Thermodynamics And Kinetics Of Materials

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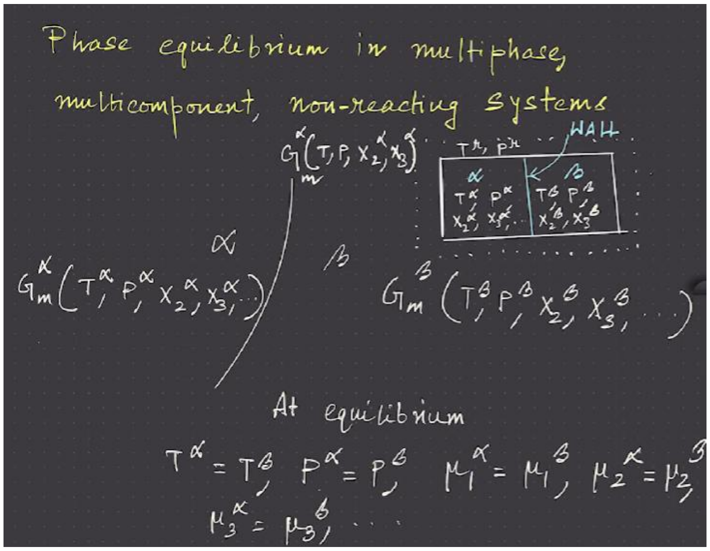
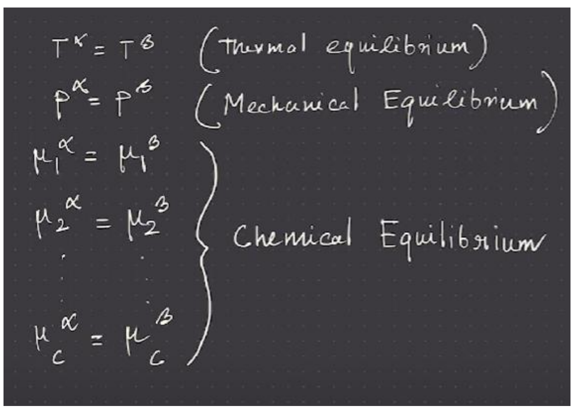
Lecture 31

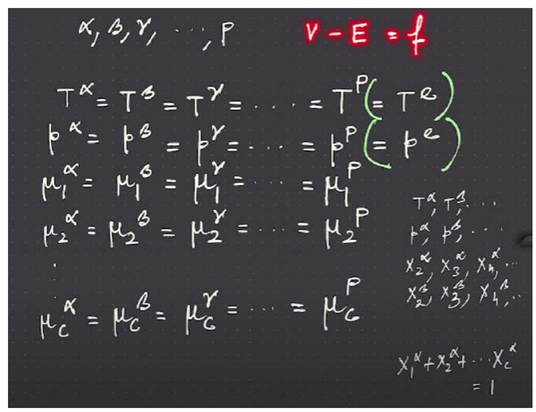
Phase equilibria in multiphase, multicomponent, non-reacting systems

So, we are looking at the phase keeping ah problem, phase keeping problem, multiphase, multiphase case of a multi component, non proactive right, multiphase, multiphone and non reaction systems. Non reactive means there is no reaction right, between there is no reaction in phases there will be no new phase form the result of reaction. So, if it is not so, but you have two phases say multiple phases suppose you have two phases alpha and beta and each in phases are ah formed by say several components. So, several components formed up from these phases and these phases are in equilibrium then part of the phase if you do not conditions if you remember, if you remember when you looked at this composite subsystem problem, when you looked at this composite subsystem problem where you had this composite subsystem and then this was basically isolated composite system and so you had say for example, let me draw it properly, if you look at that, if you remember this you had a basically a isolated composite system, so why composite? Because you are having basically several subsystems, say for air and say for air condition or a valve, so this we call valve, this we call as valve and then we had defined say for example, alpha subsystem and beta subsystem, we also told alpha is characterized by say something like u alpha and v alpha then n a alpha n b alpha and so on. Similarly, you had u beta v beta then n a beta and n b beta. Now, instead of u v n type of a description and then we told that s is a function of u v n and we told that you had d s has to be equal to 0.



So, that is how we basically would solve this problem and we made the valve, so basically we removed constraints from the valve, so what is the great part of the constraints? So, for example, we removed constraints such as, you know, we made it diathermal, right, it was adiabatic constraint, adiabatic means no heat transfer, you remove that constraint and you allowed heat transfer, right, you made it diathermal, you made it flexible, flexible or basically movable, so basically the volumes can be exchanged and then you also made the valves, you also made the valve, this was, basically it was made flexible, it was made diathermal and also it was made permeable. So, initially it was impermeable then it was made permeable and in the absence of all these internal constraints, we looked at how the, how the equilibrium conditions will be arrived at, right, what will be the phase equilibrium conditions or what will be the equilibrium conditions that will be arrived at by making sure that, so S is a function of U, V and N, then extremizing the entropy or maximizing the entropy and basically when we maximize the entropy, we found out what are the volume, what are the properties assumed, like for example, we found some equilibrium conditions like its temperatures, temperature of alpha, P alpha should be equal to P beta, so P alpha should be equal to P beta and chemical potential of each component in the alpha phase should be equal to the potential of each component in the beta phase, right. The same thing you can do instead of using this condition U, V, N, as you know, we can now consider a system, now you can consider the same system in contact with the surroundings basically you have a surrounding room, right, we have a surrounding room and the surrounding is nothing but a reservoir, a reservoir of temperature and pressure that means a thermal and mechanical reservoir, right, so you have basically properties like P r and P r, okay, alpha and beta are both in equilibrium with that and then initially, so basically before any exchange happens, so you had say for example, P alpha and P alpha and you have compositions like say for example, in terms of mole fraction, I am talking about X2 alpha, X3 alpha and so on and then here you had P beta, P beta and then you had X2 beta, X3 beta and so on and now basically you are describing this with the free energy, so you are using G as a function of or G, if you write G then you do not write, you write P comma P and then if you write Gm, say molar free energy then you are telling that okay, you have X2 alpha, X3 alpha and so on, right, so this Gm you are writing for the alpha phase and also for equilibration and then when you look at the equilibrium, the equilibrium is specifically the same, the equilibrium basically you arrive at is the same that T alpha equals P beta, P alpha equals P beta, mu1 alpha equals P1 beta, mu2 alpha equals mu2 beta, mu3 alpha equals mu3 beta and so on, right. When you look at equilibrium, the equilibrium that we arrived at, the equilibrium conditions, the thermal equilibrium, mechanical equilibrium so T alpha equals P beta for example is thermal equilibrium, T alpha equals P beta is mechanical equilibrium and this for each component, the chemical potential, the equilibrium potential is basically a chemical equilibrium.





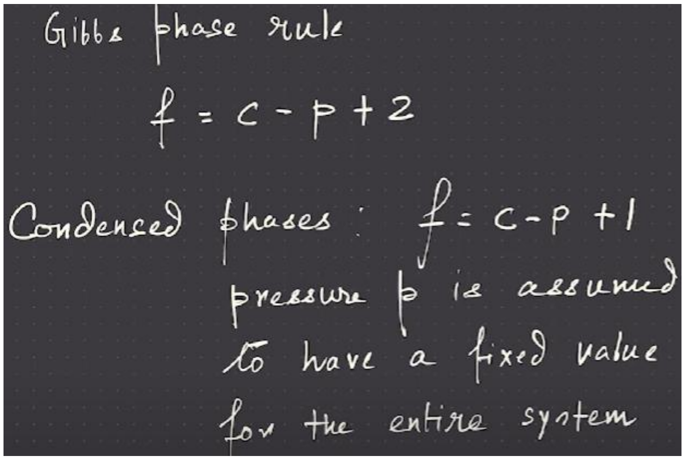
So, you are looking at the same types of equilibrium here, right. So, basically when you look at phase equilibrium in multi phase multi component non-reactive systems, we are looking at the total free energy to be minimized and the total free energy, total Gibbs free energy is a function of temperature, pressure and the mole number of components in each phase and we are again assumed there is a phase boundary and this phase boundary, so you have this phase boundary and across this phase boundary there tend to be, so this phase boundary you can have this different components like 2, 3 and 4 taken the fuse across the phase boundary, that is they are permeable. So, this boundary is permeable to the diffusion of these components, so it is permeable to the diffusion of these components, right. So, for example, one can diffuse this way, two can diffuse this way, three can diffuse, means anyway, so basically from higher chemical potential to lower chemical potential they will diffuse until the driving force becomes 0 and you achieve this equilibrium conditions, right. You achieve this equilibrium conditions like mu 1 alpha plus mu 2 beta, mu 2 alpha plus mu 3 beta, mu 3 alpha plus mu 3 beta.

Basically the exact same phase equilibrium that we arrived at with this concept of composite system with subsystems separate by a wall and basically removing the constants from the wall is exactly applicable here, right and you can get into these types of equilibrium conditions, right. This equilibrium conditions is called normal equilibrium. So, if you have several phases we have also done it as the demonstrated for several phases like you have to like say for example, you have alpha phase and then beta phase and then gamma phase. Now, if you have several phases and each phase contains several components across these you will have p alpha equals p beta equals to p gamma, p alpha equals to p beta equals to p gamma which is mechanical equilibrium. Again you will have mu 1 alpha equals to mu 1 beta equals to mu 1 gamma if these phases are in equilibrium, right.

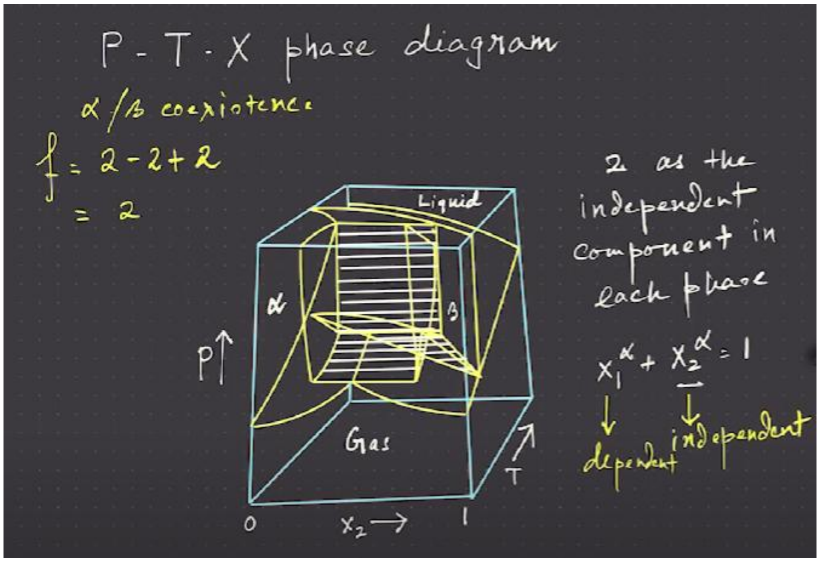
So, basically as I am telling you, so all these mu chemical potential equality are basically chemical potential, chemical equilibrium conditions. Chemical equilibrium, mechanical equilibrium and thermal equilibrium are the three major equilibria that we will look at. This equilibria we have already arrived at, right, using this concept of isolated composite system containing several subsystems that are separated by walls and in the walls you physically impose constraints and then you started removing the constraints and in the absence of all these internal constraints the values attended by each subsystem, right, the values of all temperatures or values of pressures attended by each subsystem or the chemical potentials are basically defined the equilibrium because that maximize the total entropy of the system or you can tell that it minimizes the Gibbs free energy of the system considering that the instead of considering instead of an isolated system if we tell that overall composite system is in contact with the thermal and mechanical reservoir, right. So, basically we are looking at now Gibbs free energy minimization when the system is in contact with a surrounding which is nothing but a infinite thermal and mechanical reservoir. So, in such cases we basically use something called Gibbs free energy and we look at Gibbs free energy minimization.

When we look at total Gibbs free energy minimization, ultimately what we are looking at is dG equals to 0 and d2G is Credence. So, that is what we are looking at and G is a function of like G alpha and G beta, right, there is a total, so basically it is a function of all the, so it is a summation G is the extensive property here, right, unlike GM. So, G extensive property is a summation of G alpha, G beta, G gamma and G alpha, G beta, G gamma again are extensive properties, but although these are extensive properties G alpha, G beta can be basically written as T alpha a function of temperature pressure, right, instead of looking at S, right, entropy we are looking at the conjugate. So, we are looking at temperature pressure and also the mole number of different components, right, whole numbers of components, right. So, basically we are looking at this condition where dG equal to 0 and d2G equal to 0, in this case we are telling that the system, the overall system is in contact with the temperature and pressure reserve or thermal and mechanical reserve, right.

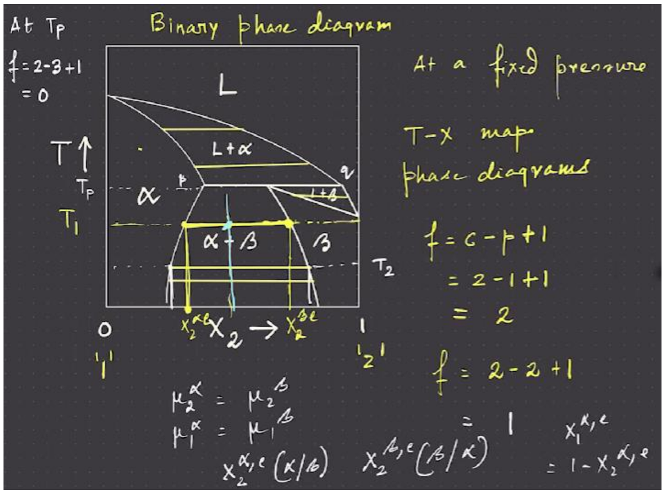
So, the idea is the same and we are looking at the same equilibrium we arrive at the same equilibrium conditions with the phases, that is in phases if heat transfer is allowed you have P alpha, P beta, if volume change, if volume redistribution is allowed, that is the phase boundary is allowed to move then you would have P alpha equal to P beta, right at equilibrium is called mechanical equilibrium and obviously if diffusion is allowed, if diffusion across the phase boundary is allowed, so basically for components 1, 2, 3 and so on you will have mu 1 alpha equals to mu 1 beta at equilibrium, mu 2 alpha equals to mu 3 beta at equilibrium, mu C alpha equals to mu C beta at equilibrium. Basically you have achieved diffusional equilibrium, so diffusion will happen as long as mu 1 in alpha is greater than mu 1 in beta or otherwise like mu 1 in alpha is less than mu 1 in beta, so basically one can move either from, one will always move from, the component 1 will always move from higher potential to lower potential, means chemical potential, similarly for component 2 and component C, so basically it will move unless the driving force goes to 0, that means the driving force is given by the chemical potential difference goes to 0, that means that the chemical potentials of components in each phase, chemical potentials of components in each phase becomes equal, right and that is called chemical equilibrium, right. So basically if you have alpha, beta, gamma and up to phase P, then you have also seen this, right, T alpha equals P beta equals P gamma up to P P which is equal to T equilibrium, say for example this is equal to T equilibrium and for pressure, so basically this T equilibrium or P equilibrium is that of the reservoir, right, these are the basically the temperatures and see all of the subsystems will assume the temperature, that is all, right, so basically at equilibrium, right, so you have P alpha equals P beta equals P gamma up to P P, P alpha up to P P, right, because we have phase P also, so again for chemical, for each component you have this chemical potential in, for component 1, chemical potential in alpha should be equal to chemical potential in beta, equal to chemical potential in gamma, up to chemical potential in P, right, similarly for component 2 and up to components, right, so basically if you have that, then basically what you see, you can derive by looking at number of unknowns, like looking at the number of unknowns, say for example that unknowns are like P alpha, T beta, so on and then P alpha, P beta and so on and then you have like X2 alpha, okay, that is the mole fraction of, the equilibrium mole fraction or equilibrium composition of component 2 in the alpha phase, then equilibrium composition of component 3 in the beta, component 3 in the alpha phase and say 4 in the alpha phase and so on, similarly the same equilibrium of component 2 in beta, component 2 in, so beta, component 3 in beta, component 4 in beta and so on, right and you are also looking at, so remember we are not writing component 1 because we are assuming component 1 to be, the component 1 mole fraction is the dependent, component 1 is the dependent component, so the, because X1 plus X2 plus X3 plus X4 for each phase, so for example X1 alpha plus



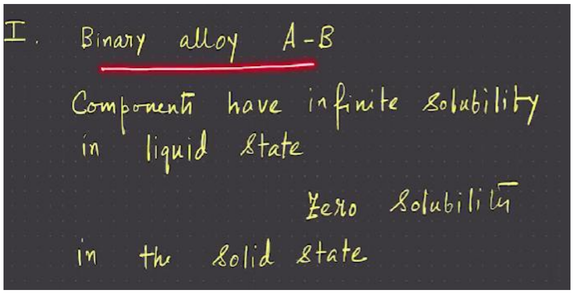
X2 alpha plus dot dot dot plus Xc alpha should be equal to 1, so now if I take component 1 to be dependent then I can tell 2 to c, all these are independent, right, so basically you have c minus 1 variables in each phase, in each phase you have c minus 1 variables or c minus 1 composition variables, right, which are expressed in mole fraction and then also the variables t and t, right, so basically you have c minus 1 plus 2 variables, right, for all the p phases, right, you have, so basically now if you look at the number of variables minus number of equations what you get is called the use of freedom and from which we have already derived and we found out this key phase rule, this is equal to c minus t plus 2, now when you have condensed phase we are assuming the pressure to be fixed for the entire system, right, we do not really consider the pressure volume more because it is negligible for condensed phases like liquids and solids, but then articles of freedom because we are not considering these set of equations at all, we are not considering these set of equations at all and we are telling that there is a fixed pressure, then basically f becomes c minus t plus 1, c is the number of components, p is the number of phases and you have plus 1 and these basically give you the degree of freedom, right, so that, right, now if you want to look at phase stability map, right, you often want to look at a phase stability map because this phase stability map if you think that it's, whether it is, see if you have gas phase you cannot use the condensed phase diagram, now if you look at a very simple binary system, binary system, so you have binary system, that means you have two components x1 plus x2 is equal to 1 and therefore for in any phase, so basically you are taking x2 as the independent, so basically x2 as the independent, right, so basically you have to do 2 as the independent component in each phase, means their compositions are 3 component in each phase, that means the concentration of 2 is independent in each phase, then the concentration of 1, so basically if you look at say alpha first, you have x1 alpha plus x2 alpha equal to 1, right, it's a binary system, but you are telling x2 alpha is your independent variable, so x1 alpha automatically becomes your dependent variable, now if you have, right, so basically if this is independent, if this is considered as independent variable, that's your choice completely, then this becomes a dependent variable in a binary system, in a binary system you can have 2 independent variables, if you have 4terary system you have 3 independent variables in each phase, right, 3 independent concentration variables in each phase, so in a 4terary system, but the fourth one, right, is basically dependent on the other 3, right, on the 3 independent concentration variables, right, so now if you look at that, you have gas phase for existence, so if you have a p-th diagram, you have a pressure axis,

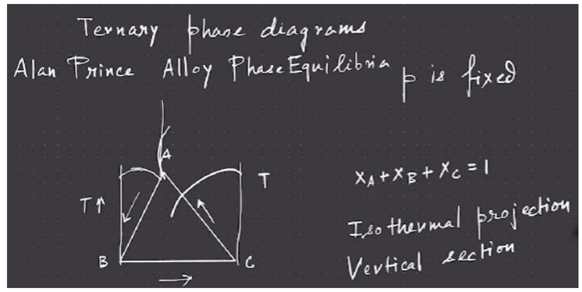


you have a concentration axis, so you have pressure axis, you have pressure axis, right here, you have concentration axis, right, it is here from 0 to 1, x2 equal to 0 to x2 equal to 1, and you also have the temperature axis, and see you have this phase boundaries, right, you have this phase boundaries, but this becomes very difficult and very complex to understand such 3 dimensional phase dimension, right, so we start making, we start making projections, so basically we start making projections, so basically we fix the pressure, and if we fix the pressure then we have one cut that we will just, right, we will take one cut of fixed pressure, and at fixed pressure we will basically look at the phases that coexist and the phase boundaries, so if you look at that there is also this, some phase coexistence for example like here you have alpha plus beta, here it is like beta plus something, beta plus liquid or something like that, so basically what I am trying to say is that in such a phase, right, in the p-th diagram, again this F is equal to C minus P plus 1, or sorry, in this case the degrees of freedom relation, right, if you look at this, for example if you look at the alpha phase field, so you have the alpha phase field, so if you are taking any point, so in this phase field you will see F equal to C is 2 minus, you have 1 plus 2, basically you have 3 degrees of freedom which is basically equal to 3, right, degrees of freedom equal to 3, now if you look at the single phase field you have a degree of freedom 3, that means this alpha phase field in this p-th diagram is represented as a volume, right, it is like a space, it is like alpha occupies some space, right, it has volume and in this volume if you want to specify pressure, temperature you can specify, you can specify all the three, right, pressure, temperature and composition, however when you go to a phase boundary, phase boundary means alpha, beta coexistence, immediately you will see that it becomes the degrees of freedom due to the stick tip, right, so if you go to a phase boundary where you have alpha, beta coexistence then you see in this p-th diagram it will become 2 minus 2 plus 2 which is basically equal to 2, so the degrees of freedom has no stick tip, right, so now instead of pressure, temperature, composition, phase diagram it becomes very complex, we look at temperature composition phase diagram at a fixed pressure if you have only condense phases, if you do not have the gas phase, if you have gas phase also, liquid phase also as well as the solid phases, so you have say solid, liquid and gas phases then you cannot get rid of pressure, right, you have to construct pressure, however if you do not have gas phase and if you have only condense phases to deal with, right, for example solidification problem, you have a liquid and you have several solids of different pressure structure, they are basically liquid and solids and you can have also different liquids as a composition with different liquids, right, so in such a things you can basically assume the pressure to be fixed because the pressure volume work is basically in the equation, right, so this is at a fixed pressure, say for example these are the fixed pressure, it is now much more clear, right, the diagram is much more clear because it is in 2D, right, you have a temperature axis like the y axis is your temperature axis and you have the composition axis, again you can make it temperature versus activity diagram, right, there are various ways you can look at phase stability maps, right, but one of the most convenience, convenient ways of looking at phase stability maps particularly in condensed systems where you have liquid phases and solid phases is basically looking at this Tx maps and this Tx maps at a fixed pressure they are called basically phase diagrams and this phase diagrams can be compiled experimentally and then they can be calculated also using some computational techniques and that computational procedure is called CALFAT, okay, Calculation of Phase Diagrams from all the available thermochemical data which is stored in databases, right, so for various alloy systems or various oxides or various high temperature materials and stuff, right,

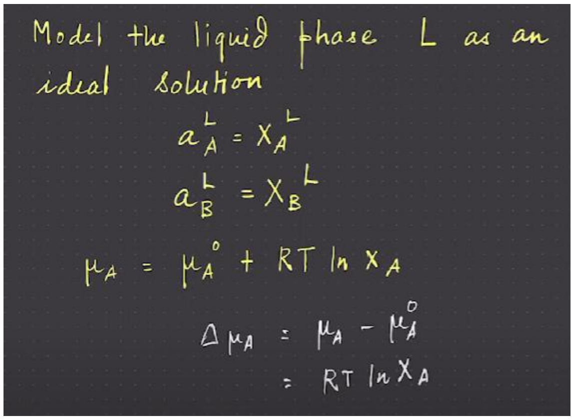


so you have a typical phase diagram here, if you look at this phase diagram, if I looked at fixed pressure then basically we are looking at this first rule which is F equal to C minus E plus 1, now if you look at the diagram you have two components, so this is called a binary, so this is a binary, binary phase diagram, binary means binary components, right, you have two components, component 1, component 1 and component 2, now component 1 has a X2, now X2 is your independent variable, X2 is your independent variable, so for when you have pure component 1, X2 is going to be 0, right, if you have pure component 2 then X2 is this, we are going to do that, now if you look at that you have different, you have different regions, right, if you look at the alpha regions for example and I am set picking some point here in the alpha region, so basically if I apply this phase rule at the alpha region and then this 2 minus 1 plus 1 which is basically 2, so degrees of freedom I find is 2, why is that so? Because if I am specifying a point I am basically specifying temperature as well as composition, right, so basically when I fix a point I have temperature here, right, we are reading it from the Y axis and we can now read from the, read the composition from the X axis, however now I can also have say alpha phase field and here there is a beta phase field and here it is alpha plus beta coexistence, now if there is coexistence that means there is some equilibrium, right so now if I look at a phase boundary where alpha and beta coexist for example the degrees of freedom has changed, here also the degrees of freedom are in the same, again you go to the beta phase region it becomes different, now 2 basically, so in a 2 dimensional diagram, 2 basically represents also an area, right so basically if the degrees of freedom are 2 then the region is represented by an area like alpha or liquid or beta if you look at alpha, single phase alpha this is basically an area, a single phase beta is an area, single phase liquid is an area now if you look at these phase boundaries, they are now coexistence boundaries, right, they have like coexistence of 2 solids or coexistence of a liquid in a solid for example, now if you have that, right, for example this phase boundary is a coexistence between alpha and liquid, right, from the coexistence region you have F, in the coexistence region you have F is C is 2 minus 2, right, you have to plus 1, so basically in the coexistence region if I specify composition my temperature is already fixed or so on, if I specify temperature then my compositions at liquid are already fixed, right, say for example if I specify temperature 1, now here I have drawn this dotted line here you can see at T1 this composition of the alpha phase that you can write here, this is basically the phase 2 alpha equilibrium and this composition at this temperature, this composition is another phase boundary, right, alpha plus beta, beta phase boundary here, so this X2 beta equilibrium, these are basically the equilibrium compositions of the coexisting phases at the alpha phase and the beta phase, similarly you have, so this line that we draw here is for the time right, and you can basically, so basically if you have certain other compositions, for example, certain other compositions here, say I have another composition here, then I can tell for this other composition what is the amount of beta phase I have and what is the amount of alpha phase that I have, but remember whatever be the composition within the two phase region you have a degrees of freedom which is basically equal to 1, right, it is basically equal to 1, so that means if I fix temperature, I already know the equilibrium compositions of alpha phase that is equilibrium with the beta phase right, so this is basically read by these points, right, these points here, so these points, for example, temperature 1 this is the point and this is the point, these points represent the composition of alpha phase that is equilibrium with the beta phase and this point represents composition of the beta phase that is equilibrium with the alpha phase at temperature T right, at temperature T1, this is the composition, this is the composition that we equal, that means at this temperature T1 you basically are solving say for example, mu 1 alpha equals to mu 1 beta and you are solving also mu 2 alpha equals to mu 2 beta and these two, the solutions of these two equations, so basically if I have these two equations at temperature T1, mu 2 alpha equals to mu 2 beta and mu 1 alpha equals to mu 1 beta then this is again x2 alpha equilibrium where we are looking at the alpha with the beta and we also get another x2 beta equilibrium, again we are looking at this value now remember, now this is something that you have to be very careful, if I know x2 alpha and if I know x2 beta then basically x1 alpha equilibrium is nothing but 1 minus x2 alpha so you have two, basically you have see at a fixed temperature T1, you have these two equations because pressure is anyway fixed so at a fixed temperature of T1, we have these two equations and these two equations, these two variables, and these are the two variables and solutions basically make some value of these variables, T1 and these are the values these are the values, means these are the points and corresponding to these points you drop a vertical line, exactly vertical line and these points in the x axis basically give you the equilibrium compositions of alpha and beta at temperature T1 similarly if I go to temperature T2, say for example I go to temperature T2 so let us say this is temperature T2, then again I have this tie line, this horizontal line in the two phase region and again the ends of the tie line that where it meets the phase boundary these two points basically give me the equilibrium, right, the equilibrium between alpha and beta or the equilibrium compositions of alpha and beta right at temperature T1, right so that is what it means, right, also additionally if you know the alloy composition in a two phase region it gives you what is the phase fraction, what is the amount of alpha phase what is the amount of beta phase, right, that is also something gives me similarly for example here you have another tie line in the liquid plus alpha region so here the equilibrium is between alpha and liquid, right this is something that you often see when you are basically say for example often you have to solve such problem when you are looking at say for example a process where liquid is cooled and once the liquid is cooled the liquid is solidifying and as the liquid is solidifying you are forming this alpha nucleus and these alphas are growing inside and as they are growing inside the composition of the liquid is also changing, right because say for example when I am here, when I am exactly here then basically you have just started nucleating some alpha phase type of this composition, of this composition, right you are here but the fraction of alpha phase is almost negligible, it is very very small it is the nucleation state, now you go pull further then you basically so as you are pulling further you are basically seeing the solid is enriching in solid, right so solid is speaking up, so basically if you look at it, if you look at the pulling curve you are seeing that the solid basically now becomes richer in x2 and liquid basically is now, the liquid was here and now solid is also rejecting some amount of solid, right when it becomes, when it is solidifying, right so basically as you go down you see the liquid and solid compositions are changing, right so here what is happening, so you are going, so this side is like linear in B this is richer in B and as you go further you are getting richer and richer in B, right so you are getting an alpha which is much different than the alpha that you got when you first solidified so alpha composition here and the alpha composition here are possibly different in B here alpha contains less solid B or the component 2 so alpha at this composition has less of 2 than at this composition at this composition you have more 2 here and also if you look at that at this composition the liquid also, say for example this is the solid composition and the liquid composition also has also a lot more solid so you are basically rejecting that as solidification progresses, right as solidification progresses you are basically seeing a solid, seeing a liquid that is richer in solid, right it is rejecting, so basically as it solidifies it rejects solid but it also picks it up, right you can see on this curve, right, so that's the idea so this is the solidus, so solidus basically is called solidus the solidus separates the single phase from the liquid plus alpha coexistence and the single solid phase alpha from the liquid plus alpha coexistence so that is called, this is called solidus and this guy is basically called liquidus, right, this guy is called liquidus and you can see, this is basically a very interesting diagram so you have one particular temperature if you look at that so I am just giving you some characteristics, I will go through each of these details but you can see that there is one very special temperature a very special temperature at which, so this is like say P, that's called P P is special temperature at which if you go to one point like this say if I go to one point like this, right, at this temperature remember we are going exactly at this temperature this temperature you see a very interesting thing you see at these points, for example at this point or at this point or in fact

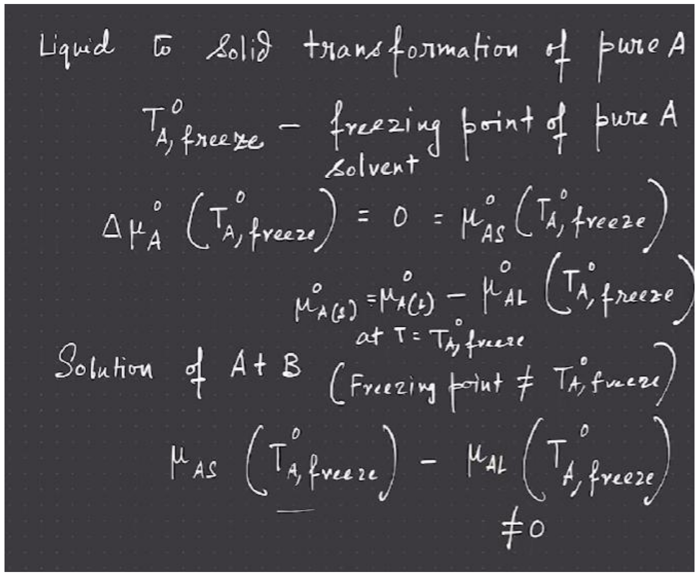




at this point or this point you see that there is a beta phase, there is an L phase and there is an alpha phase so there are three phases coexistence so F at this T P, at P P along the line, right, at P P obviously not here, not here, not here but as soon as you go along this line, along this line say let's recall this line, say some P P line if you go along this P P line, any point on the P P line you will have F which is equal to two components minus three phase coexistence plus one two minus three plus one is zero so basically these points are invariant points these points are such that once you have this point at this point three phases coexistence and at this point you cannot specify anything, you cannot specify the temperature or composition, everything is automatically fixed so basically you have the degrees of freedom basically becomes zero, right so if you see within the two phase region and also at the phase boundary degrees of freedom become one, right, it reduces in the single phase region you have degrees of freedom two and in the three phase region for a binary system you have degrees of freedom zero so that means that is like an invariant reaction that you are looking at, at any point on this basically is fixed, the composition, temperature, everything is fixed, right so that is called basically the invariant points these are the invariant points in a binary system where the degrees of freedom basically go to zero now we look at different types of phase diagrams so one of the phase diagrams that we can think of is like, right, is like you have this binary alloy B so I am basically constituting currently so if you look at, you can in principle look at ternary phase diagrams, so you can look at ternary phase diagrams I will not discuss ternary phase diagrams here if later time permits from your G1 or 2 examples so in ternary phase diagrams as you can see even if pressure is fixed, so P is fixed then also you have two independent compositions so basically what we do is basically construct a triangle okay, this is called basically a Lewis triangle so this is an equilateral triangle so this one, so I saw series one of electron here so you have this Q-strangle, so where in the Q-strangle you have like one A, this is pure A, this is pure Bn and this is pure Cn but if you see, you have now, say for example if I tell from B to C this is your, so xB and xC, right, basically this is from C to A and say B, right, so now if I tell xB to be one variable, so xB to be one variable if I am looking at that and we are looking at xC so basically xA plus xB plus xC equal to 1 right, for any phase, so you have some several phase coexisting then if you see, you have only composition here, right you have composition here, so I can draw a simpler diagram so basically you have this type of diagram, this type of composition axis but where is the temperature axis, the temperature axis is that we draw then again we have to look at a 3D picture we have to look at a 3D picture, right, so we have to look at the 3D picture because temperature is increased, right, we are looking at the 3D picture right, so basically now you are saying that there are phases and these phases are coming inside, coming inside say for example you have the kind of the field coming inside so it becomes very complex, right, it becomes very complex to understand so what you do, again in internal phase diagrams you look at projections right, what are the projections that you looked at, often looked at two types of projections, one is called isothermal projection that is at a given temperature, this is called isothermal projection so you map on the Gibbs triangle that equilateral triangle that you have drawn so there is, these are called isothermal projection, I will come to this later and then there is also something called vertical section or I will say, leaf okay, so vertical section which looks similar to a binary phase diagram but with lot of differences, right, with lot of differences you do not really obey any G-spaces there, they are very, very different sections, right so basically these are things that, these are the nuances that you have in ternary phase diagram and if you are basically interested in ternary phase diagrams you can look at the book by Alan Creams on alloy phase equilibrium which is available now, it is a classic book, this book is now available online I think by MSI Fort, MSI Fort has given you this alloy phase equilibrium book for free and it is a wonderful book on phase diagrams and particularly if you are looking at or interested in ternary phase diagrams, okay, that also works now the idea is that, if you go there, now let us look at binary alloy diagrams and we are looking at it in a more intense and systematic way so you can look at this binary alloy, we understand binary alloy phase diagrams it will be also, so the knowledge basically can be applied to ternary diagrams and you can, or you can look at say some quaternary systems where again you can look at some pseudo binary or quasi binary sections and you can make sense of this, right so you have like this binary alloy V and you have, and in these type of phase diagrams so we call it type 1 and in these type of phase diagrams the components have infinite solubility in the liquid state but zero solubility in the solid state so infinite solubility in the liquid state and

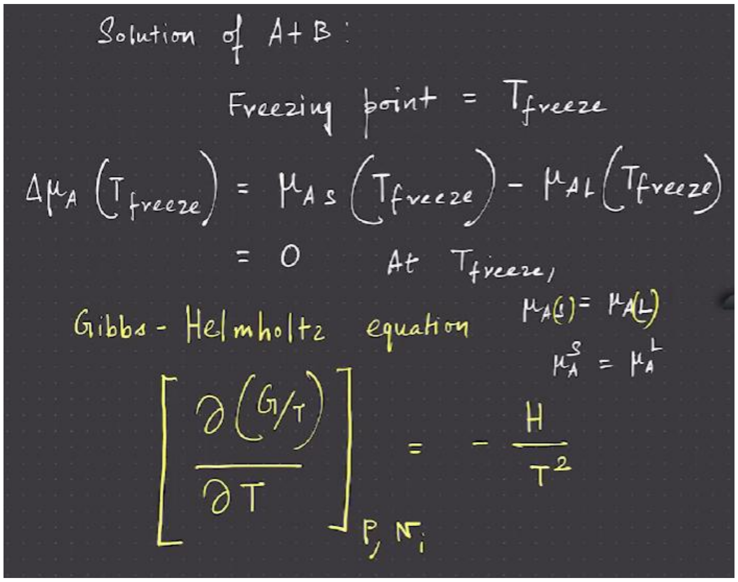


zero solubility in the solid state so basically the infinite solubility in the liquid state or liquid phase and we assume that the liquid phase is an ideal solution now if it is an ideal solution as you know from Raoult's law the activity of A in the liquid phase is equal to the mole fraction of A in the liquid phase even activity of B in the liquid phase is equal to mole fraction of Mu in the liquid phase now as you know that, then that is so, then for in each phase, in the liquid phase for example Mu A is Mu A is zero, Mu A is zero is some the chemical potential of A in the standard state or this standard can be pure A, right for some pure A solvent, right if you think of a pure A solvent, the standard state is given by Mu A zero, right so this is basically for Mu A zero and this is the chemical potential of A in solution so chemical potential of A, component A in the solution is equal to component A in pure state or that of pure solvent plus RT ln x, right that is what is the definition, right, that is what we have seen so far, right you have a solution, in a solution basically you have now A and B both so basically it deviates from Mu A zero, right and we have looked at this like delta Mu A equals to Mu A minus Mu A zero now if I look at delta Mu A, what will I write? delta Mu A which is this is Mu A solution minus Mu A zero in the standard state which comes out to be RT ln x, right this is delta Mu A, for delta Mu B the architects, right so now you are looking at say for example the liquid to solid transformation of pure A, right you are looking at say liquid to solid transformation of pure A and then let us call that liquid to solid transformation of pure A is given by this temperature which is called for pure A this is the freezing point and this is given by T A, T A comma freeze in the A comma freeze in the substrate and zero in the solid state, right so basically this is, so zero in the substrate basically points to pure A solvent and it is telling me this entire guy is a very freezing point of pure A solvent, right now if I look at delta Mu A zero, delta Mu A zero say for example when you are looking at pure A and you are looking at liquid to solid transformation delta Mu A zero is equal to zero equals to delta Mu A zero now at the T A zero freeze the delta Mu A zero that is the relative partial molar quantity or the chemical potential difference between A in the solid state and A in the liquid state so A in the solid state is given by A s substrate, A in liquid state is given by A in liquid state is given by A l substrate and zero indicates pure or zero indicates standard, right so Mu A zero A s minus Mu zero A l so basically Mu zero A in the solid state Mu zero A in the liquid state so this is the difference Mu zero A so basically since the solid and liquid are at equilibrium at T A zero freeze right this is the freezing point at the freezing point since the solid and the liquid A are in equilibrium you can tell Mu A s zero, A s zero basically means this pure solvent in the solid state that is the pure solvent in the liquid state now this minus this has to be equal to zero why because Mu A in solid is equal to Mu A in liquid right in the pure state right it has to be at, at T equals to T A naught because it is the freezing point of T A naught T A naught right so basically what we are telling is that chemical potential difference between the chemical potential difference between the solid and the liquid at the freezing point for pure solvent has to be zero right now if I look at now solution of A and B, now if I look at solution of A and B then if I now in that solution if you are now looking at Mu A s and Mu A l so at T A zero freeze so if you are looking at Mu A s and Mu A l but if you are looking at it so when you have a solution of A and B then basically Mu A zero and Mu A l zero the difference between the chemical potential of pure A right in the solution so chemical potential of

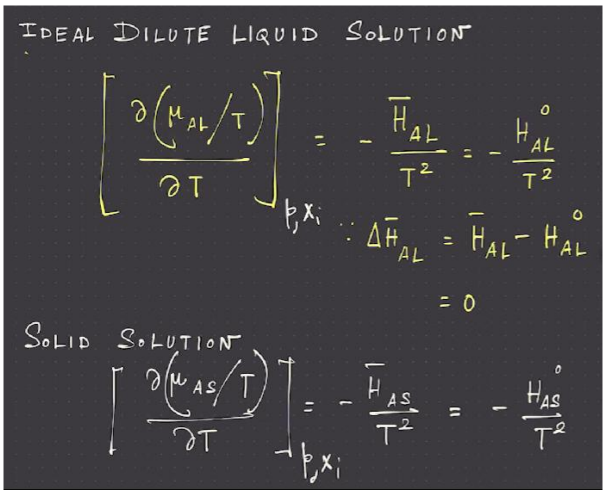


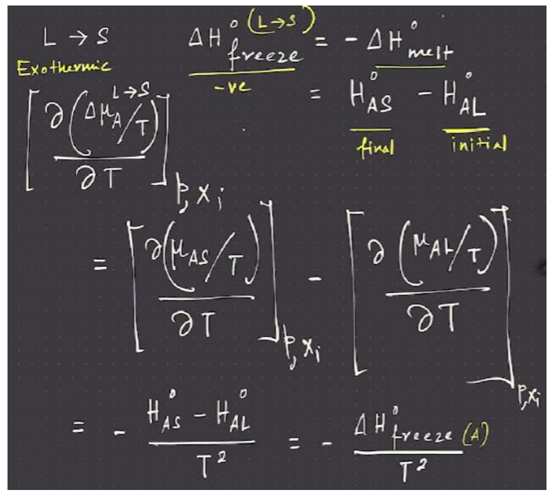
pure A in the solution in the solution in the solid state is minus the Mu A l zero in the liquid state that is not going to be equal to zero right that is not really equal but what is equal is in the solution of A plus B let us assume there is a why it is not equal because T A zero freeze is no longer the freezing point as soon as you have a solution of A and B as soon as B solid is entering the solution then T A zero freeze is no longer the freezing point of the solution the freezing point is different now they are different now as you can see the solid liquid coexistence even if you think of the pure state means we are looking at pure A the solid liquid coexistence because it is not really pure A you have a little amount of solute here so you basically see this Mu A s and Mu A l are no longer equal to zero at this temperature right so but if you look at Mu A s so basically you can get rid of this zeros here because zeros assume pure state but what I am telling is Mu A s minus Mu A l at T A zero freeze right because for solution of A and B freezing point is different freezing point is not equal to P A zero freeze P A zero freeze is the freezing point of the pure solvent A but at P A zero freeze if you have a solution then Mu A s is the chemical position of A in the solid state and in the solid phase and Mu A l which is the chemical position of A in the liquid phase at this temperature P A zero freeze because this is no longer a freezing point at this temperature they are not equal right they are not equal so the difference between them right they are not equal right as you can see not equal to look at that is a so what we are telling now is like delta Mu delta Mu that is the difference there is a finite delta Mu delta Mu can be positive delta Mu can be negative but the point is because depends on what is the new freezing point whether the freezing point is depression whether the freezing point is basically elevated we do not know so if I look at a solution of A and

B if we define a new freezing point which is P freeze then we can now take delta Mu A that is the relative partial molar free energy or the chemical potential of A right in the solution the difference in chemical potential of A in the solid chemical potential of A in the solid and that in the liquid right so basically the difference between the chemical potential of A in the solid and Mu A L that is at that in the liquid is equal to zero at P freeze because of P freeze again you have if T freeze the solution freezes right solution freezes means there is a so at T freeze you have an equilibrium between the solution in the solid state and solution in the liquid state now if that is so then delta Mu A which is the relative partial molar free energy of component A which is basically equal to the difference between the chemical potential of component A in the solid state and then chemical potential of component A in the liquid state so basically for each component as you remember from equilibrium you will have for each component at the T freeze at the equilibrium temperature T freeze at the equilibrium temperature T freeze right for the solution so at T freeze is the equilibrium temperature solid equilibrium temperature means at T freeze solid and liquid coexist right solution and liquid solution coexist right so in such a case you will have Mu A S should be equals to Mu A L right often you would also write this Mu A in the solid is have to be equal to the Mu A L right just for convenience I have put Mu A S and Mu A L sometimes in books they also put this way this practice Mu A S and Mu A L right you can write this way but I have gotten rid of the bracket I have just written this as A S here and A L Q Q so the bracket is already in fact right

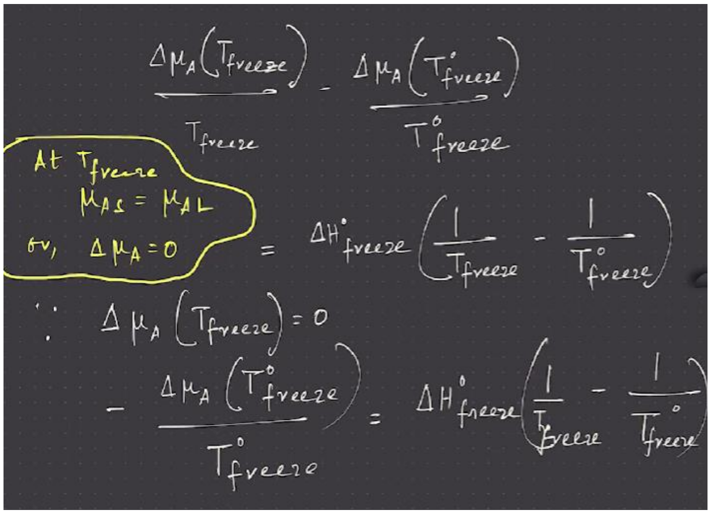


now you have this Gibbs-Helmholtz equation okay this Gibbs-Helmholtz equation which basically even proof and you will see that this basically del G by T del T that is the partial derivative of G by T G normalized with temperature with respect to partial derivative of this quantity okay with respect to temperature keeping pressure and the mole number of components constant is equal to minus H by P square right minus H by P square so similarly so basically Mu A L so Mu A L is a partial molar free energy of A in liquid right partial molar free energy of component A in liquid divided by so partial molar free energy is also with the same equation so if you have partial molar free energy of A in liquid by T and you have you are taking this partial derivative with respect to temperature keeping pressure and the components the concentration of components fixed that is equal to again based on the Gibbs-Helmholtz relation it is equal to minus H bar A L so basically it is H bar A H bar A is the partial molar enthalpy of component A in the liquid so A L basically means A in the liquid state right partial molar enthalpy of component A in the liquid state by T square but this is also equal to minus H A 0 by P square why?

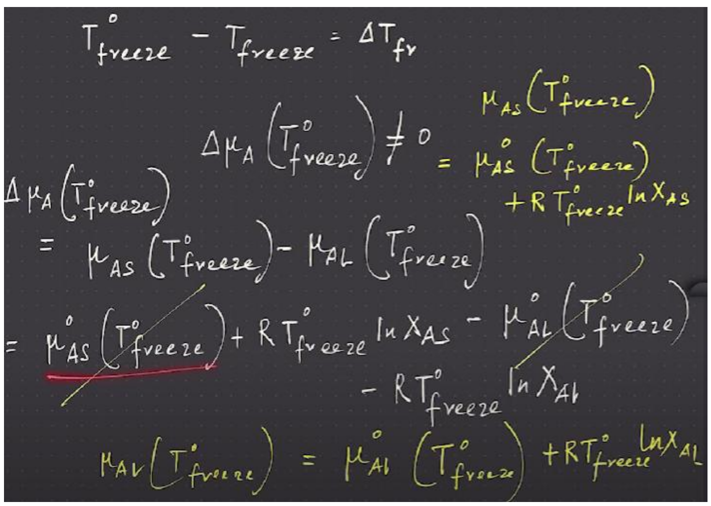




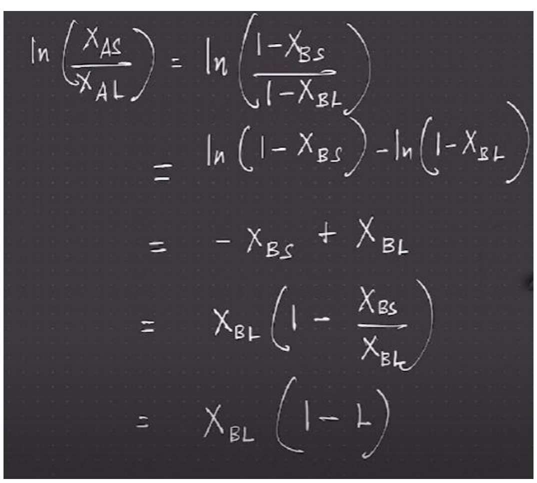
Because as you know since in ideal solutions so for if it is an ideal solution right we are adopting an ideal solution then the change in partial molar enthalpy of component A right the change in partial molar enthalpy of component A the change is here what we are looking at? if we are looking at this is in the liquid solution right this is in the liquid solution and this is in the 0 basically means it is a pure state right so it is like after mixing and this is before mixing so this is the after mixing enthalpy minus before mixing enthalpy or delta H A L this is nothing but it is basically like partial molar enthalpy of mixing of component A partial molar enthalpy of mixing of component A I know the partial molar enthalpy or the molar enthalpy of mixing basically for an ideal solution is equal to C so basically delta H by A L is equal to H by A L which is the partial molar enthalpy of component A in the liquid solution minus partial molar enthalpy of or molar enthalpy of component A in the pure state in the liquid basically the difference between them is going to be 0 because you are assuming ideal solution right that we have already discussed similarly for mu A S we can write it is H bar A minus H bar A S by T square which is basically minus H bar A S 0 by T square which basically means that at the partial molar enthalpy of component A in the solution by T square then the partial molar component of enthalpy of or molar enthalpy of component A in the pure state so basically the difference between them does not exist they are going to be the same because delta H basically the change in delta H means the delta H mix is basically 0 right delta H mix is 0 for ideal solutions right whether it is an ideal solid solution or a ideal liquid solution right. Look at liquid to solid transformation you see liquid to solid transformation is basically an exothermic transformation it is an exothermic transformation. Exothermic means gives out that liquid or it gives out heat of transformation and that is called H delta H 0 freeze now if it is giving out that means delta H 0 freeze is negative which is basically negative of delta H 0 melt because melting process is an endothermic process right the solid has to absorb it to convert to liquid right so this delta H 0 melt is nothing but so this is from liquid so basically delta H 0 freeze is nothing but it is transforming from liquid to solid right it is transforming from liquid to solid so this will be solid minus liquid so final state is solid right final state is solid and then this is final so this is in the 0th state remember this is a 0, 0 means pure state so you are looking at pure A right pure A solid the enthalpy of pure A solid right and enthalpy of pure A liquid is what we are looking at and the difference between them is basically so this is the liquid to solid transformation so this is the final state this is the initial state right this is final state right H A is 0 and right in a freezing experiment this is the final state the solid state is the final state and this is the state that you start with that is the liquid right and the liquid is freezing and you get the difference and this difference is basically nothing but delta H 0 freeze which is negative which is negative of the delta H 0 delta H 0 is very positive right now if you look at that now think of this now again you can apply for the relative partial molar partial molar frequency of A or the difference in the potential of A when you go from liquid to solid if you are looking at that so that is basically given by del mu A by T del T right so del mu A by T del T because you are looking at that right mu A from A to S the delta mu A right delta mu A that is for component A from A to T so now it is basically partial molar free energy of component A in the solid so that is what you have written here or in the potential of component A in solid by T and you have chemical potential of component A in the liquid by T which del T which is basically again given by if you look at that you apply this relation right you have this relation minus H A 0 by T square here it is minus H A 0 by T square so this basically becomes minus H A 0 by H A 0 by T square which is minus delta H 0 freeze by R T square right so why R came why does the R come or is it there is no R here currently there is no R so we can remove the R here so this

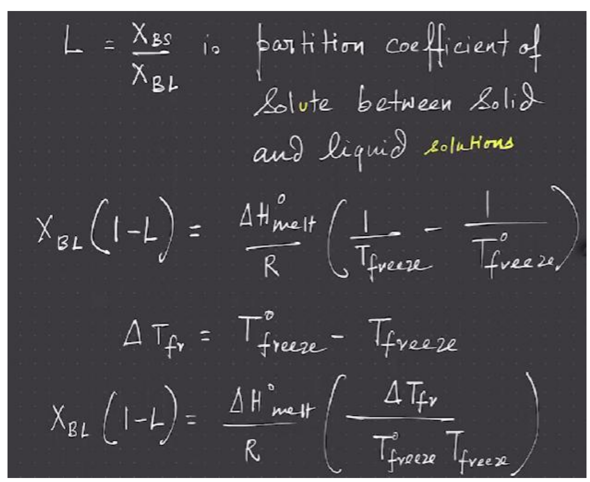


basically becomes minus delta H 0 because there is no R here I don't see any R here so basically this comes from the again the q cell moles relation so this is nothing but delta minus of delta H 0 so basically you are looking at liquid to solid transformation so del delta mu A by T that is the chemical potential of component A by T and so this we will call as delta H 0 freeze delta H 0 freeze of component A remember this is for component A this is the agreement for component A right so now if you are looking at that if you are looking at this equation so you can now integrate it right you have delta mu A at T 0 freeze right basically at delta mu A T 0 freeze and you have like delta mu A T freeze now you see the difference the difference is that in one case you are looking at the relative change in the potential of component A which is in the solution right so if you look at this, this is the solution step T freeze is the new freezing point of solution and this is at T 0 freeze and you are looking at D of delta mu A by T right so this is the T of delta mu A by T equals to minus delta H 0 freeze by T square so delta H 0 freeze by T square T T right so basically I am taking that so delta H 0 freeze we are assuming that it does not change with temperature and we have T 0 freeze which is the freezing point of the pure solvent and T freeze is the freezing point of solution and you have now D T by T square so basically you can write delta mu A T freeze by T freeze minus delta mu A T 0 freeze by T 0 freeze right so basically equal to delta H 0 freeze 1 by T freeze minus 1 by T 0 freeze right how does it come? D T by T square equals to minus 1 by T and you are looking at T freeze here and T 0 freeze here and this minus sign and there is a minus sign here right and then there is another minus sign because of the equation so minus sign is plus so these terms and this term but here be very careful if you look at that this is delta mu A and this is also you can call it delta mu A only so you have delta mu A at T 0 freeze and delta mu A T freeze remember these guys delta mu A T freeze is where you are looking at the chemical potential difference of components so basically you are looking at so you are looking at chemical potential difference of component A between the solid state and the liquid state or the liquid state in the solid state right liquid state is the initial state and solid state is the final state so it is basically solid minus liquid so if you are looking at final minus initial so delta mu A T freeze by T freeze right because that's the thing the delta mu A T freeze by T freeze is your one of the remember this is not mu A 0 don't put 0 because 0 means this A is in the pure solvent state we are not looking at that we are looking at delta mu A only that is the mu delta mu A is the delta mu A is the relative partial or relative partial molar free energy of component A or you can tell that there is a difference in chemical potential of component A in between solid solution and liquid solution right so that is the delta mu A so delta mu A is the difference so I am not keeping it here because it becomes clumsy so what I am trying to say delta mu A as you have seen delta mu A is basically mu A solid minus this is what we are doing mu A I have given bracket but it need not so I am following this condition mu A A S minus mu A A right so basically I didn't give this bracket so I just write this way so this is basically now this we are evaluating at two different temperatures we are evaluating at T 0 freeze also T 0 freeze is the freezing point of the solution right

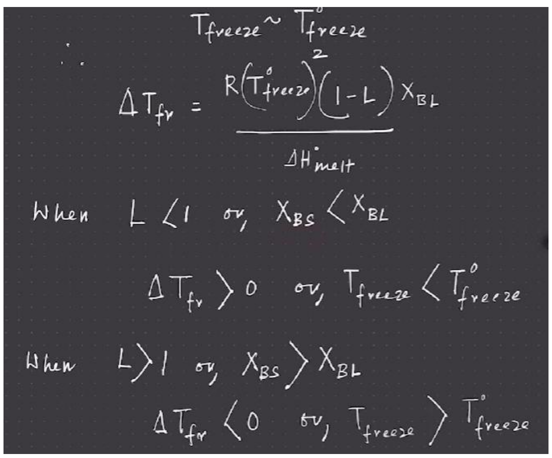


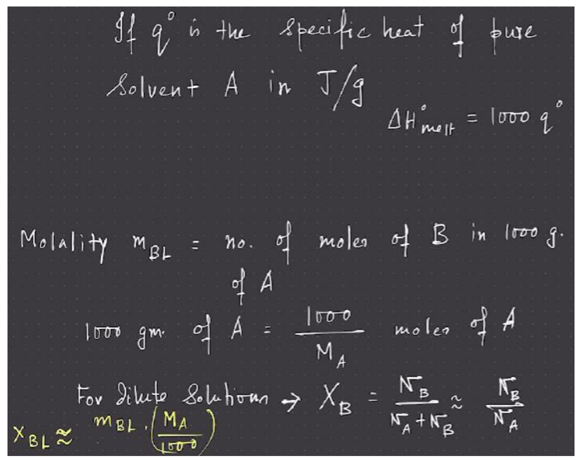
now if you do this integration you do this integration and you assume that delta H 0 freeze is not actually changing as a function between T 0 freeze and T freeze then basically delta H 0 freeze can come out of the integration and the dT by d square is minus dT by d square if you look at that is minus T minus 2 dT by d square is minus 2 plus 1 by minus 2 plus 1 and there is no minus sign here right minus 2 plus 1 this is it becomes equal to minus 1 by 2 and then minus 1 by 2 and then you take the limit of that and there is a minus sign here and there is a minus sign here that becomes plus ok now so you have delta mu A T freeze by T freeze right we were looking at this delta mu A T right so that one so delta mu A T freeze by T freeze minus delta mu A T 0 freeze by T 0 freeze is basically delta H 0 freeze 1 by T freeze minus 1 by T freeze now at T freeze at T freeze mu A at T freeze the new freezing point mu A equals to mu A L that is the or delta mu A is equal to 0 excuse me right at T freeze but at T 0 freeze delta mu A is not equal to 0 right so because delta mu A is 0 at T freeze right at T freeze this is a very important balloon right I am just taking it as a balloon here at T freeze mu A A S it goes to mu A A L right because the mu A S is basically the chemical potential of A in the solid state and this chemical potential of A in the liquid state or liquid phase and if they are equal right at T freeze they are equal because T freeze is the new freezing point so at that freezing point at the mu freezing point of the solution delta mu A is equal to 0 this is very very important point here so this guy goes to 0 so there is a minus delta mu A T 0 freeze now delta mu A T 0 freeze is not equal to 0 right we have already told and we can also realize that that mu A S T 0 freeze mu A L T 0 freeze here T right so basically at the freezing point of pure A freezing point of pure A is no longer the freezing point of the solution right so at the freezing point of pure A or which is basically now I am just writing it as simply as T 0 freeze right T 0 freeze is the freezing point of the solution so I wrote as T A 0 so basically please note that T 0 freeze is nothing but T A 0 freeze right it is a pure solvent so T 0 freeze is the freezing point of the pure solvent right at this temperature the chemical potential of A in the solid mu A S is not equal to mu A L so as a result this guy does not go to 0 as a result since mu A S is not equal to mu A L at T 0 freeze therefore delta mu A S is not equal to 0 so you have this term so this term vanishes while this term remains right so this term is remaining which is equal to minus delta mu A T 0 freeze minus delta mu A T 0 freeze because delta mu A T 0 freeze is 1 by T freeze minus 1 by T 0 freeze now T 0 freeze minus T freeze let us call it as delta mu A bar so basically it is like T 0 freeze minus T freeze is the deviation right which is the deviation or in the freezing point it can be an elevation it can be a depression we do not know so we are just telling T 0 freeze minus T freeze is delta T A bar and we are telling that delta mu A T 0 freeze is not equal to 0 right obviously now delta mu A T 0 freeze is nothing but mu A T 0 freeze minus mu A T 0 freeze right now if you have that you have that and you now assume that mu A S T 0 freeze equals to mu A S 0 that is the pure solvent in the solid state T 0 freeze plus R and you have now T 0 freeze R T ln and you have x in the so this is the composition of mole fraction of component A in the solid solution right, mole fraction ln x A S right is the solid solution and you also have similarly for mu A L T 0 freeze we are writing mu A L T 0 freeze that is the freezing point of the solvent but now we are looking at the solution which is equal to mu A L 0 now mu A L 0 means that is for the pure solvent right mu A L 0 T 0 freeze remember right plus R T 0 freeze and then x in the liquid state and then x A is basically the composition of A or mole fraction of A in the liquid state that is why x A l you can also put x A you can write this as x A l or you can write this as x A and l whatever way you want to write does not matter so basically x A so this term now you see if you have that if you expand this guys if you expand this guys this way mu A S T 0 freeze is this guy plus this guy right mu A 0 plus R T 0 freeze and then x A S and again this one is minus the mu A 0 T 0 freeze minus R T 0 freeze then x A l right this is x A S this is x A l now if you look at that x A S is basically the concentration of component A in mole fraction in the solid state and x A l is the composition of component A in the liquid state right at this T 0 freeze temperature right now if you look at this mu A S 0 T 0 freeze and mu A L 0 T 0 freeze are right this is because of this pure solvent right 0 means this is pure solvent your solvent at T 0 freeze T 0 freeze is the freezing temperature at this temperature mu A S 0 is equal to mu A L 0 so you can basically cross them out because this has to be equal to this one and this minus this has to be equal to 0 so this guys go up now if you have that now you have only this term and this term remaining right so basically you have minus R T 0 freeze and then x A S by x A l right because you have this right R T 0 freeze by x A l by T 0 freeze right because you have by T 0 freeze right if you look at this equation you still have by T 0 freeze equals to delta A 0 freeze 1 by 2 prignals 1 by 2 0 so basically if I write further R n x A S by R n x A l is basically delta A 0 freeze by R and then there is a minus sign here so this is minus sign right this minus sign comes here so minus sign delta A 0 freeze by R 1 by 2 freeze minus 1 by 2 0 freeze now since delta H freeze itself is basically negative of delta H 0 melt so I can write minus of delta H 0 freeze is nothing but delta H 0 melt is positive by R 1 by 2 freeze minus 1 by 2 0 so that is exactly what we are looking at if you do that ln x A S by ln x A l this can further be written as ln 1 minus x B S 1 minus x B l right plus x A S plus x B S should be equal to 1 right x A in solid state in a solid plus x B in the solid should be equal to 1 so that means x A S is 1 minus x B S and x A l is 1 minus x B l now this is like ln 1 minus x B S minus ln 1 minus x B l now basically if you think of this as a very dilute solution like ideal dilute solution that is the amount of this very small then ln 1 minus x B S can be written as minus x B S and this can be written as minus x B S however there is a minus sign ahead so it becomes plus x B S so this becomes x B l 1 minus x B S by x B l x B S by x B l we can consider it as l or we can often here I am writing it as l which is basically x B S by x B l is nothing but l is near the partition right if l you can call it p also right you can call it p also but here I have called it l which is x B S by x B l it is the partition position of solid partition position of solid between solid and



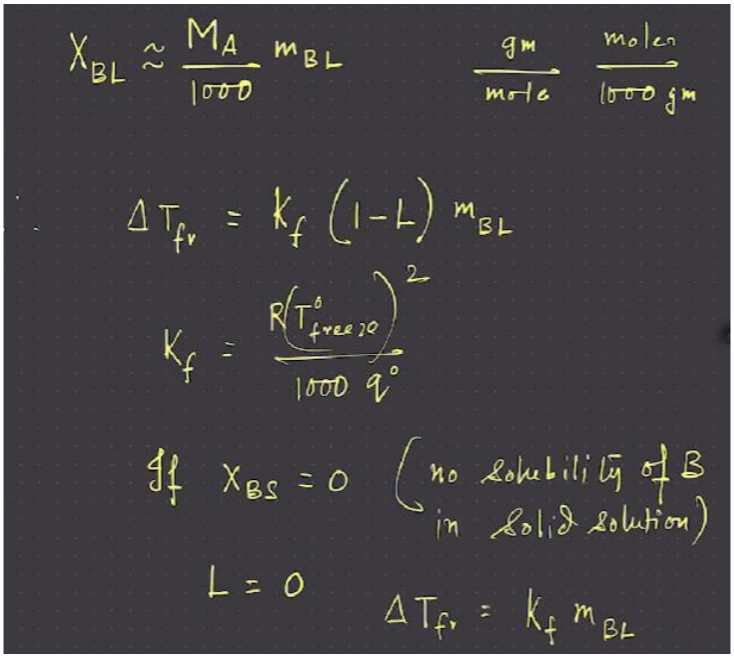


liquid right so partition between solid and liquid solutions so if that is so we can further the simplification because ln x S by x B l is this guy so basically if you do further simplification you can write x B l 1 minus l is basically nothing but right because x B S is basically so if I look at this why did this come this comes because you have x B l right this is x B l 1 minus l right so basically you are writing this guy so this one that you have in this this equation this is now replaced by this guy right so this becomes x B l 1 minus l plus delta x B l by r delta t increasing by t zero freeze times t freeze now you are telling that t zero freeze and t freeze are very close right they are very close now if I tell t zero freeze and t freeze are pretty close then you can approximate this t freeze and t freeze the product can be approximated as t zero freeze square right so you have t zero freeze square you have r and you have 1 minus l x B l by delta x B l right basically you are looking at delta t f r basically as a function of all these parameters now this product we are calling as t zero freeze square and you are taking this guy here r goes up and you have this term so basically delta t f r is this right so when l now if you look at that if you look at that when l is less than 1 that is x B s by x B l is less than 1 that is x B s is less than that is the amount of B partitioning solid is less than the amount of B partitioning liquid then in that case you have the delta t f r which is greater than zero or t freeze is less than t zero freeze which gives you depression right this gives you depression of the point right which is in general the freeze in general this is the freeze right then you have depression of freezing point right

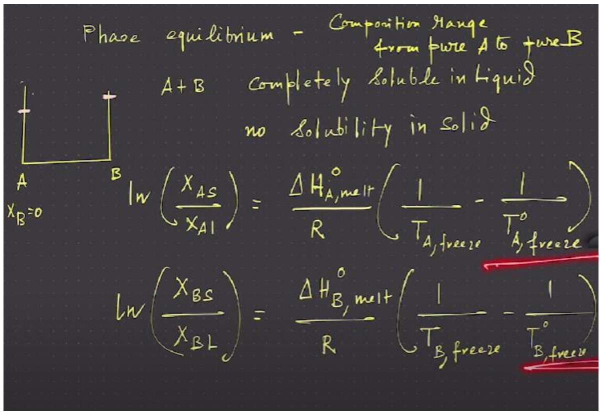


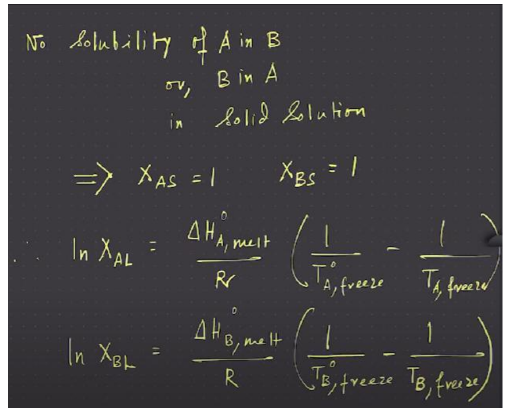


when you put this is a colligative property that we have learnt for solutions right so basically depression of freezing point when l is less than 1 mind that when l is less than 1 you have x B s less than x B l then in that case B that we have got 0 and you have depression of the point however when l is greater than 1 x B s is greater than x B l that is the amount of solid the partitioning is such that amount of B or amount of solid in the solid state is more than that in the liquid state generally not really common but it may happen in such a case delta t f r will both be less than zero or t freeze basically the freezing point of the solution freezing point of the solution will be greater than the freezing point of your solution so p zero freeze is that of your A or your solvent so you are telling the freezing point of solution is now elevated so there is an elevation so this is basically leads to elevation of the freezing point now if you look at that now if you see q naught I can go further if you tell q naught is the specific heat specific heat is per in joule per gram specific heat of your solvent A in joule per gram then delta H0 Mel delta H0 Mel is nothing but 1000 joule per gram because it is joule per gram and we are looking at delta H0 Mel and we can write it as say if I look at 1000 grams basically 1000 grams why did I do 1000 grams because I want to look at per kg of the solvent we are going to use molality, molality is number of moles of being 1000 grams or 1 kg of solvent A so 1000 grams of A is nothing but 1000 by m a, m a is the current rate of the molecular weight of the solvent A so 1000 by m a moles of A, so you have 1000 by m a moles of A and for that solutions x d which is basically nothing but n b by n a plus n b which is nothing but n b by n a and you can write x b liquid for example is nothing but approximately m b l m b m is the molality of B in the liquid state times m a by 1000 right you have 1000 by m a here you can easily put this 1000 by m a is contained is 1000 by m a most of they are contained in 1000 grams of the solvent now if you look at x b l, x b l so because by using this definition x b l is approximately equal to more m b l times m b by 1000 you are neglecting the amount of B right so if that is so, so you have this equation right it is m b l, so m b l is the molality of solvent and so if you look at that m a by 1000 is basically m a is the atomic weight or molecular weight of A component A right A can be what, A can be some compound right so that is why I am telling m a is the molecular weight of A right it is not a compound it is an air component basically it is a pure atomic species then basically it becomes an atomic but you see this is in grams and then this is in mol right m a is grams per mol and you have 1000 and here you have m b l which is moles per gram right 1000 grams moles per kg basically or moles per 1000 grams so basically gram gram cancels out, mol, mol cancels out basically mol, mol cancels out and you basically get x b l x b l of which is mol by mol right which is basically mol by mol because mol by 1000 is basically m b l right so basically mol by mol and therefore that is mol by mol is nothing but mol fraction right moles of b in the liquid by total moles of, total number of moles of the liquid right, total number of moles of liquid is basically n a l so basically n a liquid square plus n b liquid square basically gives me n b l now you are telling n b l by n b l is nothing but x b l right so if that is so we can basically write so this is just a convenience so delta p f what can be



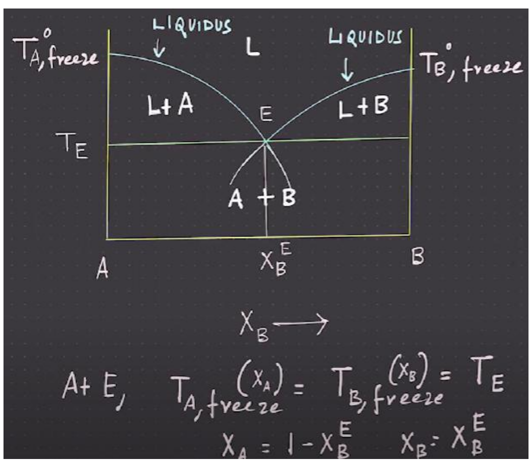
written as this with this in terms of molality right and where k f is r T 0 full square by 1000 q 0, q 0 is the specific heat right specific heat so instead of looking at enthalpy of transformation if we are not given enthalpy of transformation but we are given specific heat then it causes phi s right now if x b s equal to 0 now when does x b s go to 0 x b s goes to 0 when there is no solubility of being the solution right by the way when we are looking at the phase diagram when we are trying to cross the phase diagram we are assuming no solubility of being the solution so basically in such a case l which is x b s by x b l will be equal to 0 so in that case delta T f bar that is the change in phase point is nothing but this k f where k f is r T 0 full square by 1000 q 0 where q 0 is the specific heat of pure right of the pure solubility now you have which is is proportional delta T f bar that is change in phase point is equal to this k f which is this constant times the molality of being the molecule right molality of being the molecule if you look at phase equilibria now you are looking at all the ranges right we are now basically see we did it for ideal dilute solution but if I want to use the same equation that is why I did all these derivations to show you that we have done it for ideal dilute solution where b is like very small amount of b is present in a right so a is like a major solvent and you have minority in solute instead of that if you look at now phase equilibrium condition where you are looking at like the

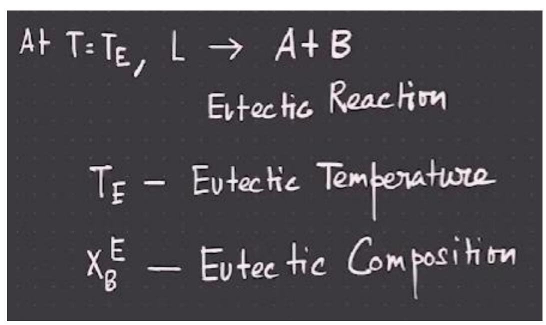




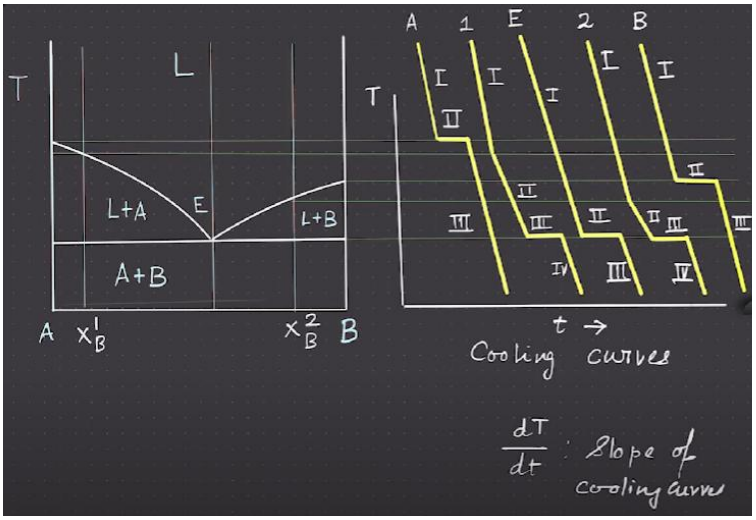
complete composition range from pure a to pure b you are looking at phase equilibrium you are looking at composition range from pure a to pure b the entire composition now you are telling a plus b and we have given this condition a plus b completely soluble in liquid but no soluble in solids so if I look at now ln xas by xa l we get this equation right delta H a 0 that is the partial molar relative partial molar enthalpy of component a right but there is a 0 so this is delta H a 0 means this is basically the changing molar enthalpy of component a of right this is delta H melt only right so basically 0 so basically this is the transformation heat of transformation or heat of melting or latent of melting of pure solvent right latent of melting of pure solvent by R right so this is the pure solvent a right or not pure solvent in this case we can tell this is the latent of melting of component a right and you have 1 by p a phase because a can have a different freezing point than b right you have 2 components a and b, a has a different freezing point than b and you are now looking at component a now if you look at component a you are looking at the component in pure state right you are basically in the phase diagram as you have seen before you have 1 axis and you have the other one so basically you generally use both right so basically this is your a side and this is basically pure a side and this is pure b side now if you look at that we are looking at the pure a axis so basically where x b equal to 0 so that is the pure a axis now in that case you have delta H a 0 melt by R and 1 by p a freeze say for example the p a freeze is somewhere here and say p b freeze is somewhere here that is always possible right so now this is pure a axis and this is the pure b axis right so this is your b axis and this is your p a axis now you are saying so if you see we are looking at delta H a 0 melt which is basically for pure a the heat of transmission during melt heat of transmission the positive heat of transmission during melting or latent heat of melting by R and 1 by p a freeze minus 1 by p a 0 freeze now for p it will be just delta so we are looking at p delta H b 0 right now that is the latent heat of melting so that will be your p right and you have p b freeze or p a freeze are basically the freezing point of a or b in the solution and you have this p a 0 freeze and p b 0 freeze p a freeze and p b freeze are that of the components a and b now you see if you look at that no solubility of a in b or b in a in solved solution so in solved solution x a s is 1 or x b s is 1 basically right in the solved solution x a s is 1 or x b s is 1 right these are pure components so if x a s is 1 and x b s is 1 then you have this equation where x a l is this right where p a 0 freeze comes in here because now you are now looking at you are looking at x a s which is basically x a s is basically pure right so then 1 minus ln x a l so then 1 is also considered this becomes minus ln x a l so minus so this becomes minus ln x l but then this should be p a freeze minus t 0 freeze but this minus is absorbed here right here because this is 1 by p a 0 freeze minus t 0 freeze similarly you have a 1 by p a l which is delta l by delta l by r p b 0 freeze and then it comes to p a freeze right so basically you are looking at p b 0 freeze now see p b freeze is like this ok and so basically p b 0 freeze here is what we are looking at right we are looking at p b 0 freeze and p a 0 freeze these are the pure right pure components but we are also looking at change in b rich solution and change in a rich solution but if you see the liquid has complete solvility of a and b right so you have liquid which is completely solv- a and b are completely solv- however if you see the solid state right this is a solid state if you look at the solid this is solid when you see in solid there is no solution at all in solid there is no solution at all it is pure a and pure b right so if a and b do not mix at all right you have pure a and pure b and then you have also this liquid plus a and you have liquid plus b that is fine you have liquid plus a and liquid plus b and these are called liquidus lines which separates liquid plus a there is a solid from the liquid and you have also a very special point here where basically T a freeze right T a freeze that T e f is equal to T b freeze right basically you can see as you go from pure b you are coming to a mixture you can see that your T b freeze is changing but at this point T b freeze and T f freeze are basically the same T f freeze equal to at the point T f freeze equal to T b freeze equals to T b right this is T b right this is basically equal to T b right and this is a special point or this is a special line or you take the point in that you take the point T f freeze and T b freeze that you have the solution these equations T f freeze and T b freeze becomes equal and that is basically the intake of temperature and you have X a which is basically 1 minus X e at a particular point so at X e right so X a and so X a is nothing but 1 minus X e right so that is what is X a so the composition of a at the composition of or the composition of the the composition of the eutectic right the composition of e is basically X e right so this is X e right and that is what we have written X b is basically X b and X a is nothing but 1 minus X b so at T equal to T e as you can see here at T equal to T e you have liquid which transforms to pure air and pure T so liquid transforms to pure air and pure T and liquid going to A plus T is a eutectic reaction right it is called an eutectic reaction but T e is the eutectic temperature and X b e is the eutectic reaction right so you got one type of phase diagram now this phase diagram very quickly I will just end here so this phase diagram can be also obtained experimentally say for example if I look at this different the phase diagram and now I look at say for example here say for example for pure B the freezing point is different for pure A the freezing point is different that is changing T a freeze is changing as you go from the pure component to here and again T b also changes like that so T b changes this way T a freeze this way and here somehow T a freeze happens here T a freeze becomes equal is an invariant point or an eutectic point right now if I have to determine this phase diagram what

I can do is I basically can use a cooling carbon experimentally so we have A and B mixture ok and I have the A and B mixture in the liquid state and we are just basically say for example we have pure A so this is pure A so pure A in the liquid state and I am pulling it under a furnace and see at one I am pulling under a furnace and it has del T so this is basically I think T t by T t is the slope of the cooling curve the slope of the cooling curve will be different in the solid so if you look at the solid arm or the liquid arm you will see the slopes will be different right because the conductivities the thermal conductivity is different or thermal diffusivity is used so basically you know this relation del T by del t if you just look at conduction del T by del t is equal to alpha so alpha is assumed to be a constant del T by del t and alpha is thermal diffusivity which is basically k by rho c e now if you look at that A in the liquid state will be different from the conductivity of the liquid state or density or the heat capacity the liquid state will be different from that of the solid state so as a result so basically this del T by del t or so we are looking at the cooling curve that we have obtained so cooling curve is basically we have described the cooling rate and as a result so basically the furnace is getting cooled so as I told you this is an experimental technique this cooling curve technique now as soon as you reach the temperature here at this temperature you see a liquid solid goes and then again it falls and this fall again is proportional to the proportional to the conductivity of the thermal conductivity of the solid right which will be different from that of the liquid so there slows to be different, but in 2





there is something very interesting that is happening, in 2 what is happening is furnace cooling is happening, furnace cooling means the furnace is expelling heat outside right, furnace is expelling heat outside however in 2 what is happening is although the furnace is expelling heat outside there is some heat evolved right heat evolved when heat absorbed right, there is heat absorbed so if you are looking from this to this so here the heat is evolved so you are looking from, so that is what we are looking at right we are looking at cooling curve right, we are looking at cooling curve so as a result when this transmission takes place when this transmission takes place right, this stage 2 for A is here when the transmission takes place it becomes basically a flat or horizontal region right, it does not change right because in this region you are basically releasing the heat right, now you look at 1, in 1 there is no such thing, it is there so if you are looking at this composition 1 so you are now looking at this cooling curve so you have one slope here, now you hit here and now you have another slope that starts and this is the simple because there is a very simple A right and then again 3 when you come to 3 3 is basically you are coming to here so basically in this case you have like again the slope change and this guy goes down but see before it does so you have 1 so basically you can look at this here 1 and then you have 2 but then there is a 3 and 3 is where liquid is transformed to solid, see in this case when liquid it is pure liquid now there is some nucleation that is happening say but now once you go here you have liquid to solid transmission right, here you do not have liquid to solid transmission right, you have some A nucleating inside the liquid but as soon as you come here you have liquid to solid transmission so here again you will have a if you use a liquid to solid transmission you have a evolution of it and you see that for 1 you have this similarly for E if you look at E so if at E continuously it is continuously reducing right then the liquid state is reducing now as soon as you reach 2 you are basically giving up right, you are basically giving up heat right and as a result you have this again which is compensating for the heat that is the furnace is giving up heat and you have some heat evolution because of this transformation from the liquid to solid right if this heat evolution is basically now balancing the heat released by the furnace to the cooling right heat release by the furnace to the cooling is now balanced by the heat that is involved right as a process of this in terms of freezing right at E right so and that is why you get this horizontal line free and then once you just cross the eutectic moment again you have to do in accordance with the conductivity of the solid like entire solids right, entire solid mixture so basically here also you can see that right there is this 3 here you have 3 and 4 because there is also 2 here right but here there is no 2 so if you look at this part there is a 2 here right there is some change but change here is not liquid to solid transmission the change here is that from here if I go here what we see is the nuclei of A solid A start nucleating inside the liquid right so this is for component E now for 2 it will be very similar 2 it will be very similar as 1 so you have 2 obviously it will be slightly different why it is like different slopes are different because you have a very different composition you have a very different composition with very different properties right but as you can see for 2 also for 2 also from here to here you have a slope change right and then you have 3 again the 3 comes here right so it is a horizontal and then it goes to 4 now in the case of pure B it is like 2 comes here right because that 2 corresponds to the temperature here right so these horizontal lines are basically using the temperature so this cooling curve is for easy and



convenient way to calculate surface diagrams using experiments you are basically making buttons of different compositions like composition corresponds to pure A or pure B or something corresponding to 1 the composition corresponds to point 1 and composition corresponds to point 2 and you are melting them and once you have the melt in a crucible you are just allowing the melt to freeze at a given cooling rate at a given as the furnace is getting cooled down right the furnace is giving out the heat and only during the transformations that take place you have this evolution of heat which compensates for this dropping temperature and as a result you basically get this all these changes and these changes can be plotted and you get back basically this change corresponds to this line right this line corresponds to the chain right you can see for different compositions you have these points that you get this point you get this point and this point and this and this so if you have these changes so immediately you can see the only thing for pure A there is no such change right pure A you have liquid then it just goes to solid right for pure A you see only one slope here right and these here you see the melting point of pure A right or freezing point of pure A similarly for pure B you see only one or a little change here so that is what I will talk about so in the next lecture we will talk about another type of phase diagram where you have infinite solubility in both liquid and solid state so here you have zero solubility in the solid state right A and B remains as A and B so xA equal to 1 and xB equal to 1 and right A and B remains as exactly as pure A and B but liquid has infinite solubility right of A and B but here we are looking at infinite solubility in both liquid and solid state which is basically and in such cases the components are isomorphous that is they have the same structure for example one of the example of this type of diagrams is basically copper nickel diagram classic example like copper nickel both are isomorphous they are basically having the same FCC structure and they form a complete liquid solution and complete solid solution across the entire composition range from 0 to 1 so I will talk about this in the next lecture