaces in between the lattice sides where a is sitting earlier.

So, let us say you have something like this. All these a are there. So now let us say b is coming and sitting in the interstitial spaces something like this, then it is known as the interstitial solid solution form. So, these interstitial spaces are not part of the crystal structure, obviously.

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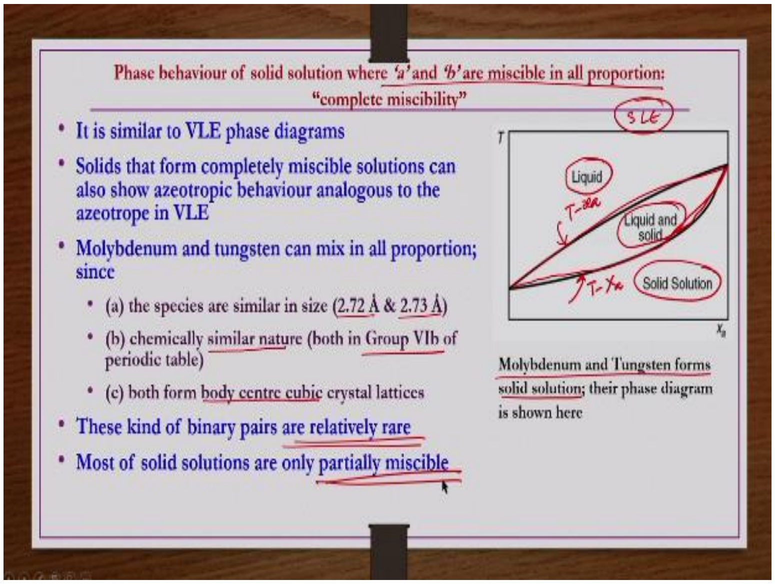

Phase behaviour of solid solution where 'a' and 'b' are miscible in all proportion: "complete miscibility"

- It is similar to VLE phase diagrams
- Solids that form completely miscible solutions can also show azeotropic behaviour analogous to the azeotrope in VLE
- Molybdenum and tungsten can mix in all proportion; since
  - (a) the species are similar in size (2.72 Å & 2.73 Å)
  - (b) chemically similar nature (both in Group VIb of periodic table)
  - (c) both form body centre cubic crystal lattices
- These kind of binary pairs are relatively rare
- Most of solid solutions are only partially miscible

Molybdenum and Tungsten forms solid solution; their phase diagram is shown here

So now we see phase behavior of solid solution where a and b are miscible in all proportions that is complete miscibility can take place, but we take a case where partial miscibility is there, that case also we consider. So the phase diagram of such kind of system where the miscibility of solids take place in all proportions then for such conditions, if you see this SLE curve, then it will have similar structure like VLE curve and the VLE curve T-X_a diagram.

If you draw something like this, so then we have a vapour at the top and then liquid at the bottom in between we have a kind of that is in between this and closed area we have a kind of a vapor and liquid. Similar to that one here the liquid would be at the top. At the high temperature and then solid solution we call it solid solution because the solids are miscible in all proportion for that case we are doing.

So those solid solutions will be at the bottom at lower temperature and then this curve would be T-x_a small x_a am writing. This curve is nothing but T-X_a am writing because now solids are also transferring. Previous case, we have taken pure solids now we have taken a case, partial to complete miscibility is taking place and then transfer is taking place both the sides. So, the liquids are coming into the solid solution.

And then solid solutions are going into the liquid solutions and there is a transfer of species either side and there is an equilibrium. So, whatever the enclosed area is there between these two curves that is having both solids and liquids. It is quite similar to whatever we have seen in the VLE case. So, this is example of Molybdenum and Tungsten form solid solution and then this is the typical phase diagram for such kind of system we can see here.

It is similar to VLE phase diagrams. Solids that form complete miscible solutions can also show azeotropic behavior analogous to azeotrope in VLE. So here in this case, we have not shown any kind of VLE cases but even in SLE also azeotropes can form and then those phase diagrams would also be looking similar to VLE of azeotropic mixtures. So, molybdenum and tungsten can mix in all proportions.

Because this we are taking miscibility in all proportions so, why these two solids can mix in all proportions? Because of the obvious reasons that we have discussed. Their size has to be same and there the crystal structure has to be similar electro negativities valencies have also be same. So that is then only a complete miscibility will take place. So, this molybdenum and tungsten can mix in our proportions because of such regions.

That the species are similar in size one is having 2.72 Angstrom size another one is 2.73 Angstrom size almost same. And then chemically similar nature also because all of them belong to group six b of periodic table so that chemical nature would be same and then both form bodies center cubic, bcc crystal lattice. So, because of such regions this, two solids completely mix into each other in all proportions.

So, but these kind of binary pairs are relatively rare, so in general we have partially miscible solid solutions. This what we have to do? We have to see the phase diagram for partial miscible solid solutions. What we have to do?

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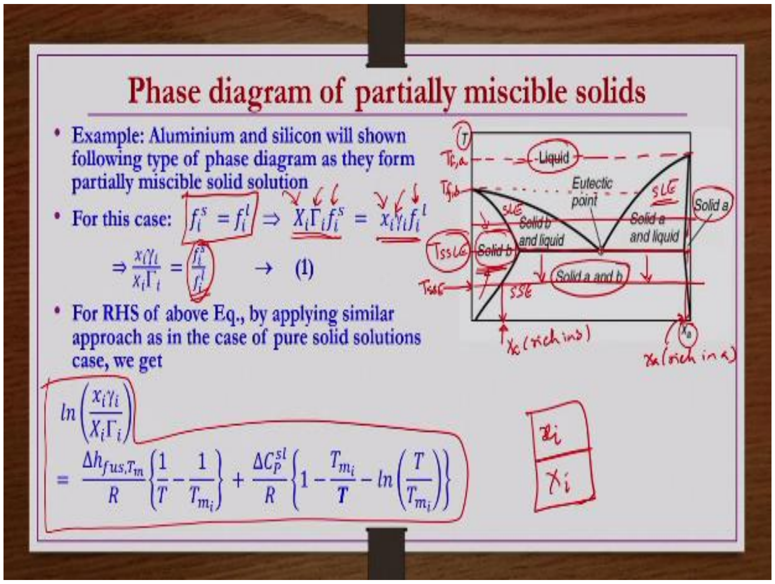

Phase diagram of partially miscible solids

- Example: Aluminium and silicon will shown following type of phase diagram as they form partially miscible solid solution
- For this case: $\boxed{f_i^s = f_i^l} \Rightarrow \underline{X_i \Gamma_i f_i^s} = \underline{x_i \gamma_i f_i^l}$

$$\Rightarrow \frac{x_i \gamma_i}{X_i \Gamma_i} = \frac{f_i^s}{f_i^l} \quad \rightarrow \quad (1)$$

- For RHS of above Eq., by applying similar approach as in the case of pure solid solutions case, we get

$$\boxed{ln\left(\frac{x_i \gamma_i}{X_i \Gamma_i}\right) = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_i}}\right\} + \frac{\Delta C_P^{sl}}{R}\left\{1 - \frac{T_{m_i}}{T} - ln\left(\frac{T}{T_{m_i}}\right)\right\}}$$

We have to see phase diagram of partially miscible solids so that looks like if you draw a T-x-y diagram it looks like this it is something similar to so called VLLE curve we can see here, so now T versus X_a, if you plot so it looks like this. Example is aluminum and silicon will show following type of phase diagram as the form partial immiscible solid solution. So here how many of two phase regions are there?

One is the SSE this one solid a and then solid b partially miscible, SSE system is there and then solid b and then liquid SLE system is, this is also two phase region and then there is a solid a and then liquid SLE region is also there and there these are the three phase reasons. So, there is a liquid at higher temperature only single liquid solutions is available, so up to these things are very common as in the case of pure solid solutions in equilibrium with a liquid.

Now but partially miscible solid solutions in equilibrium with liquid then we have additional two phases. So that is one solid phase solid b phase may be there and then solid a phase may be there. At lower composition solid b can exist as a kind of single, phase solid b phase depend at different temperature levels are shown here in this range. Also, at higher mole fractions what we can have a pure solids at different temperatures as shown in this region.

So that is the additional thing that is coming into the picture, compared to the SLE phase diagram of a pure solids in liquids. Now here a partially miscible solids in liquid so there is a equilibrium shown diagram T-X_a diagram looks like this. So this line wherever this all three phases, are being separated all wherever these all three two phase system that is solid a and solid b system is separated from SLE of solid b and liquid system and then SLE of solid a and liquid system are being separated this by this line, so that is the line is known as T_{SSLE} there.

So, this is what we have and then here also we have the eutectic point this is T lowest possible temperature. This T_{SSLE} is also lowest possible temperature where liquid can exist. Below this temperature liquid is not going to exist it is going to be only solid whatever may be the composition, if the composition is in between this region then both solid a and solid b would be there if the mole fraction is small then only solid b will be there.

If the mole fraction is large then only solid a may be there. If the intermediate mole fractions of a both solid a and solid b may be there, but there will not be liquid below this temperature T_{SSLE}. And then above this temperature, depending on the system to system, about this one we can have a pure liquids anyway, so that is at $T_{f,a}$ freezing point of a is this one and then freezing point of b is this one.

So now what happens? Below either of these, temperature we can have a kind of only liquid phase. Only liquid phase is possible below the freezing point temperature of both of these components, that is also possible same as in the case of previous slides. So, this is about the phase diagram of partially miscible solids and then again if you wanted to find out the composition of our different phase regions, what you have to do?

You have to draw a tie line at a constant temperature, you draw a horizontal line and then accordingly you have to find out. So, let us say if you wanted to find out the equilibrium composition of solids a and b at temperature T_{SSE} you have to draw a line, horizontal line like this. This is the tie line, so whatever this fraction is there that you have to find out. So, this composition is nothing but the composition of that particular component a but in a phase in which b component is rich.

Now here both two solid phase are partially miscible, they are in equilibrium. So, one of the phase, may be rich in b another phase region a. So this composition whatever is there, here so this is rich in b and this component here whatever you get that is that X_a only rich in a. Like this you can find out. If you draw a tangent horizontal line here accordingly, you can find out the composition of other phases as well.

And then here also we can see as the temperature above this T_{SSE}. What you can have? If you have a tie line, so then you can have a different phases. As X_a increases, different phases are possible, so that is at lower X_a only solid b may be existing. And then further if you increase the X_a there is SLE of solid b and then liquid is existing and then further increasing the composition and the same temperature, then you have only pure liquid then again further if you increase the mole fraction of this component.

Then it is possible that you have a both solid a and then liquid as SLE and then further a very high large X_a values, you can have a only solid a as a kind of single solid phase. So, at one different temperature different kind of phase composition that you can find out here. Equilibrium composition, you can find out from this phase diagrams, this is quite similar to whatever the case that VLLE that we have seen so it is quite similar to that one.

So, for this case also at equilibrium what we should have $f_i^s = f_i^l$ because fugacity of that component a has to be equal in neither of the components. So for the solid phase capital X_i am using as a kind of mole fraction of that component i in the solid phase and then capital Γ_i am using to estimate or designate the non-ideality of the system in the solid phase and an f_i^s is the reference fugacity of that at reference conditions.

What is the fugacity of that particular component? And then for the liquid standard once we are using for the small x_i gives the composition of that component i in the liquid phase. And then gamma is nothing but the activity coefficient of that liquid coefficient which display the non ideality of that liquid phase. Then $f_i^l$is nothing but the fugacity of that component i at certain referenced it.

So now, what we can have here, we can have $\frac{x_i\gamma_i}{X_i\Gamma_i} = \frac{f_i^s}{f_i^l}$then, this one right hand side, what we can have this right hand side term of this equation, we can use the approach that we have used for the pure solids, in the first case in order to develop the equilibrium relations to calculate equilibrium composition.

Whatever we have that method we adopt here also and do this simplification calculation etc. after developing all that, thermodynamic pathway etc. exactly similar way and we do this simplification then you get this equation for the ln $\frac{x_i\gamma_i}{X_i\Gamma_i}= \frac{\Delta \mathrm{h}_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_i}}\right\} + \frac{\Delta C_p^{sl}}{R}\left\{1 - \frac{T_{m_i}}{T} - ln\left(\frac{T}{T_{m_i}}\right)\right\}$, this is what we get.

So, if you have this information of a small x_i and then capital X_i that means you are having the equilibrium composition of that particular component that is coexisting in two phases. Two phases solid and liquid phases that is present in both the phases and then it is at equilibrium, but if you wanted now these things you need to know what is small γ_i? What is capital Γ_i? That also you should know.

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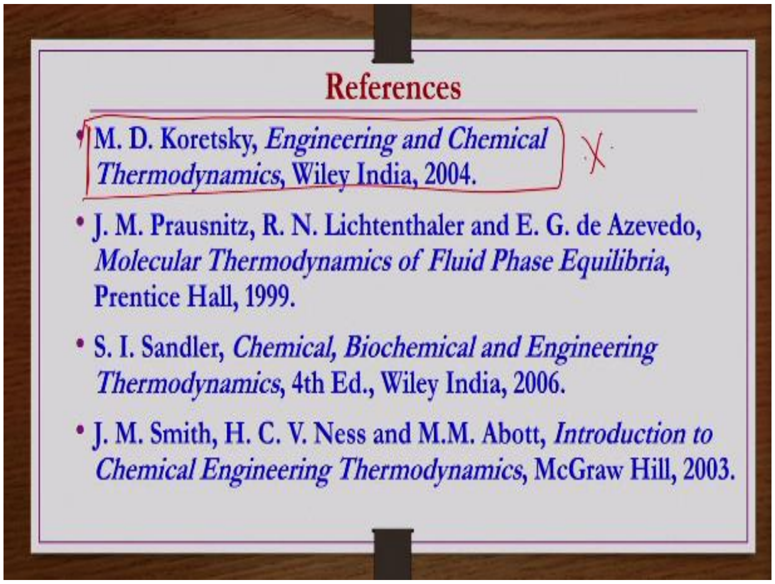

References

- M. D. Koretsky, *Engineering and Chemical Thermodynamics*, Wiley India, 2004.
- J. M. Prausnitz, R. N. Lichtenthaler and E. G. de Azevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, Prentice Hall, 1999.
- S. I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics*, 4th Ed., Wiley India, 2006.
- J. M. Smith, H. C. V. Ness and M.M. Abott, *Introduction to Chemical Engineering Thermodynamics*, McGraw Hill, 2003.

So the references for this lecture are given here. Engineering and chemical thermodynamics by Koretsky. Then Molecular Thermodynamics of Fluid Phase Equilibrium by prausnitz et al, then Chemical Biochemical and Engineering Thermodynamics by Sandler and Introduction to Chemical Engineering Thermodynamics by Smith et al. So however, this entire lecture is prepared from this reference book, which is a very good reference book for this particular lecture that is engineering and chemical thermodynamics by Koretsky. Thank you.