Thermodynamics And Kinetics Of Materials

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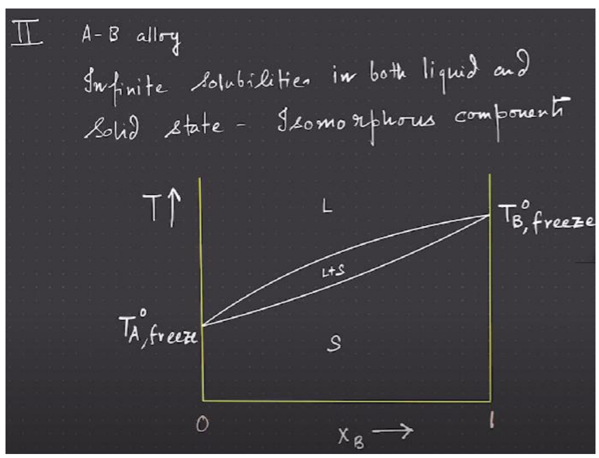
Lecture 32

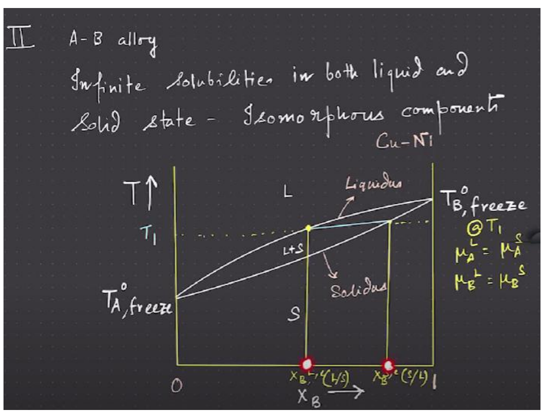
Binary phase diagrams and lever rule

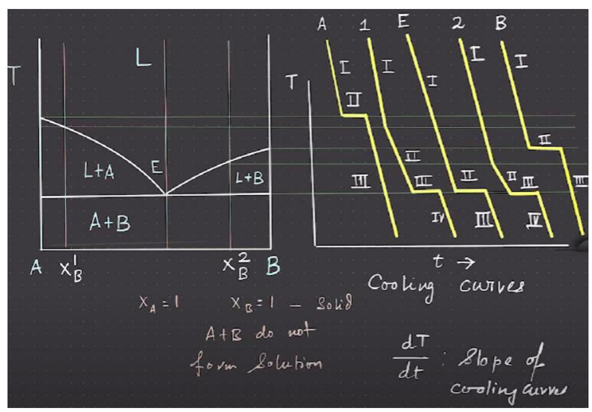
So, the last part of week 10 of this week's lecture right this is the week 10. So, we will now look at the another type of face diagram where basically. So, we have looked at the face diagram where we have 0 solubility in the solid state, but infinite solubility in the liquid state right and we have looked at this and we have basically assumed the liquid to be an ideal solution and we have found out how it looks like and we have defined an impact point and told that there is 0 solubility in the solid state. So, if you remember we told 0 solubility means basically XA equal to 1 in the solid state or XB equal to 1 in the solid state. So, in the solid state there is no right when the solid phase. So, solid is basically pure A and pure B right.



So, basically A and B do not mix A plus B do not mix because are not solubilant one another right. So, A plus B are not form do not form a solution do not form. So, in this case A plus B do not form solution and where when XA basically if I look at that we told this basically XA S equal to 1 or XB S that is in the solid state A and B. So, this is for the solid state right this is the solid state, but in liquid you have infinite in liquid you have infinite solubility right in liquid is complete a complete mixture of A and B.

Now you have in the second case basically an AB alloy. So, in the second case we are talking about an AB alloy again a binary alloy with infinite solubility in both liquid and solid and you have isomorphous components as I told you isomorphous means having the same structure one of the. So, and you get some sort of a lens diagram and this lens diagram basically is very common for example, and you can see them in copper nickel for example, copper nickel is one of the one very important example in this type of a diagram where copper and nickel have the same structure and they form an entire for the over the entire composition range they form a solid solution or a liquid solution right. Over the entire composition range copper and nickel will form a liquid solution or over the entire composition range copper and nickel will form a solid solution and they are isomorphous that means copper is SCC, nickel is SCC and they form and the structure remains the same right they have the same isomorphous means isomorph means the same structure and the same structure is there from 0 x b equal to 0 to x b equal to 1 and you basically get this type of a lens shape diagram. So, this lens has one part which separates liquid from the two phase liquid to solid and there is another part which basically separates liquid to solid from solid.





So, this part basically has one name and this part has another name. So, basically the part that separates here. So, this curve this guy basically is called liquidus. So, it is basically separating the two phase region from the liquid plus solid and this part is called solidus and again as you know within the so in the single phase solid or in the single phase liquid you cannot draw tie line and you have the degree of freedom which is basically 2 right it is basically 2 but within the liquid plus solid region you can basically draw a tie line. So, at a given temperature say for example, I have a given temperature say look at this temperature here basically remember you cannot draw tie line in the single phase region now you can see this is happening at some temperature.

So, I will just mark the temperature. So, let this be T1 and this T1 temperature this is the name you have this tie line right this tie line is there this is the temperature T1 and now at this tie line. So, from this tie line that is that we draw in the two phase region you can now basically draw this vertical lines right with the parallel to dot basically you can have this line here and you can have another line drawn here and this basically tells you that this is the at temperature T1 right at temperature T1 at temperature T1 you basically have this is the composition so this is XB this is the liquid composition which is in equilibrium with solid so liquid solid and this is basically XB solid which is in equilibrium this is the solid right. So, this is solid liquid equilibrium right. So, you have these two compositions right this composition and this composition at temperature T where the chemical potential.

$$\ln\left(\frac{X_{AS}}{X_{AL}}\right) = \frac{\Delta H_{A,melt}}{R}\left(\frac{1}{T_{A,freeze}} - \frac{1}{T^{o}_{A,freeze}}\right)$$

$$\ln\left(\frac{X_{BS}}{X_{BL}}\right) = \frac{\Delta H^{o}_{B,melt}}{R}\left(\frac{1}{T_{B,freeze}} - \frac{1}{T^{o}_{B,freeze}}\right)$$

$$X_{AS} + X_{BS} = 1$$

$$X_{AL} + X_{BL} = 1$$

Solve to get $X_{BS}(T)$, $X_{BL}(T)$

$\downarrow$ Solidus $\quad \downarrow$ Liquidus

So, at this temperature the chemical potential of this of the liquid phase and the chemical potential of component B in the liquid phase is equal to the chemical potential of component B in the solid phase. So, basically if I want to look at what is out of these we are basically going to solve two equations one is called mu A liquid equals to mu A solve at temperature T1 at T1 remember this is at temperature T1 and then we are also going to solve another equation to make the liquid in the solid. Now, if you have that then you basically get these two compositions. So, if you solve this you basically get these two so if you solve once you solve this you get this composition and this composition. So, this is the composition of the liquid which is equilibrium with it.

So, this is the composition I mean so at temperature T1 at temperature T1 at temperature T1 this is the composition of the liquid phases, this is the composition and the liquid phase right this guy. . So, you read the compositions from the X axis. So, this is the composition of the liquid phase and this is the composition of the solid phase and these two compositions are basically solution of these two conditions or technique and this composition is equilibrium in these composition. So, these composition of the liquid phase in equilibrium with this composition of the solid phase right.

So, that is the idea right, but it is a length shape diagram. Now, if you look at this you have now in both cases complete solubility right infinite solubility. Now, again you look at the same thing ln XAS by XAL. So, you are now looking at ln XAS by XAL which you have delta H is the melt that is the pure pure a melting transformation, latent heat is the latent of melting of pure a, this is the latent of melting of pure b, your R is gas constant, your Ta freeze minus Ta0 freeze and Tb freeze minus Tb0 freeze right. Now, if you have that so basically Tb freeze or Ta freeze like the freezing point of component a or freezing point of component b, but since it is infinitely soluble in both.

So, basically Ta freeze and Tb freeze are basically going to be the same across all right they will vary right, they will be the same width they will have the same T freeze. So, if you instead of writing Tb freeze or Tb freeze we can directly write T freeze and the T freeze is basically foreign alloy which is not pure a neither pure a nor pure b. In such case you see another thing that XAS plus XBS equal to 1 XAL plus XBL equal to 1. So, basically what I am trying to say is that if I look at vertical line if I am looking at a vertical line say for example, I can write get a very thin line here draw very thin line here and then we can look at the freezing point. So, basically if you look at this, this T is the this point is Ta0 freeze and this point is Tb0 freeze and as you can see Tb0 freeze is greater than Ta0 freeze that is the melting point of B or freezing point of B is greater than that of A right that is what we are basically looking.

Now, if you look at this line you have one point where B field starts changing to solid right B field starts. So, basically is not that it could be transferred to solid but it is transferred to solid because some amount of solid is starting to be input right some amount of solid is starting to be input. Now, remember that when this T to solid transmission took place here for example liquid plus A now this remaining liquid now will completely go to B and so that is where you saw this horizontal segments right in the cooling curve. Now, here how will it happen we have to see right we have to see. So, we will one thing XAS plus XBS is equal to 1 and XA plus XB is equal to 1.

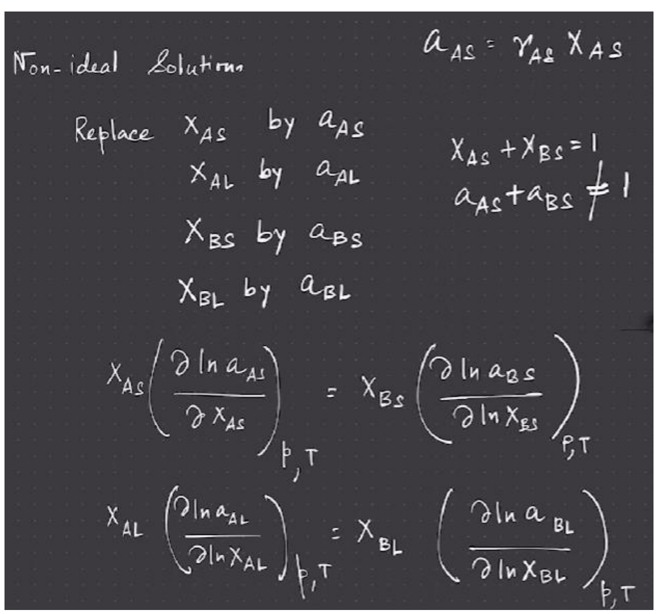
So, as a result we are now looking at only XB the variation in XB. So, this is your A right this is your A your A and this is your A right. Now, you have XAS that is the XA in the. So, basically S again is the solid right this is solid. So, you can take a bracket here if you want but I generally prefer this.

So, you have XAS and you have XBS. So, this is the solid phase this is basically. So, S denotes solid phase there is only one solid phase because we have an infinite solid phase in the solid solution. So, one S is a solid phase and one L is a liquid phase but if you see the previous diagram you had your A solid and you have your B solid right. But here you have A is the solid phase it is a mixture of copper and nickel.

So, it is all A and B solution right isomorphous mixture isomorphous mixture of A and B or isomorphous mixture if you think of copper and nickel system. So, it is a copper nickel system then isomorphous solid solution of copper and nickel. So, here it is isomorphous solid solution of. So, this S is isomorphous solid solution of A and B right. So, you have that and you have L.

So, similarly you have for liquid XA plus XB I could be 1. So, this is the liquid phase L is stands for liquid phase and there is infinite solidity both. Now, if I want to so you have equation number 1 here, equation number 2 here and you have equation 3 here and you have equation 4 here. Now, if you solve them you basically get XBS and XBL right you get XBS is the equilibrium competition of the not even the solid competition the solid competition right the mole fraction of B in the solid. Mole fraction of E in, the solid in function of temperature right you get mole fraction of B in the solid with time of temperature or mole fraction of B in the liquid as a function of temperature.

Now, these guys this XBL T is what basically. This is the liquidus equation. So, you can see this is the liquidus equation and XBS T is the solidus equation right because at different temperatures right it is basically having as a function of temperature right goes from one temperature that is pure melting point of pure A to melting point of pure B it is basically to the solidus the way it changes like this or liquidus actually changes right. So, that is the idea. Now, we can also replace basically if you want you can basically if you this is where we are basically assuming ideal solution.



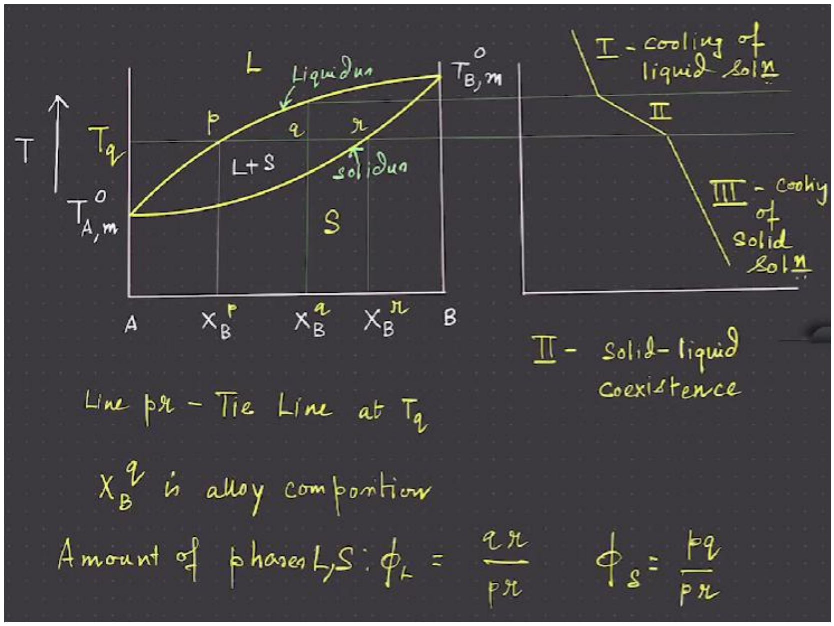
So, I am telling ideal solid solution and we are also looking at ideal liquid solution. But we can also do the non-ideal now. So, basically if you look at non-ideal then XAS is the physical activity of A in the solid and XAL that is the mole fraction of A in liquid is replaced by activity of A in liquid. Similarly, XBS is replaced by A XBS is replaced by ABS and XBL is replaced by ABS. Now, you have this relation that you can write right del N and AS del XS.

So, basically this comes from the Bistu and right. So, if you if you write this equation as a counter temperature. So, keeping pressure and temperature fixed right you have to make sure that pressure and temperature fixed you can basically write del LN AS by del XS and this is del N ABS by del XBS and you have XS and XBS which basically comes. Similarly, you can this is for the solid right this is for the solid and you can also write this for the liquid. So, you have now for liquid you have XAL del LN.

So, basically del LN A del LN X and this is del LN A del LN X for B right. So, this is for B and this is for A and if you have this two equations. So, this is basically coming from the Bistu and relation and you also have the XA. So, basically remember AAS so this is something that you have to remember although XAS plus XBS equal to 1 AAS plus ABS for a non-ideal solution right it is not equal to 1 because this has a gamma right A and so basically AAS is gamma AAS in the sub solution into X. So, in the result this is not equal to because activities do not sum up to 1.

So, basically you have two equations so basically you cannot directly solve it right it is not so easy to solve right that is one thing that you have to remember when you have a non-ideal solution you have this two equations and you can write XAS plus XBS is equal to 1 and XAL plus XBS is equal to 1 and you will get now you have how many variables you have these variable right and this is also variable this is also variable and this is also variable right. So, you have four variables but you do not have any other equation right you have only this equation and this equation right. So, as a result it is not straight forward it is not very straight forward you get the liquidation of this curves but however there are ways to basically obtain this curves there are ways to obtain this curves but it is not as trivial as here. So, here you have the clearly four equations and you have basically using these four equations you can just equate XBS as a function of temperature and XBL as a function of temperature again you will also tell me that if I do this XBS as a function of temperature or XBL as a function of temperature I have basically two variables right why do I require this two this three and four. So, three and four gives a restriction and which you can use to basically get XBS and XBL right.

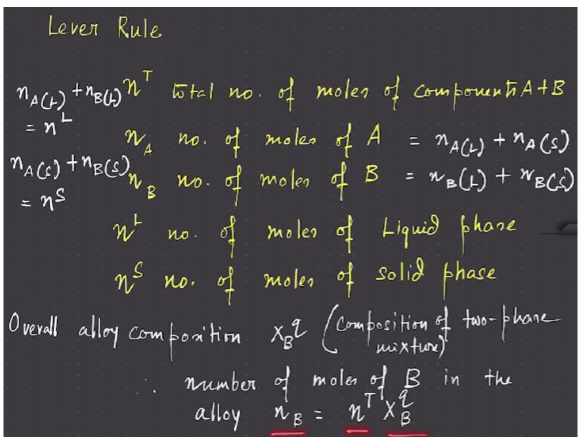
So, as a result you can get XAS and XL. So, here also basically you are looking at two equations but remember you have to measure the activities right you have to measure the activities you have to know how the activity is done right for this non-active case you can always assume some measure assumption model right you can assume. So, in this case non-active solution is an approximate. So, you can approximate using a regular solution model is one approximation regular solution approximation. Now, if you do that you can use regular solution approximation that is one type of an approximation there are many other non-active solution models but regular solution is a well known positive model and is unusual.

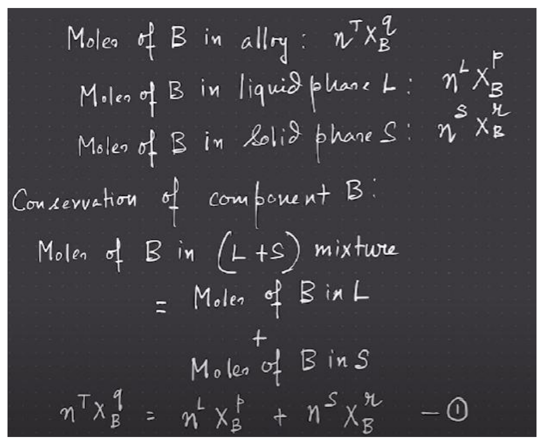


Now, if you look at the lens again as I told you have this sky line. So, you have this sky line this guy at temperature pq right at temperature pq at this sky line and you have p and r and q, q is your alerting position. Now, if you see line pr line pr is a line that is drawn this is a sky line at pq. So, basically I can draw a sky line it is slightly quicker you can draw a sky line here right. So, this is the sky line that you only draw the two phase region.

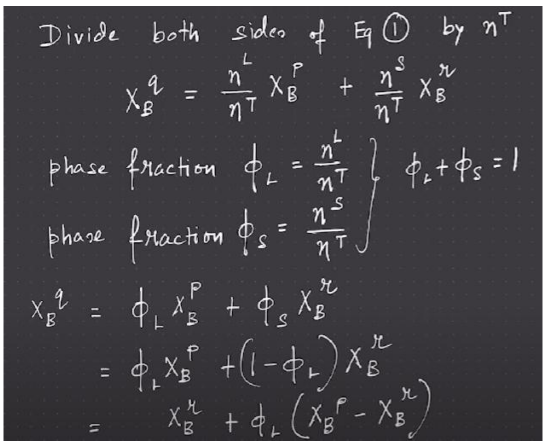
Now, in this two phase region this sky line intersects the liquidus curve at p and intersects the solidus curve at r and basically you can see if XBq. So, XBq is the alloy composition then amount of phases liquid. So, basically q so basically the amount of liquid phase right amount of liquid phase is given qr by pr right qr by pr and amount of solid phase or fraction of solid phase is given by pq right. Now, how does it come? So, you can look at the lever rule and derive. So, this is basically if you look at this pL plus pS equal to 1 you can see that because qr plus pq is nothing but pr and pr by pr equal to 1 right.

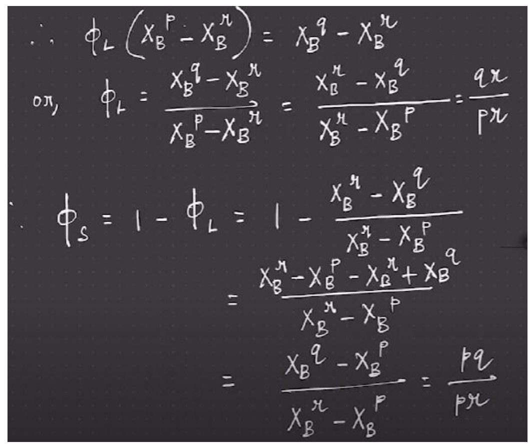
Now, I will just end this with the derivation of lever rule I will just end this with the derivation of lever rule and you have like nT which is the total number of moles of components A and B and nA is the number of moles of A, nB is the number of moles of B and nL is the number of moles of liquid phase and nS is the number of moles of solid phase. So, nA is the number of moles of A. So, nA this is the if I look at them you can write it as nA in liquid plus nA in solid right and here also liquid plus nB solid right. So, basically these are distributed but nL basically if I tell nA L plus nB L equal to n similarly nA S plus nB A equal to nB so there is the amount of or the number of moles of solid phase right or number of moles of liquid phase right but these are like nA is the number of moles of A that is distributed between the liquid phase and the solid phase, nB is the number of moles of B that is distributed between the liquid phase and solid phase. Now, overall alloy composition as I told you is xBQ right.



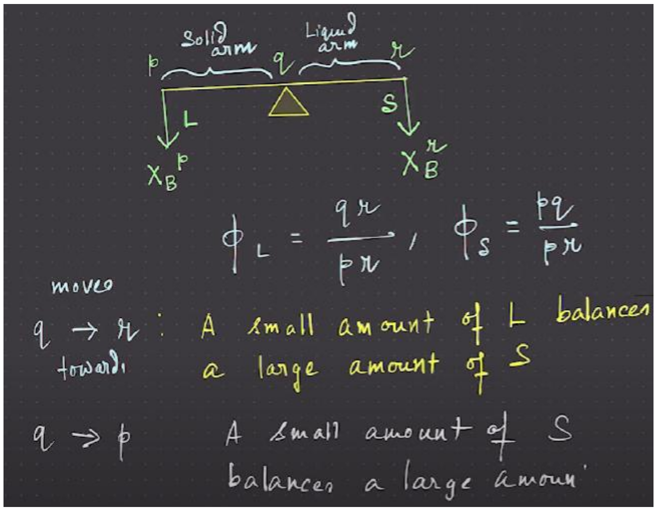


Now, if you look at that so basically it is a composition of two phase mixture. Now, if you see xBQ as the mole fraction of P and that is the overall alloy composition right at temperature pQ then the number of moles of P is basically equal to total number of moles like total number of moles times xBQ right total number of so nB number of moles of P or nB is equal to nothing but nP and is the total times xBQ right times xBQ times nK gives me nB right. So you have moles of B in alloy which is nP xBQ and most of B in liquid phase is nL xBQ so moles of B in the liquid phase which is basically given so if you look at moles of B in the liquid phase so if you look at moles of so this is xBp right in the liquid phase composition xBp at this temperature and xBr is basically the moles of so mole fraction of the mole fraction of the so basically this is the composition right this is the solid composition equilibrium in the liquid composition so xBr is the solid phase composition right xBr is the equilibrium solid phase composition at temperature pQ this is the solid phase composition so basically if I look at that you have nL xBp and ns xBr is the moles of B in solid phase right so moles of so ns is the number of moles in the solid phase now you multiply with xBr then you basically get moles of B in the solid phase and for liquid phase again you are looking at the equilibrium composition in the liquid at temperature pQ which is basically given by xBp x nL where nL is the number of moles of nL is the number of moles of the liquid phase now if you see moles of B here is the conservation of component B as a result moles of B will be the solid mixture because most of B in L plus most of B in S so if you see that nT xBq equals to nL xBp plus ns xBr right so basically nL xBp and ns xBr where ns is the number of moles of solid and nL is the number of moles of liquid multiplied with the equilibrium composition of this xBp is the equilibrium composition of the liquid and this is the equilibrium composition of solid at temperature pQ so if you do that this basically gives me number of moles of p in the solid phase right number of moles of solid phase and this number of moles of p in the liquid phase and together that is basically the total number of B in the solution right.





Now if you divide both sides then in p what you get is that the q is nL by nT x Sbq plus ns by nT x Br now phase fraction pL is nL by nT and phase fraction pS is ns by nT so basically now if you look at that xBq is pL xBp plus pS xBr now pL plus pS as you can see from here pL plus pS is equal to 1 so you can now write xBq and you have xBp you have xBr right and you can write this as pL plus 1 minus xBr so basically this becomes now if I do that so you have xBr into 1 and xB minus so basically you have minus pL and here xBr plus pL you can take pL common this is xBp minus xBr alright xBp minus xBr if you look at that this is basically xBp minus xBr or xBr minus xBp only thing p minus xBr will be negative xBr minus xBp is the is positive now if you look at that so you get pL so you have this equation so this equation is there this equation is there so you get pL as xBq that is the p minus so basically you are doing a rearrangement here you are doing a rearrangement here you basically get pL which is xBq minus xBr by xBp minus xBr which is basically if I can take the other way so I can take xBr minus xBq right xBr minus xBq is nothing but qR and xBr minus xBp is nothing but qR so basically I can do pS also which is again coming out to be pq by pR right you can do this as reflection and see and basically you get pS and pL so pL is qR by pR and pS is pR pq by pR so basically if you look at that if you look at that you are looking at why is it called as rule because see you have q which is the alloy composition which is your fulcrum and you have p which is your equilibrium solid composition and this equilibrium liquid composition and this is the liquid



arm and this is the solid arm as you can see pL basically is liquid arm by the total length right of the lever the total length is pR and this is basically the solid arm by pR and if you see that if you look at that if you move from q to R that is the fulcrum is moving this way right you are going in here then you have a small amount of liquid as you go towards R as you go towards the solid phase then what you are telling is a small fraction of liquid is basically balancing a large amount of solid now if q moves the other way for example then you look at that it is moving more towards the liquid so if it moves more towards the liquid then you have a small portion of solid is balanced by a very large portion of liquid right so when q moves towards R it is small amount of liquid balance a large amount of solid and the other way it is the small amount of so when q moves towards p say for example q is moving towards p if q moves towards p then small amount of solid balances large amount of liquid so small amount of solid balances are large right so we will basically so we will basically the tenth pick all these lectures I wanted to finish till lever rule because there is still a free energy composition diagram that is remaining and there are some other phase diagrams where you have solubility which is limited right solubility in the solid is limited or solubility of A and B in the solid is limited but solubility of A and B in the liquid is infinite so this is a special case where the solubilities of the in liquid are both infinite but lever rule applies to any right a lever rule applies to any timeline okay for any composition and that's why I derived the lever rule here and remember here we just one quick thing that if you now look at the phase diagram here so as you can see there is no horizontal line here are you seeing that there is no horizontal line here because as you can see the composition is varying right so basically if you look at say for example only here only for the pure A and pure B you will see such a logical line but other than that you will see there is a continuous change because as you can see as you go from here to here as you are coming down right you are here say for example your compositions are here but as soon as you come here then the composition has changed right so basically the composition is changed no longer the cooling curve because the continuity has changed everything has changed it cannot be a single horizontal line right the single horizontal line cannot come here right you will have this sloping line and you have this continuous change in slope right this continuous change in slope is happening for any alloy which lies between A and B right if you are in pure A or pure B again you will see a horizontal line right but when you are going as a mixture or a solution of A and B then basically you can see the cooling curve that 2 which is in the 2 phase region you see a continuous change in slope and 3 is basically cooling out solid solution ok so we stop here for the 10th week and we will continue with this more of phase diagrams and free energy composition diagrams basically the thermodynamics of these phase diagrams.