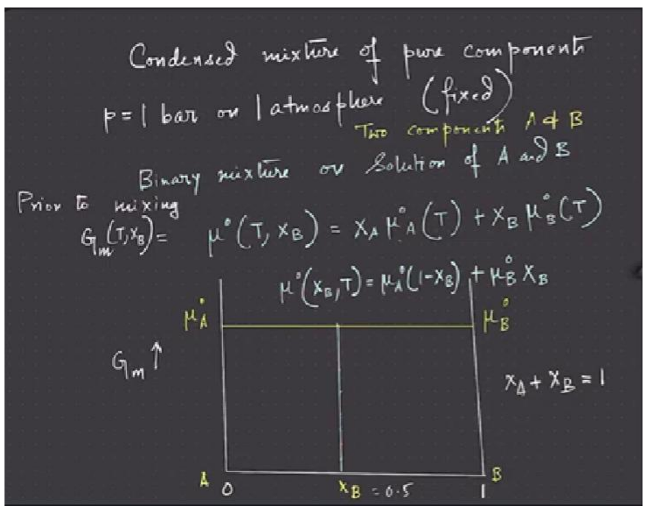
Thermodynamics And Kinetics Of Materials

Prof. Saswata Bhattacharya
Dept of Materials Science and Metallurgical Engineering,
IIT Hyderabad

Lecture 24

Thermodynamic properties due to mixing

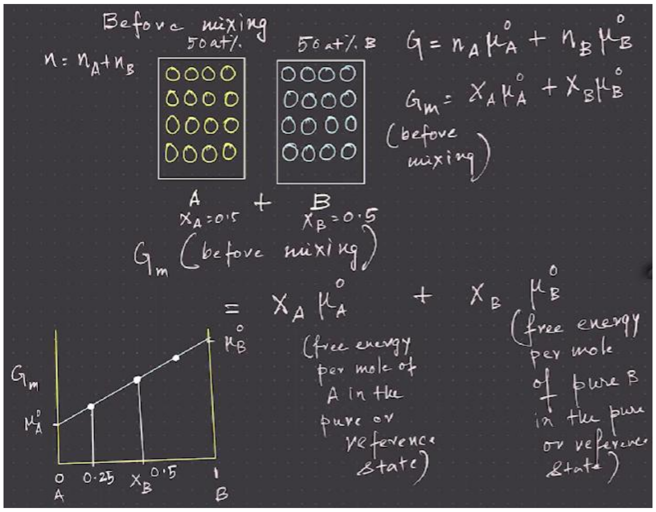
This is the process that I am talking about is before mixing. So, you have before mixing you basically have. So, this is before mixing as you can see here. So, at and again I am looking at a context mixture of pure components. For example, in the liquid state or in the solid state that means the PV work is negligible. So, we are assuming P equal to 1 bar, we are assuming P equal to 1 bar or 1 atmosphere, we are assuming that and we are fixing it.



Now you have two components A and B, two components A and B that are mixed. Now, your binary mixture or solution of A and B. Now before mixing, prior to mixing let us call it prior to mixing, the molar free energy of A and B will be given as XA mu A0 plus XB mu B0. Now XA and XB basically is for example the composition.

So, XA mu A0, XB mu B0 is going to be the molar free energy that is prior to mixing. So, basically I have taken some A atoms, I have taken some P atoms, I am trying to put them together and then I am trying to mix them. So, basically before mixing them if you look at that this is what we had. So, this is before mixing. If you look at the process before mixing, you had a box of A atoms and you can imagine them as like some yellow spheres and you had a box of B atoms and you are adding them together.

So, this is before mixing, we are just adding them together, we have not allowed them to mix A and in that case gm before mixing will be XA mu A0. Now what is mu A0? mu A0 is the free energy per mole of A in the pure or reference state. So, this is basically free energy per mole of A in the pure or reference state. Reference state may not be pure state, but we are assuming so and then you will have XB mu B0 again this is free energy per mole of A in the pure state. So, basically this is XA, XA and XB are the concentration.

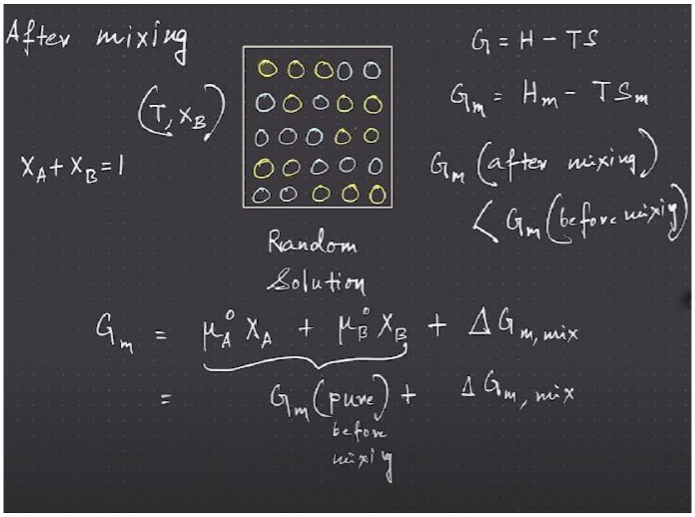


So, basically if I think of g say which is basically nA mu A. So, g is the extensive property plus nB mu B. Now divide by n, n is equal to nA plus nB and now divide by n. So, g by n becomes gm equals to now here it is mu A0, here it is mu B0, mu A0 indicates pure state, B0 indicates mu B0 the superscript 0. So, please note that the superscript 0 indicates pure state.

Now gm equals to XA mu A0 plus XB mu B0 because I am dividing by n. So, nA by n is XA, nB by n is XB. So, you have this and this is the gm before mixing. So, this is before mixing. So, now if you plot this, if you plot them then say for example mu A0 is this point and mu B0 is this point. Say we are assuming for simplicity mu A0 and mu B0 to be at the same level then basically if you look at this, this is gm. Now you see this is your composition XB. So, if they are at the same level this is your composition say XB equal to 0.5. Say you have like here you have 50 atomic percent, 50 atomic percent and 50 atomic percent B then basically XA equal to 0.5, XB equal to 0.5, XA plus XB equal to 1. So, I am taking that composition XB equal to 0.5. So, XB equal to 0.5. So, I have my energy of mixing here, right? This is my y-axis. Now since they are at the same level whatever be the composition say XB equal to 0.25 my energy is here. XB equal to 0.75 my energy is here.

See that this is along the same horizontal line. So, basically the elevation is the same if the elevation because gm is right from the y-axis. Now if you have mu A0 and mu B0 at the same level exactly then here or here or here it does not make difference. So, before mixing the energy remains the same means here or here or here. However, it is also possible that mu A0 and mu B0 are at the different levels.

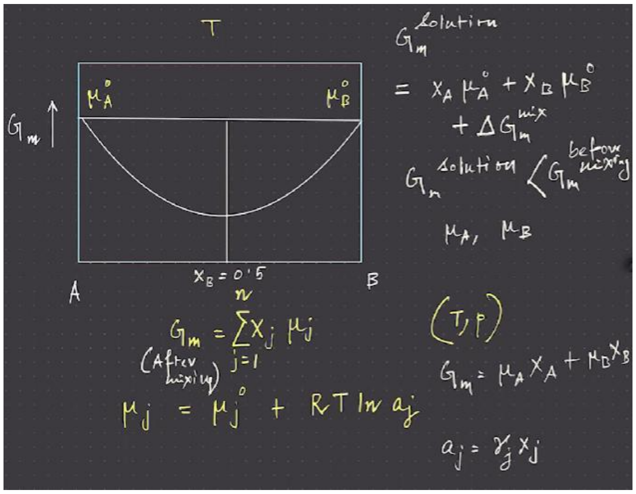
Say for example, I can think of say some sort of here is mu A0 and here is mu B0. So, I have like this. So, when I am mixing just before mixing also there is a difference, right? So, that is also possible. Say for example, let us think of a case like this. So, here you have say some sort of but it is still a straight line.



So, it is now your mu A0 it is your mu A0 it is your mu B0. Now you can see the more B you add you have slightly higher free energy more A you add you have the slightly lower free energy. But however, that is why for simplicity I drew a horizontal line to show you the concept of mixing. What happens? In mixing after mixing there is a decrease in this energy, the initial energy that you have for the mixture. So, as a result just to make you understand it has been drawn that mu A0 and mu B0 at the same reference level.

The reference levels can actually be arbitrary mu A0 can be less than that of mu B0. However, the important part here is after mixing, right? Important part here is after mixing what happens, right? So, that is why just to avoid any confusion I am please note generally there is a possibility that you can have an axis like this. So, basically generally it is possible to have this and you have say here you are plotting say gm this is before mixing, gm before mixing and you have xB here and xB equal to 0 means B over A and xB equal to 1 means B over B and you have mu A0 here and mu B0 that is understood that is here or otherwise the other way also is possible like mu A0 here, mu A0 here somewhere and mu B0 somewhere here, whatever you can do. Now, if you have that before mixing it is just given by a line, right? It is given by a line connecting mu A0 and mu A0, right? It is just a line connecting that. Now, if you have that you have a line.

Now, if you have a line now you see this is not exactly it is not a horizontal line and as a result for different values of xB say for different values of xB say here or here or here you will have some difference, right? Say for example this is for xB equal to 0.25, okay? xB equal to 0.25. So, this is 0.25. So, this is the free energy before mixing. Now, say here say xB is 0.5. So, this is the again the gm before mixing, right? All of these points that you are lying on this line for different xB, okay? This is basically a mixture of A and B but A and B have not yet mixed, right? They have not yet mixed to form a random solution, right? So, they have not yet formed a solution I can tell, okay? So, A maintains its distinct A nature and B maintains its distinct B nature, right? You can basically easily distinguish one partition that is completely A, the other partition that is completely B. You have removed the partition but you haven't allowed them to mix.



So, as a result along this horizontal line that connects mu A0 and mu B0 is where the free energy of the mixture will lie. That is just before mixing. Now, after mixing, now let us consider the scenario after mixing. Let us consider the scenario after mixing. Now, you see that the yellow, so yellow atoms were representing A and the blue borders were representing B.

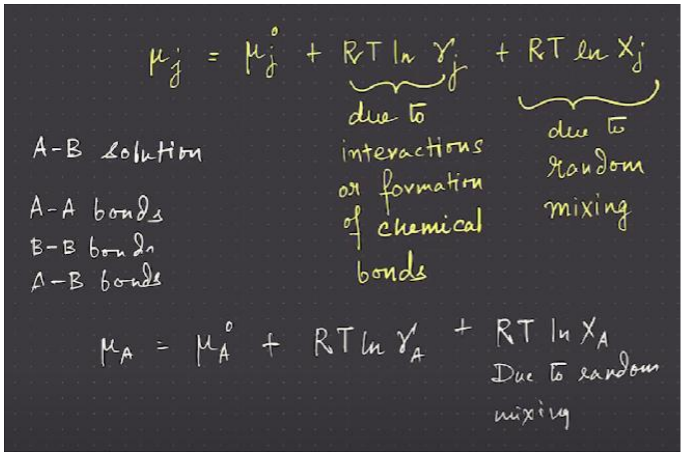
Now, as you can see now, yellow and blue have thoroughly mixed and it is a random solution, right? This is random, right? You cannot go to one point and tell, go to an atom and tell whether it is A or B. You have to look at it and see whether it is A or B and it is almost like in a solution we call it or in a liquid solution we call it like an average atom, right? It is a random solution. It is a random. The solution has become random.

So, random solution. Now, if you remember the statistical interpretation of entropy, the randomness increases, entropy increases, isn't it? Randomness increases, entropy increases. So, if you have a random solution then you have basically an entropy term that is increasing. Now, g is h minus T s, right? g is equals to h minus T s. Now, think of this, g m is also h m minus T s m. Now, think of g m that is before mixing which is mu A 0 x A plus mu B 0 x B plus I am telling there is some additional delta g m mix.

Now, this delta g m mix say has say a delta h mix, h m mix and there is a delta s m mix. Now, as you can see due to mixing there is randomness and as randomness increases, right? As the randomness in the configuration increases the entropy contribution also increases. So, delta g m mix is in general negative and as a result, so g m after mixing means after this randomness, right? Or after mixing is generally smaller than g m before mixing. So, then mixing basically reduces the energy of the system, right? Mixing reduces the energy of the system. If g m after mixing is greater than that of before mixing in general these atoms would not like to mix.

They do not want to mix, okay? At that given temperature. Again, I am looking at a given temperature condition, okay? And say at a given overall x B, right? T and x B are given. Now, I am telling why x B? Why not x A? Because x A plus x B equal to 1. So, if I fix x B, x A is automatically fixed, right? So, this delta g m mix, so you have this part.

This is like the pure part. So, pure part, right? So, you can think of this like g m pure where each part maintains its purity and then you have the purity means, purity means that the distinct characteristic like A atoms you can distinguish as A atoms, B atoms you can distinguish as B atoms. You have a partition, but you haven't removed the partitions to allow them to mix. You have a total system, okay? Containing two subsystems. One subsystem contains A, okay? Like this picture. One subsystem contains A, the other subsystem contains B that's at the same temperature and pressure.

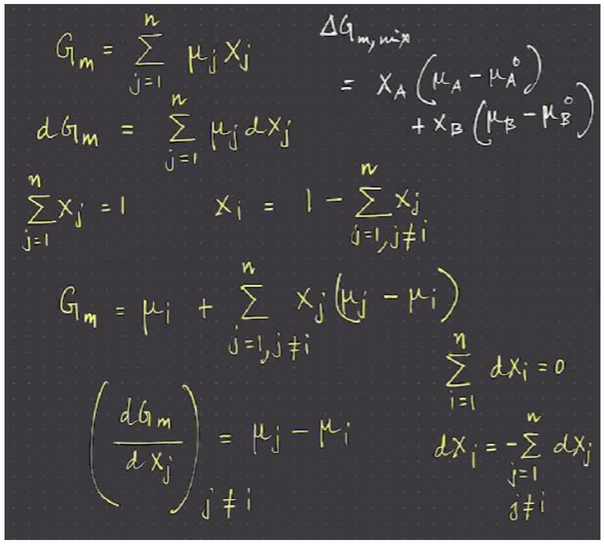


Again, at same temperature, pressure, okay? And the way the subsystems are added is like you have added 50 atomic percent of A and 50 atomic percent of B, but the partition, okay? The partition, it is still impermeable. That is, it is not allowing A and B to mix, okay? Once the partition is removed, now A and B are completely mixing, then you have this g m, this pure components plus that is before mixing and then you have the delta g m mix that comes after mixing and that part, basically that part, it basically reduces the energy. So, if you look at this very hypothetical simplistic situation, as I told you, so you had this reference energies, right? You had this reference energies, mu s 0 and mu b 0 and you had say some composition, say let us classify some composition here. So, let us specify some composition here and this composition is say x B equal to 0.5. Now, look at this. Look at the energy before mixing. This is before mixing, this is the energy after. Now, you see after is less than before, right? g m goes up this way. So, this is before, this is after. So, after is less than before, right? So, it is allowing the mixing, it favors mixing.

So, g m solution, so it favors forming a solution of A and B, random solution of A and B and it is less than g m before mixing and as a result of mixing, what has happened? Now, the g m has now become the g m after mixing, g m after mixing, right? This is g m after mixing. Now, after mixing in the solution, you have for each component, you have the chemical potential, right? So, basically like chemical potential. So, basically the chemical potential now is like mu A and mu B. Now, g m is now mu A x A plus mu B x B. Previously, it was mu A 0 x A plus mu B 0 x B.

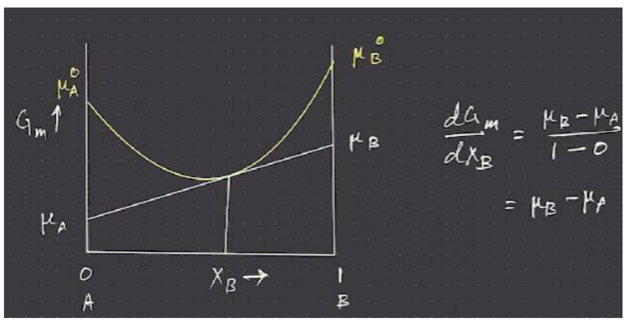
So, mu A minus mu A 0 and mu B minus mu B 0 is the excess part, okay? Is a relative change, relative partial molar free energy. Is that relative partial molar free energy, right? So, this is the idea and if you look at this, if you look at this, you have mu J, see you have mu J. So, I am defining mu J as this, of component J goes to mu J 0. Mu J 0 is the standard or reference step plus RTLN A J, right? You remember the last lecture, I have defined A

J. A J is the activity of J in the solution, activity of J in the solution, okay? Now, you see that this A J, as I told you, A J is nothing but gamma J x J.



Now, you see if I now write individually for the component J, so this is for component J. So, for example, for component A, it will be mu A 0 plus RTLN gamma A plus RTLN x A, okay? Which you can write as RTLN 1 minus x B. But see, this is due to random mixing, and this part is due to interactions or due to interactions between other atoms. So, A is interacting with B, so this part comes due to interactions between A and B and formation of chemical bonds. So, what type of chemical bonds A and B? Say, if I have AB, if I have an AB mix, right? AB solution, then what are the chemical bonds that can form? You can have AA bonds, you can have like pairwise, if I consider only pairwise bond formation, then you can have AA bonds, you can have BB bonds, and you can also have AB bonds, right? So, all of these bonds can form and you have this bonding part and you have, and these bonds means these are the interactions, right? This formation of chemical bonds and this RTLN gamma A or RTLN gamma J for the component J, basically this RTLN gamma J contributes to the or basically is due to the interactions between A and A, A and B and B and B, right? So, these interactions are basically resulting from the formation of chemical bonds like AA, BB and AB bonds, right? And there is this RTLN X, which is just due to random mixing, okay? Now, think of this as I told you, so GM mixing, after mixing you have mu A XA plus mu B XB.

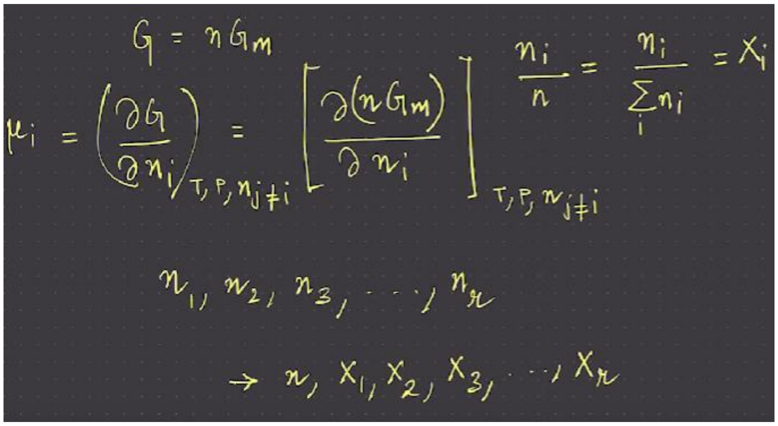
So, if you look at, if I tell you delta Gm, so this is another thing you have to understand, delta Gm mix is XA mu A minus mu A 0 plus XB mu B minus mu B 0, where mu B and mu A are basically the potentials of A and B in the solution, right? Chemical potentials of A and B or partial molar free energy of A and B in the solution and mu A 0 is for the pure form and or the standard form and mu B 0 is for the partial molar free energy in the pure form of A or mu B 0 is in the pure form of B or the standard form of B, right? So, you have, so basically you can write this way, you can try to derive this way, Gm is summation of mu J X J over all components N, okay? You can call all components say I equal to 1, 2, so you have say C components, okay? C components because N I am talking about total number of moles, right? So, this way I am telling you have C components, so J equal to 1, 2, C, component 1, component 2 like that component C, okay? So, up to component C. So, D Gm as you know is mu J DX J because the other part is basically 0 because of Gibbs relation, right? X J D mu J is 0, right? X J D mu J is 0. Now, D Gm is mu J DX J and summation X J equal to 1, X I is 1 minus summation X J where J equal to 1, 2, C, J equal to 1, 2, C and J not equal to I, right? Obviously, it cannot be equal to I. So, 1 minus summation of all the other X J's. So, Gm is mu I plus J equal to 1, 2, C, so I put C here, okay? J equal to 1, 2, C, J not equal to I, X J mu J minus mu I, right? It is mu J minus mu I.



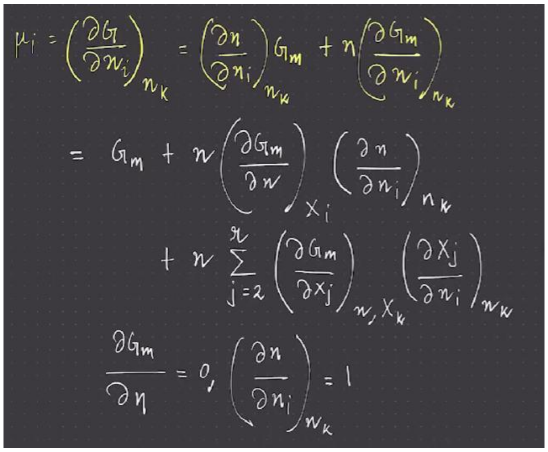
So, D Gm by DX J, okay? J not equal to I is mu J minus mu I. See, this is something that I have drawn when I did the tangent construction, right? We basically did this. I just want to reprise. So, if I show you when I did this for binary system, what we told that, okay, let us have this curve. Let us have this diagram where you have plotted Gm this way and XB this way such that this is 1, that is pure B and this is 0, pure A and then I got a free energy curve.

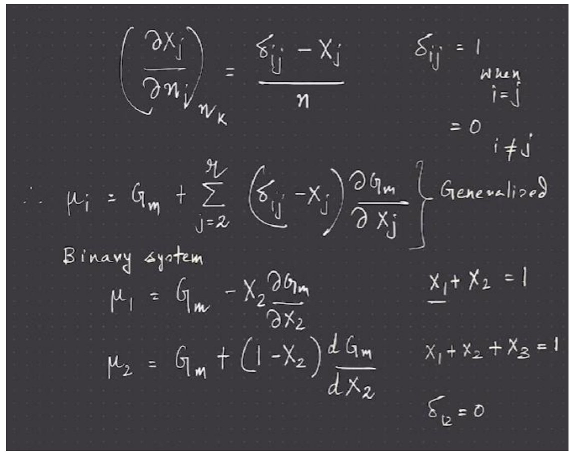
So, just drawing a free energy curve like this, right? So, it comes here, it comes here. So, basically this part, this point is mu A 0, this point is mu B 0 and this is after mixing. So, if you look at a tangent to this, if you want to draw a tangent line to any composition, you guys do any composition, you want to draw a tangent line. So, I will just push it and make it a tangent at some composition, say at this composition, at this composition, okay? So, at this composition, it is a tangent. Then the intercepts are, this is mu A, this is mu B of the solution.

See, this is mu B 0, see this is higher, mu B is less and mu A is less and you can also see that this is your Gm and this tangent basically gives you dGm dxB, the slope of this tangent line is dGm dxB which is mu B minus mu A by 1 minus 0 which is equal to mu B minus mu A.

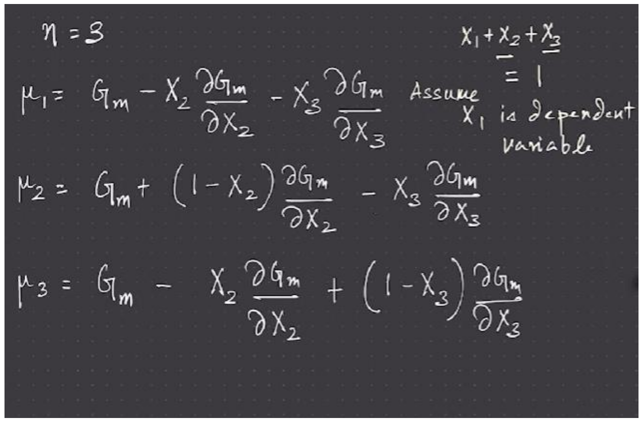


So, if you want to do it for a ternary system, quaternary system, how do you do that? So, you basically see del Gm del xj, so from this derivation, you can easily see just by partitioning this xi and xj and xj where j is not equal to i, I can write del Gm del xj I get is mu j minus mu i, right? And remember, dxi is equal to 0, dxi equal to 0, right? So, if you look at del Gm del xj, okay? So, it is mu j minus mu i and dxi is equal to, so because you have mu j dxj, right? So, mu j dxj is there. Now, if you have that, you have mu i dxi and mu j dxj and xi is 1 minus some xj and dxi is minus some dxj, right? Because the sum of dxi equal to 0, right? And again, here this j indicates j is not equal to i, right? So, we can write this way and so we can write it for any number of components, the same curve that we have shown in the previous lectures, okay? And you can derive it in a very general form like you can start with the definition of mu i since it is the chemical potential of component i which is the derivative partial derivative of free energy that the extensive free energy with respect to the change in mole number of component i, keeping mole number of component j not equal to i that is all other mole numbers of all other components constant, temperature constant, pressure constant. So, now g is nothing but ngm, right? g is nothing but ngm, gm is the molar free energy of the solution, gm is the molar free energy of the solution and n is the total number of moles of some of all the components, right? So, and so if that is so and ni by n is nothing but xi and so from n1, n2, n3, if you're mapping this way, okay? And say there are r components, so I am talking about r components, so if you do that and if you continue to derive, so you have del g del ni which is del n del ni gm plus n del gm del ni, we have done this and gm comes in n del gm del n del n del ni and now if you have j equal to 2 because see this is for ith component, now you are going from 2 to r, right? One component you have already considered here, right? So, i you have considered here, now you are going to 2 to r and this is del gm del xj, del xj del ni, now del gm del n, basically this term del gm del n, right? Equal to 0, right? Del gm del n, n is the total mole number, right? Del gm del n equal to 0 and del n del ni equal to 1, right? So, this term goes to 0, so you have now this term, okay? You start from j equal

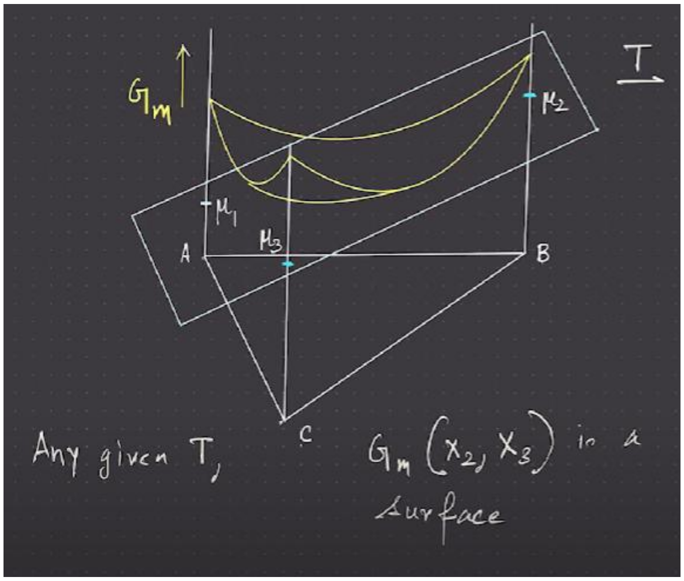




to 2 to r, you have del gm del xj and del xj del ni, then basically you get del xj del ni which is a Kronecker's delta, this is again, what I am doing is I am expanding this proof, okay? To the two systems more than binary, more than two components, so it becomes delta ij, delta ij is Kronecker's delta, remember delta ij equal to 1 when i equal to j, okay? And equal to 0 when i not equal to j, right? When i not equal to j it is 0, so basically what you get is mu i equal to gm plus j equal to 2 to r, r is the number of components, okay? R means you have starting from component 2 you have up to component r and you have delta ij minus xj del gm del xj, right? Del gm del xj is the generalized loop, right? It is the, remember it is better to write instead of writing this del gm del xj, I do not like this because del gm del xj is, I mean sometimes it is acceptable but it is better to write b gm del xj or actually this one of the components, so basically yeah, it is better to write this way here because these are all independent, these are all means x1 plus x2, say if I think of that, if I think of x1, if I want to fix x2 that is not possible because x1 plus x2 equal to 1 for a binary system, right? So, basically these are not all independent, right? So, basically if I look at x1 plus x2 plus x3 equal to 1, so that is why this partial in general for multi component systems is possible because x2 and x3 are independent, right? Not x1, right? One of them is not, so basically if you look at multi component systems where the number of components is greater than 2, then this is fine because one of the x's is a dependent variable, all other x's are independent, right? But now let us look at a binary, so here I am giving for the same formula I am talking about binary, generalization, so this is the generalized formula, this is generalized. Now, if you have this generalized formula, then for a binary system, binary system means containing two components, you write i equal to 1, so mu 1 equals to gm and now j equal to 2 to r, so you have anyway r equal to 2, right? You have two components only, right? You have two components only.



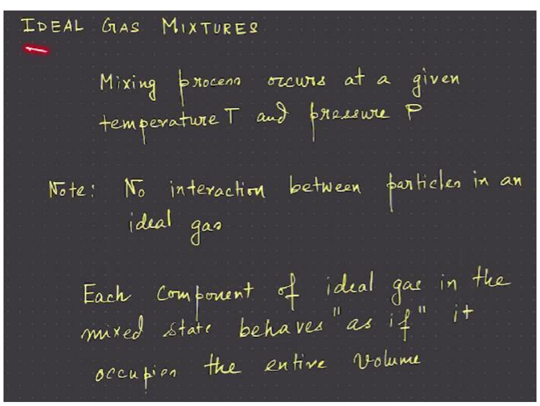
Now, if you have put i equal to 1, so if you see i equal to 1, so and if you look at that, you do not have, if i equal to 1, you start with 2, right? So, if there is no other, so j is always 2, so j starts with 2, so delta 1 2 is equal to delta 1 2 will be equal to 0, right? And so there is a minus, so it's 0 minus xj, j again, j actually r here is equal to 2 and it starts from 2, are you seeing that? So, basically if it is so, then this is 2, so for a binary system this is 2, this is also 2, so you have 2 here and since i is 1, 1, 2, this is 0, so you have minus x2 dgm, so here you see, I cannot write del gm del x2 keeping x1 fixed because x1 plus x2 equal to 1, right? You have to write dgm dx2, right? So, and the other part, say if I put i equal to 2, now you see delta 2 2, delta 2 2 equal to 1, delta 2 2 equal to 1, so 1 minus x2 dgm dx2, so you get both the intercepts mu1 and mu2. Now, if you look at a, so basically as I have done here, so mu A and mu B or mu1 and mu2. Now, if you put n equal to 3, apply that formula, now there is an interesting part that see x1 plus x2 plus x3 equal to 1, so I can now tell x2 and x3 are independent, so when I write del gm del x2, what I mean is x3 is fixed and when I write del gm del x3, then x2 is fixed, right? x1 is the dependent variable, x1, so 1, so if I write this way, so x1 is dependent, so x2 and x3 are there, so x2 when I do del gm del x2, x3 is fixed and when I do del gm del x3, x2 is fixed, so now if you have that and x1 is dependent, so again you have gm minus x2 del gm del x2 minus x3 del gm del x3, mu2 will be gm plus if you apply the formula, if you see this, you have 2, 2, 3, right? R equal to 3, 2, 2, 3, so delta, so for example for mu1, so this is 0, so that's why minus x2 del gm del x2 minus x3 del gm del x3, but here when you do 2, then in one case it is 0, so delta ij is 0 for this case, for this term, right? When mu, when i equal to 2, but this term is not 0, see there are, so you have one intercept at mu1, mu2 and mu3, now if you have that, you have mu1 that you got, again it's a ternary system, so x2 and x3 I can take as independent, right? x1 is dependent, I cannot take 2 as dependent, right? x2 plus x1, since x1 plus x2 plus x3 equal to 1, I can take any 2 to be independent, it can be 1 and 3, it can be 2 and 3, we have chosen 2 and 3, okay? We have assumed, so assume x1 is, so in this case what I've done is I assumed x1 is dependent variable, but you can also assume x2 is dependent variable, then x1 and x3 are independent, okay? You can also assume x3 as dependent variable, so then x1 and x2 are independent, right? You can assume anyway, now you have that, then you have these three equations, three equations, mu1, mu2 and mu3, these are basically the equations for the intercepts, right? And if you look at this gives triangle, see if you look at this gives triangle in three component system, you have three components A, you have three components A, B and C, okay?

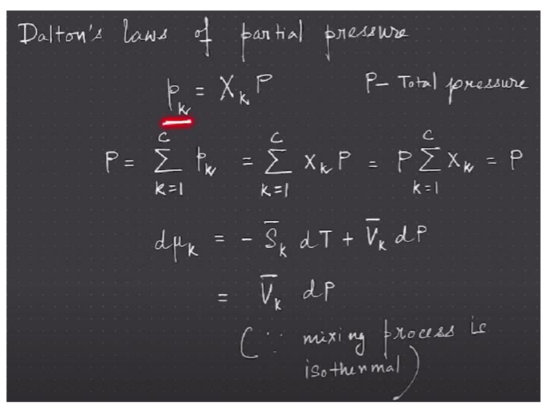


And if you look at it, this is at a fixed temperature, okay? Again, we are looking at a fixed temperature and this is a condensed phase, I don't care about pressure, pressure is not an axis, so GM is plotted, the GM now has become a surface, right? It's a function of, GM is a function of x1, x2 and x3 but x1 is dependent variable, so GM is a function of, I can tell that x2, x3 and T. Now, T I have fixed, T I have assumed, so at this T, GM is just a function of x2 and x3, now I have plotted this, so you can see this is your triangle where A, this is 100 A and this is say 0 A and this is say 100 C and this is 100 B, now if you look at this axis, if you look at each of this axis, so you have this axis and then you have another axis here and you have another axis here, right? There are three axis, now if you look at the surface, this is your surface, the free energy surface, right? This yellow guy, this is your free energy surface, now at some composition, again the composition, if you have to specify composition, I have to specify, so this is, so what I am telling is at a given T, at any given T, you can write GM as a function of x2, x3, right? Now, this is a is a surface, now if it's a surface, if it's a curve, you have a tangent line, if it's a surface, right? It's a three-dimensional surface, then you have a two-dimensional tangent plane, right? So, you have this blue guy that this one is the tangent plane through a suitable composition set x2, x3, okay? Now, if it is so, this tangent plane is making intercepts, say for example, if you see that this is the intercept, so if you look at it, it's a slightly perspective joint, so you have like, if you look at this, this is gone through like the surface and if you look at that, that this plane has got this axis at mu1, the A axis at mu1, the C axis at mu2 and the B axis at mu3, okay? So, you have A, B, C, so or you can write this also, this is also fine, you can tell this is mu2 and means it's just a convention and say this is mu3, C is 3, so this is mu3, so this blue point that you can see here, right? The blue point that you can see here or the blue point that you can see here or here, these are the intercepts on this axis, on this axis, these are the intercepts by the plane and these are the intercepts, one intercept here, mu1, so for the A axis, for the B axis, it is mu2 and for the C axis, it is mu3, right? These are the, these intercepts are the chemical potentials of the solution at a given composition and you can set x1 as x2, x3, okay? x1 is automatically determined because I have assumed x1 to be dependent value, okay? So, basically you can, so what we are telling here, again, let us go back to this, this is a generalized form, okay? Generalized form for the expression of mu and mus are nothing but the chemical potentials and this chemical potentials of component I and as you can see, if you want to visualize, if you want to visualize for greater than 2, then it becomes, for example, for component 3, you have a surface, you have a tangent plane, for component 4, you have a hypersurface, you have a hyper tangent plane, so basically, it's very difficult to visualize but using this approach, you can always get mu1 and mu2 as a function of gm and x2, right? So, that's the idea. So, if you look at this, so basically, this is a very generalized way, okay? It can apply to n equal to 2, n equal to 3, n equal to 4, n equal to 5, any number of n and you can get all these mus, right? Mu1, mu2, mu3, mu4, mu5.

Only thing, remember that if it is a 4 component system, then 3 components are independent, one of them, 3 components like x2, x3, x4 are independent and x1, say, we can assume to be dependent, so we cannot have all 4 as dependent, right? When we are expressing in terms of mole fraction, right? But this is a generalized formula. But if you can see, if you apply this generalized formula, you get for the binary system, the common tangent that the not common tangent construction, you get the tangent intercept method, so you get the intercepts, right? You get the intercepts in the binary system, okay? Excuse me, common tangent will come when we will discuss phase equilibrium, okay? We haven't yet discussed phase equilibrium in binary systems, which will soon, although we have discussed equilibrium between subsystems and there's a same idea that will apply, but I haven't shown it in the form of free energy composition diagrams, but this is a very, very important diagram that you should remember, okay? And this is a diagram that I will apply when I also explain the phase equilibrium subsequently, okay? Not right now, but subsequently. So, only thing that I wanted to tell you that this approach that which starts with the definition of chemical potential, right? It starts with the definition of chemical potential and then G, I write as NGM and then we go on, right? Del N, del Ni and N del Gm del Ni and then del Gm del Ni is again split into one is like del Gm del N and del N del Ni and then there is this, this is the chain rule, okay? When I am having Xi, Xi is the dependent variable and then for other independent variables, J equal to 2 to R, these are the independent variables, I have this del Gm del Xj and del Xj del Ni and since this is del Xj del Ni, this is basically del Xj del Nj, del Ni. So, as a result, you can see that there is a delta Ij automatically that comes in and that's why you have this delta Ij, this is called Krone-Kirch delta, okay? This is also called, this is known as Krone-Kirch delta. It's a very useful mathematical function, you can actually see that it's an identity matrix basically.

Delta Ij equal to 1 when I equal to J or 0 when I is not equal to J, right? And as you can see here, you have this expression which becomes basically 1 minus X2 here and 0 minus X2 here, right? So, this expression as you have is multiplied with the generalized slope, right? With respect to X1, not X1, X2, X3, X4 and so on, right? Del Gm del Xj, right? When I am writing del Gm del Xj, I am telling not the dependent variable but other independent variables are fixed, right? For higher order multi-component systems, okay? For example, a higher order system here is N equal to 3. I have assumed X1 is dependent and X2 and X3 are independent. So, when I am writing del Gm del X2, understand that X3 is fixed, not X1. Dependent variable cannot be fixed, right? And when I am writing del Gm del X3, X2 is fixed, right? So, this is the idea. Okay, so now I give an example of ideal gas mixtures, okay? In ideal gas mixture, what happens? If you have ideal gas, you have all these components which behave, all the components in the ideal gas mixture will not interact.





There is no interaction between particles in an ideal gas, right? There is no interaction between particles, right? That's what we have assumed. No interaction between particles in an ideal gas and mixing process occurs at a given temperature and pressure. Again, we have fixed the temperature and pressure, no interaction, that is Ln gamma i term, that gamma term, that RTLm gamma term goes to zero, right? Because there is no interaction. So, each component of ideal gas in the mixed state behaves as if it occupies the, so if there is no interaction, each component of the ideal gas will behave as if it occupies the entire volume, right? Each occupies the entire volume, right? Because see, there is no interaction. Now, if there is no interaction and I have these different components, now each component acts as if, because the other, each component, these components, molecules or atoms are not interacting with the other molecules as a result, they act as if they occupy the entire volume, right? Now, and it is again, if you think of Dalton, now if you remember Dalton's laws of partial pressure, then what does it tell? The partial pressure of component K in an ideal gas mixture is proportional to xK times P, where P is the total pressure and xK is the mole fraction of component K.

So, partial pressure of component K is mole fraction of component K times the total pressure, right? Partial pressure equals mole fraction into total pressure, that's the Dalton's law of partial pressures, right? And if you see, P is K equal to 1 to C if you have C components, PK, okay? So, PK is nothing but xK P, right? From this relation, right? So, PK equals nothing but xK P and P is the total pressure which is fixed. So, total pressure is coming and some xK, K equal to 1 to C, which is nothing but 1, right? This is equal to 1. So, this is nothing but P, right? P equal to P. So, as you can see here that this, so this proves that this is a consistent relation, right? And now, if you have that, you know, d mu K or dGK bar is a partial molar Gibbs free energy of component K, which is equal to d mu K is equal to minus SK dt plus minus SK bar, right? You remember the bar because it's the partial molar entropy of component K plus VK bar dP. So, this comes from dG, so we already know the relation dG equal to minus SDT plus V dP.

Okay, so in the next lecture, I will continue this. In the next lecture, I will continue this and this ideal gas mixture stuff.