Advanced Thermodynamics

Prof. Nanda Kishore
Department of Civil engineering
Indian Institute of Technology, Guwahati

Lecture -31
Solid - Liquid Equilibrium - 2

Welcome to the MOOCs course, Advanced Thermodynamics the title of this lecture is solid-liquid equilibrium part 2. Since it is a continuation of our previous lecture on solid liquid equilibrium will be having a kind of recapitulation of what we have studied in the previous lecture. So in the previous lecture we have taken different SLE problems where a pure solids in equilibrium with liquid then what is the corresponding phase diagram that is what we have seen.

And then corresponding equilibrium relation in order to find out the equilibrium composition for such case of pure solids in equilibrium with liquid those things also we have develop, and then analogously phase diagram of partially miscible solids in equilibrium with liquid those things we have seen and then for such case also we have seen what are the equilibrium relation that can be used to obtain the equilibrium composition for the case of partially miscible solids in equilibrium with liquid as well. Those two cases we have seen.

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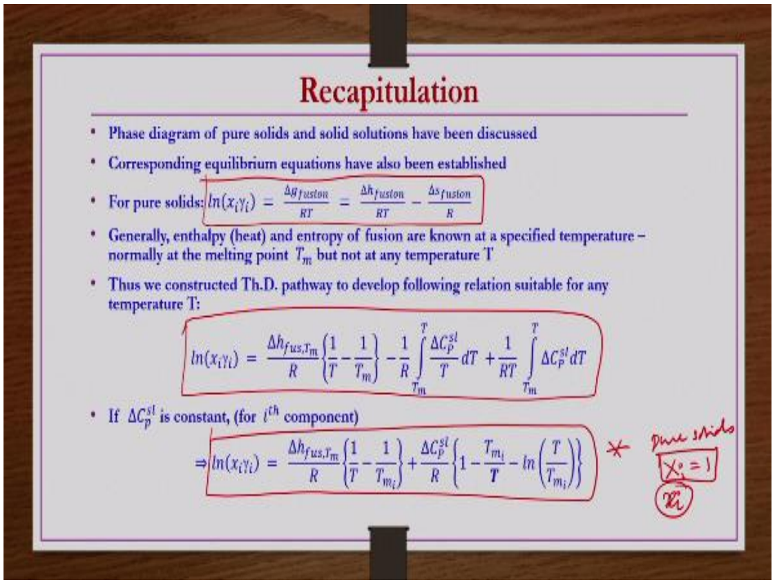

Recapitulation

- Phase diagram of pure solids and solid solutions have been discussed
- Corresponding equilibrium equations have also been established
- For pure solids: $\boxed{ln(x_i\gamma_i) = \frac{\Delta g_{fusion}}{RT} = \frac{\Delta h_{fusion}}{RT} - \frac{\Delta s_{fusion}}{R}}$
- Generally, enthalpy (heat) and entropy of fusion are known at a specified temperature – normally at the melting point T_m but not at any temperature T
- Thus we constructed Th.D. pathway to develop following relation suitable for any temperature T:

$$\boxed{ln(x_i\gamma_i) = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_m}\right\} - \frac{1}{R}\int_{T_m}^{T}\frac{\Delta C_P^{sl}}{T}dT + \frac{1}{RT}\int_{T_m}^{T}\Delta C_P^{sl}dT}$$

- If ΔC_p^{sl} is constant, (for i^{th} component)

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

Pure solids

$\boxed{x_i = 1}$

x_i

So that is phase diagram of pure solids and in solid solutions in equilibrium with liquid have been discussed, then corresponding equilibrium equations have also been established for pure solids we have obtained this information that is ln x_i γ_i = $\frac{\Delta g_{fusion}}{RT}$that is $\frac{\Delta h_{fusion}}{RT}$- $\frac{\Delta s_{fusion}}{R}$but in general this Δh_{fusion} and Δs_{fusion} are available at standard temperature something like at melting temperature etc.

So but we need at certain in temperature any temperature T so what we have to do we have to construct a thermodynamic pathway and then obtain this information at any other temperature T as well that is what we have done. So when we have done that one then we got this expression in the previous lecture that is ln x_i γ_i =$\frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T}-\frac{1}{T_m}\right\}-\frac{1}{R}\int_{T_m}^{T}\frac{\Delta C_p^{sl}}{T}dT+\frac{1}{RT}\int_{T_m}^{T}\Delta C_p^{sl}dT.$

So if you assume this ΔC_p^{sl}as a constant and then do integration substitute the limits and then do some kind of simplification then for ith the component we got this relation, that is ln $\frac{x_i}{\gamma_i}$ = $\frac{\Delta h_{fus,T_m}}{R}$ $\left\{\frac{1}{T}-\frac{1}{T_{m_i}}\right\}+\frac{\Delta C_p^{sl}}{R}\left\{1-\frac{T_{m_i}}{T}-ln\left(\frac{T}{T_{m_i}}\right)\right\}$. This is what we have seen this is for the pure solids.

That is even the solids are being transferred into the liquids, liquids are now transferring into the solid phase, so even during the course of species transfer solid species remaining pure that is capital X_i is remaining 1 maybe then weight may be decreasing our amount may be decreasing because they are transferring to the liquid phase. We have seen in the previous lecture capital X_i we have indicated for the mole fraction of component i in the solid phase.

And then small x_i as usual we have taken the mole fraction of component i in the liquid phase so in the case of pure solids we have this x_i = 1 always. So that is what we have then but in general there may be a kind of partial miscible solutions also. Then this x_i cannot be equal to 1.

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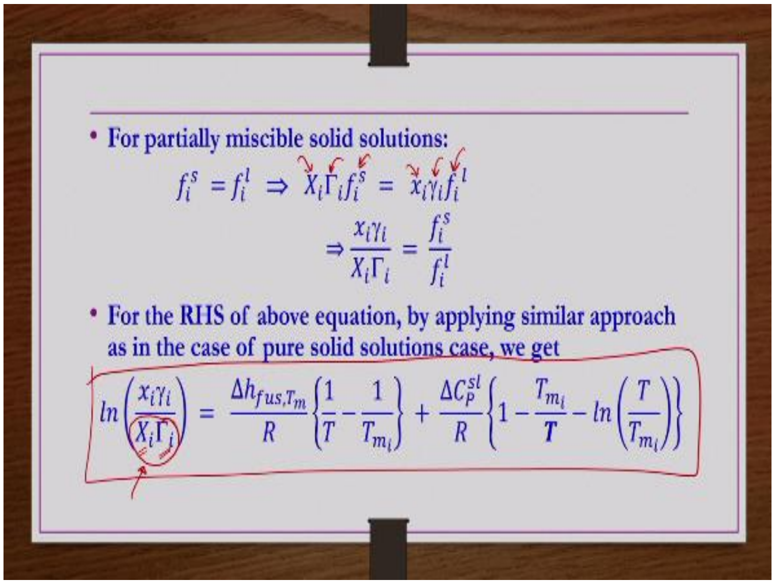

- **For partially miscible solid solutions:**

$$f_i^s = f_i^l \Rightarrow X_i \Gamma_i f_i^s = x_i \gamma_i f_i^l$$

$$\Rightarrow \frac{x_i \gamma_i}{X_i \Gamma_i} = \frac{f_i^s}{f_i^l}$$

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

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

So for such conditions also we have developed these relations for partially miscible solid solutions we have f_i^s= f_i^lthen we have capital X_i capital Γ_i f_i^s= x_i γ_i f_i^lcapital X_i is nothing but the mole fraction of component a in the solid phase and then capital Γ_i is nothing but that indicate or display the non-ideality in the solid phase and then $f_i^s$is nothing but the fugacity of that component i in the solid phase at certain different conditions.

Whereas small x_i is nothing but the mole fraction of that component i in the liquid phase γ_i is nothing but the activity coefficient of that particular component in the liquid phase which indicated the non ideality of the system and then this $f_i^l$is nothing but the fugacity of component i in the liquid phase at certain reference conditions. So, now this we can write it as $\frac{x_i \gamma_i}{X_i \Gamma_i}= \frac{f_i^s}{f_i^l}$.

And then for this one also in the case of pure solids in equilibrium with liquids whatever the way that we have followed for the derivation of equilibrium relation; if you follow entirely the same pathway here also and do the simplification, then you get this ln of this then you get this relation ln $\frac{x_i \gamma_i}{X_i \Gamma_i}= \frac{\Delta \mathrm{h}_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_i}}\right\} + \frac{\Delta C_P^{sl}}{R}\left\{1 - \frac{T_{m_i}}{T} - ln\left(\frac{T}{T_{m_i}}\right)\right\}$.

So only difference compared to the pure solids case is this this additional thing is coming here capital X_i and capital Γ_i are coming into the picture. In the case of partially miscible solution whereas in the case of pure solid solutions in equilibrium with liquids then this capital $X_i = 1$ and then if it is a pure solid then it is a kind of ideal solid so then capital Γ_i is also equal to 1.

Remember ideality in the case of a solid is defined in the similar way as in the case of liquids that is if the component is pure then or if the component is almost pure then we can say that is a kind of ideal system. So if the solids are partially miscible so then they are not pure solids so then obviously they are not ideal so there would be some capital Γ_i information as well and then X_i cannot be 1.

So they what is that X_i that we have to find out in general so this is what we have seen and then corresponding phase diagrams for whether of the cases also we have seen in the previous lecture now what we do we take a few example problem based on the discussions that we had in previous lecture. So, that we can find out the equilibrium composition or a eutectic composition etc. or how we can make use of these relations to get other kind of information? Those things we are going to see in the form of a few example problems.

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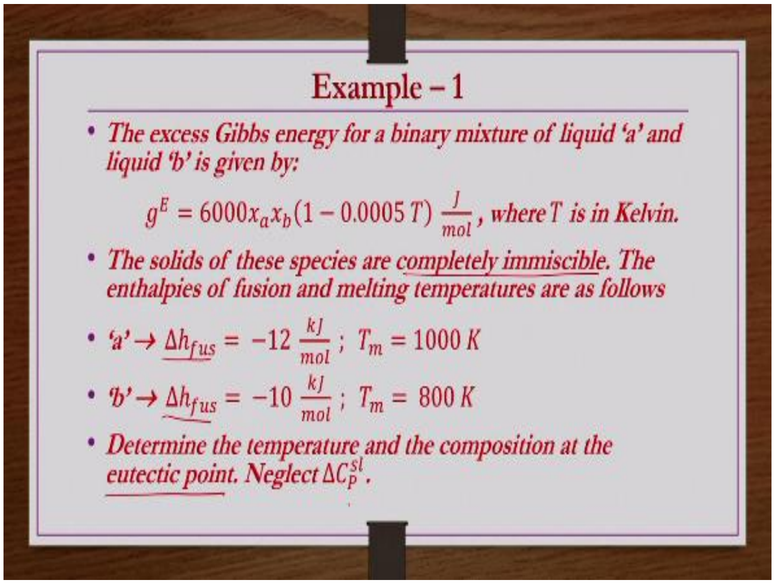

Example – 1

- The excess Gibbs energy for a binary mixture of liquid 'a' and liquid 'b' is given by:

$$g^E = 6000 x_a x_b (1 - 0.0005\,T)\,\frac{J}{mol},$$ where T is in Kelvin.

- The solids of these species are completely immiscible. The enthalpies of fusion and melting temperatures are as follows
- 'a' → $\Delta h_{fus} = -12\,\frac{kJ}{mol}$; $T_m = 1000\,K$
- 'b' → $\Delta h_{fus} = -10\,\frac{kJ}{mol}$; $T_m = 800\,K$
- Determine the temperature and the composition at the eutectic point. Neglect ΔC_P^{sl}.

So example 1 the excess Gibbs energy for a binary mixture of liquid a and liquid b is given by $g^E = 6000\ x_a x_b\ (1 - 0.0005\ T)$ Joule per mole where T is in Kelvin. The solids are completely immiscible the enthalpies of fusion and melting temperatures for either of the components are given for component a Δh_{fusion} is - 12 kilo Joule per mole and then melting point is nothing but 1000 Kelvin.

Whereas for component b Δh_{fusion} is nothing but - 10 kilo joule per mole and then melting temperature T_m is nothing but 800K. Now determine the temperature and the composition at eutectic point but neglect ΔC_p^{sl}. So ΔC_p^{sl} that is C_p^s - C_p^l is 0

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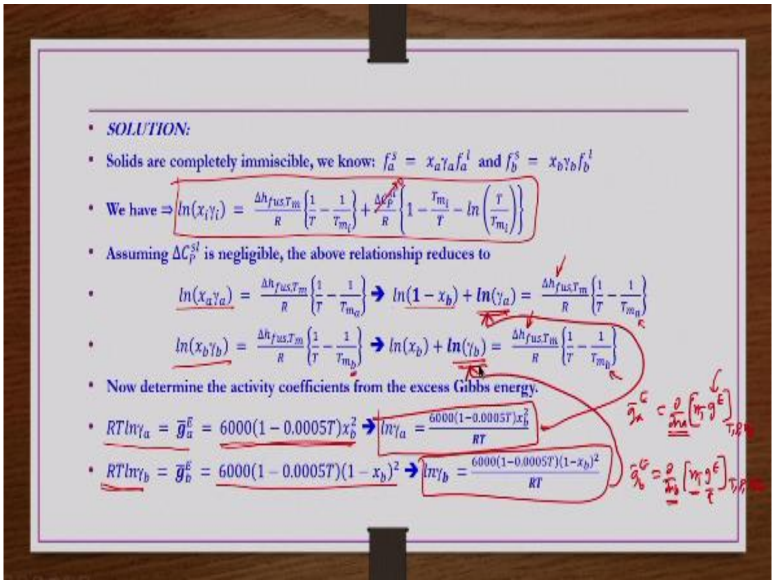

- *SOLUTION:*
- Solids are completely immiscible, we know: $f_a^s = x_a\gamma_a f_a^l$ and $f_b^s = x_b\gamma_b f_b^l$
- We have ⇒ $\ln(x_i\gamma_i) = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_i}}\right\} + \frac{\Delta C_p^{sl}}{R}\left\{1 - \frac{T_{m_i}}{T} - \ln\left(\frac{T}{T_{m_i}}\right)\right\}$
- Assuming ΔC_p^{sl} is negligible, the above relationship reduces to
- $\ln(x_a\gamma_a) = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_a}}\right\} \rightarrow \ln(1 - x_b) + \ln(\gamma_a) = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_a}}\right\}$
- $\ln(x_b\gamma_b) = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_b}}\right\} \rightarrow \ln(x_b) + \ln(\gamma_b) = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_b}}\right\}$
- Now determine the activity coefficients from the excess Gibbs energy.
- $RT\ln\gamma_a = \bar{g}_a^E = 6000(1 - 0.0005T)x_b^2 \rightarrow \ln\gamma_a = \frac{6000(1-0.0005T)x_b^2}{RT}$
- $RT\ln\gamma_b = \bar{g}_b^E = 6000(1 - 0.0005T)(1 - x_b)^2 \rightarrow \ln\gamma_b = \frac{6000(1-0.0005T)(1-x_b)^2}{RT}$

$\bar{g}_a^G = \frac{\partial}{\partial n_a}\left[n_T g^E\right]_{T,P}$

$\bar{g}_b^G = \frac{\partial}{\partial n_b}\left[n_T g^E\right]_{T,P}$

So solutions in solids are completely miscible then f_a^s= x_a γ_a f_a^l and then f_b^s is nothing but x_b γ_b f_b^l. So then we have for completely immiscible system that means system is pure system that means solids are remaining pure solids they are completely immiscible so they are completely pure so then we have that capital X_i = 1 and then capital Γ_i is also 1.

Then whatever the pure solids in equilibrium with liquid cases say that expression we have to use so that expression is nothing but this one that is ln x_i γ_i $=\frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_i}}\right\} + \frac{\Delta C_p^{sl}}{R}\left\{1 - \frac{T_{m_i}}{T} - \ln\left(\frac{T}{T_{m_i}}\right)\right\}$ but in the problem it is mentioned ΔC_p^{sl} is 0. So the second term is not going to be there and now this expression, if you write for two components so that is component a and b.

So ln $x_a\ \gamma_a = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_a}}\right\}$ and then this ln $x_a\ \gamma_a$ I can write ln x_a + ln γ_a and then x_a I am writing 1 - x_b so ln of 1 - x_b + ln of γ_a = right hand side as it is. So now T_{m_i}in place of i I am writing a similarly for component b if you write ln $x_b\ \gamma_b = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_b}}\right\}$ for component b.

So here also ln $x_b\ \gamma_b$ I can write ln x_b + ln γ_b so then we have right hand side as it is without any change. So now we have to solve this equation actually now this Δh_{fusion} are given for both the components $T_{m_a} T_{m_b}$are also given so we have to find out these temperatures and then this x_b compositions. So two equations or two unknowns are there but you know what is this information activity coefficient that we do not know.

But molar excess Gibbs energy expression is given so that is we can use that expression to get this ln γ_a because we know RT ln γ_a = - $\bar{g}_a{}^E$. So that is $\bar{g}_a{}^E$is nothing but$\left[\frac{\partial}{\partial n_a}(n_T . g^E)\right]_{T,P,n_b}$ if you do that you know you can if you find out this differentiation whatever g^E that is given that g^E you write in terms of moles; g^E is given in terms of mole fraction that you write in terms of moles and then multiplied by total number of moles n_T.

And then whatever that product is there you partially differentiate with respect to n_a then again you convert that expression in terms of the mole fraction, so that you get this one these things so many examples we have done in LLEK, so similarly when you do this you get so that RT ln γ_a is nothing but 6,000 (1 - 0.0005 T) x_b^2. So from here ln γ_a is this one that is $\frac{6000\ (1 - 0.0005\ T)\ x_b^2}{RT}$.

Similarly RT ln γ_b is nothing but $\bar{g}_b{}^E$, so that is $\bar{g}_b{}^E$ is nothing but $\left[\frac{\partial}{\partial n_b}(n_T . g^E)\right]_{T,P,n_a}$. So whatever g^E expression is given in the problem that is given in mole fractions you convert in terms of moles by taking $x_a = \frac{n_a}{n_T}$ and $x_b = \frac{n_b}{n_T}$. Then whatever the g^E expression in terms of moles is said that you multiply by n_T, so whatever the product expression is coming that you partially differentiate with respect to n_b.

So then whatever the final expression that comes in terms of moles that again you convert in terms of mole fractions then you will get $\frac{6000\ (1 - 0.0005\ \mathrm{T})\ (1 - x_b)^2}{RT}$, $(1 - x_b)^2$ = x_a square but $(1 - x_b)^2$you can write and then that part is nothing but equal to RT ln γ_b. So ln γ_b is nothing but $\frac{6000\ (1 - 0.0005\ \mathrm{T})\ (1 - x_b)^2}{RT}$.

So now this expression you can write here in place of ln γ_a and this expression you can write in place of ln γ_b here.

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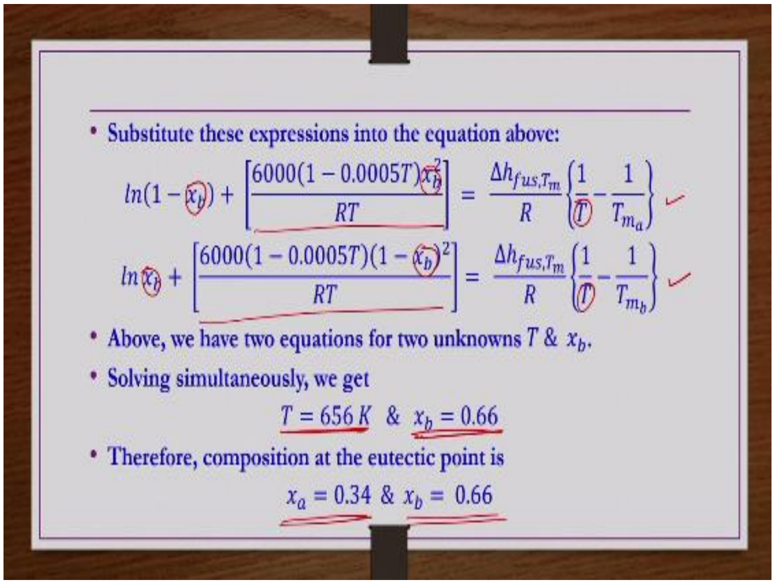

- Substitute these expressions into the equation above:

$$ln(1 - x_b) + \left[\frac{6000(1 - 0.0005T)x_b^2}{RT}\right] = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_a}}\right\}$$

$$ln\, x_b + \left[\frac{6000(1 - 0.0005T)(1 - x_b)^2}{RT}\right] = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_b}}\right\}$$

- Above, we have two equations for two unknowns T & x_b.
- Solving simultaneously, we get

$$T = 656\,K \ \ \&\ \ x_b = 0.66$$

- Therefore, composition at the eutectic point is

$$x_a = 0.34 \ \&\ x_b = \ 0.66$$

Then what you have you have this expression ln (1 - x_b)+ ln γ_a is nothing but $\frac{6000\ (1 - 0.0005\ \mathrm{T})\ x_b^2}{RT}$ = right hand side is as it is for the component a similarly for the component b ln x_b + ln γ_b is nothing but $\frac{6000\ (1 - 0.0005\ \mathrm{T})\ x_a^2}{RT}$ so that is $\frac{(1 - x_b)^2}{RT}$ and then right hand side is same as it is for a component b, so now only thing unknown is in these two equation is the temperature and then this x_b.

So we have two equations two unknowns, so when you solve these two equations you can get you know whatever the temperature and then x_b that we get as this temperature you get 656 Kelvin and then x_b you will get 0.66. So that means eutectic composition or the composition at the eutectic point is nothing but x_a = 0.34 and then x_b is nothing but 0.66 this is how we can solve problems on SLE.

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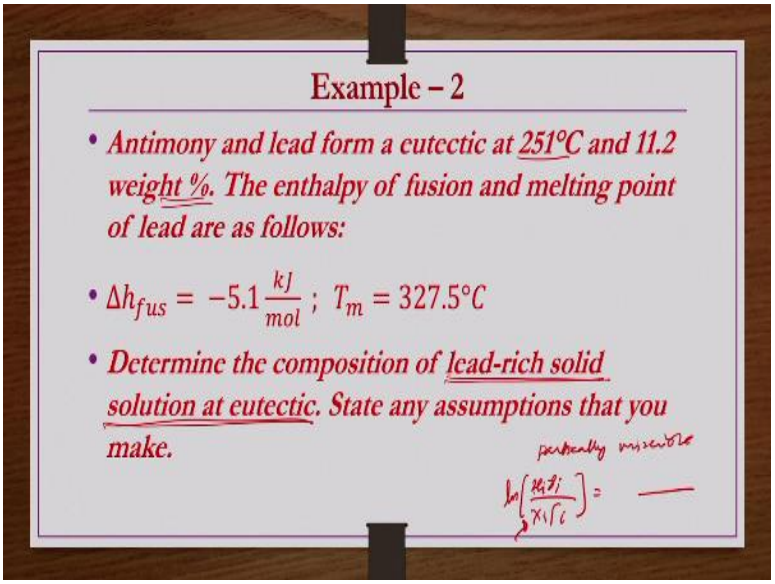

Example – 2

- *Antimony and lead form a eutectic at 251°C and 11.2 weight %. The enthalpy of fusion and melting point of lead are as follows:*
- $\Delta h_{fus} = -5.1 \frac{kJ}{mol}$; $T_m = 327.5°C$
- *Determine the composition of lead-rich solid solution at eutectic. State any assumptions that you make.*

partially miscible

$\ln\left[\frac{x_i\gamma_i}{X_i\Gamma_i}\right] = $ ——

Now we take another example problem antimony and lead form a eutectic at 251 degree centigrade so temperature is given and 11.2 weight percent so weight percent of this antimony is given the enthalpy of fusion and the melting point of lead are as follows for the lead they are given as Δh_{fusion} is - 5.1 kilo Joule per mole and then for the lead melting point is 327.5 degree centigrade.

So determine the composition of lead-rich solid solution at eutectic. State any assumptions that you make, so nothing has began has been given. So it is actually mentioned lead rich solid solution at eutectic so actually one of the phase reach in one particular component if it is mentioned like that that means it is partially miscible system or partially miscible solid solutions are there, so then ln $\frac{x_i\gamma_i}{X_i\Gamma_i}$= whatever that expression that we have to use. And then we have to find out what is this X_i capital X_i.

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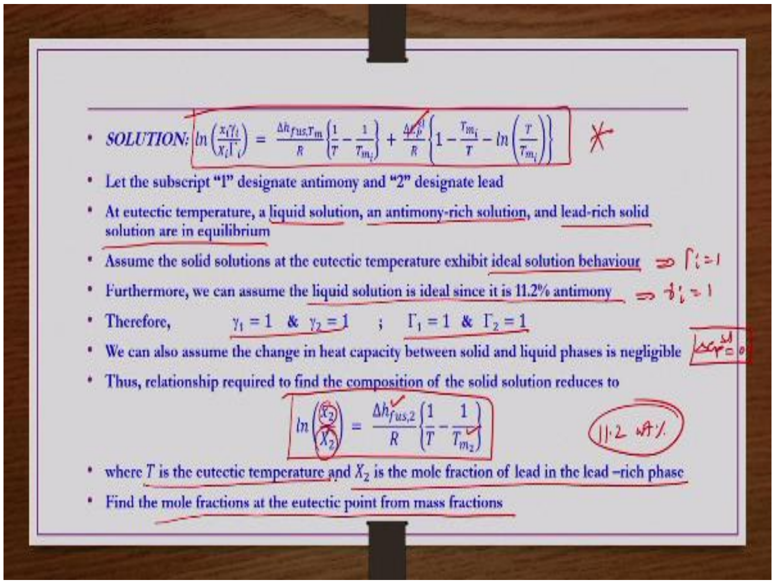

- **SOLUTION:** $\ln\left(\frac{x_i\gamma_i}{X_i\Gamma_i}\right) = \frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_i}}\right\} + \frac{\Delta c_p^{sl}}{R}\left\{1 - \frac{T_{m_i}}{T} - \ln\left(\frac{T}{T_{m_i}}\right)\right\}$ *
- Let the subscript "1" designate antimony and "2" designate lead
- At eutectic temperature, a liquid solution, an antimony-rich solution, and lead-rich solid solution are in equilibrium
- Assume the solid solutions at the eutectic temperature exhibit ideal solution behaviour $\Rightarrow \Gamma_i = 1$
- Furthermore, we can assume the liquid solution is ideal since it is 11.2% antimony $\Rightarrow \gamma_i = 1$
- Therefore, $\gamma_1 = 1$ & $\gamma_2 = 1$; $\Gamma_1 = 1$ & $\Gamma_2 = 1$
- We can also assume the change in heat capacity between solid and liquid phases is negligible $\boxed{\Delta c_p^{sl} = 0}$
- Thus, relationship required to find the composition of the solid solution reduces to

$$\boxed{\ln\left(\frac{x_2}{X_2}\right) = \frac{\Delta h_{fus,2}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_2}}\right\}}$$

11.2 wt%

- where T is the eutectic temperature and X_2 is the mole fraction of lead in the lead –rich phase
- Find the mole fractions at the eutectic point from mass fractions

So this is the expression that we have to use in this expression whatever the things are there are provided or not that we have to see if not provided we have to make certain kind of assumption that is also clearly stated in the problem. So let the subscript 1 designate antimony and 2 for the lead, so at eutectic temperature a liquid solution and antimony rich solution and then lead rich solid solution not in equilibrium all three phases are at equilibrium that is the eutectic point.

So assume the solid solutions at the eutectic temperature exhibit ideal solution behavior because nothing is given about non ideality of the solid phase and then that is also possible further we can assume the liquid solution is ideal since it is only 11.2% of antimony. So it is a small fraction it is there not negligible but small fraction only there, so then we can say that the liquid solution is almost kind of pure solution and then we can take the liquid solution is also as a kind of ideal behavior.

So from here capital Γ_i = 1 and then from here small γ_i = 1 then we have for both the component if you write we have this one small γ_2 = 1 capital Γ_1 = 1 capital Γ_2 = 1 we can also assume the change in heat capacity between solid and liquid phases is negligible, ΔC_p^{sl}= 0 because no information is given.

So we have to assume there is no option so that second term in the RHS is gone in this equation this relationship required to find the composition of the solid solution reduces to this form $\ln \frac{x_2}{X_2} = \frac{\Delta h_{fus,2}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_2}}\right\}$ because we wanted to find out you know this x_2 this is the final relation.

And then we have to find out this capital X_2 how much it is this is given this is also given, so a data for a required temperature we have to find out this capital X_2 but what is this small x_2 that is not given but weight fraction of these two items are given. So antimony 11.2 weight percent so what we can have we can convert them into the mole fractions and then get that small x_2 so here T is the eutectic temperature that is given, x_2 is the mole fraction of lead in the lead rich phase.

That is what we have to find out and then find the mole fractions at the eutectic point from the mass fractions whatever this 11.28% antimony and then remaining lead is there. So that weight fraction basis we can use but these are given in the weight fraction. So, we have to convert them into the mole fractions. So, how we can do? We need to have the molecular weight information about these components so that we can get from the reference books.

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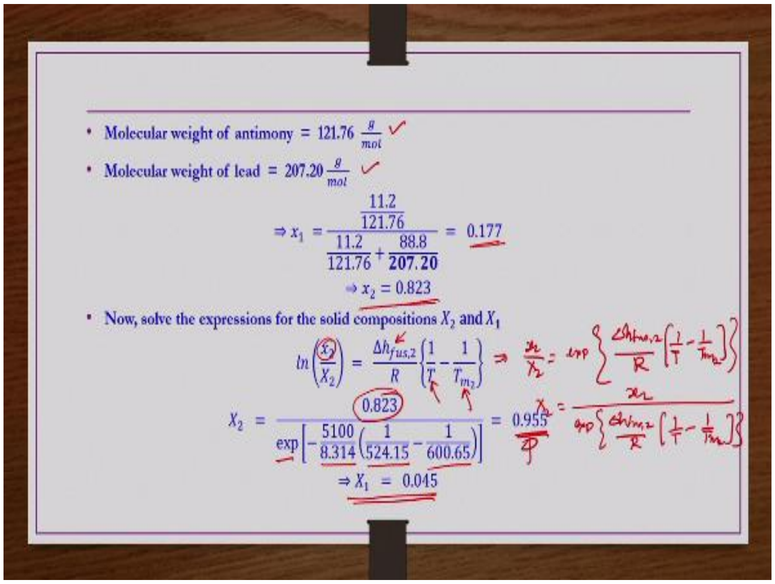

- Molecular weight of antimony = $121.76\ \frac{g}{mol}$ ✓
- Molecular weight of lead = $207.20\ \frac{g}{mol}$ ✓

$$\Rightarrow x_1 = \frac{\frac{11.2}{121.76}}{\frac{11.2}{121.76} + \frac{88.8}{\mathbf{207.20}}} = \underline{0.177}$$

$$\Rightarrow x_2 = 0.823$$

- Now, solve the expressions for the solid compositions X_2 and X_1

$$\ln\left(\frac{x_2}{X_2}\right) = \frac{\Delta h_{fus,2}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_2}}\right\} \Rightarrow \frac{x_2}{X_2} = \exp\left\{\frac{\Delta h_{fus,2}}{R}\left[\frac{1}{T} - \frac{1}{T_{m_2}}\right]\right\}$$

$$X_2 = \frac{0.823}{\exp\left[-\frac{5100}{8.314}\left(\frac{1}{524.15} - \frac{1}{600.65}\right)\right]} = 0.955 \qquad X_2 = \frac{x_2}{\exp\left\{\frac{\Delta h_{fus,2}}{R}\left[\frac{1}{T} - \frac{1}{T_{m_2}}\right]\right\}}$$

$$\Rightarrow X_1 = 0.045$$

So molecular weight of and antimony not given from reference books we can get this one 121.76 gram per mole and then molecular weight of lead is 207.20 gram per mole then x_1 should be because antimony we have taken as component one so x_1 should be 11.2 divided by 121.76 and whole divided by 11.2 divided by 121.76 + 88.8 divided by 207.2 that comes out to be 0.177. So that means x_2 is 0.823.

So only unknown in the previous equation that is to be solved to get the capital X_2 is this small x_2 that is also now we got it so this if you substitute here in this equation and then give this eutectic temperature this T_{m_2} is given and Δh_{fusion} is also given x_2 you just obtained so from here if you write $\frac{x_2}{X_2} = \exp \frac{\Delta h_{fus,2}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_2}}\right\}$ and then from here X_2 is nothing but $\frac{x_2}{\exp \frac{\Delta h_{fus,2}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_2}}\right\}}$.

So this is what we have so this is X_2 is 0. 823 divided by exponential of Δh_{fusion} is - 5100 it is given 5.1 kilo Joule, it is given so - 5100, R is 8.314 and then eutectic temperature T is given and then T_{m_2} is given so all that you substitute so then you get 0.955. So that means X_1 is 0.045. So in the lead rich phase lead is very high almost 95.5% by moles but this is all we can solve the different types of problems initially we can take one more example problem.

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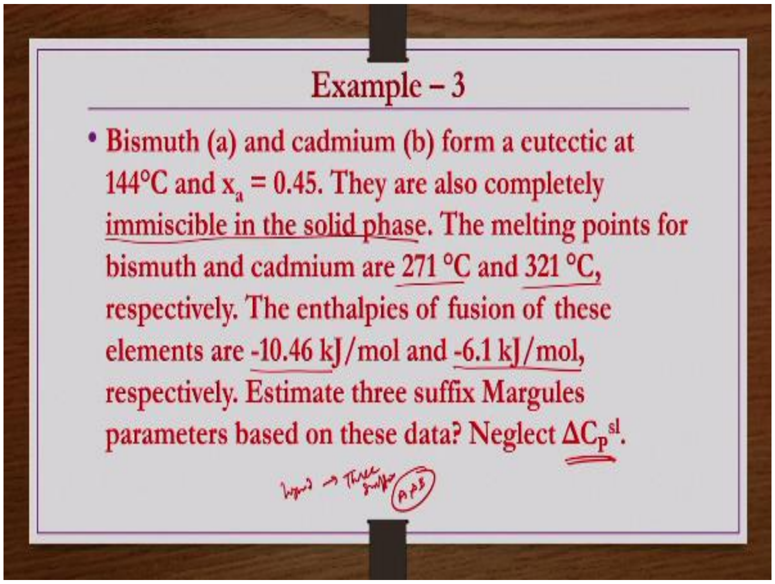

Example – 3

- Bismuth (a) and cadmium (b) form a eutectic at 144°C and $x_a = 0.45$. They are also completely immiscible in the solid phase. The melting points for bismuth and cadmium are 271 °C and 321 °C, respectively. The enthalpies of fusion of these elements are -10.46 kJ/mol and -6.1 kJ/mol, respectively. Estimate three suffix Margules parameters based on these data? Neglect ΔC_p^{sl}.

liquid → Three suffix APB

Example 3 Bismuth and cadmium form a eutectic at 144 degree centigrade and $x_a = 0.45$ they are also completely immiscible in the solid solutions; they are also completely miscible in the solid phase, that means pure solids we have to take the melting points for these two components are given as 271 and 321 degree centigrade respectively.

The enthalpies of fusion of these two elements are - 10.46 kilo Joule per mole and then - 6.1 kilo Joule per mole respectively estimate 3-suffix Margules parameter based on this data. Let us say the liquid phase whatever is their liquid phase non-ideality, if you described by 3-suffix Margules equation whatever they 3-suffix Margules parameters A and B are there, that you have to find out neglect ΔC_p^{sl}that is C_p^s - $C_p^l$is 0. So it is a pure solid system that equations we have to take pure solids in equilibrium with liquid.

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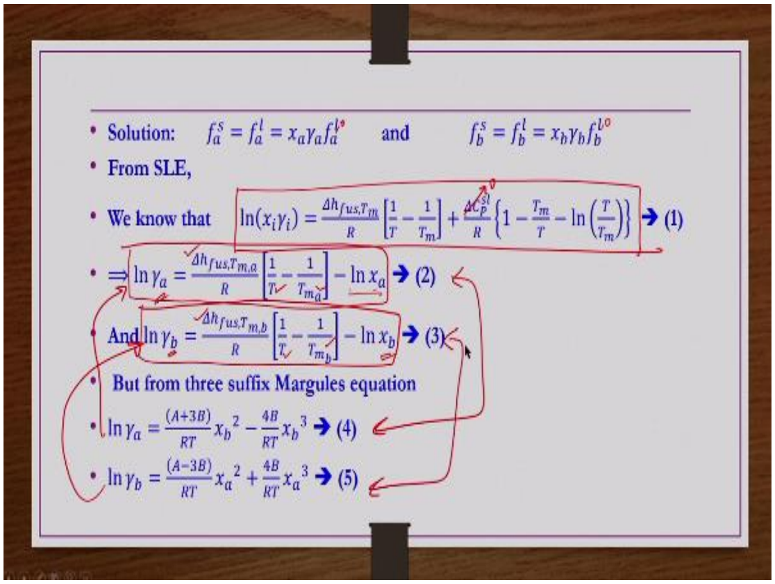

- Solution: $f_a^s = f_a^l = x_a\gamma_a f_a^{l^o}$ and $f_b^s = f_b^l = x_b\gamma_b f_b^{l^o}$
- From SLE,
- We know that $\ln(x_i\gamma_i) = \frac{\Delta h_{fus,T_m}}{R}\left[\frac{1}{T} - \frac{1}{T_m}\right] + \frac{\Delta C_p^{sl}}{R}\left\{1 - \frac{T_m}{T} - \ln\left(\frac{T}{T_m}\right)\right\}$ ➔ (1)
- $\Rightarrow \ln\gamma_a = \frac{\Delta h_{fus,T_{m,a}}}{R}\left[\frac{1}{T} - \frac{1}{T_{m_a}}\right] - \ln x_a$ ➔ (2)
- And $\ln\gamma_b = \frac{\Delta h_{fus,T_{m,b}}}{R}\left[\frac{1}{T} - \frac{1}{T_{m_b}}\right] - \ln x_b$ ➔ (3)
- But from three suffix Margules equation
- $\ln\gamma_a = \frac{(A+3B)}{RT}x_b^2 - \frac{4B}{RT}x_b^3$ ➔ (4)
- $\ln\gamma_b = \frac{(A-3B)}{RT}x_a^2 + \frac{4B}{RT}x_a^3$ ➔ (5)

So f_a^s= x$_a$ γ$_a$ f_a^l and f_b^s= x$_b$ γ$_b$ f_b^l. So this actually reference there something like a you know not we can have here something like that, like this at reference temperature from SLE that is when pure solids are in equilibrium with liquid then we have this derivation ln x$_a$ γ$_a$ = $\frac{\Delta h_{fus,T_m}}{R}\left\{\frac{1}{T} - \frac{1}{T_m}\right\}$ + $\frac{\Delta C_p^{sl}}{R}\left\{1 - \frac{T_m}{T} - ln\left(\frac{T}{T_m}\right)\right\}$.

This is what we have it is said that this $\Delta C_p^{sl}$is negligible or neglected that is what given in the statement, so this part can be ignored. So now if you write this equation for two components component a and component b so ln x$_a$ γ$_a$ =$\frac{\Delta h_{fus,T_{m_a}}}{R}\left\{\frac{1}{T} - \frac{1}{T_{m_a}}\right\}$. So whatever ln γ$_a$ x$_a$ that we can write ln γ$_a$ + ln x$_a$ so that ln x$_a$ if you bring it to the left hand side we have - ln x$_a$.

Similarly for the second component if you do ln γ_b = $\frac{\Delta h_{fus,T_{m_b}}}{R}\left\{\frac{1}{T}-\frac{1}{T_{m_b}}\right\}$- ln x_b. So these two relations are there, so here this Δh_{fusion} are given $T_m's$ are given $T_{m_a}T_{m_b}$ are given and then T is also given x_a is also given. So x_b is also known so only thing that you know ln γ_a ln γ_b are not known. So far we do not need them we need corresponding 3-suffix Margules parameters A B.

So whatever the 3-suffix Margules equations are there, so corresponding ln γ_a ln γ_b equations we how to use. So from 3-suffix Margules equation we have ln γ_a = $\frac{A+3B}{RT}x_b^2-\frac{4B}{RT}x_b^3$ and then we have ln γ_b = $\frac{A-3B}{RT}x_a^2+\frac{4B}{RT}x_a^3$. So now in place of this ln γ_a you substitute this one and then in place of ln γ_b you substitute this one then what we will have are substituting or maybe equating this equation 2 and 4 and then equation 3 and 5 if you equate.

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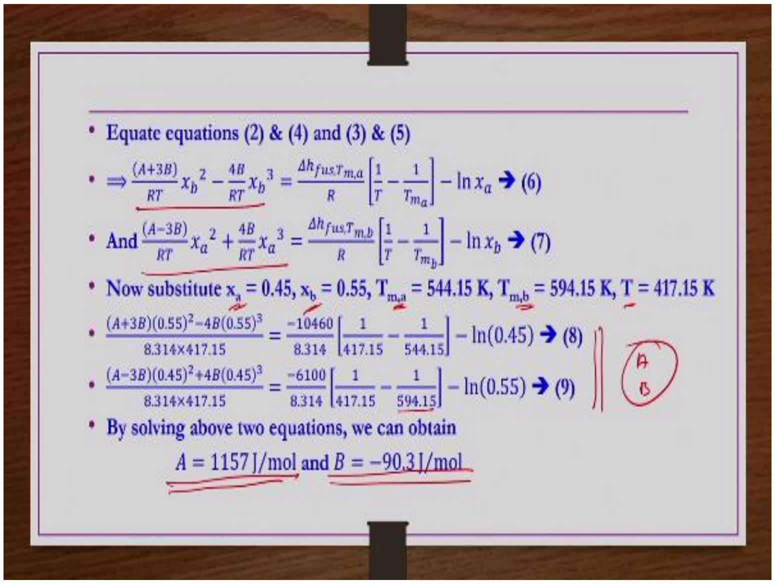

- Equate equations (2) & (4) and (3) & (5)
- $\Rightarrow \frac{(A+3B)}{RT}x_b^{\ 2}-\frac{4B}{RT}x_b^{\ 3}=\frac{\Delta h_{fus,T_{m,a}}}{R}\left[\frac{1}{T}-\frac{1}{T_{m_a}}\right]-\ln x_a \rightarrow (6)$
- And $\frac{(A-3B)}{RT}x_a^{\ 2}+\frac{4B}{RT}x_a^{\ 3}=\frac{\Delta h_{fus,T_{m,b}}}{R}\left[\frac{1}{T}-\frac{1}{T_{m_b}}\right]-\ln x_b \rightarrow (7)$
- Now substitute $x_a = 0.45$, $x_b = 0.55$, $T_{m,a} = 544.15$ K, $T_{m,b} = 594.15$ K, $T = 417.15$ K
- $\frac{(A+3B)(0.55)^2-4B(0.55)^3}{8.314\times417.15}=\frac{-10460}{8.314}\left[\frac{1}{417.15}-\frac{1}{544.15}\right]-\ln(0.45) \rightarrow (8)$
- $\frac{(A-3B)(0.45)^2+4B(0.45)^3}{8.314\times417.15}=\frac{-6100}{8.314}\left[\frac{1}{417.15}-\frac{1}{594.15}\right]-\ln(0.55) \rightarrow (9)$
- By solving above two equations, we can obtain

  $A = 1157$ J/mol and $B = -90.3$ J/mol

A
B

Then we have ln γ_a is nothing but $\frac{A+3B}{RT}x_b^2-\frac{4B}{RT}x_b^3$ = right hand side of equation 2 that is $\frac{\Delta h_{fus,T_{m_a}}}{R}\left\{\frac{1}{T}-\frac{1}{T_{m_a}}\right\}$- ln x_a then equation number 3 that is ln γ_b = we are having. So ln γ_b is nothing but $\frac{A-3B}{RT}x_a^2+\frac{4B}{RT}x_a^3$ for 3-suffix Margules equation and then = right hand side whatever we have $\frac{\Delta h_{fus,T_{m_b}}}{R}\left\{\frac{1}{T}-\frac{1}{T_{m_b}}\right\}$- ln x_b.

So here we know this x_a is given so x_b is also be known T_{m_a} is given T_{m_b} is also given eutectic point temperature T is also given so in this equation everything is known except A and B. So we have two equations, so in these two equations except A and B you substitute all these values here so then A + 3B when you substitute all these values in the equation number 6 you will get $\frac{(A + 3B)0.55^2}{8.314*417.15} - \frac{(4B)0.55^3}{8.314*417.15} = \frac{-10460}{8.314}\left\{\frac{1}{417.15} - \frac{1}{544.15}\right\}$ - ln 0.45.

Then these values if you substitute in equation number 7 then we have $\frac{(A - 3B)0.45^2}{8.314*417.15} + \frac{(4B)0.45^3}{8.314*417.15} = \frac{-6100}{8.314}\left\{\frac{1}{417.15} - \frac{1}{594.15}\right\}$ - ln 0.55. So, these two equations we are having and then these two unknowns A and B are there so if you solve these equations two equations then you will get a as 1157 Joule per mole and then B as - 90.3 joule per mole.

So 3-suffix Margules parameters A and B you can obtain like this. Like this different types of SLE problems can be solved using the equation equilibrium relation that we have established in the previous lecture.

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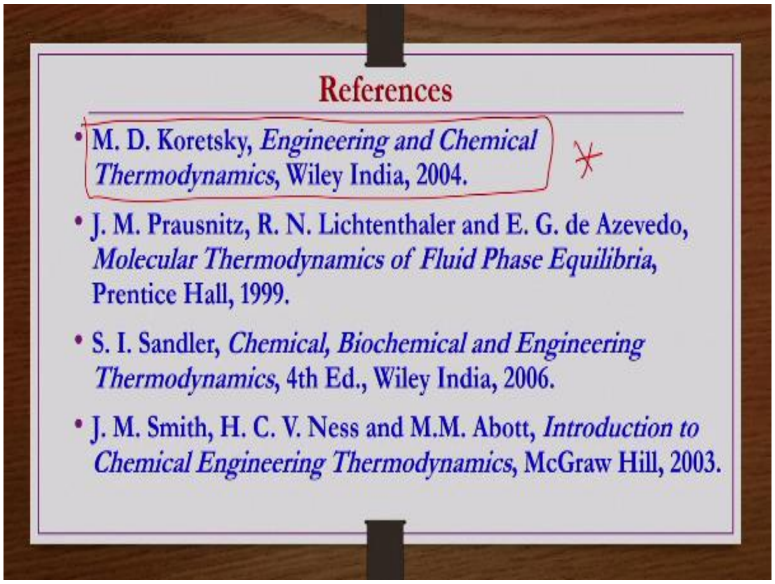

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So the references for this lecture are Engineering and chemical thermodynamics by Koretsky, Molecular Thermodynamics of Fluid Phase equilibria by prausnitz et al, Chemical, Biochemical and Engineering Thermodynamics by Sandler and Introduction to Chemical Engineering Thermodynamics by Smith et al. However this entire lecture is prepared from this reference book

Engineering and chemical thermodynamics by Koretsky; which is an excellent book for SLE problems with this we have completed all the lectures of this course advanced thermodynamics thank you very much for your attention. Thank You