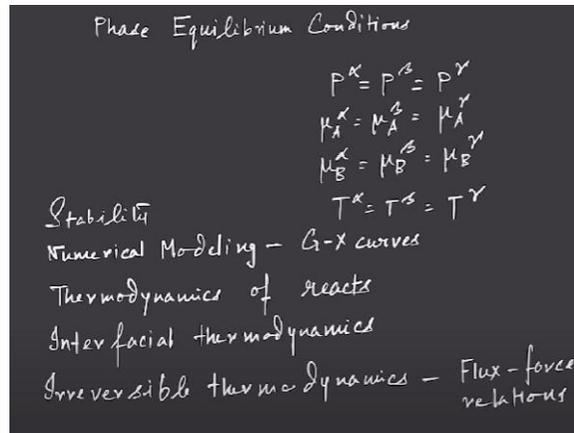**Thermodynamics And Kinetics Of Materials**

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Lecture 36

**Thermodynamic Stability and Numerical Modeling**

Welcome to the twelfth week that is the last week lectures and of this course, Thermodynamics and Kinetics of Materials and this is Shashwatha and so in the last week in the concluding week we look at so we have so far looked at equilibrium right phase equilibrium so we have looked at phase equilibrium we have looked at phase diagrams we have looked at binary phase diagrams we did not look at the ternary phase diagrams but in ternary phase diagrams it is basically as you know we use isothermal section and if required later if you want some pointers to ternary phase diagrams please contact me so I will be ready to help you. So we looked at phase equilibrium conditions we looked at unary systems we looked at multi phase multi component systems we looked at the fundamentals of thermodynamics principles how they apply to phase change how they apply to solutions and different solution models however we had to look at so we always talked about extremization of entropy as one of the criteria and then we looked at all this for simple systems we looked at arrived at the different thermodynamic conditions for example, P alpha equals to P beta if alpha and beta are in equilibrium you have P alpha equal to P beta equal to P gamma say alpha beta gamma are in equilibrium then we looked at also for each constituents say you have two constituents mu A alpha equals to mu A beta equals to mu A gamma so this is another equilibrium condition similarly for the other component if I have a binary system mu B alpha equals to mu B beta equals to mu B gamma we also looked at the thermal equilibrium T alpha T beta T however we need to discuss about stability which is related to secondary equilibrium stable equilibrium whether the equilibrium is a stable equilibrium such as meta stable equilibrium we have discussed meta stability but we have discussed even unstable systems right we have discussed instability gap below at a temperature below which a solution becomes unstable and phase separates we have looked at that but how we formally treat stability is something that we will discuss and instability in the context of stability we look at some aspect like numerical modeling so if I numerical modeling means we basically will use new period model and then we can use something called from the GX curves that is from the solution models GX curves you will see some GX curves and from that if we can use count engine construction so basically that is something that we will do right GX curves and counting construction and also we look at thermodynamics of reacting systems we initially at the

Phase Equilibrium Conditions

$$P^{\alpha} = P^{\beta} = P^{\gamma}$$
$$\mu_A^{\alpha} = \mu_A^{\beta} = \mu_A^{\gamma}$$
$$\mu_B^{\alpha} = \mu_B^{\beta} = \mu_B^{\gamma}$$
$$T^{\alpha} = T^{\beta} = T^{\gamma}$$

Stability
Numerical Modeling — G-X curves
Thermodynamics of reacts
Interfacial thermodynamics
Irreversible thermodynamics — Flux-force relations

initial stages we discussed from the thermochemistry thermodynamics of reactions in terms of reactions so that the endothermic or the mesothermic but here we will go a little bit more detail we will look at Ellingham diagrams as example and finally we will look at some examples of interfacial thermodynamics so these are the three lectures are there so over the interfacial   thermodynamics and a brief introduction to irreversible thermodynamics which is basically the basis of kinetics and there we will look at particularly how it applies to this flux force relations right and this is where we will conclude although the irreversible thermodynamics part if you want further information because it is just an introduction a very preliminary introduction so if you want to go further deep into the irreversible thermodynamics part as you can see in the layout of the course we initially had lot more on diffusion however we changed it the layout a little bit on because you see there is a we discussed all thermodynamic principles in details so we basically did not want to get into a lot of kinetics but we wanted to get into the idea behind kinetics the principles of kinetics and that is what I will talk about and that is where irreversible thermodynamics comes about however as you can see that these are very involved and detailed and it may require a separate set of lectures and we can also have discussion offline so as you know you can reach me at my email id and if you have any doubt and also there is a forum right now but in the forum mostly what is discussed in the class is what will be discussed further but beyond the forum if you want to know something more advanced you can always contact me by my over my email and send me an email and I will try to help you as much as possible now I will start with the criteria for stability now you know when we talk about stability one of the easiest ways to understand stability is by using a mechanical analog so if I take a mechanical analog think of a piece of material which is in the form of this box as you can see here so this is like a rectangular parallelepiped so if you look at this it's not a bar it is like you know in a cross-sectionally you think of this is like a book to see so and you are looking at a book so basically you are looking at something like this and then you have this and this right so you are looking at that now if you look at this this this square is bar or bin or if you can call it a this this material you can immediately see here there is a long edge and there is a short edge of this

material right you you are looking at the cross section here you are looking at the cross section here but if you can think of it is like like like a column a small column rectangular column like this think of a rectangular column if you have played a game of jenga you will see in the jenga there are these pieces these wooden pieces you think of these three-dimensional wooden pieces or blocks so I am talking about one block which has a long edge and which has short edge right which has some thickness and which has which is also having some height and some width okay so I am not looking at the width as such but we are looking at the thickness section and the height now if you see the long edge if the long edge rests and my center of mass is somewhere here see at the lowest level where the long edge is resting on the ground or on the surface so this is your surface this guy is your surface on which the long edge is resting now if you the long edge is resting if you look at this orientation here is your center of mass roughly here is your center of mass right this is the weight of the block now however you can also set the block in such a way that it is resting on the short edge instead of the long edge instead of the long edge it is resting the the surface the the the it is resting on the short edge now in this case in this case for example
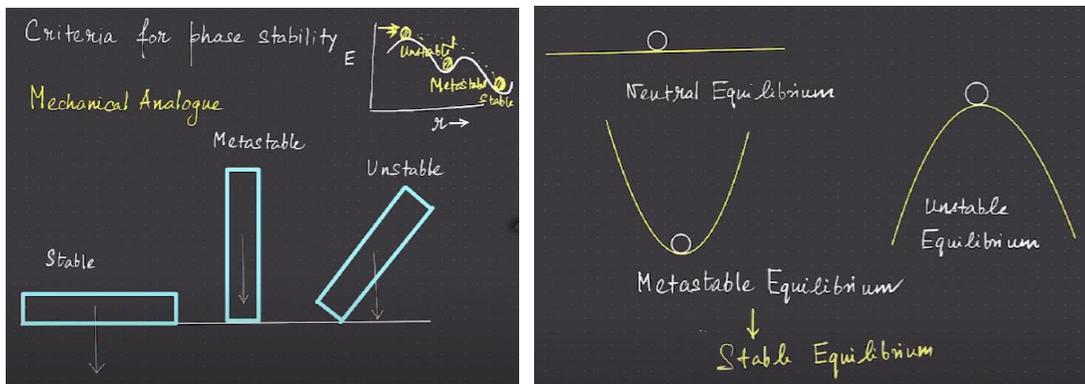
even if I move if I try to force it if I try to apply some force on it if I try to apply some force on it it will move here and there slightly but it will not destabilize right it will not destabilize it's a stable equilibrium right it will just remain as it is however if you look at this the metastable the if you see you can immediately understand why it is metastable because as you can see the center of mass has gone up of the right the way I have tested it on the short end center of mass is somewhere here and if you push it slightly then right not very slightly but yeah you give it give a little show then basically if you if you if you give a little show then it falls right it falls such that it again so if I if I say for example produce a force like this it will fall and once it falls it will rest on this stable equilibrium so if you see stable is the lowest if you look at the stable equilibrium this is the lowest energy state now if I push it or shove it a little bit then it will fall in such a way that it comes to a more stable equilibrium so the metastable equilibrium so that is why this is called metastable

because from metastable I can go to for the more stable now if I look at unstable say there is something called unstable equilibrium this unstable equilibrium something like I am basically somehow I am balancing it on one corner somehow I know or somehow like like like a magician I have balanced it on some corner and it's just barely there so you can see a small touch a small touch or small disturbance even a small sound it can immediately if you will see it will immediately fall on the long edge right it will fall on the long edge it will again the unstable one will tend to go so there is there are two things that can happen this unstable one can fall like this and then it will rest on the long edge it becomes a stable equilibrium so this guy if it falls like this however there is also a possibility that I force it like this then it will just go up and it is possible that it will come to a metastable equilibrium so the unstable one can either be metastable or be stable right the unstable one can either be metastable can either reach a better stable equilibrium if I basically force it this way if I force it this way if I just touch it this way immediately it will fall to the stable equilibrium right so stable equilibrium is the one that it does not want to change at all unless we have regressed it disturbed it unless we have moved it from there and we have we have we have forced it to be metastable or unstable it will remain in stable equilibrium forever however when it is in metastable equilibrium if there is an energy or a driving force better civil equilibrium will change to stability correct better stable equilibrium will change to stable equilibrium if I look at this from an energy point of view if I look at this from some energy point of view then it is the energy and think of this you are somewhere here now here I'll call it locally stable equilibrium but if I mean here for example the ball will roll either this way or this way right I have a ball I have a ball here if you can see there is a ball here the ball can either roll this way right you have a heel here you have put a ball here and this is the energy so this has the highest energy as you can see this is the energy landscape right this is the energy landscape that I am talking about and say this is my position coordinate r okay position coordinate r so if I have such a coordinate and if I have some particle here resting the particle here will be in a highly unstable step a little push can either push it down this hill this hillside or along this hillside now if you see the driving force for going here is much more than the driving force for going here however if it starts rolling this direction if it starts rolling in this direction it will reach metastable equilibrium rather than the stable equilibrium correct it will reach metastable equilibrium in fact I can think of a better diagram say for example I have this now you see our ball here okay so let me just this now if the ball is rolling uh this part is becoming a neutral equilibrium so that means where I want to change it a little bit to a stable equilibrium so basically make it till unstable now you are here somewhere the ball is somewhere here okay now you have just given a little displacement means you have displaced a little from the position so you have given a little displacement from this position what happens it falls in and it goes here right the ball has gone here right it is going here however if I force it a little more if I give it a more than a slight push if I make it a larger push then it is possible that the ball will basically directly follow this trajectory and come here now as you can see this is the stable stable

equilibrium this is the metastable equilibrium and this is unstable right so you have made stable metastable and unstable so as you can see here so if I want to apply this mechanical analog or this energy surface how do I basically understand it in terms of phase stability in terms of phase stability is what we will discuss now right so we have given a mechanical analog see look at this you have given a mechanical analog of facility and you have also given energy surface you have drawn some imaginary energy surface we look at the energy surfaces we generally encounter and this is an energy surface of functional position right on the energy surface so if you see there are positions where the the equilibrium will be unstable there are positions where the equilibrium will be metastable and there are positions where the equilibrium is the most stable one and once you have gone to the to the unstable one you do not sorry to the stable one the most stable one once you have gone here you don't want to there is no way unless there is a big external force you cannot go to the unstable one or the metastable right however a very little disturbance to the unstable equilibrium will lead it to either a adjustable equilibrium or it may lead it to the more stable most stable equilibrium right so this is what we are talking about and here is an example here and I am talking about an another interesting case here so you have a very flat surface and the if the particle is here the particle is here and you have very flat surface now this has same energy this has same energy so if I am here same energy if I am here if I am here in all these points along this surface the energy remains the same so this is called a neutral equilibrium right you just remain there if you displace it slightly the energy does not change so it's called a neutral equilibrium now look at metastable equilibrium why am I calling this metastable because there is a possibility that there are there is a a further means there is a further downward slope somewhere so you have say for example some more downward slope there right. So it is possible right so that is why we call it a meta stable equilibrium right we call it a meta stable equilibrium you can also call it stable equilibrium if there is no such meta stability if this is the lowest energy position of the ball if this is the lowest energy position of the ball then this metastable equilibrium becomes a stable equilibrium right meta stable it becomes a stable equilibrium.

$$G_{m,mix} = RT\left(x_A \ln x_A + x_B \ln x_B\right) + \omega x_A x_B$$

$$x_A + x_B = 1$$
$$(1-x) \quad x$$

$$= RT\left\{(1-x)\ln(1-x) + x \ln x\right\} + \omega x (1-x)$$

$$\frac{dG_{m,mix}}{dx_B} = \frac{dG_{m,mix}}{dx}$$

$$= RT\left\{-1 - \ln(1-x) + 1 + \ln x\right\}$$
$$+ \omega - 2\omega x$$

$$= RT \ln\left(\frac{x}{1-x}\right) + \omega (1-2x)$$

$$\frac{dG_{m,mix}}{dx} = RT\left\{\ln x - \ln (1-x)\right\} + \omega (1-2x)$$

$$\frac{d^2 G_{m,mix}}{dx^2} = RT\left\{\frac{1}{x} + \frac{1}{1-x}\right\} - 2\omega$$

$$\frac{d^3 G_{m,mix}}{dx^3} = RT\left\{\frac{1}{(1-x)^2} - \frac{1}{x^2}\right\}$$

However have a look at the instability say have a look at this position where you are at the top of the hill the peak and if you are the peak of this energy barrier so if you are in the peak this peak is basically the giving you the unstable equilibrium condition unstable because if I displace it this way or this way the ball will just roll right I displace it very slightly the ball starts rolling a little disturbance it will just go to either a metastable equilibrium or a stable equilibrium right so that is the idea. Let us look at that in the context of this solution model right we have already looked at something called phase separation right we have looked at the regular solution model where we looked at something like phase separation where A atoms favor A atoms and the B atoms favor B right so basically if I want to write the excess energy due to mixing or the energy due to mixing then it has one delta S mix right it has a delta S mix this is your delta S mix contribution and there is a T delta S mix right so minus T delta S mix basically gives you RT xA ln xA plus xB ln xB for a binary solution if I take a binary solution this term is basically minus T delta S mix right this has an S and then you have the regular solution parameter so this is the delta H x delta H x right xA and xB are the mole fractions of n in fact if I if since xA plus xB is one I can take 1 minus x and x so basically this becomes RT 1 minus x ln 1 minus x plus x ln x there is a same term here and then this guy becomes omega x 1 minus x just writing it this way right now I want to basically take a derivative I want to take a derivative so dGm dx basically comes out to be RT ln x by 1 minus x plus omega 1 minus 2x okay so basically this basically gives me a slope right of the curve the slope of the curve at any point right it basically gives me a slope of the curve at any point see if I have a curve like this so if I have a curve like this in one single curve so if I have a curve like this right and then basically this is my so if I have this curve for example as a function of x so if I look at this as x x is the composition of some mole fraction of B say and this is my the y-axis y-axis is say Gm now this is Gm mix for example the energy of mixing now I take any point here I take any point here I take any point here and then I draw a slope and the slope is basically given by this relation right the slope is given by that so this is the slope of the curve so I can take this point here I can take the same point somewhere say here I just take that if I want a slope like couple tangent then this is the tangent this is how the so basically this is the the first derivative is the slope of the tangent drawn at some composition this is the slope of the tangent drawn at some composition x or x B okay so that is the first derivative and see the first derivative if you can understand this so basically if you can have a look at this but you see so this is exactly what I want to tell there are some points where the slope becomes zero see there is one point where the slope becomes zero there is another point here where the slope becomes zero right you can notice that point so this is one point where slope is zero this is another point this is another point so basically if I draw three tangents like this and this is another point right there are three points on this curve where slope is zero now let us have a look there is something other than slope that is changing here right and we will try to look at that okay so basically what I told you have
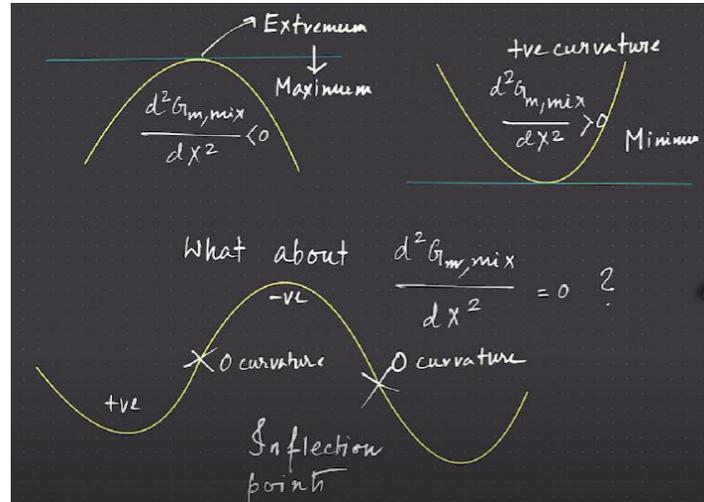
dgm mix right which is rt so which have which is rt ln x minus ln 1 minus x plus omega 1 minus 2x remember when you plot this curve when x equal to 0 ln 0 is undefined when x equal to 1 ln 0 is again undefined so as a result when you plot this first derivative right you can plot the first derivative you can plot the free energy and if you plot these points remember to use an axis but the limits are between 0 and 1 but not exactly 0 and 1 because at 0 and 1 the logarithm terms are undefined now have a look at the second derivative now you have the first derivative so you can go further and you go to the second derivative so you have rt remains rt remains and you have ln x becomes 1 by x and this becomes plus 1 minus 1 by 1 minus x why because you have a 1 minus x and here you have minus sign so ln 1 minus x if you take differentiation so it becomes 1 by 1 minus x with the minus sign outside so but there is already a minus sign so minus minus becomes plus so you have a plus sign you have a plus node that there is a plus sign right so this one has a plus sign here and then you have the third derivative I go further I take the third derivative then you have rt so if you look at that you have rt and then 1 minus x whole square right 1 minus x whole square right 2 omega, omega is a constant right so this goes to 0 now you have 1 by x square so minus 1 by x square see minus 1 by x square but here it is minus 1 by so this is 1 minus x whole so minus of 1 minus x whole square but there is also minus x here so this becomes plus so plus 1 minus x whole square minus 1 by x square into rt now if you look at the third derivative and basically put x equal to 0.5 now you see you have 1 by 1 minus 0.5 which is 0.5 1 by 0.5 whole square minus 1 by 0.5 whole square so at x equal to 0.5
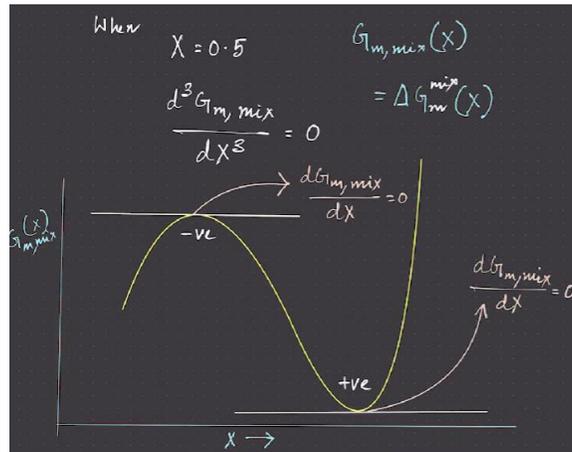
 this guy basically goes 0 now these guy if you see if you have d2 so basically you have d2g dx square d2gm dx square as some quantity say let us call it some quantity say y now if that is so d3 this is basically d3gm dx cube which is nothing but dy dx right so basically this is a slope of the secondary right say low slope of the curve slope of the curve that is

of the secondary right so basically now if you look at this if you look at this so you have gmx say for example you have gmx here so you have gmx here and you have one point where the dgmx dx equal to 0 this is one point where it is and this is another point where dgmx dx equal to 0 and these points are basically where the tangent line becomes parallel to the x axis tangent line is parallel to the x axis the slope is basically 0 but when you look at the d3gm dx cube equal to 0 then you get a value of x equal to 0.5 what does that really mean okay so basically you have a curve and you have it slope and the second derivative basically represents its curvature second derivative represents its curvature now if you look at the curvature the second derivative so in this case the curvature is negative right these case you can see this is curvature is negative and these is where curvature is positive now if you see you have a negative curvature here you have a positive curvature here and the curvature is changing right so here so you are looking at this point this point where you are in the maximum so you have a negative curvature negative curvature means the secondary derivative is negative means the secondary derivative is negative means the function is a the the the the the extremum of the function is a if I have a function fx if I have a function of x if I tell f prime x equal to 0 and I get x equals to xe now I do f double prime x now at x equal to xe I get less than 0 that means xe is a at xe the function is a maximum right the function is a maximum if the secondary derivative is negative now the curvature is that means the secondary derivative is negative means here what we are talking about here the secondary derivative is indeed negative right the curvature indeed is negative here the curvature is positive right which has a positive curvature positive curvature means it's a minimum right when f double prime x at x equal to xe is greater than 0 that means xe is where the function has a minimum right so this is the idea right so we are just looking at the same idea so basically what we are telling is okay you have calculated the function you know the function for example energy or say free energy function now you take the first derivative and equate it to 0 what do you get you get the extremum values now you want to check whether the extremum values indicate a maximum or a minimum if it is a maximum as you can see if you remember the ball rolling example then if the ball is here then obviously this is basically an unstable equilibrium however if it's a minimum it has nowhere to go right it is already in the minimum energy level it wants to remain there if you can see the second derivative now will be positive so positive indicates minimum negative indicates maximum we can immediately see that right so this is basically the maximum this is maximum and this guy tells you minimum so you have positive curvature here you have positive curvature so this is what you have here is positive curvature that means the second derivative is greater than 0 at the extremum value right the extremum value is where the slope is this is 0 the extremum value you calculate by making the slope 0 and then at the extremum value if you calculate the curvature the curvature is positive that means the positive curvature means it's a minimum okay of the curve it's a minimum now if you again slope is 0 here also right slope is 0 here also this is an extremum value so as you can see this is the extremum value now at this

extremum the second derivative is less than 0 second derivative is less than 0 means this extremum is nothing but a maximum right in this case this extremum that you have this

Extremum
↓
Maximum
$\dfrac{d^2 G_{m,mix}}{dX^2} < 0$

+ve curvature
$\dfrac{d^2 G_{m,mix}}{dX^2} > 0$ Minimum

What about $\dfrac{d^2 G_{m,mix}}{dX^2} = 0$?

−ve
+ve
✗ 0 curvature   ✗ 0 curvature
Inflection point

extremum is nothing but a minimum right so now if you look at this term so there is also possibility that the second derivative is 0 now second derivative is 0 basically gives you the point of inflection okay this is called the point of inflection. Inflection is where from positive curvature you are changing to negative curvature so basically you are changing from positive curvature to negative curvature through 0 curvature this 0 curvature so these are 0 curvature points and these points are called points of inflection the points where the curvature becomes 0 so 0 curvature are the points of inflection by the way the 0 curvature points indicate something called as spinodal decomposition spinodal decomposition is where you have a oil-water mixture which is homogeneous now you are taking it below at some temperature it's below the spinodal it's continuously phase separates without any grinding force okay so this this inflection points but what I want to tell you what you want to what I want to emphasize is that there is this there so if you have this type of the double well potential double well means it has two wells right it has two wells one well here and one well here right and this energy I am drawing now as a function of composition tomorrow I can draw it as a function of some order parameter okay so now if you see that it has one minimum here one minimum here but there is one maximum right so there is one maximum now if it is maximum then it has negative curvature this is positive curvature this is again positive so from positive to negative if I have to travel I have to go through 0 now 0 curvature is where basically it indicates the locus locus of the points for which for which any any energy any fluctuations if I have a ball here any small fluctuation will reduce the energy see here the energy one now the energy is now if you see the energy so if it reduces if I come here then the energy has reduced right the energy has reduced

because I have this thing and this thing so average thing I can think of this and if you look at that I go further down and my energy decreases so my energy decreases until I finally reach the common tangent right common tangent basically gives me the the equilibrium states the two equilibrium states that I reached that is that the double well that this well and this one right so this is that now if you do if you use a regular solution model and you

$$\frac{d^2 G_{m,mix}}{dx^2} = 0$$

$$\Rightarrow RT \left\{ \frac{1}{x} + \frac{1}{1-x} \right\} - 2\omega = 0$$

$$\Rightarrow \frac{1}{x} + \frac{1}{1-x} = \frac{2\omega}{RT}$$

$$\Rightarrow \frac{RT}{2\omega} = x(1-x)$$

When $X = 0.5$

$$\frac{RT}{2\omega} = \frac{1}{2} \cdot \frac{1}{2} = 0.25$$

$$\Rightarrow \frac{2\omega}{RT} = 4$$

$$\Rightarrow \frac{\omega}{RT} = 2 \quad \text{(critical value)}$$

$$T_c = \frac{\omega}{2R}$$

want to basically write d 2 gm x dx square equal to 0 then what you get is RT 1 by x by 1 plus 1 minus x minus 2 omega equal to 0 now if you remember so this now if I if I do for the simplification so I get 1 by x plus 1 by 1 minus x equals 2 omega by RT right this is my this is the for the simplification so further if I do because x times 1 minus x is there so if I just make it the inverse so then what happens RT by 2 omega equals to x times 1 minus x because x plus 1 minus x equal to 1 right so now you have RT by 2 omega equals to x times 1 minus x right now when x equal to 0.5 when x equal to 0.5 your RT by 2 omega becomes x times 1 minus x where x equals 0.5 and 1 minus x is 0.5 so RT by 2 omega goes to 0.2 or 2 omega by RT equal to 4 right if I do the inverse if it is 0.25 then 2 omega by RT has to be equal to 4 or omega by RT has to be equal to 3 so now this value at 0.5 right at 0.5 gives the so first we have to understand why 0.5 why did I look at 0.5 because if I basically use 0.5 in this equation so what I get ln half minus ln half which is basically 0 so this term becomes 0 and this one 1 minus 1 right 1 minus 2x so this also becomes 0 so this is 0 and this is 0 at x equal to 0.5 and x equal to half the second derivative the second derivative because that x got to half the secondary what happens the secondary of a   text   wishes   ha   it   is   basically.

.. if I look at the second derivative x equal to half what is the secondary this is the second city so second derivative at x equal to 0.5 is basically RT 1 by x is 2 1 by 0.5 is 2 and this is 2 so 4 RT minus 2 omega now this has become 4 RT at minus 2 omega at x equal to 1 by 2 right 1 by 2 yeah so it becomes 4 RT minus 2 omega at x equal to 1 by 2 now 4 RT minus 2 omega if it is negative then only 4 RT minus 2 omega if it is negative that means if 4 RT minus 2 omega has to be less than 0 then basically 2 omega has to be 4 RT has to be less than 2 omega or 2 omega has to be greater than 4 RT or omega has to be greater than 2 RT so if omega is greater than 2 RT then basically you will start seeing that 4 RT minus 2 omega is negative that means it is a maximum right it is a maximum so the maximum now it at exactly x equal to half it is a maximum now at exactly x equal to half if I want to find if I want to go to d 2 gm dx square equal to 0 which is the inflection point I basically get a very important quantity called the critical temperature which is Tc equal to omega by 2R right we have got Tc equals to comes out to be so RT by 2 omega into x into 1 minus x now put x equal to half so then it becomes half into 1 minus half which is half into half which is 1 4 right it becomes 1 4 so RT by 2 omega equal to 1 4 right or 2 omega by RT equal to 4 or omega RT by RT equal to 2 and Tc equal to omega by 2 right this is the critical temperature so if you look at a mesindic gap phase diagram if you look at a phase diagram with the mesindic gap if you look at a phase diagram with the mesindic gap this is my gene and this is my x and I am approximately it is so if you see this is your this is not gene this is in the phase diagram this is T and this is x and this point is Tc above Tc you have alpha below Tc you have alpha 1 plus alpha right above Tc you have alpha and below Tc you have alpha 1 plus alpha now if I take these are the two phases or I can call this like I have a homogeneous mixture beta and this is beta 1 plus beta now if I tell alpha equals to omega by RT okay so that's why I do not want to use alpha because I have used alpha for denoting this parameter right so this beta is basically a phase right beta is a homogeneous solid solution and say this is A and this is B of A and B below Tc once I go below Tc what I see is that B the composes into two phases beta 1 and beta right beta 1 and beta 2 okay so there are so if when you learn about phase transformations you will see that there are two ways for beta 1 and beta 2 form in one case you have beta 1 matrix in which there is beta 2 nucleation in another case the beta for example at if the composition of beta is 0.5 then you will see that below the critical temperature beta will spontaneously decompose without any push without any driving so it will spontaneous because why spontaneous because if you look at the free energy composition diagram this is what so you are here so again as I told you you are here now if you go a little bit here or here your energy has decreased right your energy was here now the energy has come here or energy has come somewhere so energy is basically continuously decreasing okay if I basically come if I start falling like this way or and this way right so this is exactly what is the root cause of this spontaneous phase separation so if you are within the negative curvature

$$\frac{d\,G_{m,mix}}{dx} = RT\left\{\ln X - \ln(1-X)\right\} + \omega(1-2X)$$

$$\frac{d^2 G_{m,mix}}{dX^2} = RT\left\{\frac{1}{X} + \frac{1}{1-X}\right\} - 2\omega$$

$$= 4RT - 2\omega \quad \text{at} \quad x = \tfrac{1}{2}$$

$$\frac{d^3 G_{m,mix}}{dX^3} = RT\left\{\frac{1}{(1-x)^2} - \frac{1}{X^2}\right\}$$

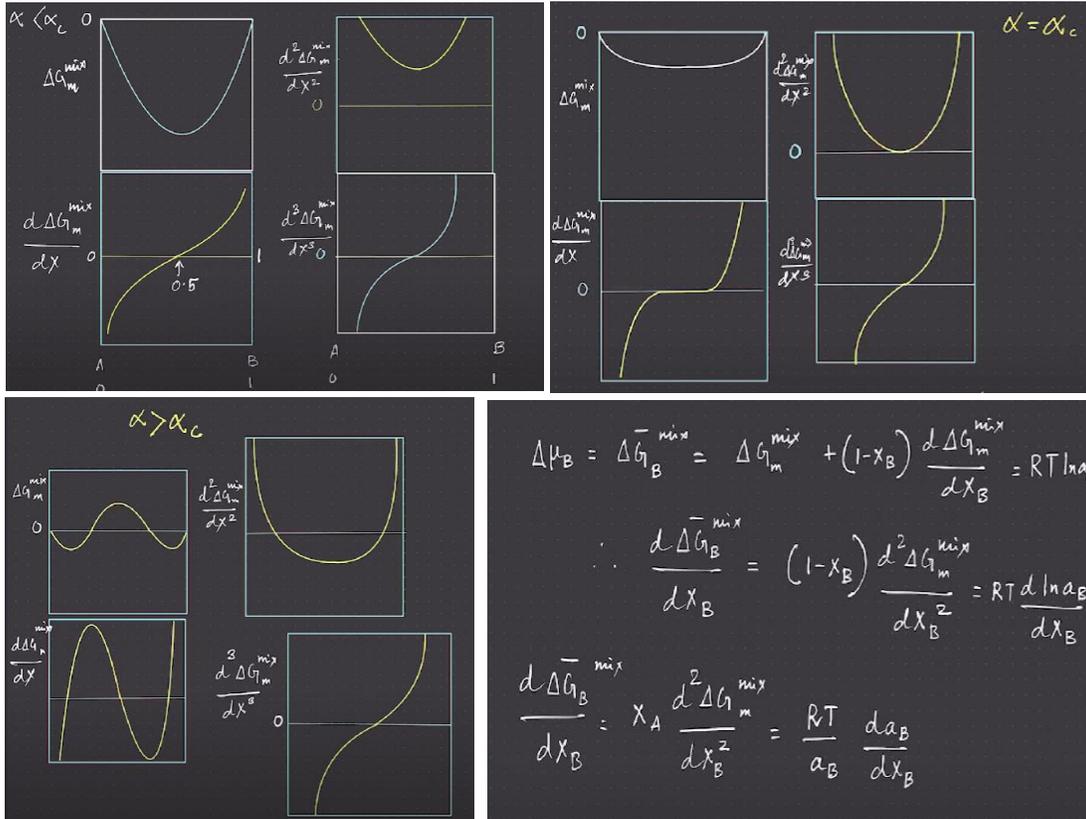$$4RT - 2\omega < 0$$

$$2\omega > 4RT \qquad \omega > 2RT$$

region even a small fluctuation will lead to reduction in free energy as a result as a result there will be spontaneous phase separation of the sub solution into two phases right one is a rich phase and another is B rich phase and as you can see here the diffusion is not so previous diffusion is down the chemical potential gradient but it is not down the composition gradient right it is not down the composition gradient because if you see A becomes richer in A and B becomes richer in B right so this is something that you will you can look at so if you see if alpha equals to omega by RT and if you see that omega by RT equals to 2 is the critical omega by RT equals to 2 is the critical and from there you can write T equal to Tc when Tc equals to omega by 2R right you take this way T you take this way so you get Tc equals to omega by 2R but you see omega by RT is a critical one now if as I told you if omega greater than RT sorry alpha C is the critical so basically if I tell omega by RT greater than 2 or as I told you omega greater than 2RT then basically what you get is phase separation right you get is phase separation if alpha is greater than alpha C alpha C equal to 2 so omega by RT equal to 2 is the critical point so if alpha is greater than alpha C what you basically get is phase separation if alpha equal to alpha C you get critical right that is the critical point so this basically gives you a critical point and if alpha less than alpha C right if alpha is less than alpha C what is what does this mean omega by RT less than 2 right so basically if you see that means omega omega is omega minus 2RT is less than 0 so in this case you basically get a homogeneous single phase this comes again from this right this is no longer if omega minus 2RT is less than 0 then basically 2RT minus omega is basically positive right 2RT minus omega is basically positive if you remember when I put this expression the secondary it becomes 4RT minus 2 omega 4RT minus 2 omega now 4RT minus 2 omega is basically the same as 2 common you take so it becomes 2RT minus omega 2RT minus omega is positive then the curvature is positive curvature is positive means it indicates that it's a minimum value if 2RT minus

omega is negative then only 2RT minus omega is negative means omega is greater than 2 RT omega is greater than 2 RT means omega by RT is greater than 2 or alpha is greater than alpha C now if alpha is greater than alpha C basically what you will see is phase separation alpha equal to alpha C you see you basically see a critical point critical point is where the beta phase coexist with the beta 1 and beta 2 so it's critical phenomenon and critical phenomenon is somewhere your free energy looks a bit like a neutral equilibrium so basically it becomes a bit degenerate and what you basically see is something like this so if I draw so it becomes much much flat right the energies become much right as you are approaching the TC the energies become start becoming flat so at one point at T equal
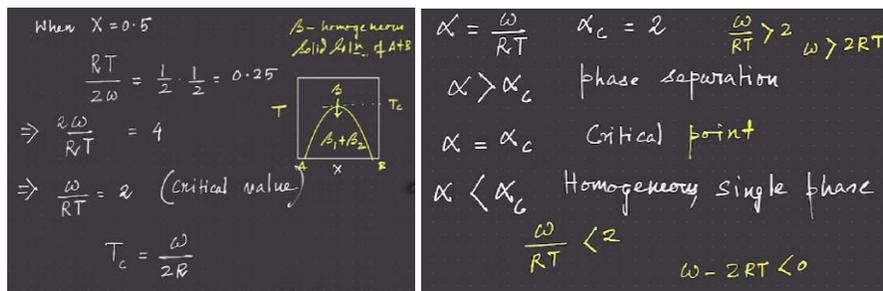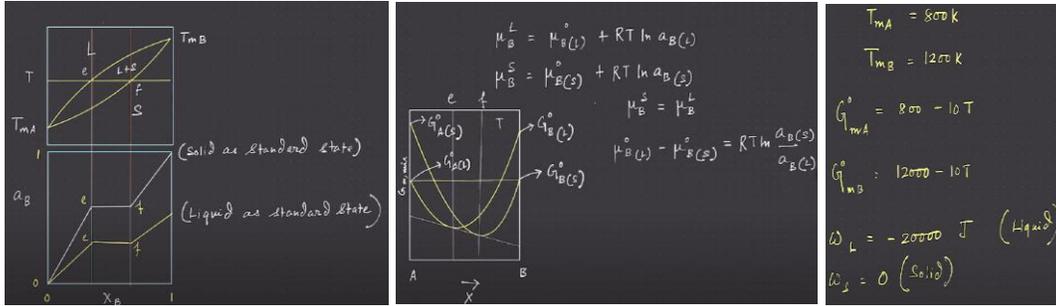

to TC you have some sort of a neutral equilibrium any state is possible right you cannot really apply the normal way of applying phononics so you use something called there is a new there is a branch to understand the critical phenomena okay so the understand the critical phenomena where you use some other more sophisticated statistical mechanical theory to understand that critical phenomena so at the critical value basically you are telling that's a critical point where you cannot basically tell what is means what is the state of the system whether it's a homogeneous state or it's a separated state you cannot really tell because all have become all of the states have become degenerate right so that is the idea so if you look at that if alpha so if I want to plot it if you see if alpha is less than alpha C what you get is a minimum right what you get is a minimum so alpha is less than alpha C and if you look at that this is how your free energy does first derivative looks like and as you can see it intersects the x axis at 0.5 correct when alpha is less than alpha C and if you see the second derivative second derivative looks this way and the third derivative again looks this way again with a value at 0. 5 right again with a period 0.5 right this is the at 0 line right now if you look at alpha equal to alpha C you see again as I told you it's not very flat and you have this type of a curve where you see it extends right it is like it's not exactly 0.5 it can be here it can be here right so this is like these are the points like it carries between 0.21 and 0.79 by the way this basically defines your negative curvature region right this is between these two points it's not exactly 0.21 and 0.79 in this case so you can basically calculate what are the these values these two end points basically tell you the confine of the negative curvature this is the negative curvature as you can see here that you have this this curvature value here that curvature value is 0 here and then the curvature value increases right so basically if you look at this critical phenomenon it

becomes slightly interesting here it becomes very flat line here the curvature becomes flat line right if you can see the front chain here right if you are seeing gmx here so it becomes a right and then you have obviously the alpha greater than alpha C where you have this inflection points right where the second derivative basically goes to 0 and then you have a maximum and you have two minima and if you look at this this plot you have one root here right this is x equal this is basically y equal to 0 or d so this is the slope right the slope

$$\Delta \mu_B = \overline{\Delta G}_B^{mix} = \Delta G_m^{mix} + (1-X_B)\frac{d\,\Delta G_m^{mix}}{dX_B} = RT\ln a_B$$

$$\therefore\quad \frac{d\,\overline{\Delta G}_B^{mix}}{dX_B} = (1-X_B)\frac{d^2\Delta G_m^{mix}}{dX_B^2} = RT\frac{d\ln a_B}{dX_B}$$

$$\frac{d\,\overline{\Delta G}_B^{mix}}{dX_B} = X_A\frac{d^2\Delta G_m^{mix}}{dX_B^2} = \frac{RT}{a_B}\frac{da_B}{dX_B}$$

of the curve becomes 0 so slope of the curve becomes 0 here the slope of the curve becomes 0 here here and here so that's the these are the corresponding roots right but at these two points at these two points you have minima this point corresponds to this point this guy corresponds to this point and this one right so similarly you have the third derivative here and the second derivative right now you can also calculate delta mu B delta mu B is basically nothing but mu B solution minus mu B where mu B solution minus mu B pure right mu B pure state so basically if you look at delta mu B delta mu B is basically delta g B bar mix right this is the partial molar this free energy but this is the partial molar this free energy of mixing so this basically equal to delta gmx plus 1 minus x B d g delta gm dx B you can look at the previous partial molar quantities lecture and you can basically see this is what we have written and if you if you calculate simplify then you will basically get this guy because it's a difference between mu B minus mu B 0 this is nothing but equals

to RT and AB where AB is active now unlike an ideal solution model where AB equals to x B here AB will be different right and if you look at this first if you look at the first derivative again you get 1 minus x B d 2 delta g dx square and this becomes RT dln AB dx B now if you do the if you do the second derivative basically what you get is this RT by AB d AB dx B or dln AB dx B basically RT dln AB dx B and that basically keeps you the thermal effect it will become very useful when you study diffusion okay but as you can see here so this one this guy this is basically d delta g B bar mix so this so you have d delta g B bar mix dx B delta g bar is this so if you look at that that becomes basically d delta g B bar mix so basically you have this one and you have this guy because you have x A and this stuff right and this is your delta g bar mix so this becomes d delta g m mix dx B but you have also plus d delta g m mix dx B so 1 minus x B into d delta g m mix dx B but there is 1 minus x B so minus so this one minus this one will go to 0 and then you will have the secondary derivative so which is basically it will take place okay so basically as you can see here you can calculate the partial molar partial molar quantities of mixing or partial molar potential of like partial molar chemical potential for mixing right for the element B as well as for the element right now basically what I want to say is that there are as you know already and we don't I don't want to again discuss because I have already discussed the standard states okay so if you look at that if you always have the standard states you can use any standard state as whatever possible however this is something that I wanted to tell you because when you look at regular solution models instead of x B right more in most of the cases we have been using ideal solution models so far but you can also use regular solution models like this but you have this state mu B s because mu B l because this is your solid free energy right this is your solid free energy and this is your liquid free energy right and if you have that so you are seeing that this guy minus this now this has to be going to this but you have this part and this part so basically this equal to this this minus this is equal to 0 so this becomes RT ln AB by AB solid by AB liquid right AB solid by AB liquid is basically if you take the other way so this becomes liquid minus right this is the pure B pure B liquid to solid so this is solid to liquid transfer so this is solid to liquid transmission or metal right so this is the transmission now this is basically again comes as a ratio of the activities right in the solid state and the liquids now if you look at that so only thing that I want to tell that you can use solid as a standard state or a liquid as standard state does not really matter the tangent construction does not change the tangent construction does not change the common tangent construction does not change that means that equilibrium values do not change whether I am using this one or this one that really does not matter as long as I am consistent that I am taking B liquid as the pure as a standard state and A also I am taking the liquid as standard state or A for A I can take the solid as standard state well that for B I can take the liquid as standard state or vice versa but whatever I take whatever I take the tangent construction which basically gives me the

$$\mu_B^L = \mu_B^o(l) + RT \ln a_{B}(l)$$
$$\mu_B^S = \mu_B^o(s) + RT \ln a_{B}(s)$$
$$\mu_B^S = \mu_B^L$$
$$\mu_B^o(l) - \mu_B^o(s) = RT \ln \frac{a_{B}(s)}{a_{B}(l)}$$

$T_{mA} = 800\ K$

$T_{mB} = 1200\ K$

$G_{mA}^o = 800 - 10T$

$G_{mB}^o : 12000 - 10T$

$\omega_L = -20000\ J \quad (Liquid)$

$\omega_S = 0 \quad (Solid)$

equilibrium compositions now that do not change right that do not change and if you see the activities if you look at activities and if you look at if you think that activity is the same is the base based on the mole fraction as you can see this activity and mole fraction you have a slope here but as soon as you go to the two-phase region right this two-phase region EF in E and F here you basically see there is no changing activity again the activity changes in the as soon as you will see the as soon as you cross F right you are in the solid state right so basically it becomes now if you take liquid as standard state what happens you go liquid is standard state so basically again you are reaching E you are reaching E and then you have EF where you have that to be constant and then from F you are going to the solid state right from F you are going to the solid state so it does not really matter only thing that matters is so EF nothing changes only thing that matters is the activity if I do it with respect to the standard solid as standard state activity goes to 1 right because the solid is the most stable state at the in the standard most stable standard state so that's why the activity goes to 1 but here if I take liquid as standard state then the activity is not equal to is not equal to the same as xB but if I take solid as standard state it becomes exactly equal to now I just show you so all these things I can basically model so I will try to find quickly tell you how to model this so just open terminal I just open terminal and show you how to model this stuff so basically terminal here here I open something called so I'll use a little bit of Python here so don't I will share this notebooks with you I have two more books here that I have written share them so last modify you Let's look at the face impression first So as I told you I haven't taken so I haven't taken 0 and 1 as I told you I have taken an array between 0.0000001 and 0.9999999 I have avoided 0 and 1 because log is undefined at 0 and 1 right and then I am taking a R value of 8.314 and the omega value that I have taken is 16,000 I have taken 16,000 as omega value 16,000 joules right as omega value joules per mole right and you have R is 8.314 and I am taking a temperature range between 400 and 1400 with steps of 100 okay, and I will show you how the As you increase the temp as you go to higher temperature and as you go to lower temperature So as you are at the lower temperature, you will basically see this double well type of curves But as you go to higher and higher temperatures basically entropy starts dominating and you will basically get into a homogeneous Solid solution or a homogeneous so as you go to a higher temperatures You can go either to homogeneous solid solution or to a homogeneous liquid solution, and I will just show that what happens so if I Start and clear out all output.
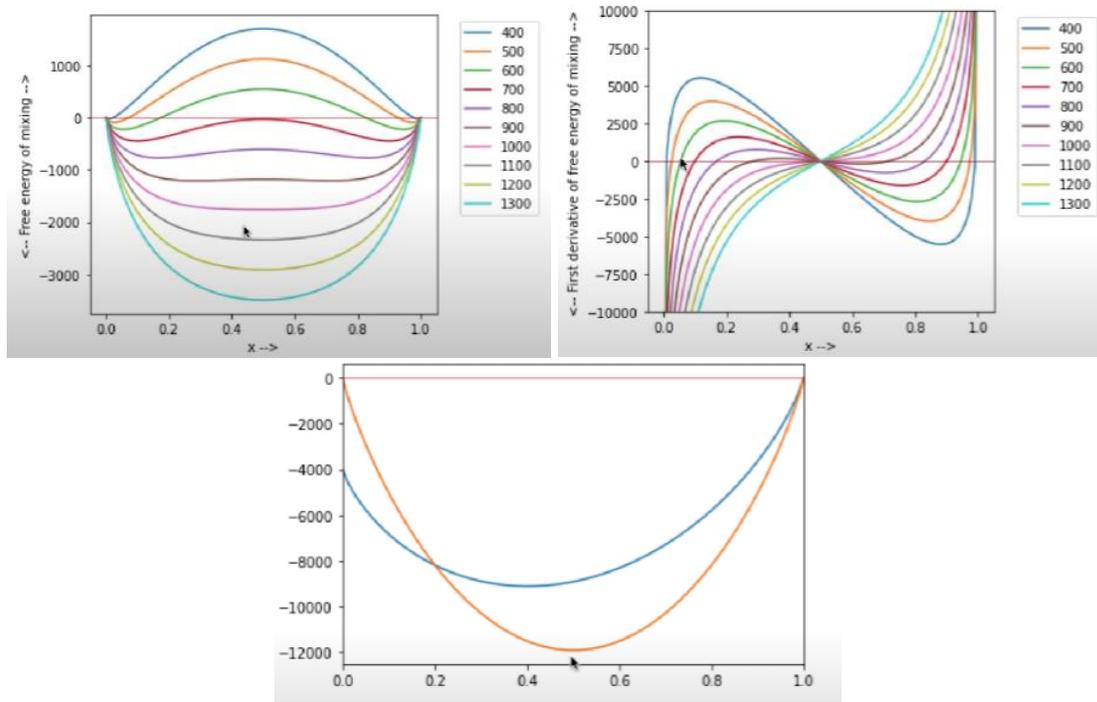
 I have already written it. I have tested it So I will just show you so this is basically a plot to show this basically see That at 400 for example 400 is this one 500 is this orange curve and 600 is this one so as you can see that you have this positive values Of your humidity free energy of mixing only at lower temperature set there you have the positive values In fiction points and you can see that these energy curves are cutting the x-axis and all and so it becomes positive However as you go to 700 800 900 and so on you start seeing that it has been becoming so if around 700 you still see Double well around 800 also or around 900 But as you go to something like 1100 thousand or so you basically see that it has become a single homogeneous phase But here you can see that if I am here if I am here if you can look at the arrow Then I will basically go into one of these compositions like this composition Now I can actually find out what of these compositions. What are basically these compositions say for example I use psi pi library and I solve for this so I am solving basically the so if since this is a single free energy And I am looking at the minima so I can directly calculate the minima minima calculation means I am taking the first derivative Right this is the first derivative, and I am setting it to 0 Okay, and I am setting it to 0 so first derivative of the free energy of mixing And if you can see the first derivative you can see how it cuts the x-axis X-axis also is something I have drawn so you can look at that you can see here So at 400 for example you are here So this is where you are cutting the x-axis now at 500 you are somewhere here in between Right and 600 you

are somewhere here this green line So it is hitting the x-axis that this position at this position Which is close to zero point say one or so right and this is this position this pink Which is close to 0.9 above slightly point and above so basically as you can see as you go to temperatures around say 1300 1200 1100 Thousand and so on you start seeing that Basically it is passing only through a point of 0.5 correct or not you are seeing only it is possible point point So that means it is no longer F 400 if I look at t equal to 400 then basically I'm just solving it for a given temperature So you see one of the points is 0.008. So if you see at t equal to 400 you are basically getting this point basically this point corresponds to point 0 0 8 7 7 9 3 and therefore this will be 1 minus point 0.008 7 9 3 which is like very very close to 0.9 now I have done it for different images like 400 500 600 700 800 900 so you can see here I have done it for different approaches right so I can actually Here So That you can see all the data so these are all data points So you have 400 you have this data point and then 500 you have this data point So this is on the C A side and C B side is basically nothing But 1 minus C A right 1 minus point 0.008 ok at 400 1 minus point 0.02 at 500 1 minus point 0.09 or 0.05 at 600 1 minus point 0.09 at 700 and so on right so basically If you see at 963 1 minus point 5 is nothing But point 5 if you go beyond 963 I go anywhere beyond 963 say let us go to something like say 965 you see that there is only one root and that root is basically equal to point 5 So it is returning to a homogeneous solution so basically we look at 965 you see you got point now if you go to 964 Again it becomes point So at 963 at 963 you see a value which is not equal to point At 963 also it is point 5 you just go below 963 like 962 you see That now it is point 486 so you are very close You are very close like that at point 962 is point 486 that means the other one is 1 minus point 486 So if I now plot this If I now plot all of these so basically if I do this and then I plot These two what I get is a phase step See this is my mesentery gap right so this is around 963 is where or nice two point something Where you basically get what alpha equal to omega equals to 16,000 you basically get this as the TC You can basically use omega by 2 R To check for that you get the correct risk right omega by 2 R So basically it will give you some value like this right so this is basically and I have made it slightly smoother here by interpolating So you can see the same curve Okay, so basically I did the free energy and looked at the first derivative and from the first derivative We're cutting the x-axis x-axis is the y equal to 0 line see y equal to 0 line So this is the y equal to 0 line and basically you can see that At lower temperatures it cuts at two points right cuts at two points and also causes a point here right This is the maximum point for the low temperatures however at high temperatures This is the only point right this green line or something which is drawn around say 1200 degrees Celsius or this yellow line that you can see here. They are only one value right there is only one maximum value So basically what you are trying to say is that if it is so then basically it's a single homogeneous phase Right single homogeneous phase say for example at 1100 if I look at the curve the 1100 curve 1100 curve is somewhere here right this this line this one this one is somewhere here So you can see here it is it is it is it is it has Become such that you have the minimum at 0.5

and basically right you have a Single homogeneous phase not a maximum remember at 0.5 now 0.5 is your single minimum point right see as you go to lower And lower temperatures your 0.5 now becomes a maximum right and you have some other values at the minimum Right so this is what we are looked at phase separation, so I will give another example. I'll give another example and That is the G versus X curve And I I'll share this course Sorry So this is the G versus X curve now. I'll give you the problem the problem is here the problem that I have is here So I have say for example I am trying to construct one of these lens curves or I am just looking at the behavior Okay, I have different temperatures of this free energies and stuff so basically if I want to do that I have TMA given 800 Kelvin I have TMB given then I have been given the G0MA right as a pure pure A molar free energy that is which is basically 800 minus 10 T Y minus 10 T So I have assumed that is 800 minus 10 T so basically that means This is basically 800 or 8,000 so this is not 800 this is 8,000 sorry This one is to 8,000 so that's what I have written here and TMA is 800 so this is 8,000 and this 12,000 minus 10 T so basically and As you can see here you have this This is the DMA and so this one contains the H part and this one contains the S part right so this is all there As you can see here these are for pure A and pure B Now I told that omega L is minus 20,000 ok joules and omega S I have taken as 0 Now I am telling that this is my equation Gm equals to Xa Gm is 0 right Y XB Gmb0 is not there So Xa Gm is 0 plus RT Xa Ln Xa plus Xb Ln Xb plus omega S Xa Xb So that is the model so I am giving you this is the model right Gm Solid is this and Gm liquid is this so these are the this is basically we are telling that here It will be only Xa Gm is 0 In this case when I am looking at solid and here Xa Gmb0 right Xa Gmb0 now if I see that This for the liquid for the liquid because the liquid will have so so so so we will see that okay, so what does that mean? Basically gives you This is the line so this is at some temperature of thousand degrees okay This is at some temperature thousand degrees. I can also do it at the temperature of say 1200 degree I can see which is more stable now if you look at that to do it at 1200 degree so you have the First curve basically if I just see the liquid curve So this is the blue curve is the liquid curve No that the orange curve is the liquid curve the orange curve is the liquid curve and the solid curve is the blue curve because I just hide this guy So you see as you can see this is the solid curve okay, which has a value of minus Yeah, so you have this value right so you have a point so you have a minimum however It is not the minimum that I am looking at What I am looking at is the tangent construction, so if I do this You Can immediately see The x is coexistence so you have a coexistence here right you have a coexistence here You can look at my cursor then you can understand that if I draw a common tangent okay, so that is the idea So if I do that You can do the tangent also So I have this for different temperatures then I create this Derivative and the tangent line equation and look at that Do that then as a some temperature? You It's not defined Don't see this Acha tangent has FX 0 AB Tangent has GML this has except You I Can make it a little bit of clean thing so if you look at this you have this term and this term Now you have to be small guy here and This is the

derivative and this is your tangent And then this becomes A Mail You On the effects I Will just look at it, but what I can tell you is that this one.

 I don't know what has happened here Look at X be and so this is good for a different temperature, and then I just leave it for Now this is the derivative equations tangent equation You You We will check this I get back to you, so I'll get back to you with this Particular error, but what I am trying to say is that for different temperatures, so basically I have done it for 1200 I can do it for thousand And I can do it for Different other temperatures, but what I am trying to say if you draw the common tangent here you can basically get that equilibrium values So this is exactly what I'm telling so again you are plotting it at different temperatures And you are able to get you are able to get it and see this is the GML value and Yeah, so III will share this with you. I'll just fix this part in the tangent line code I don't know why suddenly this problem is happening Okay, so I will I'll fix this part, and then it is telling name X is not defined But that is something that looks very weird to me because the X is definitely defined So it's X is already defined here X is nothing, but it's B. So am I doing the X be correctly? passing the X be correctly This one we have a C X be And this is like point eight and point six so this is all fine And it tells me Y equal to FX So, I will get back to you and I'll share this screen okay, so next in the next lecture I will go into the chemical reactions okay, so basically What I wanted to tell so this part Unfortunately this has some small problem here. We will fix this okay, so what I want to tell Here is that If you do the Delta GA bar so basically as I am telling you that once you know this values once you know these values You can get the from the tangent common tangent you can get the intercepts right you can get the mu a so here I have anyway calculated them. I just want to show you numerically mu a and mu B.

 Okay, so you have got it here So you get these values and you have the Delta GA bar and the Delta GB bar And you can basically get the activities right you can get the activities so if you look at this RTLNA comes up with this omega XB squared plus RTLNA and This basically that means RTLNA gamma XA is this one so RTLNA gamma A See this and this cancels out So you have RTLNA gamma A equals to omega XB square or LNA gamma A equals to omega XB square by RT And you get the gamma A value So what is gamma A at the critical temperature if I tell you so at the critical temperature you just put the T equal to What is that at T equal to Tc is nothing but omega by 2R So here you have to put omega by 2R And then if you want to find that critical temperature again at critical temperature at the critical point Then basically we are also looking at XB equal to 0.5 right so now in the next in the next part I will start with the reacting systems. Okay, so I will start with the reacting systems. I am ending it here Now and I am stopping the lecture