Diffusion in Multicomponent Solids
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Lecture - 09
Gibbs Free Energy - Composition Curves, Phase Diagrams and Gibbs Phase Rule

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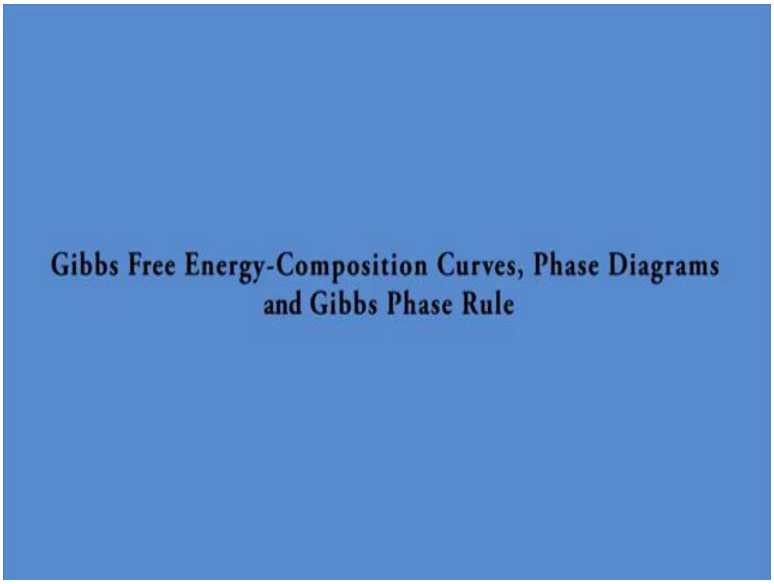

Welcome to the ninth lecture of open course on Diffusion in Multicomponent Solids. In this lecture, we will see how Gibbs free energy composition diagrams help in determining phase stability and phase diagrams. We will alsee how the constraints are imposed on the degrees of freedom based on Gibbs phase rule.

So, in last class we went over the regular solution and ideal solution models for determining the Gibbs free energy of mixing, that is the change in Gibbs free energy when we form a solution of two components.

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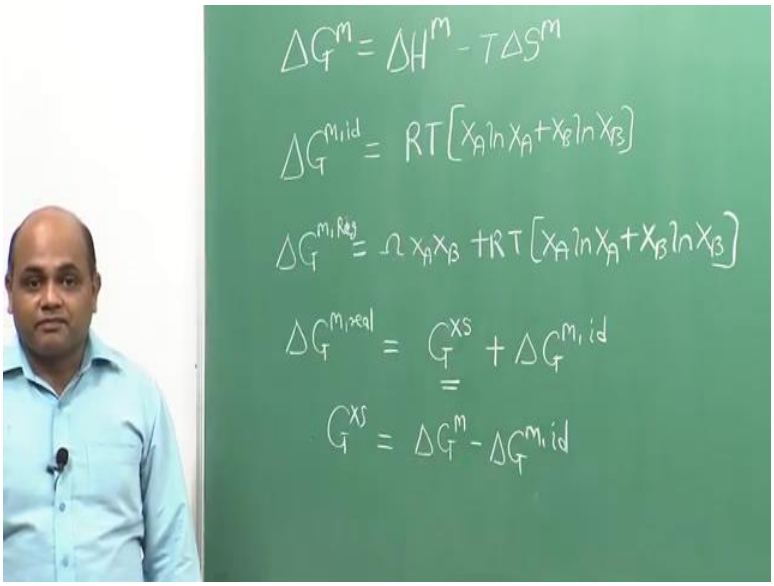

in general molar Gibbs free energy of ΔG^m can be expressed as:

$$\Delta G^m = \Delta H^m - T\Delta S^m$$

ΔH^m is the enthalpy of mixing minus temperature times ΔS^m where ΔS^m is the entropy of mixing. For ideal solution, enthalpy of mixing is 0 and for entropy of mixing, the entire contribution comes from the change in configurational entropy. $\Delta G^{m,id}$ is expressed as:

$$\Delta G^{m,id} = RT(X_A ln X_A + X_B ln X_B)$$

and for regular solution $\Delta H^m = \Omega X \ \ X_B$, so:

$$\Delta G^{m,\ Reg} = \Omega X \ \ X_B + RT(X_A ln\ X_A + X_B ln\ X_A)$$

For regular solution we assume that the entropy of mixing is only because of the change in configurational entropy and we assume random mixing. The entropy of mixing for regular solution is same as ideal entropy of mixing, but in reality if ΔH^m is not 0 then as I mentioned in the last class there will be a tendency for short-range order and whenever there is a short-range order, the entropy of mixing will not be equal to the ideal entropy of mixing, because then the mixing is not random.

So, in real solutions the way the Gibbs free energy of mixing is modeled is that we define a quantity called molar excess Gibbs free energy. The molar excess Gibbs free energy G^{XS} is nothing but difference in the Gibbs free energy of mixing of a solution and its Gibbs energy of mixing if the solution was ideal. G^{XS} is:

$$G^{XS} = \Delta G^{m} - \Delta G^{m,id}$$

In what respect the real solution is different from ideal solution? First, it has a non-zero enthalpy of mixing, and second the mixing is not random.

G^{XS} has two contribution, one is from the enthalpy of mixing and the second one is from the non-ideal part of entropy of mixing. There are various models using which G^{XS} can be modeled and then we can also determine the model for the real solutions. we will not go in details of that. Now, we are interested in understanding the stability of solutions.

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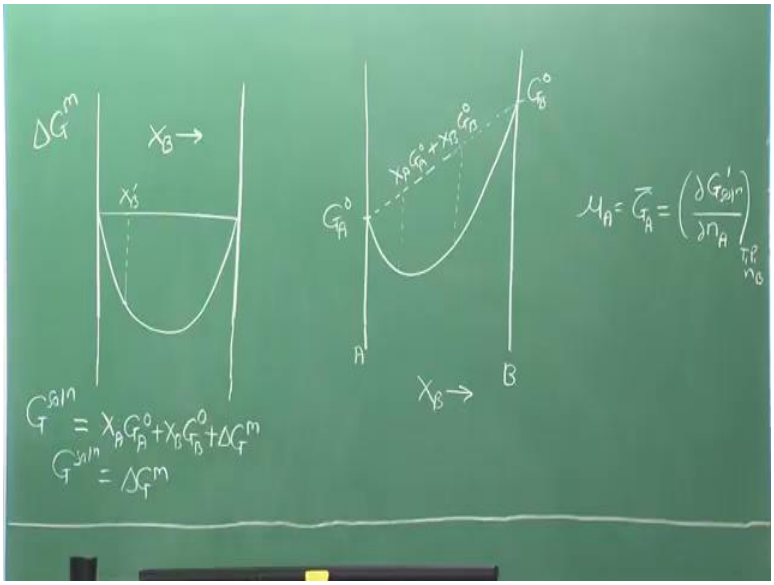

If we draw this ΔG^m versus composition curve and if the enthalpy of mixing is non-zero but has a very small magnitude then we have seen in the last class the Gibbs free energy of mixing will still be negative at all compositions and if you draw the curve of ΔG^m versus composition expressed in terms of X_B or mole fractions of B it will take a shape something like this.

Now, I have drawn this curve to be symmetric, because I am assuming constant value of Ω, but this Ω may change as a function of composition in which case, the curve will not be symmetric. But for simplicity let us just work with the symmetric curves of ΔG^m versus X_B.

Now what does this mean? That at any composition if I form a solution consider X_B Prime, if I take two components with this composition XB Prime and XA Prime and from a solution there will be a decrease in Gibbs free energy and the forming the solution will be an irreversible reaction and we see that the solution will be stable at all composition. Now this is delta G M versus XB, what about the absolute Gibbs free energy of solution?

If we draw absolute Gibbs free energy versus X_B curve, how would it look like? G^{Sol} will be basically the total Gibbs free energy of the system before mixing plus the ΔG^m. The total Gibbs free energy before mixing will be $X_A G_A^o + X_B G_B^o$. So:

$$G^{Sol} = X_A G_A^o + X_B G_B^o + \Delta G^m$$

If left axis is A rich, right axis is B rich, and if I write X_B as X axis, then I will have G_A^o marked somewhere on X_A equal to one axis. This is basically the molar Gibbs free energy of pure A and G_B^o marked somewhere on the X_B equal to one axis. I am assuming here that G_B^o is greater than G_A^o, but it can be other ways also. Before mixing the total Gibbs free energy of the system was $X_A G_A^o + X_B G_B^o$ or it varies along the straight line joining G_A^o and G_B^o. and at any given composition if you know ΔG^m then you know the absolute value of the Gibbs free energy. Plotting at each composition will give a curve something like this.

This is the absolute Gibbs free energy versus mole fraction. This is how the G^{Sol} versus composition curve would look like. However, we do not know the absolute values of Gibbs free energies. By convention we assign value of 0 to some standard state of each component and usually the standard state is taken as the pure element in its stable state at the temperature being considered. And in this case we will assign value of 0 to G_A^o and G_B^o and if we do that then G^{Sol} becomes equal to ΔG^m:

$$G^{Sol} = \Delta G^m$$

Whether we draw ΔG^m or G^{Sol}curves, they give us the same information. Now once we have established how the Gibbs free energy of solution varies with composition, our next question is then, how do we determine the individual chemical potentials from there?

Any idea, how do we go about it? It is called a tangential intercept method. if we want to determine chemical potential, μ_A, it is basically same as the partial molar Gibbs free energy of A in the solution and it is defined as partial of Gibbs free energy of solution with respect to number of moles of A at constant temperature pressure, and constant number of moles of B:

$$\mu_A = \bar{G}_A = \left(\frac{\partial G^{Sol}}{\partial n_A}\right)_{T,P,n_B}$$

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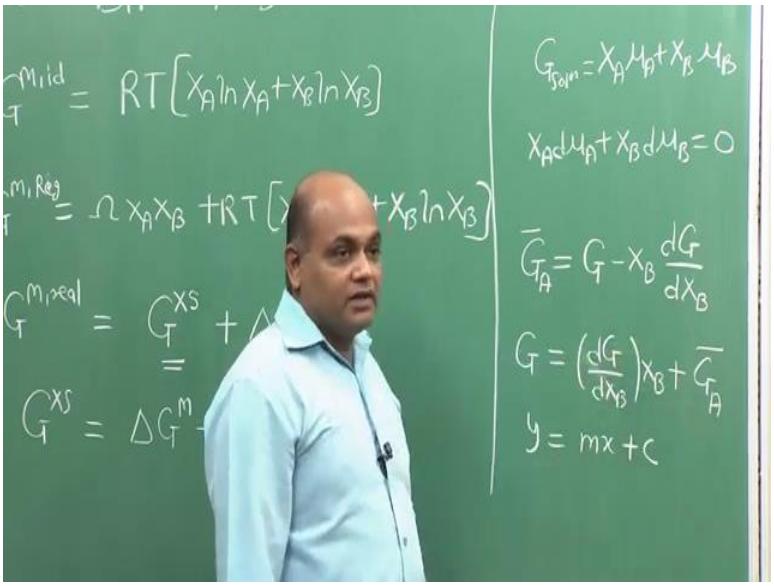

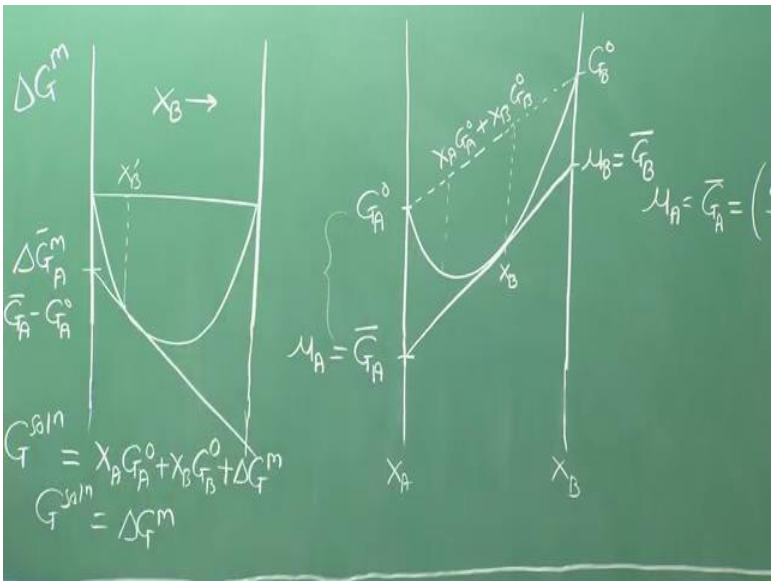

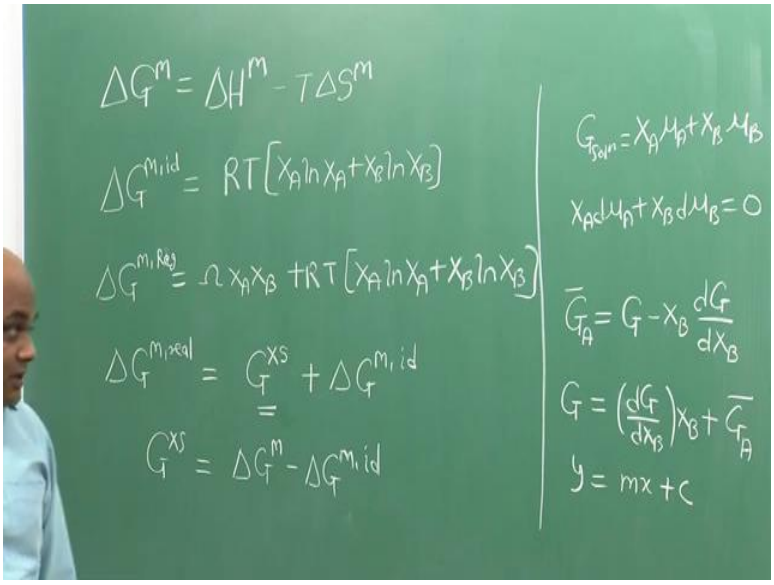

Molar Gibbs free energy of the solution can then be written as:

$$G^{Sol} = X_A \mu_A + X_B \mu_A$$

and from the Gibbs-Duhem equation we have:

$$X_A d\mu_A + X_B d\mu_A = 0$$

Now, if we differentiate this equation:

$$G^{Sol} = X_A \mu_A + X_B \mu_A$$

and then use Gibbs-Duhem equation and do some rearrangement of the terms, we will get the equation for $\bar{G}_A$ which can be written as:

$$\bar{G}_A = G - X_B \frac{\partial G}{\partial X_B}$$

We can write the same equation in a little bit different form.

$$G = \bar{G}_A + X_B \frac{\partial G}{\partial X_B}$$

This is an equation of a line, as it is in the form of:

$$y = mx + C$$

Where m is the slope of the line and C is the intercept on Y-axis. So, the slope of G versus X_B curve is $\frac{\partial G}{\partial X_B}$. Here G is Y and X_B is X. This is basically the equation of a line which is tangent to the Gibbs free energy curve at the desired composition. And $\bar{G}_A$ in this is nothing but the intercept of this tangent on the X_A equal to 1 axis.

If we want to determine the chemical potential of A at some composition X_B, we draw a tangent to the Gibbs free energy curve at that composition and the intercept on $X_A = 1$ axis is basically $\bar{G}_A$ which is same as μ_A. Similarly, the intercept of the tangent on the X_B equal to one axis gives us chemical potential of B μ_B which is same as $\bar{G}_B$.

Now, this method we can apply for determining any partial molar quantity if we know the relationship between the actual molar quantity with the composition. For example, if we want to determine the partial molar volumes, we draw the curve of molar volume of the solution versus composition and by the tangential intercept method we can determine the partial molar volumes at the given compositions.

Similarly, we can also apply this method to ΔG^m curve. At any composition we can determine the partial molar Gibbs free energy of mixing of a component. At this composition if we need to determine the $\Delta\bar{G}_A$, we draw the tangent and at X_A equal to 1 intercept, this is $\Delta\bar{G}_A$ and it is nothing but $(\bar{G}_A - G_A^o)$. This was the case when the magnitude of enthalpy of mixing was very

small, what if the magnitude of enthalpy of mixing is high? ΔH^m may be highly negative, or highly positive.

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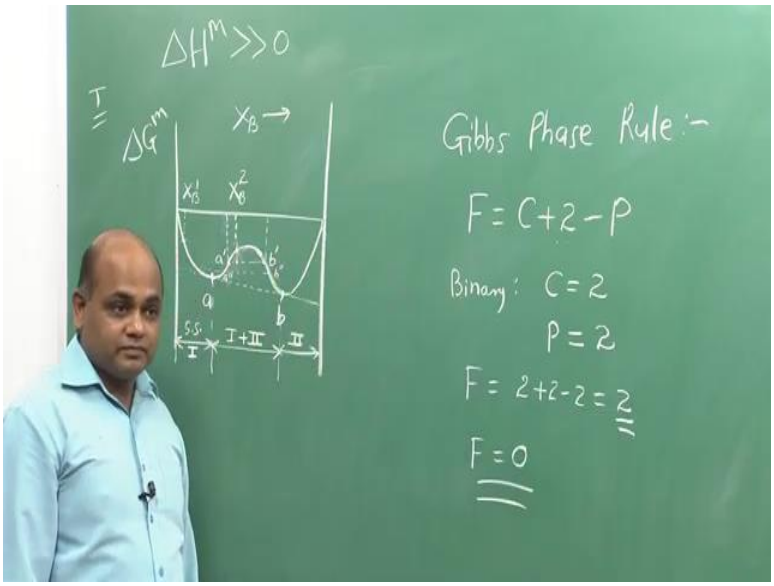

Let us first consider the case of $\Delta H^m > 0$ with a large magnitude. We have seen when $\Delta H^m > 0$ and when it has a large magnitude, ΔG^m curve will develop a negative curvature. Now, how do we assess the stability of solutions in this case? If we consider any composition towards A rich or B rich side, suppose any composition towards A rich side here, we are drawing ΔG^m versus X_B and if we consider composition X_B^1 here and we see that ΔG^m is negative. Single phase solid solution is stable in this case.

What if I consider a higher temperature, at X_B^2 there may be a single phase solid solution. And if I quench it to the previous temperature, initially there will be a metastable solid solution, but then will it remain stable ? The Gibbs free energy ΔG^m is still negative. What if the solution with thiscompositions splits into two different compositions? Obviously, in order to keep mass balance one has to be A rich, the other has to be B rich.

Suppose it splits into two compositions, let us call them a' and b', the total Gibbs free energy now is lying along this line joining a' and b' and where it intersect this X_B^2 line. By splitting into a' and b', there is decrease in Gibbs free energy. There is a tendency for this solution to split into two different solutions, one with composition which is rich in A, the other richer in B. Now, this

can continue further or it can further split. Instead of a' and b', it can split into a'' and b'' compositions and there is a further decrease in Gibbs free energy.

So,what will be the equilibrium compositions of A rich and B rich solutions? How long Gibss free energy can keep decreasing? If we analyze this, we will see that it will keep decreasing until we have A rich solution with composition a, B rich solution with composition b and these points a and b are basically the touching points of the double tangent to the curve (double tangent is the common tangent to the both parts of the curve).

Now, why not beyond A and B? If it splits further, we will see that there will be an increase in Gibbs free energy. So, the equilibrium configuration will be two solid solutions, one with composition A which is in equilibrium with another solid solution with composition B. Any solution in between will split into two compositions. At temperature T any composition between A and B will be stable as two phase solid solution, one with composition A, the other with composition B.

Upto a solid solution I is stable, beyond b the B rich solid solution or II is stable and between a and b there is a two phase equilibrium, $I + II$ and you see these compositions are fixed for the two phase equilibrium? Is it also consistent with the Gibbs phase rule? What does Gibbs phase rule says?

$$F = C + 2 - P$$

where F is the number of degrees of freedom, C is the number of components, and P accounts for number of phases, and 2 accounts for two variables, temperature and pressure.

If we are considering binary system, C is equal to 2 and the number of phases here are 2 in the two-phase equilibrium region. we basically have F=0 degrees of freedom since we are drawing this curve at constant temperature and constant pressure. Both T and P are constant.

For a two-phase equilibrium in a binary system, we cannot vary the composition of the two equilibrium phases, once we fix the overall composition. The compositions of the two phases in equilibrium is fixed, whereas in the single phase region we will have one degree of freedom which is the degree of freedom of composition, you can vary the composition and still be in the

single phase region. Now, within the two phase region what happens if I have different compositions? As I change the overall composition, what will change? The compositions of the two phases are fixed.

Student: **Out of phase.**

Professor: Right. The relative amount of two phases will change, as the composition moves towards B rich side the fraction of B rich phase that is II phase will increase and those phase fractions can be obtained by lever rule.

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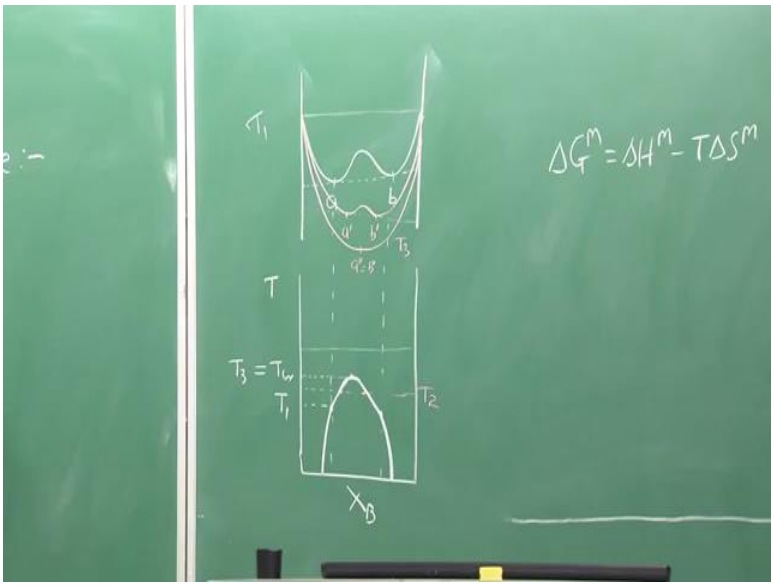

Now what happens if I change the temperature? I will redraw this curve here. Between points a and b there is no miscibility. It is called a miscibility gap which is the region between a and b. If we plot temperature versus X_B, you can plot these compositions a and b. Let us say these are at temperature T_1.

As I increase the temperature, what should happen? As:

$$\Delta G^m = \Delta H^m - T\Delta S^m$$

The entropy of mixing factor is multiplied by the factor of temperature. As I increase the temperature, contribution from the entropy term is increasing, so the miscibility gap should decrease or increase? Decrease.

Relative contribution from ΔH^m is decreasing, so the region with negative curvature should decrease as I increase the temperature. If I draw the same curve at a higher temperature T_2, it will be something like this and if I determine again the equilibrium compositions by tangential intercept method, this will be let us say a' and b'. If I keep increasing the temperature, at some point this negative curvature will vanish. During the transition somewhere at temperature T_3 the curvature will become 0 and that is called the critical point. At that point basically a' and b' are overlapping.

So when enthalpy of mixing is highly positive, temperature versus X_B curve is basically the locus of a and b, we will basically get the phase diagram with miscibility gap. At temperatures above T_3, there is no negative curvature because the contribution from $T\Delta S^m$ term is very high. The negative curvature which was because mainly which was mainly because of the highly positive value of ΔH^m has vanished and again complete miscibility will exist at higher temperature. Below the critical temperature T_3, the miscibility will be there again.

This is how we can obtain the phase diagram from Gibbs free energy of mixing curves. This is an example of phase diagram with miscibility gap. So, far we consider only one solid solution, what if there are more phases which are stable?

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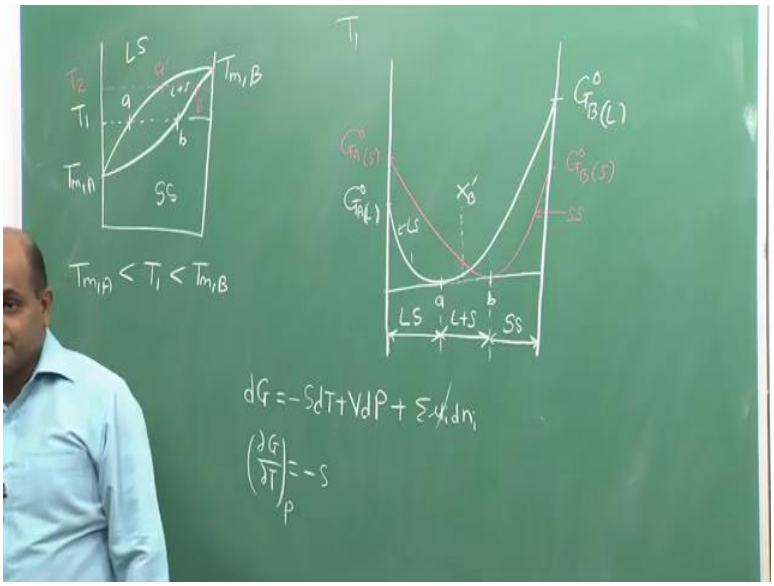

For example, the simplest of such system is an isomorphous system. In isomorphous system there is complete miscibility in the liquid solution as well as complete miscibility in the solid state and there is a two-phase region in between liquid plus solid.

There are two phases we need to consider here, liquid and solid. How do we get to this phase diagram from the Gibbs free energy of mixing curves? Since there are two phases, we need one curve for each phase, we need one ΔG^m curve for solid solution, one ΔG^m curve for liquid solution.

Let us first draw the ΔG^m curve for liquid solution, we can draw G^{Sol} curves, that way I can explain it in a better way. To calculate G^{Sol} curve for liquid we take first pure A in liquid form at the temperature which is being considered and we take pure B in liquid form and mix them to form liquid solution. Now, let us select the temperature T, let us call it T_1 which is in between the melting points of the two. T_1 is greater than the melting point of A and it is lesser than the melting point of B. On X_A equal to 1 axis, I have to first locate $G^o_{A(L)}$ the molar Gibbs free energy of A, this is in liquid form. At X_B equal to 1 axis, I locate $G^o_{B(L)}$ when B in liquid form and then we find out the Gibbs free energy of liquid solution. We then draw the curve for liquid solution and we do the same procedure for solid solution, we first take A in solid form, then B in solid form and then mix two, find out what is the change in Gibbs free energy.

Now, $G^o_{A(S)}$ where would it lie relative to $G^o_{A(L)}$? It will be above because at T_1, liquid A is a stable phase. Solid A will have higher molar Gibbs free energy than liquid A:

$$G^o_{A(S)} > G^o_{A(L)}$$

What about $G^o_{B(S)}$?

$$T_1 < T_{m\,(B)}$$

So, pure B is stable as solid.

$$G^o_{B(S)} < G^o_{B(L)}$$

and we can draw a curve for solid solution. Both the curves are intersecting at some point and we can draw a common tangent to both of them. Let us mark the touching point of the common tangent to liquid solution and solid solution as $a\ and\ b$. Up to a we can see that if we vary the composition from $X_B = 0$, up to a we will see that liquid solution has lower Gibbs free energy than solid solution. So, liquid solution will be stable, beyond composition b up to $X_B = 1$, we see that solid solution has lower Gibbs free energy than liquid and solid solution is stable, but between A and B what happens? Again, if we consider any composition in between, let us say X'_B, we see that if this composition splits into one liquid solution and one solid solution, it will be associated with a decrease in Gibbs free energy.

At X_B' it looks like liquid solution has a lower Gibbs free energy than solid solution, one would tend to think that liquid solution is stable but we also need to think about other possibilities by whichl there will be any further decrease in Gibbs free energy, and one such possibility is by splitting the same composition into liquid solution which is richer in A and solid solution which is richer in B.

And by doing this we can decrease the Gibbs free energy and one starting composition will split into liquid solution and solid solution, and the equilibrium compositions can be marked by the common tangent to the two curve a and b . Any composition between a and b there is a two-phase equilibrium, liquid plus solid.

If we increase the temperature, what should happen? will the two curves will shift up or down or one will shift up, one will shift down?

Student: Both the curves will shift down

Professor: Exactly, both the curve will shift down, why? You know this equation of state:

$$dG = -SdT + VdP + \sum \mu_i dn_i$$

At constant composition, last term will be 0 and at constant pressure:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

If you consider any composition, as I increase the temperature the Gibbs free energy should decrease because the slope is $-S$ which is always negative, so the Gibbs free energy should always decrease with temperature. But entropy of liquid is higher than entropy of solid. The liquid curve will shift down faster than the solid curve. In a way it will look like relatively the liquid curve is shifting down with repsect to the solid curve. if we try to draw that, we will see that the points a and b as I increase the temperature are shifting towards right and they are approaching each other.

Similar to here, if I determine the equilibrium compositions of liquid and solid at a higher temperature T_2 this will be a' and b' and this will continue until $T_{m\,(B)}$ and beyond $T_{m\,(B)}$what

will be the situation? Only liquid is stable. The solid curve will lie completely above the liquid curve, so at all compositions Gibbs free energy of liquid solution is lower than that of solid solution.

We looked at how to derive phase diagrams from Gibbs free energy of mixing versus composition curves for some simple systems, the one with miscibility gap and isomorphous system. Now, in both these cases solid A and solid B components in solid states had the same crystal structure.

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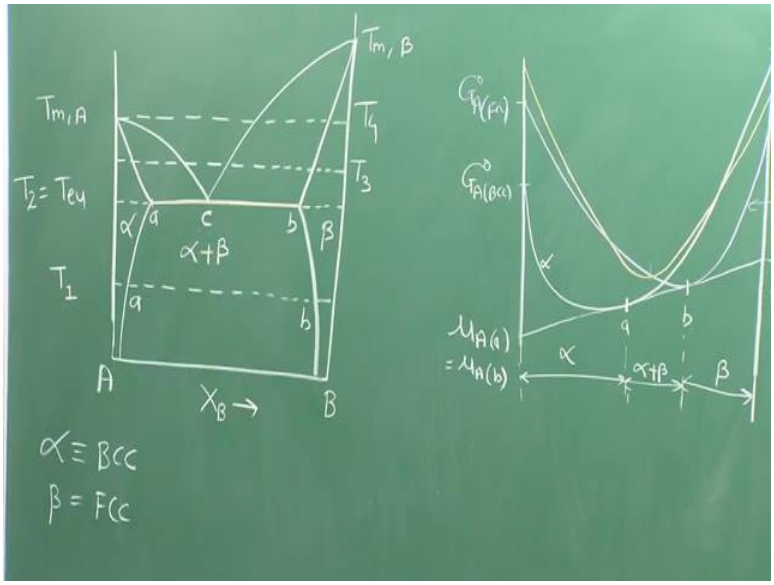

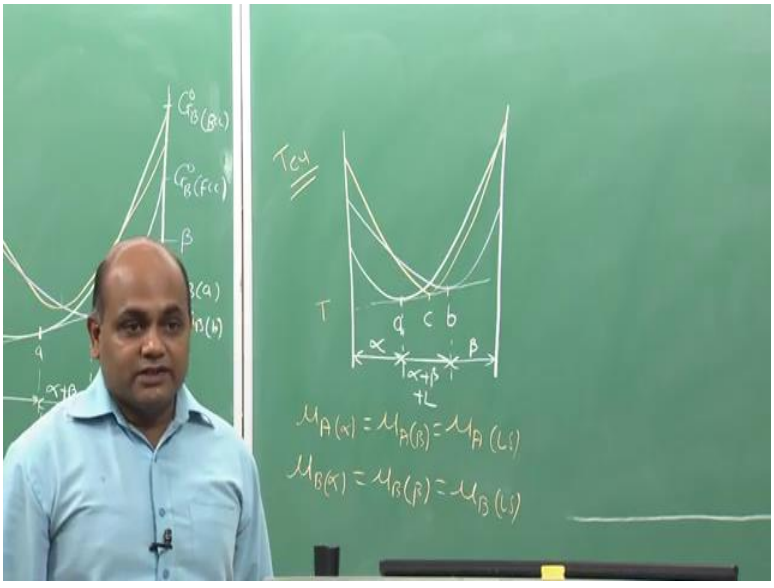

What if they have different crystal structures? Then it will give rise to little more complicated phase diagrams. One example is the eutectic phase diagram similar to what I have drawn here. This is a eutectic phase diagram between two components A and B, there is a little bit of terminal solid solubility, α is the A rich solid solution which let us say is BCC, β is B rich solid solution which let us say is FCC, and there is a eutectic point here, the three phase equilibrium between α, β and liquid.

How do we get to Gibbs free energy versus composition from the phase diagram? In computational thermodynamics essentially we evaluate the Gibbs free energy curves for different phases and then from this Gibbs free energy versus composition data we derive the phase diagram. That is the actual way we go in computational thermodynamics. But to understand the process really well, let us do it a reverse way. At a given temperature on the phase diagram let us see how the Gibbs free energy of mixing curves will look like.

Let us start with the temperature T_1. Here, you have a two phase equilibrium α and β. Now, there are three phases on the phase diagram we need minimum three curves, one for BCC solid solution that is α, one for FCC solid solution that is β and one for liquid solution. First we need the curve for α that is the BCC solid solution, we need to first mark G_A^o and A solid in BCC crystal structure and we need the point G_B^o and B also in BCC. Note B is stable as FCC but we need the value of molar Gibbs free energy of B in BCC. So, we first need to convert FCC B into BCC B and then mix A in BCC and B in BCC to form the BCC solid solution. That will give us the curve for Gibbs free energy of mixing for α.

Practically it may not be possible to determine the Gibbs free energy change associated with this transformation FCC B to BCC B but we need to know that. It may be done by the first principle calculations. Then we need the curve for β, for β which is FCC we need G_A^o for FCC that is the molar Gibbs free energy of A when it is FCC and obviously A FCC is an unstable phase. The value of G_A^o FCC will be higher than G_A^o BCC. B is stable as FCC, so G_B^o FCC will be lesser than G_B^o BCC and we can get the curve for β. We can determine the two-phase region by drawing a common tangent and these touching points a and b mark the equilibrium compositions of the two phases in equilibrium.

If we see up to point a, there is the α stability, beyond the composition b β single phase is stable because Gibbs free energy of β is lesser than that of α and between a and b there is a two phase equilibrium α+β. As I increase the temperature a and b points will approach each other. We will see that the solubilities on both sides are increasing, note here one thing there is a common tangent right at a and b. If I want to find out chemical potential in the two phases, at any composition between a and b, what would it be? You know any composition between a and b will be stable as two phase mixture, one with composition a, another with composition b.

I need to know the chemical potential of A for example in phase α and in phase β. It will be given by the tangent. Trivially since this is a common tangent:

$$\mu_{A(\alpha)} = \mu_{A(\beta)}$$

Similarly:

$$\mu_{B(\alpha)} = \mu_{B(\beta)}$$

And this is the condition for two phase equilibrium. The chemical potential of A in one phase should be equal to the chemical potential of A in the other phase. Similarly, chemical potential of B should be same in both the phases. What about the liquid solution curve? It will be lying above this tangent line. As the temperature increases the Gibbs free energy of liquid solution is decreasing faster than the solids. At a certain temperature there may be a possibility that there will be a triple tangent because this liquid curve relatively is shifting down and at some point it may touch the common tangent to both the solid solutions.

In that case, there is basically a three phase equilibrium because in this case:

$$\mu_{A(\alpha)} = \mu_{A(\beta)} = \mu_{A(L)}$$

i.e., chemical potential of A in α is same as chemical potential of A in β same as chemical potential of A in liquid solution. Similarly:

$$\mu_{B(\alpha)} = \mu_{B(\beta)} = \mu_{B(L)}$$

and this is called the eutectic temperature. At eutectic temperature there is a three phase equilibrium.

We can mark a, b and c as the three points where common tangent is touching the three curves of α, liquid and β touching points respectively at the eutectic temperature. In this case up to point a single phase α is stable, beyond point b single phase β is stable and between a and b there is a three phase equilibrium α+ β+ liquid.

This way you can assess other more complicated phase diagrams also. Now, let us look at one more case when ΔH^m is highly negative. When ΔH^m was positive, there was a tendency for phase separation, it developed a miscibility gap. Because ΔH^m is positive it means A-B bonds are weaker than average of A-A and B-B bonds, or there is a tendency to minimize the number of A-B bonds. But when ΔH^m is highly negative that means A-B bonds are much stronger than A-A and B-B or there will be a tendency to maximize the number of A-B pairs. Now, in extreme case what might happen? For example, if you are considering 50-50 percent of A and B, when will be the number of A-B pairs maximized? When all A atoms have only B as neighbors and all B atoms have only A as neighbors. This is called an ordered structure and it may form a completely different phase which is called as intermetallic phase. When enthalpy of mixing is highly negative there will be a tendency for ordering.

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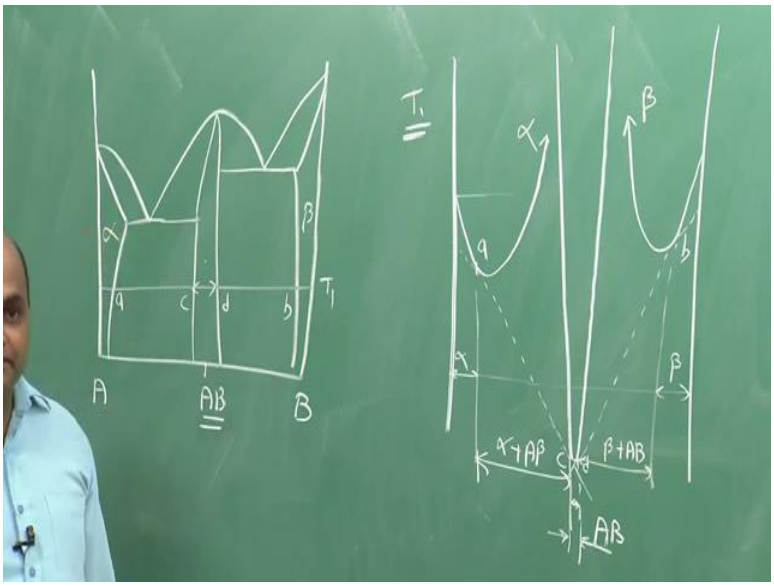

Let us consider such an example. This is an example of a phase diagram with an intermediate phase, we have A, B and this is intermetallic AB. In that case now we have three solid phases, α, β and intermetallic AB which will have a completely different crystal structure and then there is a liquid phase.

We need at least four Gibbs free energy curve, one for α, one for β and one for AB. And typically, the Gibbs free energy curve for this intermetallic will be very sharp because ΔH^m is highly negative so that it develops a sharp ΔG^m curve. Then we can draw one curve for α, one curve for β and we can determine the two phase regions by the method of common tangent. If you consider this temperature T_1 upto point a, α is stable, beyond b β is stable.

Now, we can draw two common tangents, one between α and AB, the other between β and AB. ac is the common tangent between α and AB and d is the point where the common tangent between β and AB touches the curve of AB and there is a small region between c and d where a AB is stable.

Between a and c we have α+AB between b and d we have β+AB and between this small region there is a single phase AB which is stable. So, when ΔG^m is positive there is a tendency for phase separation and when ΔH^m is negative there is a tendency for ordering.