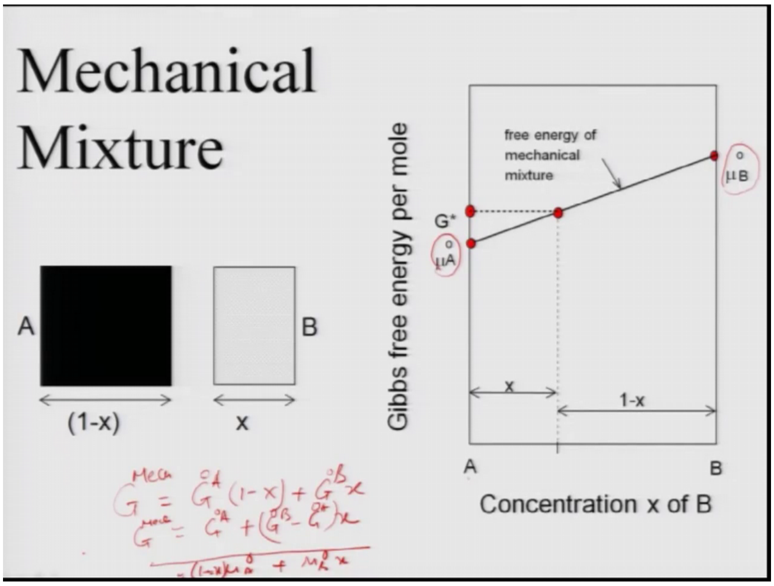
Phase Transformation in Materials
Prof. Krishanu Biswas
Department of Material Science & Engineering
Indian Institute of Technology, Kanpur

Lecture - 05
Ideal Solution, Chemical Potential

In this lecture we are going to again carry over the Thermodynamics Solution. As I have discussed in the last class that solutions actually automatically mixed solid solutions; that is what we have treated. Now, we are going to use this mathematical formalism for answering different aspects of solution.

(Refer Slide Time: 00:36)



Mechanical Mixture

$$G^{Mech} = G^{oA}(1-x) + G^{oB}x$$
$$G^{Mech} = G^{oA} + (G^{oB} - G^{oA})x$$
$$= (1-x)\mu_A^0 + \mu_B^0 x$$

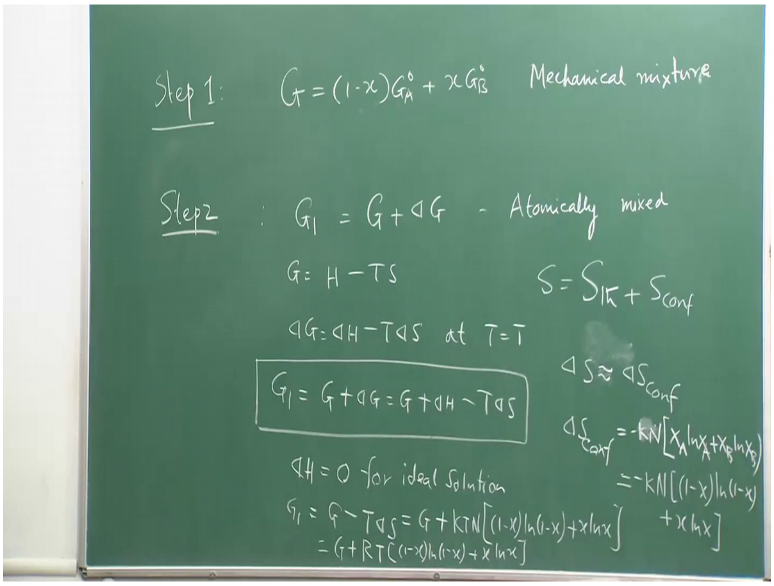
So, solutions can be formed in a many ways, but thermodynamically we can think of a solution forming in 2 steps, in the first step if a solution contains 2 by atomic species a and b then we bring them together side by side is step 1, in the steps 2 we allow them to mix mechanically. Now in the step one if the solution contains x moles of b and 1 minus x moles of a then the mixture will have free energy given by G A 0 1 minus x plus G B 0 x because we are taking x mole fractions of p.

Therefore, the free energy of the contribution of the b will be x multiplied by G B 0, where G B 0 is the free energy of pure B; similarly free energy of pure A is G A 0 and there are 1 minus x mole fractions of A in the solution. So, therefore, it is G A 0 multiplied by 1 minus x and if you take the sum then it is becomes G A 0 1 minus x plus

G B 0 x and as I told you in last lecture that is this is the equation of a straight line. If I plot G A free energy versus x is the mole fractions of B.

So, at any point on this curve within pure A and pure B the free energy is given by point lying on this line, so that is basically nothing but free energy of the physical mixture or mechanical mixture that is we have put things together, now what happens when we when we atomically mix them. So, let us do that on a board that is much easier.

(Refer Slide Time: 02:35)



Step 1: $G = (1-x)G_A^0 + xG_B^0$ Mechanical mixture

Step2 : $G_1 = G + \Delta G$ - Atomically mixed

$G = H - TS$

$S = S_{th} + S_{conf}$

$\Delta G = \Delta H - T\Delta S$ at $T = T$

$\Delta S \approx \Delta S_{conf}$

$$\boxed{G_1 = G + \Delta G = G + \Delta H - T\Delta S}$$

$\Delta S_{conf} = -kN[X_A \ln X_A + X_B \ln X_B)$

$= -kN[(1-x)\ln(1-x) + x\ln x]$

$\Delta H = 0$ for ideal Solution

$$G_1 = G - T\Delta S = G + kTN[(1-x)\ln(1-x) + x\ln x]$$
$$= G + RT[(1-x)\ln(1-x) + x\ln x]$$

So, if I consider So, I have already told you the free energy of the mechanical mixture is nothing but 1 minus x multiplied by G A 0 plus x multiplied by G B 0 ok, where this 0 transfer the pure elements free energy. Now this is my step 1, I have just mixed the 2 elements in the proportion of 1 minus x and x and the steps 2 the mixing will be done atomically. Now how do I calculate that so this to calculate that let us assume that G 1 is a free energy of the after the steps 2. So obviously, G 1 will be G plus some additional terms which is delta G is because of the mixing atomically mixing of these 2 pieces, this is just a mechanical mixture, we can write down also mechanical mixture.

Now if you add them together atomically if just like a solution, let say if you add sugar in water or if you add coffee in milk, then what will happen free energy of total system will be equal to this G plus an additional term, which will come because of the mixing atomically mixing together. So, this is because of atomically mixing because in a syrup and a sugar syrup or in a coffee and milk mixture atoms are mixed atomically. So, what is happening if I mix atomically, we know that G is given by free energy I assume you know all this stuff because I only told G is given by H minus T s, where G is the Gibbs free energy H is the enthalpy of the mixture enthalpy of any system T is the temperature and s is the entropy.

So, therefore, delta G is nothing but delta H minus T delta S as a certain temperature T equal to T right that is what we know. So, therefore, I can simply write down G 1 is nothing but G plus delta G that is equal to G plus delta H minus T delta S, this is my first equation which comes if I atomically mix 2 pieces in a proportions of 1 minus x and x.

Now, this G is directly coming from the mechanical mixture, what we need to calculate is delta H and delta S. So, that is why actually we are going to make assumptions to calculate these, the first assumption we make is that of a ideal solution. what is ideal solution? Ideal solution is one where heat of mixing is 0, that is if I put a and b together there is no change of heat if a has certain enthalpy H a and b has certain enthalpy H b and if I mix them together the enthalpy of the system is become H a plus H b minus H a b that is equal to 0. So, that is what is delta H.

Therefore, delta H is assumed to be 0 for ideal solution and ideal solution is one where, there is no heat of mixing or volume change because of mixing that is what is the assumption for the R d a solutions and if that is the case if delta H is 0 for the ideal solution then G 1 become G minus T delta S. That is at a particular temperature, where T is the temperature and delta is the change of entropy. So obviously, to calculate this we need to know what is the change of entropy, the reason I am just going step by step is because calculation of enthalpy requires many important aspects to be understood, but calculation of entropy is much easier.

Now as you know entropy has 2 important parts, what are this parts one is the thermal entropy, what is known as a vibration part of entropy. Other one is known as configurationally entropy. So, what is vibration entropy if I heat a system the atom starts vibrating, so therefore energy levels of atoms will have different characteristics and that is contributed to entropy because of the thermal aspects.

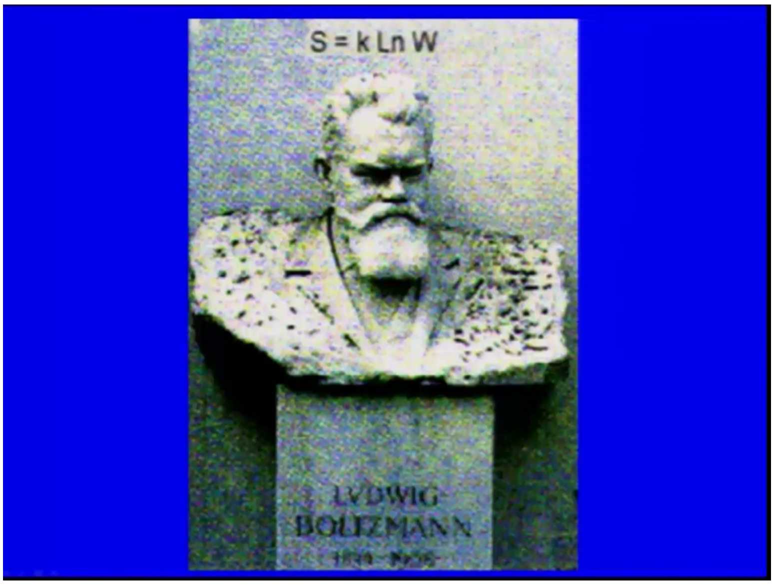
Normally in metallurgical thermodynamics, we ignore this part because this is not a substantial amount in case of solid solutions and second important part therefore, entropy is equal to this plus this as I wrote total entropy and as I told you the thermal part is ignored because of it is contribution is not very high that is why and what is the second part this is known as configuration part. Now if I take 2 atoms a and b different types and start arranging them in a lattice, that is why you form this solid solutions. There is change of configuration as compared to pure A and pure b, if I have only pure atoms and try to arrange them in a lattice then there is only one possible of arrangements, similarly by the pure B try to arrange them in a lattice there will be only one possible arrangement of pure B in the lattice because the atoms are similar or same.

But the moment I have 2 atoms different chemically different species and try to arrange them in a lattice I can have many ways of arranging them, that depends on what are the different probabilities of arranging them in the atoms in the lattice. So, that is what actually contributes to the configurationally entropy, configuration means different types of arrangements and this different types of arrangements will have different probabilities; obviously, the one which has the best or highest probability of all the arrangements it will be observed in the real systems.

So, this is the part which is now normally contributes the entropy and that is the part we need to calculate. So, therefore, delta S which is shown here in this term is directly coming from change of configuration entropy, this part is ignored it has been observed that this part the thermal part contributes only 1.5 to 2 percentage of the total entropy change, that is why this is not considered in a general sense.

But specifically we should write down this is almost equal to configuration entropy change. So, then how I calculate that is what I am not going to do in details, but I am going to tell you how it is done for Boltzmann equation. Again Boltzmann equation is what I showed you in the last lecture this is s equal to k ln w.

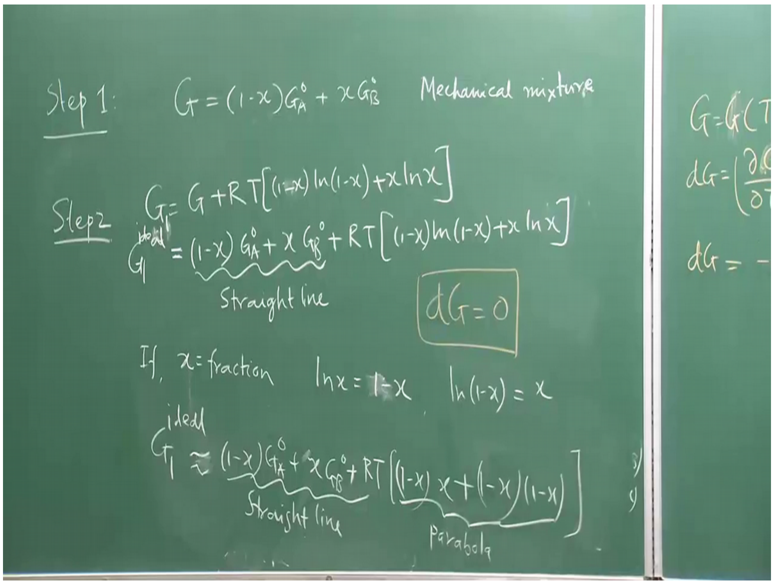
(Refer Slide Time: 09:53)



So, k is nothing but a Boltzmann constant and w is the different possible elements of the atoms in the lattice, that is the probability actually and log is it is log of that probability what determines the entropy. So, it is a standard derivation which is there you are in the books and what we one can do also, it is not very difficult task using sterling approximations one can calculate that and it for a binary alloy is equal to k multiply by N in to x a log of a that because of that log comes here x b log of x b. For our system we can write down, minus k n multiplied by 1 minus x log of 1 minus x because x a mole fraction is 1 minus x, that is why and x log of x that is for b. So, that is what actually you get if you do that detail calculations.

So, I am just skipping it because it is there in my phase diagram course also it is available in the books. So, then I can write down that is nothing but G plus k T n multiplied by that factor 1 minus x log of 1 minus x plus x log of x and that is become G plus k and n if you multiply Boltzmann constant with the atomic Avogadro number, that is becomes the gas constant gas constant is what R that is the universal gas constant, that is value say 8.314 joule per Kelvin mole, R T 1 minus x log of 1 minus x plus x log of x; so that is what is the equation we should use. So, I will just erase the steps 2 part to write down the equation properly So that it is visible.

(Refer Slide Time: 12:22)



Step 1: $G = (1-x)G_A^0 + xG_B^0$ Mechanical mixture

Step 2 $G_1 = G + RT[(1-x)\ln(1-x) + x\ln x]$

$$G_1^{ideal} = \underbrace{(1-x)G_A^0 + xG_B^0}_{\text{Straight line}} + RT[(1-x)\ln(1-x) + x\ln x]$$

$$\boxed{dG=0}$$

If, x = fraction $\ln x = 1-x$ $\ln(1-x) = x$

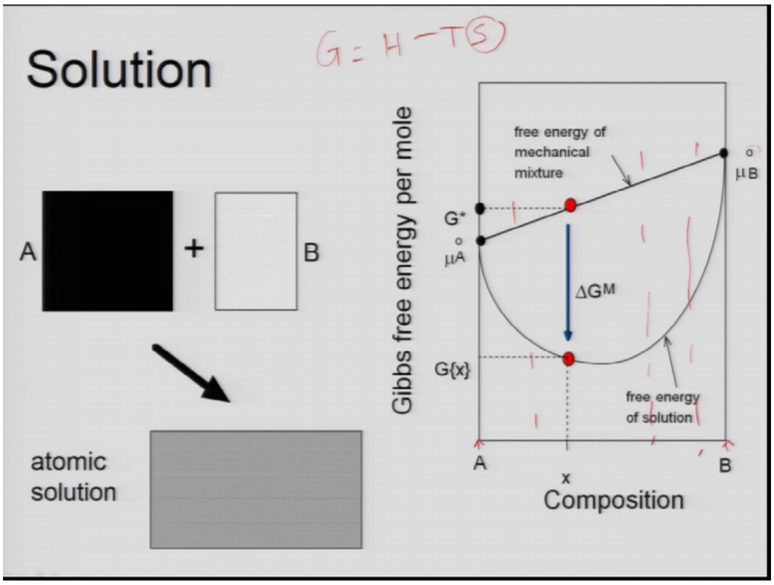
$$G_1^{ideal} \approx \underbrace{(1-x)G_A^0 + xG_B^0}_{\text{Straight line}} + RT\left[\underbrace{(1-x)x + (1-x)(1-x)}_{\text{Parabola}}\right]$$

Say at the end of steps 2 what I get G is equal to G 1, actually G plus R in to T 1 minus x log of 1 minus x plus x log of x. So, that is nothing but if I write completely this term, that is nothing but 1 minus x G A 0 plus, I am just plugging this value of G from the top equation x G B 0 plus R in to T 1 minus x log of 1 minus x plus x log of x. So, that is the free energy of ideal solid solution. That is why I write here G 1 ideal that is the free energy of the ideal solid solutions, if I mix 1 minus x mole fractions of A and x mole fractions of p. Now if you clearly see this is an equation of a straight line right, whatever the next part let see what happens to the next part. We know that if it is x is a fraction, where suppose if that is the case here then, log of x is nothing but x or 1 minus x rather not x that is what happens.

So, if I simply use that form that analogy So, then I could see here that that equation G 1 ideal can be written a straight line functions 1 minus x G A 0 plus x G B 0 plus R T. So, if I write down this so therefore, one my log of 1 minus x is nothing but x again. So, that is become 1 minus x multiplied by x so, let us write down this is almost equal to plus 1 minus x multiplied by 1 minus x. So, it is a very clearly this is straight line equation that I have written already and this is an equation of a parabola because we have one x squared term correct that is why.

So, that is why whenever we plot whenever we plot this free energy is there, here let us better we do that that is becomes an inverted parabola that is what you can see here.

(Refer Slide Time: 15:17)



Solution

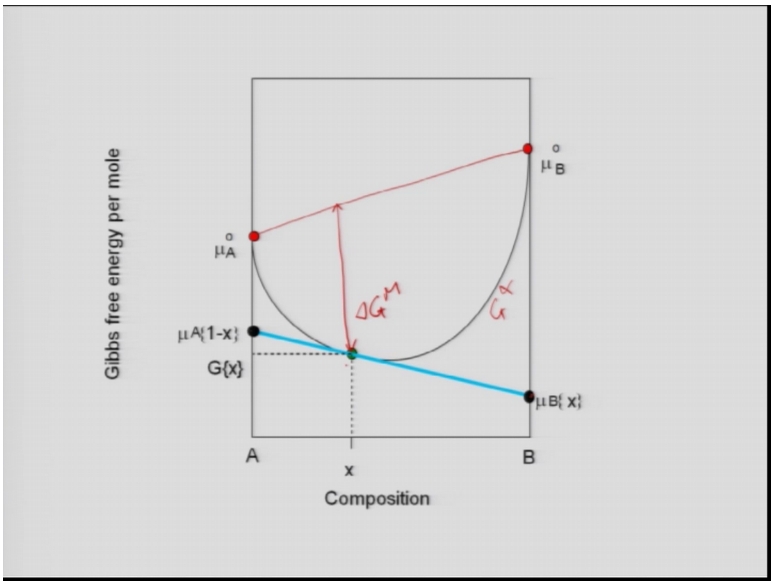
$G = H - T S$

This is inverted parabola and delta G this term here delta g, what I have written this term this is the term for the ideal solution delta G is because of entropy change is shown like that delta G m that is the delta G of mixing. Therefore, whatever you see in the books and the books whatever you see that the delta G mix or delta G m, we will see delta G small delta G either M superscript or m superscript that is basically, because of the atomic mixing and the top line top still line is basically the rule of mixture that is the step 1, the moment you put 2 atoms side by side they are mechanically mixed. And this mechanical mixing will lead to increase of change of free energy given by this straight line.

So, if you add them together you get the total free energy of the system that is what is shown on the y axis in this plot. See here twice then x axis is nothing but x. So, that is what the real meaning of this kind of curves. So that means, if I have any solutions any number of components, So that 2 or 3 or even more I can actually I will be able to calculate the free energy mixing for the ideal solution, but actual solutions are not ideal. So, we have to do something else that we will do in the next few lectures. How we can calculate delta H which we have missed here, which we have ignored here actually, which I have taken as a 0. We will see how it is to be done to calculate that we need to use some models and these models are already dealt in the books, but we will see how we can use is different models and modify delta H equations.

In fact, most of the thermodynamics of solid solutions or solution actually are based on different models to calculate delta H, delta S is calculated and given by this equation what I have derived, I have shown you just now. Only thing we are going to we are going to improve on is to calculate different parameters contributing to delta H, that is the that is the way things are done in the books. So, let us move on.

(Refer Slide Time: 17:39)

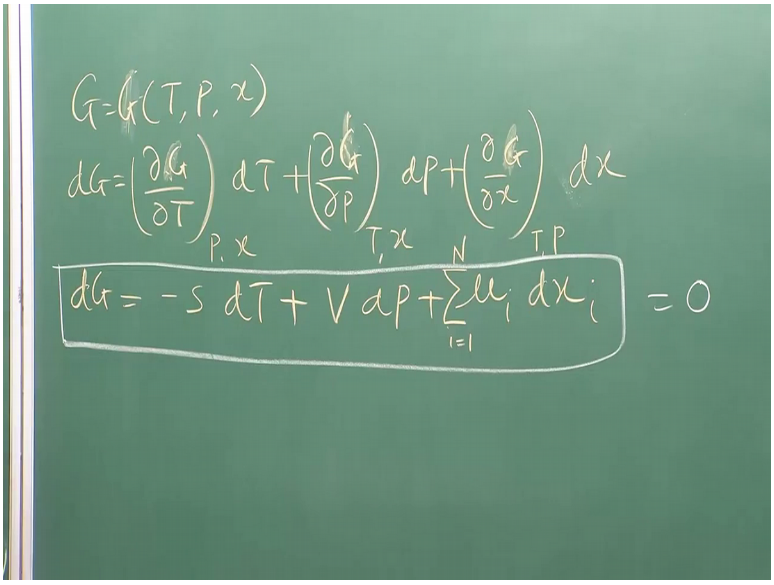


Now so, if I have a solid solution this is what I have shown you of alpha. Alpha is a Greek alphabet, we use alpha beta gamma delta in the phase diagram because they are easy to indicate solid solutions or liquid solutions whatever it is; but we use always pure components for these non solutions, like pure A b or pure A atoms. So, distinguish between these 2 is possible only by using Greek alphabets. So, here it is shown like this is a parabola. So, it is a parabola inverted and this line is missing here there is no need to drawing it again. So, at any composition x, the free energy change because of atomic mixing is given by this value correct.

The total free energy is given by we are drawing a dotted line these and marking as a G within capital within curly bracket x and as I mentioned we always try to use a symbol mu for the pure components, instead of G A 0 in the literature you will find mu, but there is nothing wrong if you use G A 0 also, G A 0 is also used. But conventionally rather you know across the world, the symbol which is primarily used to indicate they kept the free energy of a pure component is mu and mu a 0 is nothing but a free energy per mole of component pure A mu b 0 is free energy of component, pure B per mole only when you add them together free energy this will go change.

So therefore, the our basic condition that equilibrium conditions, is what equilibrium condition is I have already told equilibrium condition is always given by d G equal to 0, that is your minimum free energy conditions, the differential of G must be equal to 0. Now if I differentiate G in terms of what in terms of temperature in terms of x, because there are 2 variables and if you look at carefully even if I do not have some pressure to be constant, there will be 3 variables pressure. Will be also built in here within G A 0 or G B zero. So, therefore, G is a nothing but a function of 3 variables here.

(Refer Slide Time: 20:01)



$$G = G(T, P, x)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,x} dT + \left(\frac{\partial G}{\partial P}\right)_{T,x} dP + \left(\frac{\partial G}{\partial x}\right)_{T,P} dx$$

$$\boxed{dG = -S\,dT + V\,dP + \sum_{i=1}^{N} \mu_i\,dx_i} = 0$$

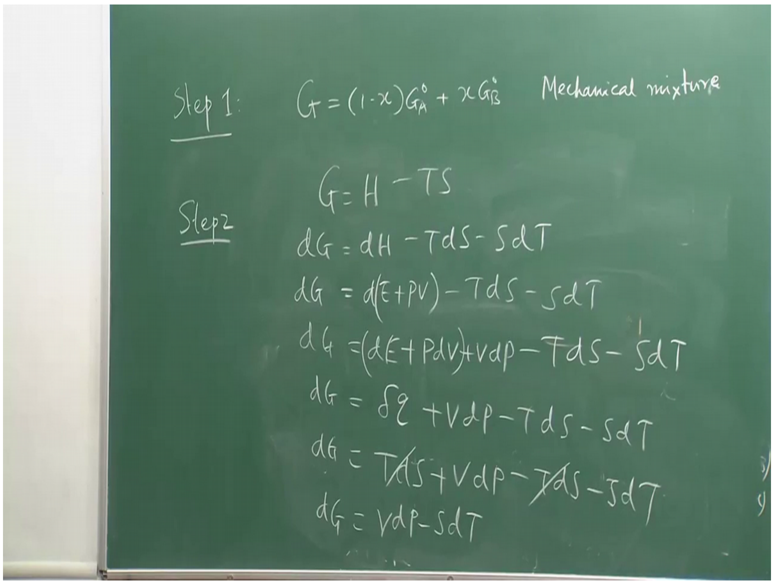
G is nothing but a function of temperature pressure and x am I clear, that is what is the complete analogy picture of the free energy of any solid solution, that free energy is a function of temperature is very clear composition also is very clear as well as it will be pressure composition of pressure of fractional pressure. So that means, if I take a total differential d G that is nothing but d f d T at a constant pressure and composition multiplied by d T plus d f this is del not d sorry del f del p at a constant temperature and composition d p plus del f by del x at a constant temperature and pressure multiplied by d x. This is a mathematically correct equation total differential is nothing but partial differential multiplied by these differentials added together.

Now we know that this is nothing but minus s, this better actually we write G that is then it is become easier to understand otherwise it will be confusing better. So, these del G by del T at constant pressure we know that that is equal to minus s, even if you do not know I will just write how it is done plus this one is nothing but volume multiplied by d p what about this term is what is known as chemical potential. That is what we have been discussing, this is known as mu of any components multiplied by T x that is what we write so; that means, total change of free energy is equal to this.

Now, if I have many components I write this is the way, summation I equal to 1 to n mu I d x I. Suppose you have 3 component solid solutions, then you will write mu 1 d x 1 mu b plus mu 2 d x 2 mu 3 d x 3, that summation is what is taking care of atomic mixing atomic mixing part is coming from these summations.

Well, as I told you may have problem in understanding these how do I consider this parts that is very easy to understand. Let me just explain to you, you will realize very soon, how it is obtained we know that G is fundamentally given by H minus T s.

(Refer Slide Time: 22:53)



Step 1: $G = (1-x)G_A^0 + xG_B^0$ Mechanical mixture

Step2: $G = H - TS$

$dG = dH - TdS - SdT$

$dG = d(E+PV) - TdS - SdT$

$dG = (dE + PdV) + Vdp - TdS - SdT$

$dG = \delta q + Vdp - Tds - SdT$

$dG = \cancel{TdS} + Vdp - \cancel{TdS} - SdT$

$dG = Vdp - SdT$

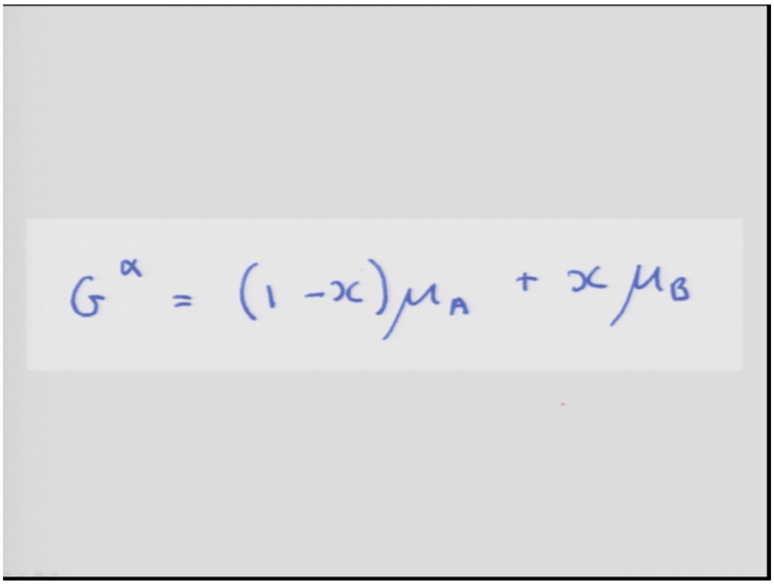
So, total differential is nothing but T H minus T d s minus s d T remember this is total differential this is not partial. So, I can modify this equation based on first and second law of thermodynamics, this is what del H is always equal to d e because d e plus p v H is e plus p v minus T d s minus s d T. So, I can write down d e plus p d v plus v d p, that is equal to total differential of that the moment d e, put that d e is meaning that is total differential.

Therefore, it has to be differentiated through and through now we know that d e plus p d v as per first law of thermodynamics is equal to del q and this del is different from these d e because, this del tells you that it is a path dependent function, but this is not a path dependent function. So, this is because work done is a path dependent function that is why del q; so v d p minus T d s minus s d T that is what you get. Now, we know that as per second law of thermodynamics del q is nothing but T d s, why it is because second law thermodynamics tells you the definition of entropy and d s is nothing but del q divided by t.

So, if you do that carefully T d s T d s get cancelled. Therefore, you get v d p minus s d t. So, therefore, if I take a simple differential, del G by del p is equal to volume there you can see at del G by del T is equal to minus of entropy. So, that is what we use. So, therefore, for a solid solution or a liquid solution this is the fundamental equation of the free energy change. Now I like to hence I like to ask myself a questions that, if I have to know the stability condition for solid solutions, then I must put in that equation this should be equal to 0. So, how do I solve this equation then that is why we face problems, all of us face problems in solving the equations? We do not solve it we are very clever persons, what we do we simply put a tangent rule to the curve and tangent rule helps us things very easily.

So, if I make a tangent across the sorry at a particular point on this curve, that is tells me the chemical potentials of these 2 components, when where this straight line meets the pure A and pure B particle excesses. So, that is why it is written mu a within curly bracket 1 minus x mu b within curly bracket x; that means, the chemical potential of b in the solution having x mole fractions of B, chemical potential of a in a solution having x 1 minus x mole fractions of A. So, that is how do I arrive, I will explain in another class. How do I get how do I use the tangent rules that is required separate discussions, we will do that slowly one by one and thus this straight line as equations is given by this is nothing.

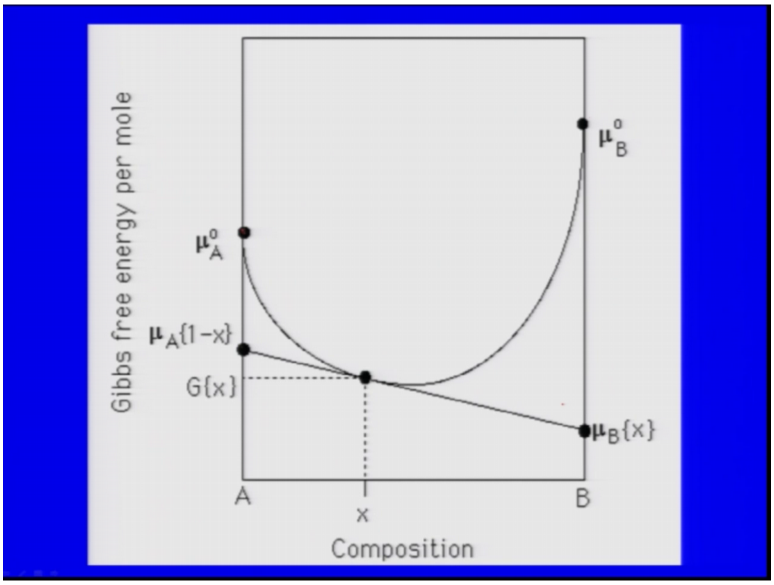
(Refer Slide Time: 26:42)



$$G^{\alpha} = (1-x)\mu_A + x\mu_B$$

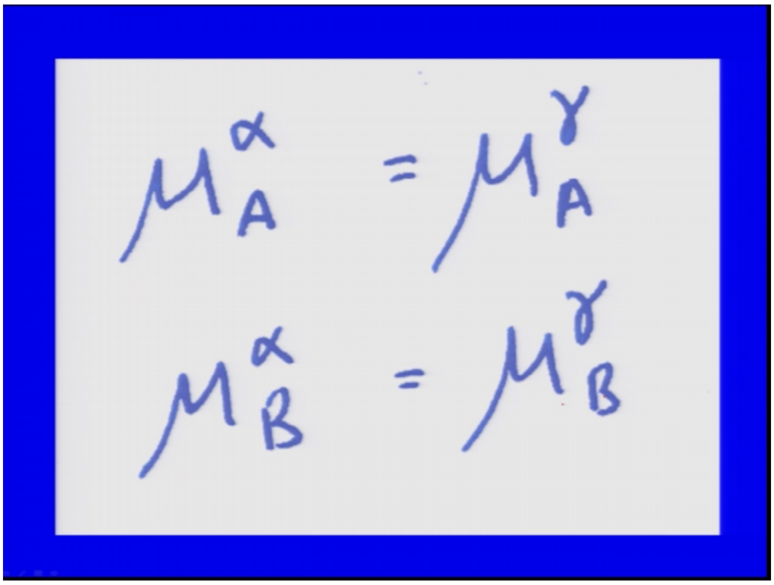
But 1 minus x mu a plus x mu b that is what is the equation of these tangent at a point x.

(Refer Slide Time: 26:48)



Now, again we shown in this curve we discussed. So, how do I consider stability the stability is considered by using Gibbs rules and they are given by mu a in the phase alpha must be equal to mu a in a phase b gamma.

(Refer Slide Time: 27:09)

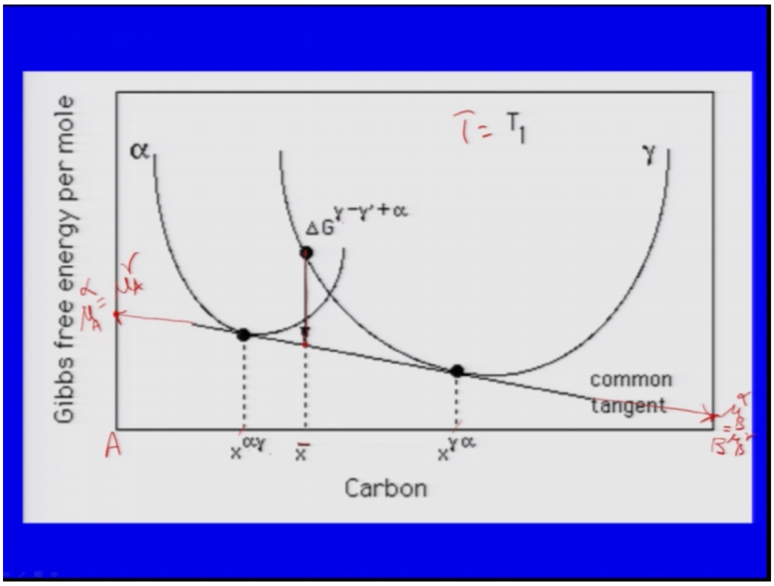


$$\mu_A^{\alpha} = \mu_A^{\gamma}$$

$$\mu_B^{\alpha} = \mu_B^{\gamma}$$

Similarly, mu b in alpha must be equal to mu b in gamma, where mu a are the chemical potentials of a mu b are chemical potentials of b correct.

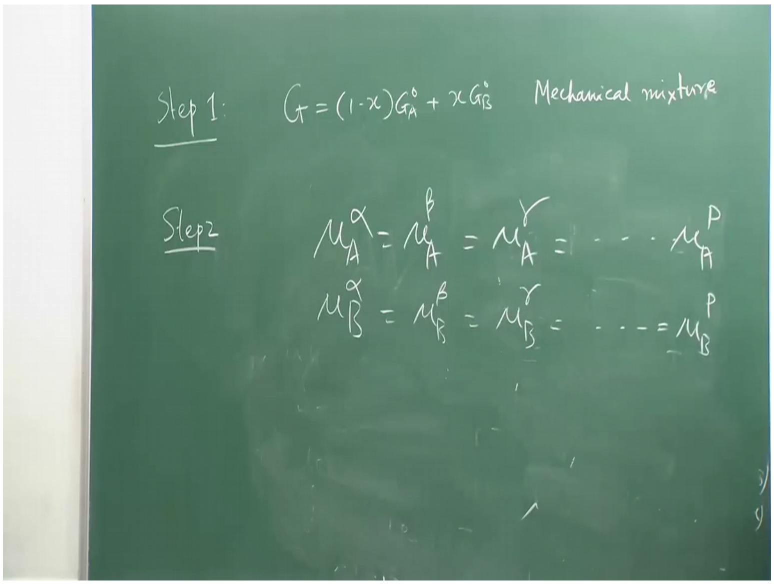
(Refer Slide Time: 27:17)



So, graphically how do I do it, draw a common tangent instead of a tangent. Suppose this is the free energy of alpha, this is a free energy of beta gamma at a temperature T equal to T one and so I draw a common tangent between them and that common tangent will tell me the stability conditions. So, the stability conditions is obtained easily by extending these 2 line, this tangent to the both the particle axis. So, therefore, they will meet at mu or the vertical axis x. So, this point is given by mu a alpha because there is a tangent to alpha, that is why similarly tangent to gamma.

Therefore, this is also be equal to mu a gamma and they are hitting they are sitting on the same point therefore, their values are equal similarly on the right axis this mu b alpha equal to mu b gamma. So, if any system it does not matter, it is suppose it is a very complex system you have many components and many phases you simply write the condition like this ok.

(Refer Slide Time: 28:11)



Step 1: $G = (1-x)G_A^0 + xG_B^0$ Mechanical mixture

Step2 $\mu_A^\alpha = \mu_A^\beta = \mu_A^\gamma = \cdots \mu_A^P$

$\mu_B^\alpha = \mu_B^\beta = \mu_B^\gamma = \cdots = \mu_B^P$

So, that must be satisfied, similarly if I have another component b again same thing, it does not matter how many components are present. So, I can simply write this equation.

So, this actually gives me in multi component systems, where solid solutions are presents or even phases are presents different phases are presents. So, alpha to p these are actually all condition to be satisfied, the chemical potential at the interface between the phases must be equal of a particular component. So, does not matter whether it is a this condition is very general, it does not matter whether it is a biomaterial nonmaterial instruction material micro material whatever it is, but this is a fundamental condition this must be satisfied, chemical potential must be satisfied.

Now, I should stop here and discuss in more detail; I will describe; what is the actual mathematical formula of mu, basically we know that mu is specific. Say is a particular functions how it is dependent on we will discuss in details in the next lecture.