Phase Diagrams in Material Science Engineering

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Lecture – 02
Heterogeneous equilibrium and Free energy Formalism

So, we will move on. As I have told you in the first lecture there are phases - equilibrium and phase diagrams. But to understand this phase diagram we need to have basic knowledge of thermodynamics, because thermodynamics is a very basic thing for many of the engineering branches. So, material science is not exception to that.

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Welcome to another glorious day of phase equilibria!!.

Just let me just tell you a very nice cartoon which I found, this is very nice picture two sills are moving in ice water mixture in north pole. As you see here the first sill is telling; the second one is telling the first one - hey, speed up in front otherwise we are going to miss the class.

The second guy is little bit of more engrossed in the atmosphere he says - I know, I know. But I am trying to figure out how we can describe these two phases, one component system in terms of measurable parameters. This guy is telling what a geek you are, you already in to science, already in to phase diagrams. So, that is what I say welcome to another glorious day of phase diagrams and phase equilibria.

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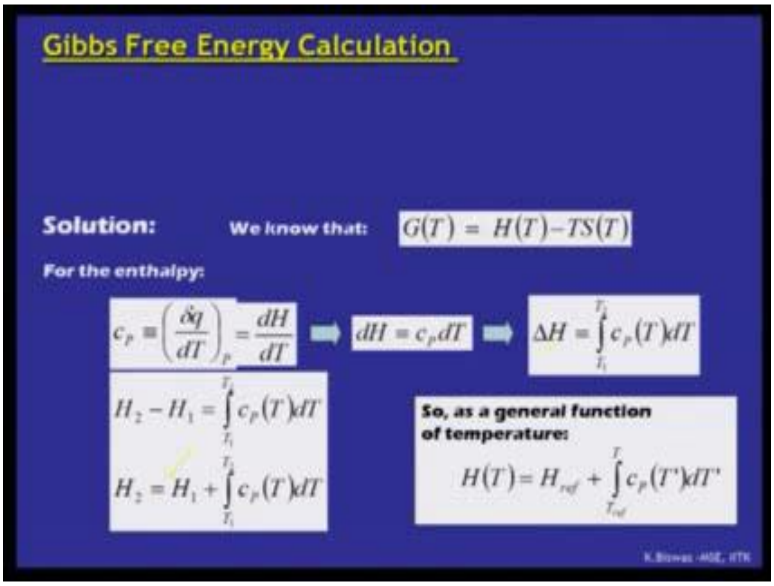

Gibbs Free Energy Calculation

Solution: **We know that:** $G(T) = H(T) - TS(T)$

For the enthalpy:

$$c_p = \left(\frac{\delta q}{dT}\right)_p = \frac{dH}{dT} \Rightarrow dH = c_p dT \Rightarrow \Delta H = \int_{T_1}^{T_2} c_p(T)dT$$

$$H_2 - H_1 = \int_{T_1}^{T_2} c_p(T)dT$$

$$H_2 = H_1 + \int_{T_1}^{T_2} c_p(T)dT$$

So, as a general function of temperature:

$$H(T) = H_{ref} + \int_{T_{ref}}^{T} c_p(T')dT'$$

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So, before I discuss let me just tell you in material science thermodynamical description is basically based on Gibbs free energy, and we know that Gibbs free energy is given by G, capital G by the names of Gibbs - he was a fascinating scientist and G is defined like this, G is a function of temperature is equal to H is a function of temperature minus T into S is a function of temperature.

What is H? H is nothing but enthalpy. Enthalpy is nothing but heat contains some people say, what is heat contained? Well we know that the most important factor or parameter rather not factor in thermodynamics which is known as heat capacity. So, if you look at any thermodynamics books even one of this book which I referred in first class you will see that C p is the prominent parameter determining almost all thermo dynamical parameters like free energy, enthalpy, entropy, everything. So, C p is defined as a del q by del T as a constant pressure there is another heat capacity also at constant volume C p, but in metallurgy and material science use C p. So, enthalpy can be written like this at constant pressure d H by d T is equal to C p.

So, therefore, you can actually simply integrate it like this way what I have written d H is equal to C p d T. So, therefore, delta H is equal to integral C p d T from temperature T 1 to T 2. Very simple and we can do this little expansion of delta H, delta H can be expanded and written like this H 2 minus H 1. So, therefore, H 2 is nothing but H 1 plus integration C p d T, so that means, it boils down that enthalpy can be easily calculated by knowing the C p of any material C p of iron, C p of any phase. If I know I can calculate easily the enthalpy.

So, now what is H T, H T is well this is the general formulation if I go to H T. H T is nothing but either reference plus T reference is at a value of suppose certain temperatures which is that 25 degree Celsius and normal pressure.

So, now, what is the Entropy?

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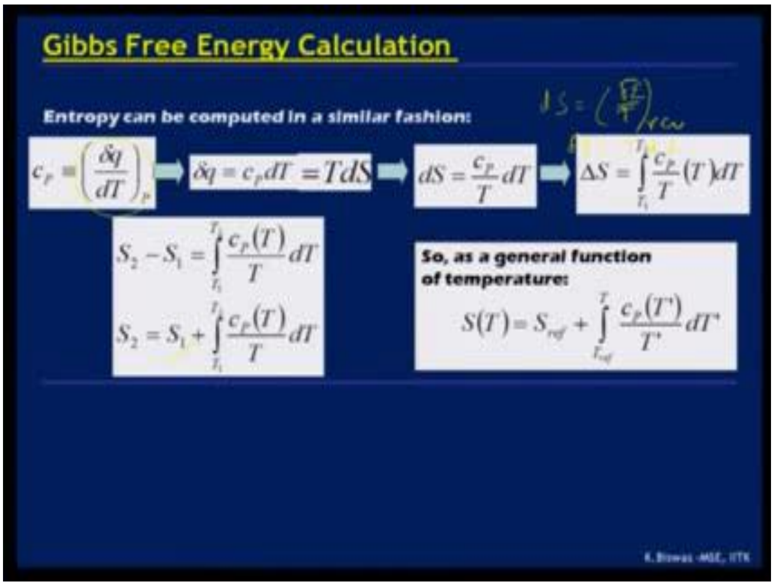

Gibbs Free Energy Calculation

Entropy can be computed in a similar fashion:

$dS = \left(\frac{\delta q}{T}\right)_{rev}$

$$c_p = \left(\frac{\delta q}{dT}\right)_p \Rightarrow \delta q = c_p dT = TdS \Rightarrow dS = \frac{c_p}{T} dT \Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{c_p}{T}(T) dT$$

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{c_p(T)}{T} dT$$

$$S_2 = S_1 + \int_{T_1}^{T_2} \frac{c_p(T)}{T} dT$$

So, as a general function of temperature:

$$S(T) = S_{ref} + \int_{T_{ref}}^{T} \frac{c_p(T')}{T'} dT'$$

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Entropy is the thermo dynamical parameter, I will discuss in detail what is its meaning, but let me just tell you what is the mathematical term. Again I can write down C p equation, C p is equal to del q by del T as you see here C p is equal to del q by del T at a constant pressure. So, therefore, I can write down del q is C p d T, also second law third law tells me that d S is equal to del q by d T. So, therefore, d q is nothing but T dS. I can write down this also here. For second law thermo dynamical (Refer Time: 04:38) dS equal to del q by T reversible. So, therefore, I can write down del q is equal to T dS del q is nothing but T dS that is what I have done here. So, we can clearly see I can get it like this the d S is equal to C p by T d T.

So, if I integrate it I can simply get delta S is equal to C p by T d T integral of T one to T two. So, that is why we can easily get entropy. So, S 2 equal to S 1 plus this integral C p by T d T. So, by this we can simply calculate both the enthalpy and entropy of any system or any phase rather by using this formalism, provided you know the C p values. C p is the most critical intrinsic parameter used in the thermodynamics and in the similar way S T can be written as S reference plus T, T reference to T will see normalize reference is the given by the forth law of thermodynamics that is what the entropy of a pure component at the absolute zero is 0, that is why actually we can actually get entropy. But remember in thermal dynamics you never ever used absolute values of enthalpy entropy. We always use relative pairs of enthalpy entropy that is what is delta G.

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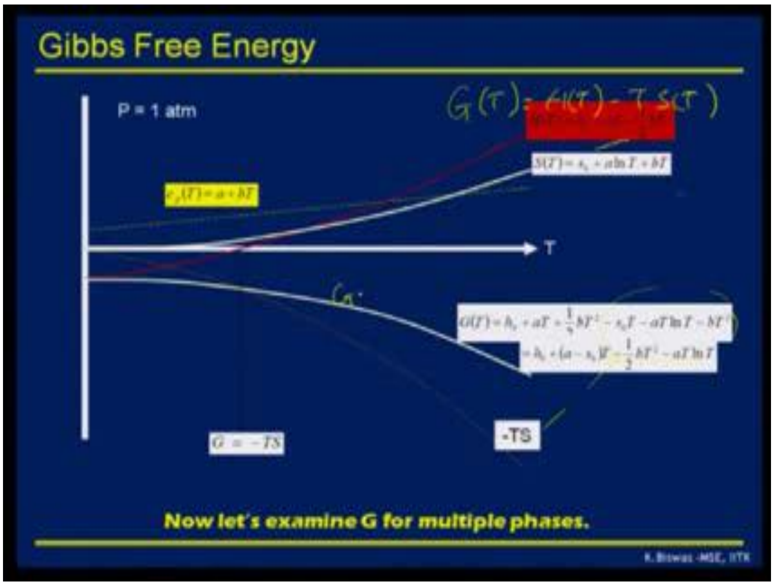
Gibbs Free Energy

Now let's examine G for multiple phases.

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So, therefore, G is as a function of temperature is nothing but H is a function of temperature minus T S T; that is what I have here. And I told you that H is nothing but C p T 1 to T 2 dT with plus H reference. So, nearly this one T minus I can write down S reference plus T 1 to T 2 C p by T d T, right. So, simply very easily I can calculate this. Now let me just erase this part because this requires me to use for the diagram. So, I erase by keep only the G equation there.

So, what you can see here I plot G as a function of temperature as a constant atmospheric pressure because most of the metallurgy system has actually constant. Let us suppose C p is given by a simple function a plus b T, remember I am just doing mathematical expressions. C p is given by simple function a plus b T, a is a constant, b is a constant so that means; C p is linearly a little bit temperature. So, if I do that I can actually create this curve which is nothing enthalpy like this, enthalpy this one you can clearly see. If you integrate that aT plus half b T square plus 80 is nothing but H reference. So, now, simply I can do the enthalpy, enthalpy will be again a log T plus b T plus H 0 is a H reference term. So, by that I can calculate now minus T S, minus T S should be like this because if you multiplied by minus T this will be negative.

So, what is G then? G is nothing but H plus a T plus half b T square minus H 0 T minus at log T minus b T square you multiply by T s, so T S is this term TS is completely this term. So, G is this. Now how it is look like? How it is look like this, this is this curve this is G. So, you can clearly see that I can get graphical representation of G as a function of temperature at a constant pressure. We will also (Refer Time: 08:35), but that I show you later not now. So, therefore, it is clear to you that we can calculate the most thermodynamic important function called Gibbs free energy, any material science system very easily, using this simple mathematical formulation. Those of you who were not this got a idea very well you can refer to this books and understand it very clearly how actually a free energy things comes in the thermodynamics of phase diagrams and how it can be deal to it with. But I have given you fair idea about how to calculate and now to use it.

Now, let us look at the examine the G for multiple phases because finally, we are going to deal with multiple phases like ice in water or you are going to discuss like you know soap bubble or you are going to discuss kerosene in water mixture or you are going to discuss steels with the complex micro structure, right. So, let us do that.

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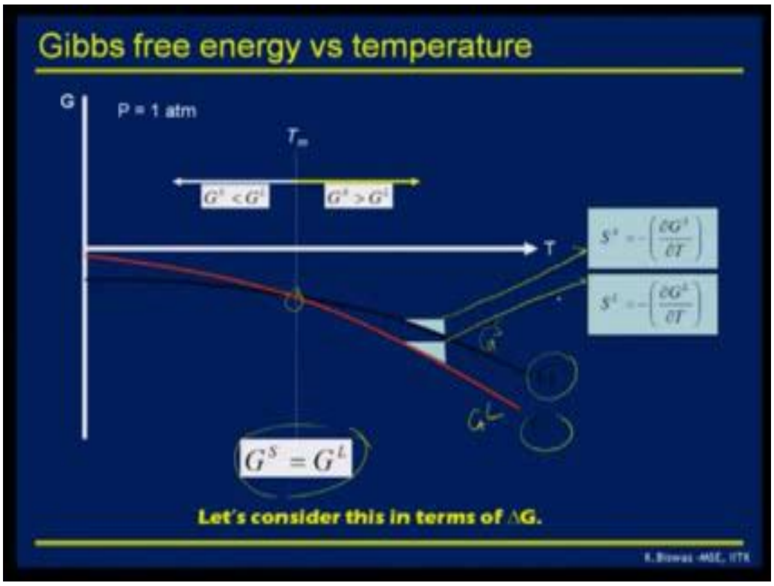

Gibbs free energy vs temperature

$G^S = G^L$

Let's consider this in terms of ΔG.

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Now, I will plot here again G versus temperature, you can see temperature in G, temperature x axis G is in y axis that are one atmospheric pressure. So, this is what the black curve is basically tells you - G for one phase because G will look like this a function of temperature I have shown you earlier, sloping down curve, G for another phase. So, this is one is known as G solid, but the black curve is for G solid I write again G solid and the pink curve is called gene liquid and They are actually making a cross over here. You can clearly see this is a cross over and you know at this cross over the free energies of both the phases are equal - solid and liquid.

Suppose water and ice, ice is solid, water is liquid. So, this is the free energy of both of them will (Refer Time: 10:25) temperature like this. So, this is the cross over point here that corresponds to dopants between free energies. The free energy of both the solid liquid are equal, what is that called? That is what I have written free energy of solid liquid equal that is what is the melting temperature of ice or freezing temperature of water that is nothing but 0 degree Celsius. So obviously, below this zero degree Celsius or below the melting temperature of any component solid has a lower free energy then the liquid and this is the why the solid is more stable, ice is more stable then water at temperature less than 0 degree Celsius because is free energy is lower than that.

So, therefore, this is more stable therefore, this is the more equilibrium or equilibrium phase, this energy is minimum. Now the other side what happens? G S is more than liquid G liquid, so that means, a temperature higher than this temperature solid will not be stable, the solid is higher energy than liquid - liquid will be stable. So, that is why if you heat ice above 0 degree Celsius temperature ice will melt to water. So, you can clearly see how nicely thermodynamics can describe all kinds of phases and Transformation that is the beauty of thermodynamics.

So, now one you can actually do many things, the slope of this curve is what? Slope of this curve is nothing but entropy. So, both of them can be written like this. So, I have written this one, slope of solid curve and slope of liquid curves like this. They are actually entropies - entropy of solid entropy of liquid. So, let us consider because G is an absolute thing let us consider the in terms of delta G, this is much easy to understand much easy to do mathematical basically.

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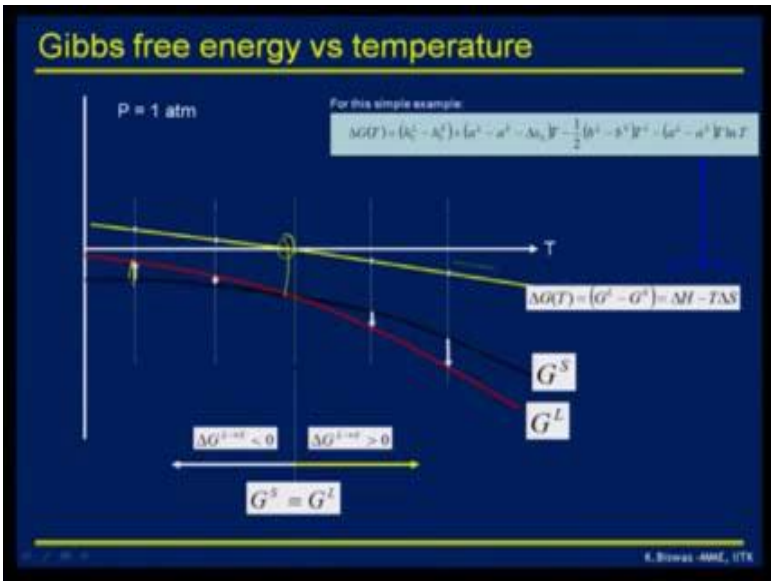

Gibbs free energy vs temperature

For this simple example:

So, what you can do? We can do a same thing what I have done, I have borrowed this curves again from the last slide again free energy versus temperature G is and G l and delta G is; then this one as you clearly see delta G is difference between the solid and liquid free energies. So, delta G is 0 at a melting temperature at 0 degree Celsius ice water there is no difference of free energy between ice and water. Then, as you go on beside you can see here is increasing - this left side also it is increasing.

So, see here I marked it like this refines with the (Refer Time: 12:59) or white arrow I get the point I get another point, I get another point; on the right side I get a points like this, so I can calculate G. So, what is the basic message you get from this? Why do you have use delta G versus temperature? It is a delta G versus temperature plot, why it is more in convenient? Because at temperature less than this equilibrium melting temperature delta G is less than 0, but above that sorry above that delta G is more than 0. What us it that mean? That means, that for liquid To solid Transformation per liquid in water to ice transformation delta G less than 0 below melting temperature that means, that liquid will easily solidify to solid; that means, water easily freeze to ice at temperature less than this. But on the other hand, if the temperature higher than 0 degree Celsius for ice water mixture, delta G is greater than 0.

So, the message is this delta G tells you the spontaneity of the process, whether a process will happen spontaneously or not depends on the sign of delta G. The sign of the delta G is negative for a particular process then this process is spontaneous and will take place. The sign of delta G is positive process is not allowed thermodynamics calls this way whether a phase transformation of a particular thing will happen or not this is what the thermodynamic way of dealing with. So, that is why from G, I have gone moved in to delta G because delta G is easy to handle, and you know how delta G is given? Delta G is given by this equation, you can see here eight zeros are your reference terms minus a l aS al's is a for liquid, a S is a for solid minus delta this zero, then temperature minus b terms temperature square half divide by 2 and then log term comes T log T. So, by knowing all this a b c or rather not c a and b and delta a H 0 and H 0 and your HS H 0 L and H 0 S we can calculate delta G. So, that is very easy to do, very simple.

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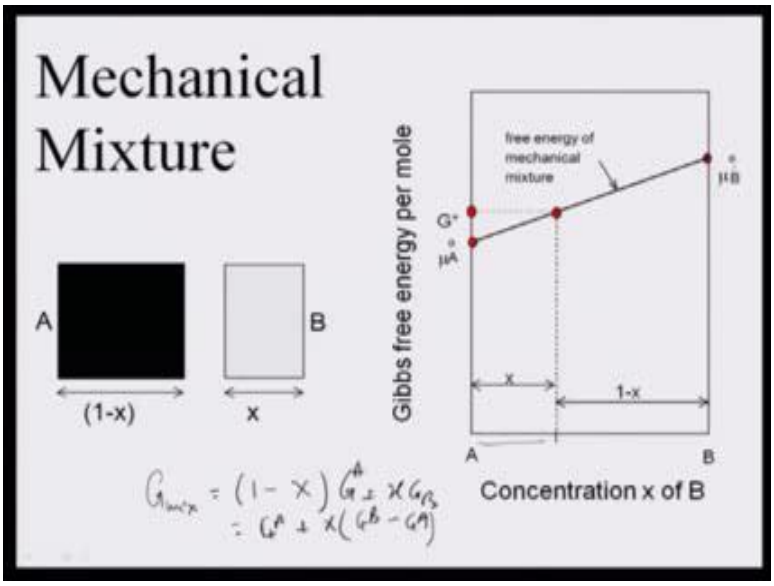

Mechanical Mixture

$$G_{mix} = (1-x)G^A + xG_B$$
$$= G^A + x(G^B - G^A)$$

Well now, I will just tell you what is the different between a mechanical mixture and a chemically homogeneous mixture. Like if I put sand and salt together it is a mechanical mixture, they do not mix each other. But if I put salt in water completely get mixed together, let us let me just explain it. Suppose I am there only I can bring about the basic concentration terms very easily, till now we are discussing about all the temperature, G as a function of temperature, G as a function of temperature constant pressure that is what we discussed.

Let us now discuss a function of composition. So, suppose I have a and b, let us assume a is sand I say a is salt and b is water. So, I have x as the fraction of water and 1 minus x is a fraction of salt, I put them together - if they are not mixing together they are mechanically mixture like they are not mixing together means they are not getting inter mixed, I will get free energy versus concentration of x, this is x like this line, because this is nothing but what? G is nothing but of (Refer Time: 16:34) let me check this thing black. G is of the mixture is what? This is nothing but 1 minus x G of a plus x G of b and this is the straight line equation, clearly see that. How it is? 1 G a plus x G b minus G a, that is what, this is x this is a straight line equation and I have plotted that. Now forget about these term mu A 0 mu B 0 and you can clearly see free energy of this composition which is 1 minus x and x is given by this point, because this is 1 minus x, this is x very simple; got it.

Now, these are the points which is (Refer Time: 17:28) mu A 0 and mu B 0 which I will discuss in future slides.

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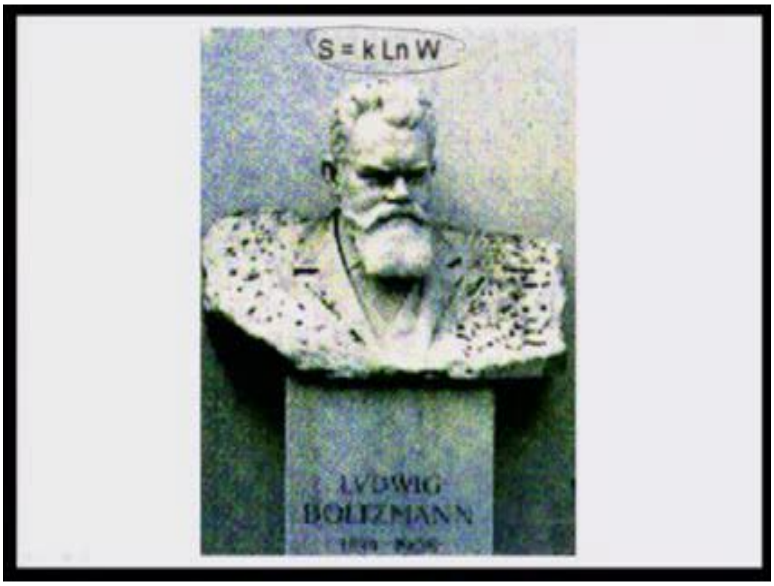

You know, before I go back into free energy terms I just want to tell you entropy which is a very important thing in this description was first time discovered by Boltzmann, all of you should know that. And in Boltzmann tombstone this equation is written, you see here S k l n W very important equation because he only draw a first time described this equation and gave us a new path. But unfortunately nobody believed him in those days. So, he has to commit suicide or rather he committed suicide, and this is a very fascinating story that how such a brilliant person was very good in those days for a one equation and he did not have any choice.

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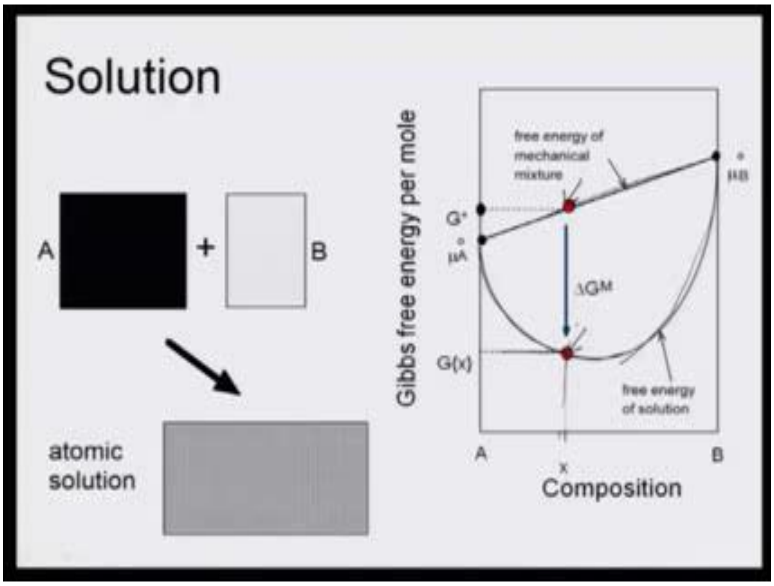

Solution

So, now, if I take a solution instead of mechanical mixture, in a mechanical mixture free energy is a system is nothing but a linear relationship as a function of composition. But suppose if I take a solution like I told you salt and water that is why I have taken the example - salt and water, a is salt b is water and I put it together they will mix nicely. You know that the atomically mixing is possible, for that the free energy will be given by this curve - the one edge were draw like this, not the straight line; why? Because of Boltzmann, that I am going to discuss now, Boltzmann only gave this equation that is why it is possible.

So, like physical mixture this is what is straight line will give for a alloy or for a solution that this will be the free energy curve. Free energy will be like a imparted parabola and for any composition free energy it can be given. So, what you understand from this picture before actually I tell you why this shape is like this, is that if I have physical mixture of free energy is given by this red thing and if I may a alloy of same composition it will be given by this one.

So, basically the energy of the alloy free energy of the alloy is to lower than the free energy of physical mixture that is why if I add salt in to water it has to mix because the energy will be lower. Instead of if they are keeping, remaining separate energy will be higher. So, better the salt get mixed into water that is why salt easily gets mixed in water, sugar easily gets into mixed in water, coffee easily gets mixed into the milk that is the reason because solution in energy of solution is lower than the (Refer Time: 19:58) of the physical mixture. And difference is quite large you see delta G means it is difference is very large.

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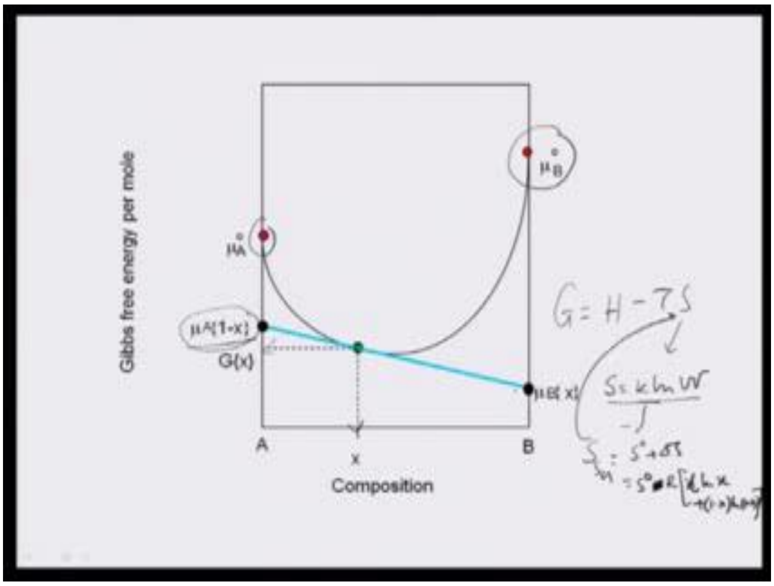

So, now why do you get that? This is mainly because G is nothing but H minus T S and S (Refer Time: 20:15) that is what it brings down the free energy curve. What is S? S is a entropy, and as Boltzmann has given S is nothing but k l n W and those of you who know (Refer Time: 20:27) little bit of this one basically this term for the solution can be written like this, solution it will be S of solution is equal to S 0 plus delta S 0 plus delta S is nothing but R; this is minus sorry R x ln x plus 1 minus x ln 1 minus x. This any under graduate book will give you this expression; this expression can be easily obtained from this Boltzmann's equation.

So, therefore, if I plug-in this S there and we know enthalpy, enthalpy can be calculated by using C p values. So, we will get a expression like this. Even if enthalpy is very not depended on much depended on composition still you will get this equation because x ln x or 1 minus x ln x, 1 minus x is nothing but a equation of a parabola and you get a negative parabola because this is a negative sign. That is why you get is this. Now G of at any composition is given by this where x is this, is easily obtainable and here mu A 0, mu A 0 and mu B 0 are the few energies at pure component like pure A will as a free energy of mu 0 pure B have a free energy of mu 0, that is why these are actually called as mu, mu terms. In fact, you can easily draw a straight line tangent, not a straight line tangent at this point and get the free energy or a mu at this point A and at pure B like this.

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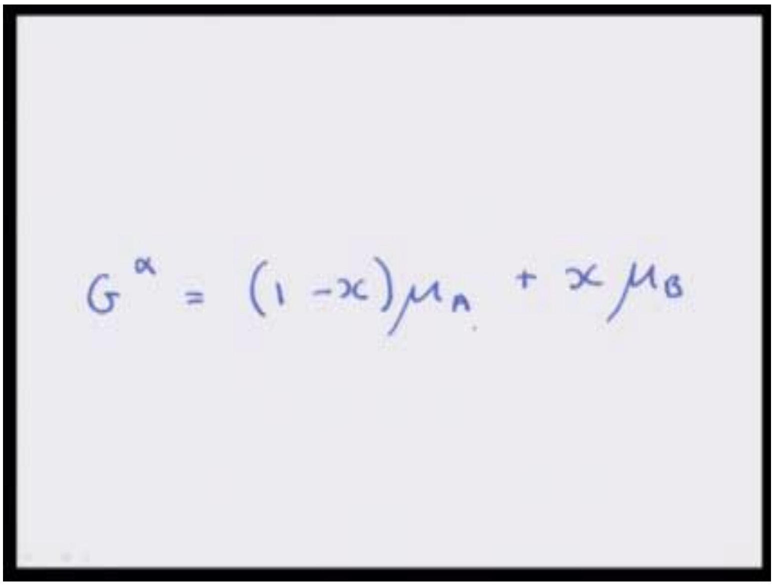

$$G^{\alpha} = (1-x)\mu_A + x\mu_B$$

So, therefore, G is nothing but 1 minus x mu A and x mu B clearly you can see, why? Because this is straight line, now straight line has this part and this part, summation of that is nothing but a free energy of x; that is why. So, this is what is known as tangent to curve rule.

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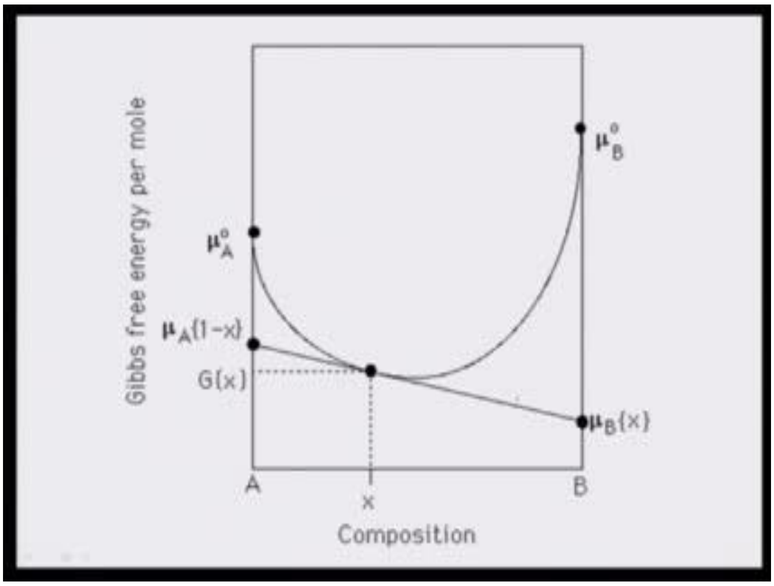

We will move forward further how to use this concept in next class. So, let me just tell you that G is as a function of temperature and as a function of composition I have described you and told you in this lecture. You should refresh your minds and by using literature internet or books and we will go forward for the further.