Chemical Engineering Thermodynamics
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Solid-liquid equilibria, Lecture-56

Welcome back in the last class I was discussing about solid liquid equilibria and how do we construct phase diagram of a such a system so okay.

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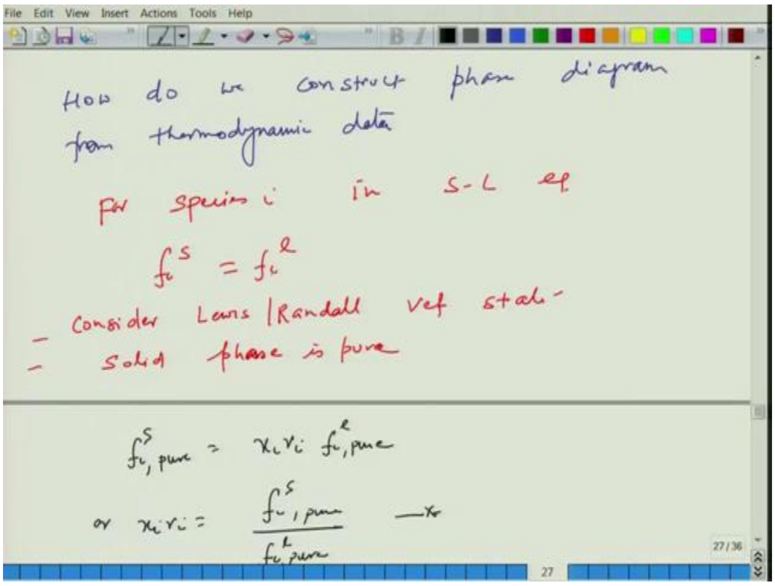


How do we construct phase diagram from thermodynamic data

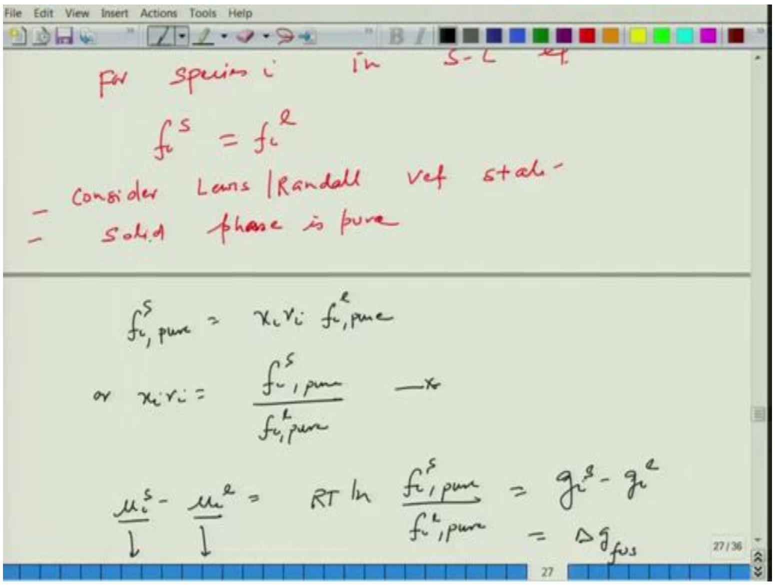
For species i in S-L eq

$f_i^S = f_i^l$

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

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

or $x_i \gamma_i = \frac{f_{i,pure}^S}{f_{i,pure}^L}$ —*



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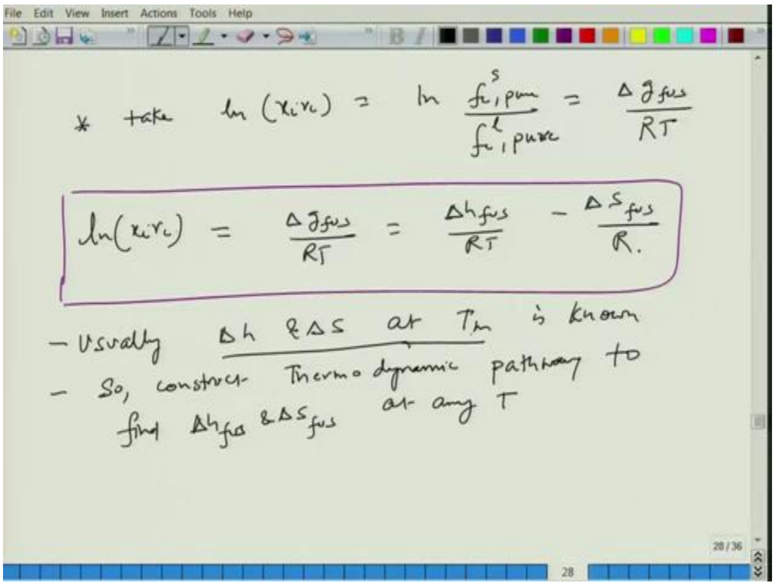
or $x_i \gamma_i = \frac{f_{i,pure}^S}{f_{i,pure}^L}$ —*

$$\underset{\downarrow}{\mu_i^S} - \underset{\downarrow}{\mu_i^l} = RT \ln \frac{f_{i,pure}^S}{f_{i,pure}^L} = g_i^S - g_i^l = \Delta g_{fus}$$



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

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

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

So we say the well we can make use of the same equilibrium criteria which is the fugacity of a component i in the solid phase should be equal to that in the liquid phase and considering a Louis Randall difference state we can present f i l in terms of xi Gama i f i l pure and you can consider for example solid phase to be pure. If you do that then essentially we have a this particular expression and this ratio of the fugacity of the component i in the solid phase divided by that in the liquid phase for the p o k can be related to the difference in the molo guess way energy for his component in different phases.

So using this we come up with the expression which relates the composition of a component i and the activity Gamma this is in the liquid phase and that is related to the delta h of fusion delta h is an change in enthalpy between the solid and the liquid at a specific temperature and that then you have this another term which relates organize to the delta s that is the change in the entropy.

But this is at the temperature T. so this particular function h and s this would be at a specific temperature T and what we usually know is delta h and delta s at a melting condition or at basically Tm. So, in all to find out this delta h fusion and delta s fusion at a given temperature were basically we interested in then we must try to use some approach to find such a thing among easiest way to do that is to construct thermodynamic path way.

This is something which we have done earlier also but now we are going to apply the similar concept to obtain this delta h fusion and delta s fusion for a given temperature using the information of delta h and delta s at T.

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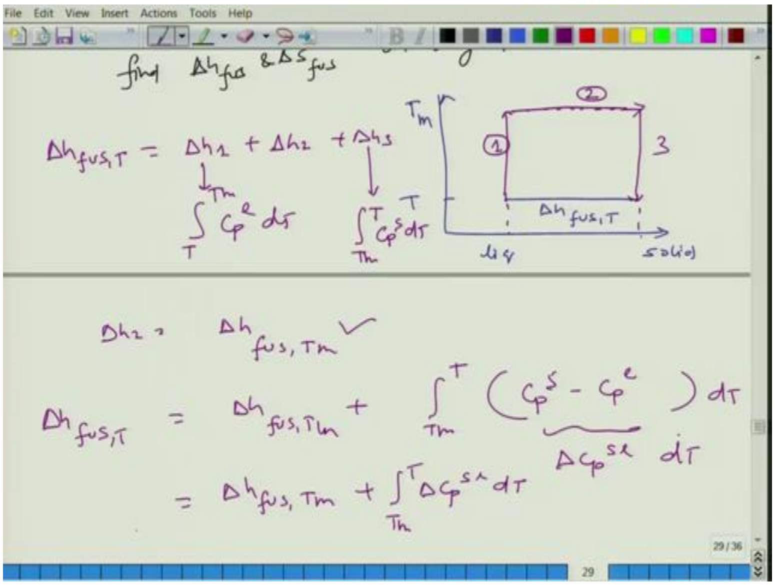


find Δh_{fus} & ΔS_{fus}

$$\Delta h_{fus,T} = \underset{\int_T^{T_m} C_p^l\, dT}{\Delta h_1} + \Delta h_2 + \underset{\int_{T_m}^{T} C_p^s\, dT}{\Delta h_3}$$

$$\Delta h_2 = \Delta h_{fus,T_m} \checkmark$$

$$\Delta h_{fus,T} = \Delta h_{fus,T_m} + \int_{T_m}^{T} \left(\underbrace{C_p^s - C_p^l}_{\Delta C_p^{sl}}\right) dT$$

$$= \Delta h_{fus,T_m} + \int_{T_m}^{T} \Delta C_p^{sl}\, dT$$

$$Find\ \Delta h_{fis}\ and\ \Delta S_{fis}$$

$$\Delta h_{f,v,s,T} = \Delta h_1 + \Delta h_2 + \Delta h_3$$

$$\Delta h_2 = \Delta h_{fis,T_m}$$

$$\Delta h_{fis,T} = \Delta h_{fis,T_m} + \int_{T_m}^{T} \left(C_p^s - C_p^l\right) dT = \Delta h_{fis,T_m} + \int_{T_m}^{T} \Delta C_p^{sl}\, dT$$

$$\Delta S_{fis,T} = \int_{T}^{T_m} \frac{C_P^l}{T} dT + \Delta S_{fis,T_m} + \int_{T_m}^{T} \frac{C_p^s}{T} dT$$

$$\Delta S_{fis,T} = \Delta S_{fis,T_m} + \int_{T_m}^{T} \frac{\Delta C_p^{sl}}{T} dT$$

$$\Delta g_{fis,T_m} = 0 = \Delta h_{fis,T_m} - T_m \Delta S_{fis,T_m}$$

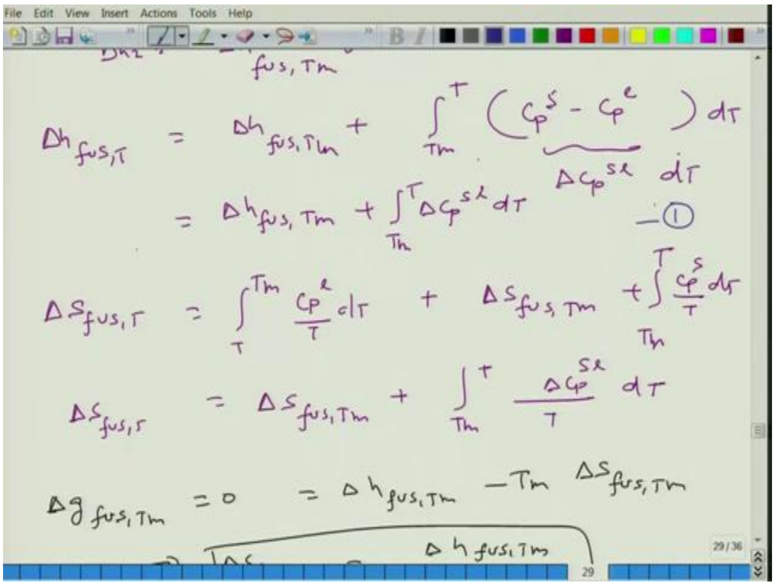
$$\Delta S_{fis,T_m} = \frac{\Delta h_{fis,T_m}}{T_m}$$

$$\Delta S_{fis,T} = \frac{\Delta h_{fis,T_m}}{T_m} + \int_{T_m}^{T} \frac{\Delta C_p^{sl}}{T} dT$$

Now substituting,

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

$$= \frac{\Delta h_{fis,T_m}}{R}\left[\frac{1}{T} - \frac{1}{T_m}\right] - \frac{1}{R}\int_{T_m}^{T} \frac{\Delta C_p^{sl}}{T} dT + \frac{1}{RT}\int_{T_m}^{T} \Delta C_p^{sl} dT$$



fus, T_m

$$\Delta h_{fus,T} = \Delta h_{fus,T_m} + \int_{T_m}^{T} \underbrace{\left(c_p^{s} - c_p^{l} \right)}_{\Delta c_p^{sl}\ \ dT} dT$$

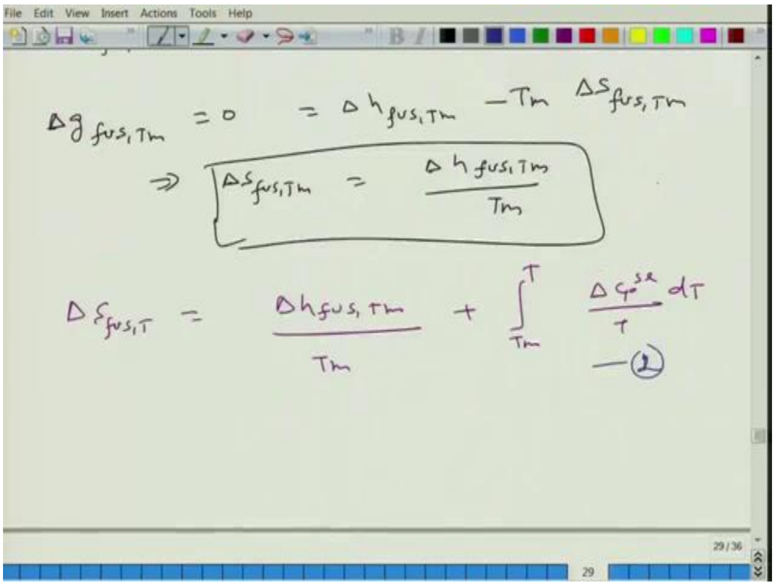
$$= \Delta h_{fus,T_m} + \int_{T_m}^{T} \Delta c_p^{sl}\, dT \qquad — ①$$

$$\Delta s_{fus,T} = \int_{T}^{T_m} \frac{c_p^{l}}{T}\, dT + \Delta s_{fus,T_m} + \int_{T_m}^{T} \frac{c_p^{s}}{T}\, dT$$

$$\Delta s_{fus,T} = \Delta s_{fus,T_m} + \int_{T_m}^{T} \frac{\Delta c_p^{sl}}{T}\, dT$$

$$\Delta g_{fus,T_m} = 0 = \Delta h_{fus,T_m} - T_m \Delta s_{fus,T_m}$$

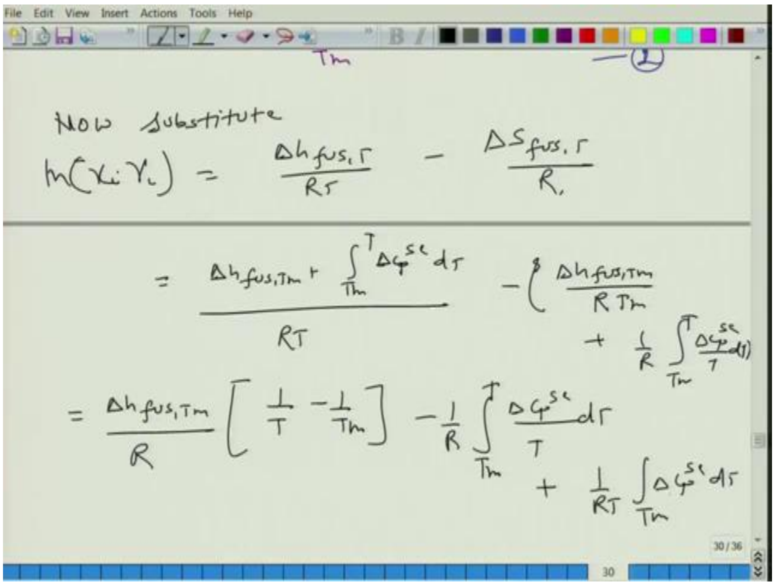
$$\Rightarrow \Delta s \qquad \Delta h_{fus,T_m}$$



$$\Delta g_{fus,T_m} = 0 = \Delta h_{fus,T_m} - T_m \Delta s_{fus,T_m}$$

$$\Rightarrow \boxed{\Delta s_{fus,T_m} = \frac{\Delta h_{fus,T_m}}{T_m}}$$

$$\Delta s_{fus,T} = \frac{\Delta h_{fus,T_m}}{T_m} + \int_{T_m}^{T} \frac{\Delta c_p^{sl}}{T}\, dT \qquad — ②$$



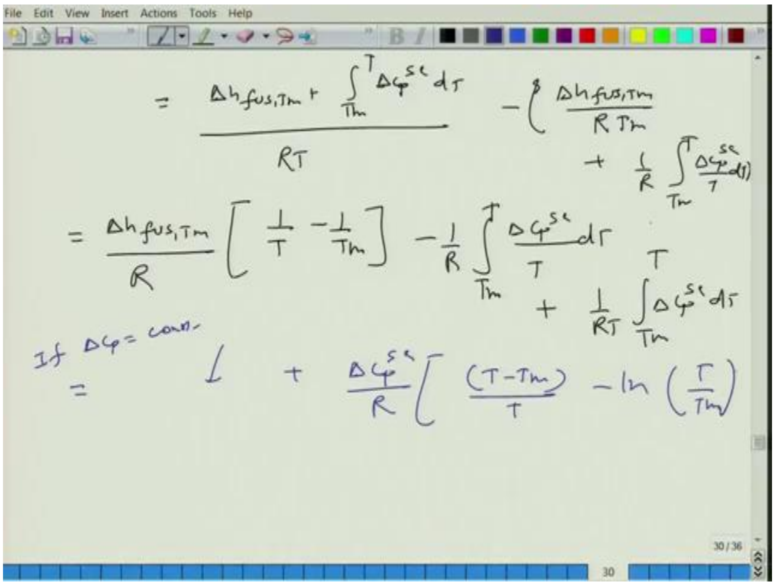
T_m — ②

Now substitute

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

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

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



$$= \frac{\Delta h_{fus,T_m} + \int_{T_m}^{T} \Delta c_p^{sl}\, dT}{RT} - \Big(\frac{\Delta h_{fus,T_m}}{R T_m} + \frac{1}{R} \int_{T_m}^{T} \frac{\Delta c_p^{sl}}{T} dT$$

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

If $\Delta c_p = \text{const.}$

$$= \quad + \frac{\Delta c_p^{sl}}{R} \left[\frac{(T - T_m)}{T} - \ln \left(\frac{T}{T_m} \right) \right.$$

So, let me just draw first a temperature versus kind of a phases, so this could be your Tm and this could be your T and this is your liquid and that is here this your solid. This is what we want we want to the information from liquid to solid that would be your delta H fusion at a specific temperature T and what we know usually is this information which is your delta h and at Tm. So, what we can do is we can connect this particular reference by gain simple path which is rectangular in nature. So, now we can say that this is a path 1 this is 2 and 3.

Now, in order to find this delta h fusion T, I can write this delta h fusion T is delta h 1 plus delta h 2 plus delta h 3. Now, what would be your delta h1 are this is can simply can connect to the basically Cp of the liquid phase because this is a liquid. So, liquid L dt T to Tm this is the specific change in the enthalpy along this particular path. Similarly, I can do the same thing for here this is the solid phase because this is the solid here and this is the liquid. So this I can write this as Tm T Cps dt.

So, because there is no specific face change along this particular path 1 and 3 and this is single phase but only the temperature is changing. So, essentially, we simply relate to the Cp. That is something which we have done earlier also but what about delta h 2? So, delta h2 is nothing but delta h fusion at Tm that is something which we are given which we are aware of it.

Now, given this you can plug in back this expression to obtained delta h fusion at T this would be your delta h fusion at Tm plus Tm by T and then essentially we are changing this limits from which Tm to T and hence, if you do that there has to be a negative sign here when you add this negative Cpl with Cps this would be something like this. So, this we can rearrange this expression this plus this and this can be written in this way.

So, this is nothing but delta Cp Sl dt. So, you have now relation delta h fusion at specific Tm plus Tm to T delta Cp Sl dt. So, that is what we have so as far as the delta s h is concerned but since we are interested not just only delta h but as well as delta s because both are required in order to get delta g which can be connected to this composition and activity co-efficient. So now we should ask about how do you get this fusion particularly at T we can use a similar path and, in that case, I will have a delta s fusion.

So delta s at for the path 1 that I can write in terms of T to Tm in terms of Cpl by T this simply we can write plus the second path which is along the phase transition this will be delta s fusion Tm plus again Tm to T. So this is what we have as well as delta s is concerned. So this we have the separately written for delta h and separately written for delta.

Now we can again then then similar way as we have done that we can again rearrange this, and this we can again write it as delta s fusion Tm change the limit to Tm by T and since T is constant you will have the difference between Cps minus Cpl which will be your delta Cp sl and this is your dt.

So we have now come up with an expression for delta h and delta s fusion at the specific temperature T. Now you note that delta g fusion Tm that is the way the system is at equilibrium at this condition you should be 0. That means delta g should be 0 and this is nothing but delta h fusion Tm minus Tm delta s fusion Tm, now this relates delta s fusion at Tm as h fusion Tm divided by Tm.

So it tells you that at a fusion particularly at Tm which is an equilibrium condition you should have this delta g must be 0 that means there is a relation between delta s and delta h in this way. So now I can plug this expression back in and I can have much less or rather more simplified expression which just depends on T because Tm we know and T, of course, we would like to find and we would like to fix the value of T in order to get the phase diagram.

Tm as we know Tm you know delta h fusion that is usually the case and, of course, delta Cp sl also you would know. So you can find out delta s, now given this delta s and delta h you cn now plug in back in this expression. So with this two key expression we have one is of course this this could be written as 2 and the other one is this. Now, use these one and two expressions to obtain the information of a Ln xi.

So we can substitute now substitute Ln sub substitute delta h and delta s in the expression of Ln xi gamma i. So again, let me write it again here. So this is your delta h fusion T divided by delta, so this is your delta h fusion T by T minus delta s fusion at T by R. Now with this we can simplify this. So now I can write delta s fusion T from 1 we have delta h fusion Tm plus Tm by T delta Cp sL dt divided by RT minus this term delta fusion T by R, so if you divide this by R you get this formation.

So this can be written as let us say delta h fusion Tm by R Tm plus 1 by R integral of Tm T delta Cp Sl by T dt. So if you simplify this if you takeout this part you are going to get the following. So let me try to simplify this, so if you look at this you have is delta fusion Tm and there is also delta fusion Tm and R Tm this is Rt so I can take out delta h fusion at Tm by R and what is common here is taken out what remains is 1 by T minus 1 by Tm.

Similarly, if you look at it delta Cp here is semester to be common here but let me just write this in this way that I can write this as minus of R this is minus 8 comes here and this is your Tm by T delta Cp sL by T dt plus here this part can be written as 1 by R T delta Cp sL dt Tm by T. So this is the total expression of xi gamma i. Now, if you consider delta Cp to be independent of temperature then this further can be written as this if delta Cp is constant.

Then you have the first term plus delta Cp comes out separately what remains is T minus Tm by T minus ln T by Tm. So this the expression which we got, now you can do with a bit of assumption and you have now a way to obtain information of a composition. When you have information of a delta s delta hat melting conditions and as well as you though heat capacity. Now how do you take this forward and solve a certain problem.

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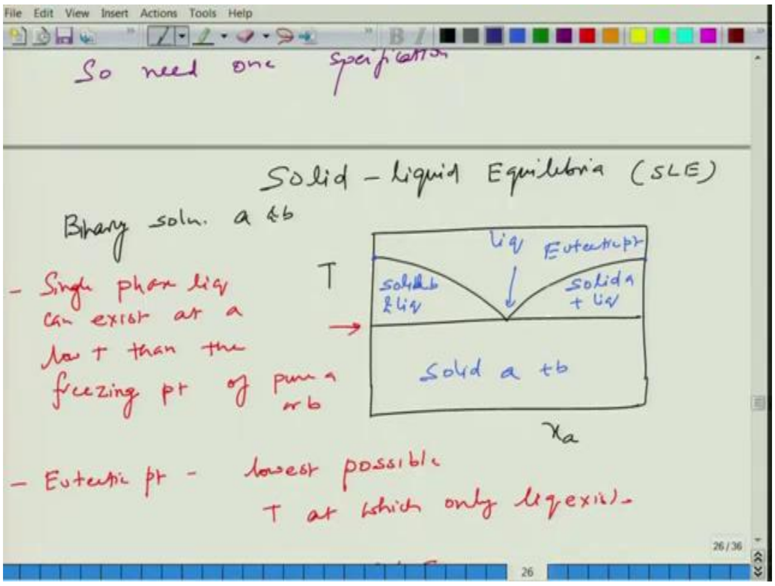

So need one specification

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

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

So let us do this exercise to understand a bit. Now one of the things which we can do is of course we can find out let us say you can find out now any equilibrium condition between solid liquid equilibria here for example. So this points you can find it out write at any given point. So if you have the information of the melting point then essentially you can find out this information and in that way you can also map this whole curve and obtain the Eutectic point. So let us try to you do this in order to get a feeling of this whole exercise.

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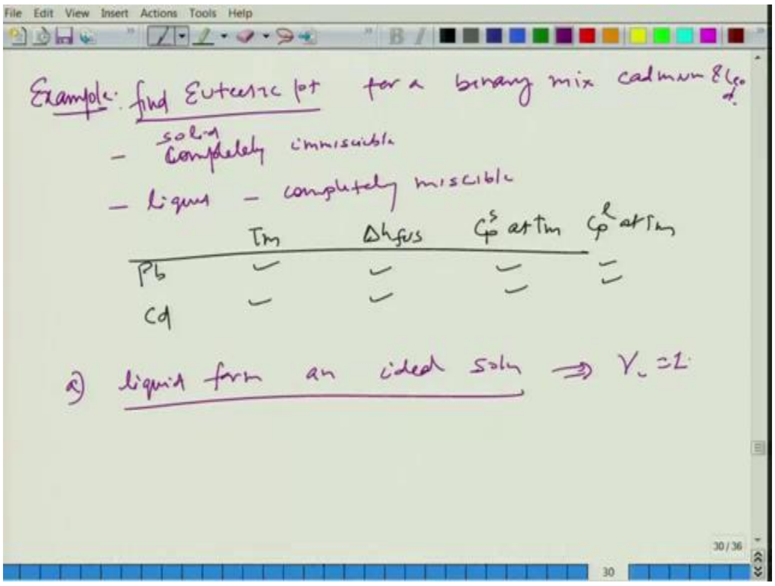
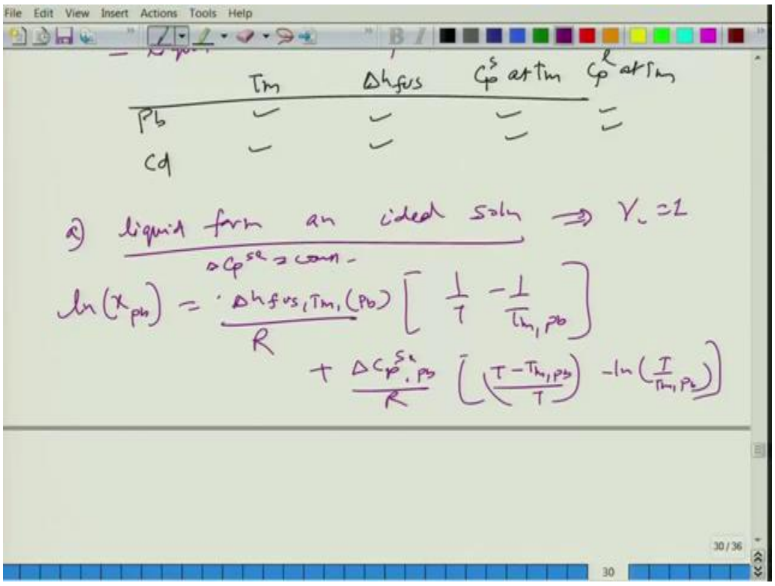


Example: find Eutectic pt for a binary mix cadmium & Lead

- solid Completely immiscible
- liquid – completely miscible

	Tm	Δh fus	C_p^s at Tm	C_p^l at Tm
Pb	✓	✓	✓	✓
Cd	✓	✓	✓	✓

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

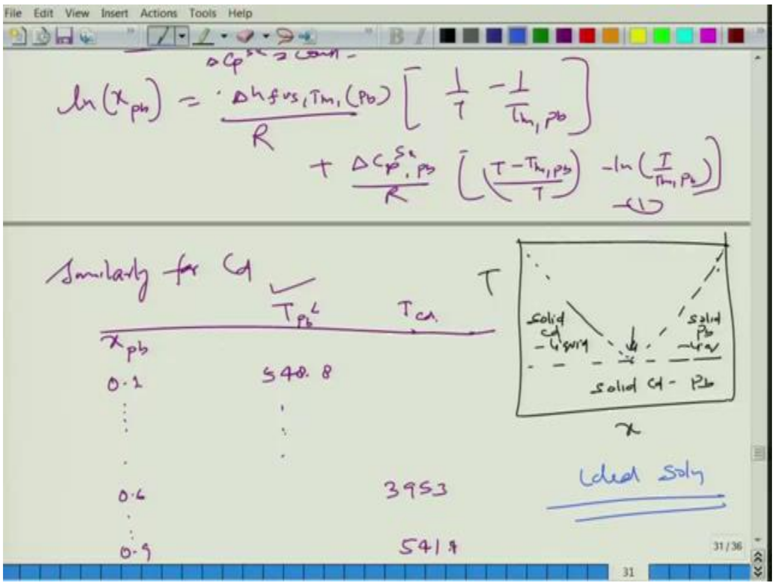


	Tm	Δh fus	C_p^s at Tm	C_p^l at Tm
Pb	✓	✓	✓	✓
Cd	✓	✓	✓	✓

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

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

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



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

So, this is a case where we have to find Eutectic point of a binary mixture which cadmium and Led. So, what is the assumption that these metals are immiscible? Completely immiscible, so solid place are solid immiscible liquid phase is a completely immiscible. So this is basically the assumption which we are considering the solid phase, do not mix at all and the liquid it mix completely.

Now information which is given to us for the case of let us say Pb led end this is a cadmium. So, this are the information given to us Tm is given. So I am not going to describe completely all the data the whole idea is to understand the process and subsequently can you can take it on the own. So Tm is information is given delta h fusion at Tm is given and Cp s at Tm is given Cp l at Tm is given.

In order to get this Eutectic point for different phases, so what we can do is we can perform two cases one A is when the liquid forms an idle solution which essentially means that gamma is good one and when this idle solution that means the left hand side is simply log gamma i and it is a binary solution. So essentially you can write this Ln of x of pb right and then we can write down the right-hand side expression is this.

Now, in this case, of course, we can also consider Cp sL to be constant and then you will have this complete information it will be simpler rather. So considering that Cp sL delta is constant I can write down final expression here which is this, this was delta h fusion R, so we can plug this information because rest of the information is given to us and so you have simply delta h fusion Tm and this is of that of pb.

So this is of pb then you have this R and 1 by T minus Tm of pb an then you have this delta Cp sL of pb by R and the rest of the other terms which is basically the same term as we are going to write it here, which is T minus Tm of pb by T minus L T by Tm. Now this is equation 1 similarly you can do the same exercise for Cd. Now Cd you can also write this same exercise now the point here is which should be noted that this particular equation gives you a clearly an expression which relates composition of a led with the temperature.

So essentially you can get a temperature versus composition plot for pb using this expression as similarly you can do the same exercise for a Cd you have to plug in all those values so if you do that you may get something like this you know that you know that is a composition of pb if it is 0.1 you may get corresponding T if you put some composition here, you will have to solve T here, right?

So that will be let us say 548.8 and similarly if you put some number let us say 0.55 and similarly, if you put let us say you know you can keep doing that and keep going getting some point here and after that there will be some issues because you cannot go beyond ascertain number because that would become they non-solvable equation and then at certain point say you may not get this value but if you look at the other equation it will provides us solution and 395.3 will come out for the temperature as a for the case of phase cadmium.

So 0.6 led means 0.4 cadmium as far as the mole fraction is concerned and similarly if you go till 0.9 some values of 0.4 will comes in like 541.4 comes in. So this is also a temperature but this temperature corresponds to let us say pb and this temperature corresponds to that Cd. Now the issue is again, remember that we would be of course solving this but at certain point this is non solvable we will not get any value because that will lead to some issues and that is something which, now when you do that you will realise that.

So if you solve this problem by putting this temperature versus mole fraction. So you will see that you have this data and then this is a case of solid Cd and liquid and then some other data is there and this would be the case of solid led and liquid. So you will have, that means you will have the situation where below this temperature you will have this solid Cd and pb, which means that this is if you draw this data point and if it intercepts at a certain point then this point would reflect to be Eutectic point.

But this is the case where we have assumed there has to be a idle solution remember that, because we have not consider gamma. So, if you consider case where you have to consider gamma then it will become a non-idle liquid surface. So, now at that this point we can consider difference models of non-idle liquid phase.

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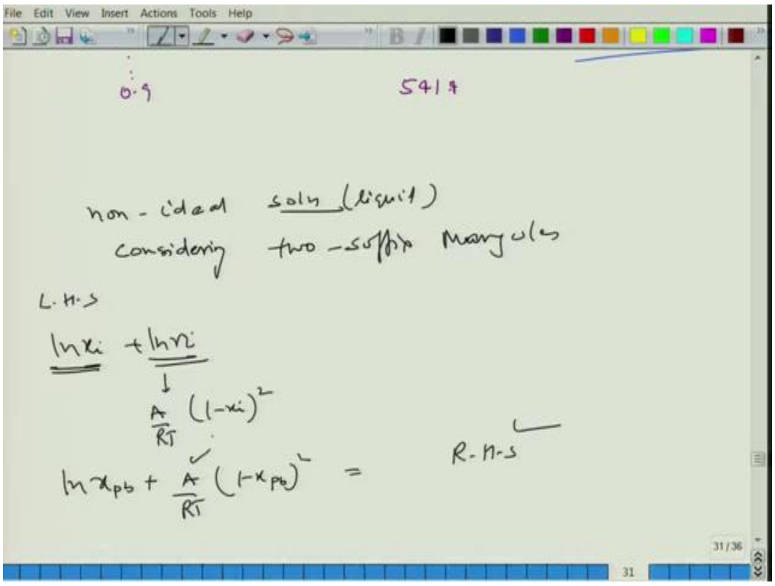


0.9 541 K

non-ideal soln (liquid)

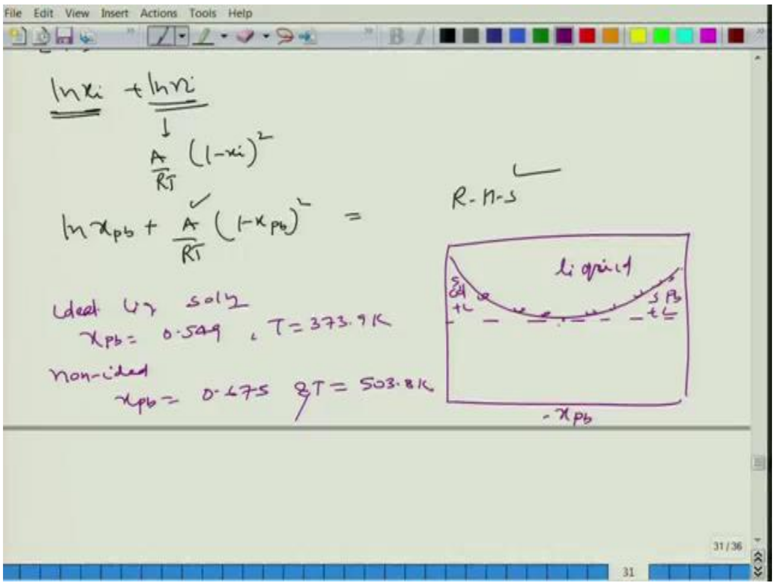
considering two-suffix Margules

L.H.S

$\ln x_i + \ln \gamma_i$

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

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



$\ln x_i + \ln \gamma_i$

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

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

ideal liq soln

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

non-ideal

$x_{Pb} = 0.475$ & $T = 503.8K$

$$LHS:\ \ln x_i + \ln \gamma_i = \ln x_{Pb} + \frac{A}{RT}(1 - x_{Pb})^2 = RHS$$

So if you have taken let us say non-idle liquid phase would be solution or liquid and if he consider non-idle liquid solution and considering two suffix Margoles equation, if you consider this then the essentially you have Ln left hand side of this equation is Ln xi plus Ln gamma i.

So, of course, this will remain the same but gamma Ln gamma can now be written as simply A by R T 1 minus xi, square in this case binary solution. So, if you ae talking about let us say R T let us say pb. So x pb plus A by RT 1 minus x pb square. So and the rest of the right hand side still remains the same, so this still remains the same you now have to solve the x as if you know plug in the x values and essentially A has to be known.

So we plug in the x values for given x you have to again solve the equation to get a temperature out of it and if you do that it turns out that for the case of non-idle of course it is not going to be simple here, so the question would be how do you get the u tactic point? So it remotes smooth here you will get more points for this, so it is the wave, if we plot let us say mole fraction of pb. So you will have this some kind of a points which is something like this it will come out to be something like this and this is your point here.

So this is your liquid and the of course this is your going to be Cd solid Cd plus liquid this is your solid pb plus liquid. So the Eutectic point in this case would be somewhere here, you can find it out also and this will be the case where you will have the different value, for example, in the first case for the case of idle solution, idle liquid solution, you had x is equal to 0.549, just to given idea and temperature is 373.9 kelvin for the case of for this non-idle case the value comes out to be 0.675 and temperature is 503.8 kelvin.

So, this tells you that so important to consider and such a case, a proper models in order to obtain a right information and those idle solution for such would not be appropriate but the methodology does not change much, it is more less than the same though the only thing is that we have to consider the appropriate models for solving these phase diagrams.

So, I think that will be the case for today and hopefully we have gone through a complete analysis we have looked into the how to generate solid liquid equilibria and particularly we looked at Eutectic mixtures where you can find out also the Eutectic compositions from simple analysis as we have done today. So with this course today and we will see you next time.