Phase Transformation in Materials

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Lecture - 11

G-X Plot for Peritectic System

Students, in the last lecture I have started the heterogeneous phase equilibria and I discussed about the free energy composition diagrams with the different phase diagrams, different types of phase diagrams. So, we are going to conclude that today. So, I showed you as few of a systems, eutectic systems and another isomorphic system with a (Refer Time: 00:51) gap. So, today I am going to take up the peritectic phase diagram. I am sure you have the free energy diagrams, will look like, in fact can be used for obtaining information stability of the different phases. As you know peritectic phase diagram is basically based on the reaction, known as peritectic which is this type.

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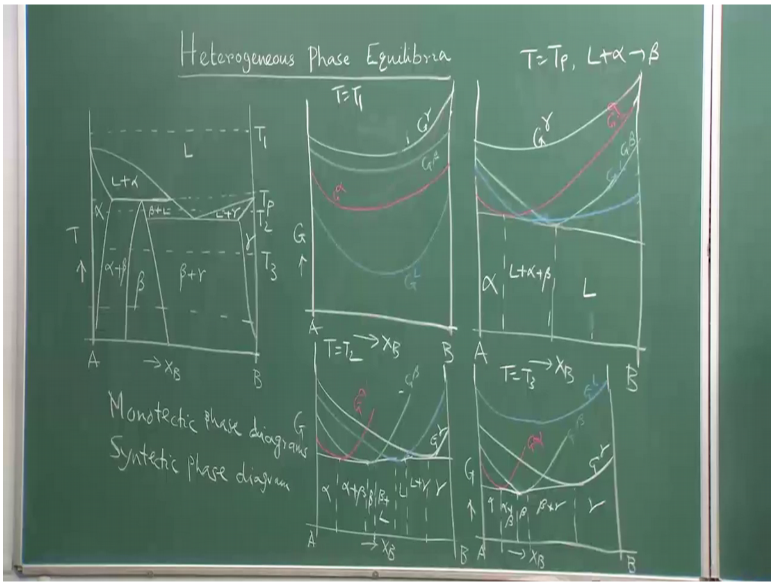

Where liquid reacts with another solid phase here it is alpha and produce, another new solid phase called beta. This is an reverse rate type of reactions. So, therefore, we always write this, but we are interested in the further reaction that is liquid plus alpha going to beta.

The phase diagram for such a system will look this. First we will have a solid solution for alpha. So, that is how it will looks like it is little bit, little complex, but not much complex. So, liquid, this is alpha phase, this is gamma phase, liquid plus alpha obviously because we are connecting that and this is the peritectic phase beta. You can see, there is a horizontal line on the phase diagram that indicates the reaction and this reaction tells you that liquid plus alpha reacts produce beta. So, therefore, this will be alpha plus beta, this is basically beta plus gamma, always in the phase diagram you will find that a peritectic reaction is most of the time followed by an eutectic reaction. So, this eutectic reaction is liquid going to beta plus gamma. Therefore, this will be beta plus liquid and this is liquid plus gamma. That is how the phase diagram looks like.

Now, let us draw the free energy composition diagram at different temperature and this is the T p. T p is the peritectic temperature, then we will draw another one here which is the most it cuts through many of the phase field and then we will draw another one here. So, therefore, through the four temperatures, we are going to draw the free energy composition diagram one at temperature T 1 is very clear. T 1 liquid is stable other phases are not stable at all. Then under temperature T, will be T p that is a peritectic reaction temperature, at which peritectic reaction now takes place. Then at temperature T 2 in which the TA line or the temperature line, actually passes through lot of temperature line, rather not TA line passes through lot of phase field. And finally, will take another at temperature 3.

Let us draw that. So, I need colour chalks to do that. I will do it, draw it one by one. So, here itself I draw temperature T 1. This is A, this is B, similarly, at temperature T 2, at temperature T p, where this reaction of the low curve, this is at temperature T will be T 2 and finally at temperature T will T 3. So, let us draw first at temperature T T 1, as you clearly see, there are only 4 phases here, liquid and 3 solid phase, alpha, beta and gamma. So, in all these diagrams, we need to consider. We need to draw the four curves 1 for the liquid and 3 for the 3 solid phases.

So, for the liquid, we are going to draw using a blue. So, here liquid is several phase. So, liquid will be at the lowest part. This is G L. Now, for alpha, we are going to use G alpha, G beta and G gamma. Let us say G beta as a blue and G gamma will be using a light colour chalk. So, I will, let us remove this temperature above, so that you can see it very clearly. Let us not cross over this always make confusion. Cross over means something else you saw the 3 4. Free energy composition curves will looks like I can do it better. In fact, fine. So, it is very clear liquid is the stable phase, because a free energy curve for the liquid is actually at the lowest positions.

Now, I go to the at temperature T p, at temperature T p, this reaction occurs. So, therefore, alpha liquid and beta all of them will be at equilibrium, but you will see alpha is stable for certain composition range, then alpha plus liquid plus beta is stable in this reaction range, then the peritectic horizontal and the liquid is stable. So, that is what you see here . So, therefore, it is very clear, that you will have curves for the liquid alpha and beta crossing over each other, because we have a region of liquid plus or this liquid plus alpha and beta plus liquid also. So, let us draw it for the liquid, liquid is low. So, liquid is kind of like this, this is G L, and then alpha, alpha will cross over. This is G L sorry, G alpha not L and then you have beta, beta will be also crossing over somewhere there. So, liquid beta is stable better to draw like this. Oops this will be no, this will not cross over here.

So, this is G beta and Z gamma as usual will be above fine, because if there is a crossover we need to draw tangents between these curves. So, first thing we will tangent between 3 curves. So, as you clearly see it is difficult to draw tangent between 3 curves. So, what we should do? You should basically, move up this curve little bit, then you can draw it, otherwise, it will look bad, still it is not proper. So, let it be down little bit. So, I draw a common tangent between these 3 curves here. And I draw a tangent here between beta, beta is for blue the green and the, oops yes and the liquid curve; so this tangent here. So, I have drawn two tangents.

Now, let us remark at the regions specifically. So, this is alpha, because alpha is stable here you see here and there is a common tangent between 3 liquid, liquid is blue. Red is alpha and the beta. So, therefore, this is liquid plus alpha plus beta and then you have a beta stable somewhere. It is not beta, this is liquid stable, this will beta, cannot be stable. So, let us remove that it is not, that is it will be liquid. So, what you do it, you remove this tangent. This tangent will come next, this will be liquid. So, this tangent is fine, that is why I was telling that there is some mistake happening. So, I will draw it and I will explain it to you again.

So, this is the liquid. So, as you clearly see here, that liquid is the bottom most curve in a composition range from here to there. So, that is why actually at temperature T equal to

T p will look like. Now, at temperature T equal to T 2, how it will look like. So, you can see alpha plus alpha plus beta, then beta plus liquid, then again liquid, then liquid plus gamma and gamma. So, all the curves will cross over. So, that is why it will look little. So, let us draw it half, then otherwise it will look clumsy. So, this is a alpha; obviously, this will go like this complete and then beta and alpha will cross over here. So, because this alpha plus beta is here then there is a range, then liquid and alpha beta will cross over. Let me write this one at the top liquid, liquid will be blue. So, liquid will come somewhere there, then only it will cross over and then you have a gamma gamma come into picture.

So, what I will do; I will do a common tangent between gamma and sorry beta and alpha, then common tangent between beta and liquid common tangent between beta and liquid is somewhat like this and then another common tangent between gamma and liquid, this is gamma. So, you have A alpha common tangent between alpha and beta, will give alpha plus beta. This is beta, this is here, no, this is beta, beta plus liquid, liquid beta plus liquid and then gamma liquid, liquid plus gamma, because there are regions in between the common tangents, where we have the position of the curve in the lowest positions therefore, tangent between alpha and beta is giving alpha plus beta, beta and liquid giving beta plus liquid, liquid and gamma is giving liquid plus gamma.

So, relative these positions will be little bit clear once you, once we look at these positions. Here you see this tangent ends there and liquid comes down, sorry beta comes down here. So, therefore, tangent will be somewhere there, similarly, here the liquid comes down there and then the tangent actually starts, little bit ahead that is why it is like this. So, at T3, let us complete it at T3 again of alpha plus beta. Beta beta plus gamma and gamma, only thing is that liquid is going to be at the higher level. So, liquid will be at a higher level. So, let us finish it there and then we will first do the alpha again, it is better to draw half, because full will always make the line difficult and then beta. So, beta will be going like, this fine and then gamma gamma will cross over obviously.

So, what I am going to do, I am going to do, only draw a common tangent here. So, beta has to be going down little bit. So, then only beta will have A and then gamma beta will have like this. So, we have alpha alpha plus beta beta gamma. So, this is G gamma, this is beta and this is G alpha. So, what we have alpha alpha plus beta beta beta plus gamma and gamma correct there are 2 tangents. Tangent may not look nice here, but it is there and in between we have a beta region, because this curve is going down . So, therefore, there will be 2 tangents. I will remove common tangent 1 tangent between this and alpha other tangent between beta and gamma.

So, that is how it looks like and any further temperature down, nothing is going to change only the stability range compositions are going to be changing. So, please practice yourselves, then only it will be clear to you; otherwise, it is going to be creating more trouble. So, we are not going further into the complex phase diagrams. You can also try monotectic and syntectic phase diagrams. These two phases is also be important, because there involves liquid viscous invincibility, but soon will be part of assignments fine. So, you can actually try yourselves then it will be clear to you.

Now, let me also continue the discussions, you know as you have seen this phase, diagrams should drawn at a one atmospheric pressure, almost all metallurgical phase diagrams are drawn at one atmospheric pressure, we do not change the pressure. In fact, that is why we have 2 axis. One is temperature axis another one is a composition axis and third axis which could have been normal to that. We always ignore, because we assume pressure to be constant, but you know many cases pressure is not kept constant.

So, it is better, that we know what is the actual effect to the pressure on the, on this you know lines; obviously, pressure will have effect both in terms of, you know temperature of these transformations also the compositions. So, first we look at what is the effect of pressure on the transformation temperatures. This is important for pure metals more, because suppose, in iron, pure iron, the gamma to alpha, the alpha to gamma transient temperature. Alpha is a Basel phase, gamma is a sepsis phase. Actually, it depends on the pressure.

Similarly, if you look at ice and water mixture, water, ice transformation that also depends on temperature of the transformation, depends on the pressure. So, how we can bring it that effect well we will discuss that in a mathematical manner first. First we know that G is basically H minus T S and we know the Gibbs free energy controls everything.

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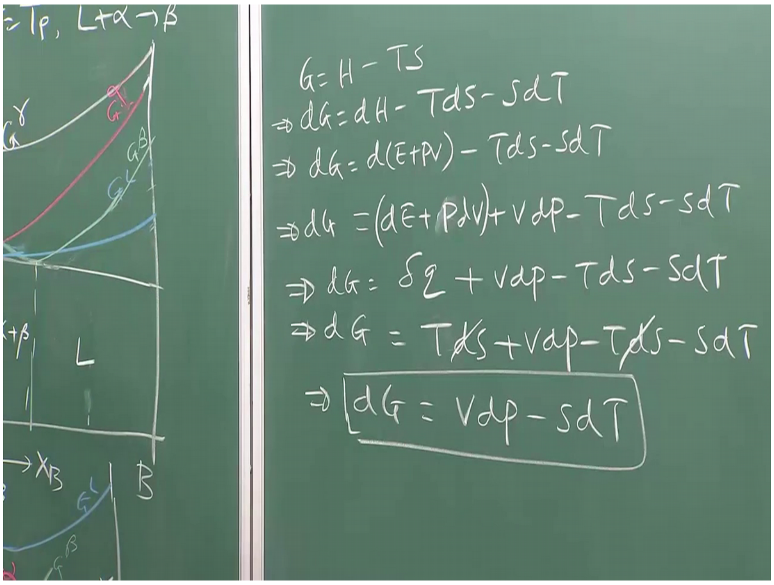

$$G = H - TS$$

$$\Rightarrow dG = dH - TdS - SdT$$

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

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

$$\Rightarrow dG = \delta Q + Vdp - TdS - SdT$$

$$\Rightarrow dG = T\cancel{dS} + Vdp - T\cancel{dS} - SdT$$

$$\Rightarrow \boxed{dG = Vdp - SdT}$$

So, we can write down that this G basically, I will write the letter, write down total differential is equal to d H minus T d S minus S d T right. Now, this d G can be further expanded, because H is nothing but E plus p V and we know that, this again further can be converted, make total differential right. So, next step is to use the first law of thermodynamics. First law of thermodynamics tells you that these two parameters within the parenthesis is nothing but heat del Q. So, that is plus V d p minus T d S minus S d T right. Similarly, we can again use second law of thermodynamics. Second thermodynamics tells you del Q is nothing but T d S. So, T d S T d S gets cancelled. So, therefore, you get total differential. G is a constant of pressure and temperature that is equal to V d p minus S d T.

Now, to derive the effect of pressure and temperature, we are going to use this particular expression alright. So, let us suppose, there are two phases one is alpha other one is beta. So, we will write down, this same expression for alpha and beta and then see what happens at equilibrium.

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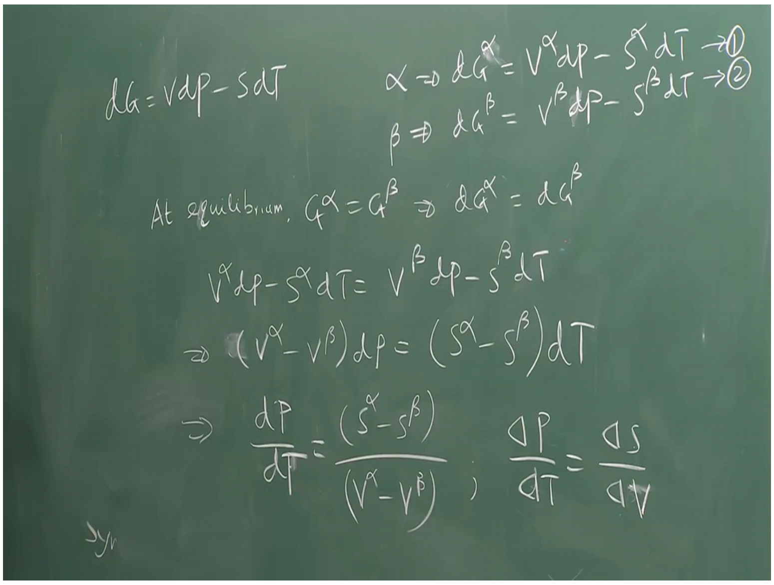

$$dG = VdP - SdT$$

$$\alpha \Rightarrow dG^{\alpha} = V^{\alpha}dP - S^{\alpha}dT \rightarrow ①$$

$$\beta \Rightarrow dG^{\beta} = V^{\beta}dP - S^{\beta}dT \rightarrow ②$$

At equilibrium, $G^{\alpha} = G^{\beta} \Rightarrow dG^{\alpha} = dG^{\beta}$

$$V^{\alpha}dP - S^{\alpha}dT = V^{\beta}dP - S^{\beta}dT$$

$$\Rightarrow (V^{\alpha} - V^{\beta})dP = (S^{\alpha} - S^{\beta})dT$$

$$\Rightarrow \frac{dP}{dT} = \frac{(S^{\alpha} - S^{\beta})}{(V^{\alpha} - V^{\beta})} \; ; \; \frac{\Delta P}{\Delta T} = \frac{\Delta S}{\Delta V}$$

So, as you see d G is nothing but V d p minus S d T and we assume, that there are two phases one alpha, one beta. So, for alpha, we can write down d G alpha or d G rather is equal to V alpha d p minus S alpha d p at nay temperature pressure p and T right. Similarly, for beta, this is G alpha, always written down alright, at equilibrium we know that G of alpha must be equal to G of beta, it has to be at equilibrium, because free energy first be at equilibrium.

And then we can write down d of d G of alpha will be equal to d G of beta; that means, in top those two equations we can equate. So, if I equate, what will happen if I equate these two equation, 1 and 2 by equating 1 and 2, we get V alpha d p minus S alpha d p is equal to V beta d p minus S beta d T. All at constant temperature pressure, because this equilibrium is happening at a temperature pressure which is given. So, we can write down. So, we can simply write down V alpha minus V beta d p is equal to S of alpha minus S of beta d T.

Therefore, we can see d p by d T or rather later side. Other way that will helps you better, d T by d p is equal to. So, d p here, it will go there, no it is better to write with p, because we are all used to the Clausius-Clapeyron equation, which we are going to derive. So, that is nothing but S alpha minus S beta divide by V alpha minus V beta. So, that is how actually, the pressure will vary as a function of, sorry, pressure will have that effect of temperature.

So, we can always write down in differential form in the other way. So, as you see here, that effect comes as a function of change of entropy and change of volume basically correct. So, we can modify the equation again, further what do, how we can modify, the equation we can modify. This very simply, very simple we can modify this equation, we know that G is nothing but H minus T S right.

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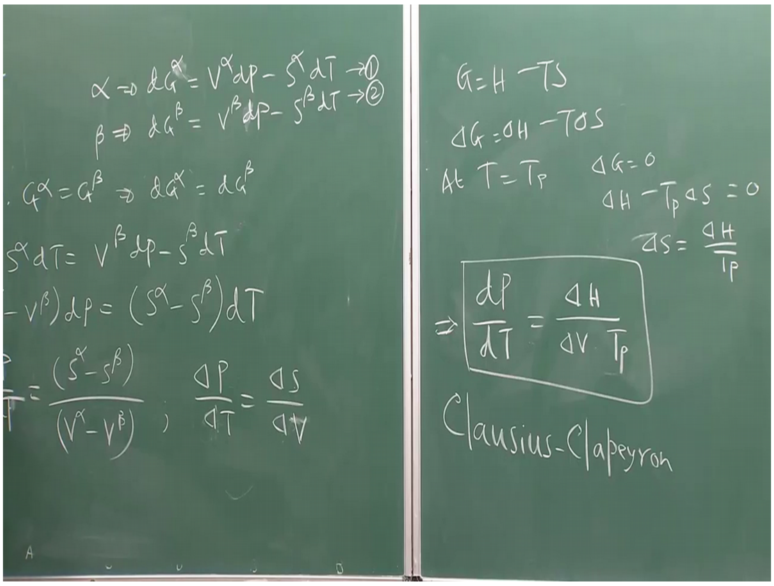

$\alpha \Rightarrow dG^{\alpha} = V^{\alpha}dp - S^{\alpha}dT \rightarrow ①$

$\beta \Rightarrow dG^{\beta} = V^{\beta}dp - S^{\beta}dT \rightarrow ②$

$G^{\alpha} = G^{\beta} \Rightarrow dG^{\alpha} = dG^{\beta}$

$S^{\alpha}dT = V^{\beta}dp - S^{\beta}dT$

$-V^{\beta})dp = (S^{\alpha} - S^{\beta})dT$

$= \frac{(S^{\alpha} - S^{\beta})}{(V^{\alpha} - V^{\beta})}$, $\frac{\Delta P}{\Delta T} = \frac{\Delta S}{\Delta V}$

$G = H - TS$

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

At $T = T_p$ $\Delta G = 0$

$\Delta H - T_p \Delta S = 0$

$\Delta S = \frac{\Delta H}{T_p}$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{\Delta H}{\Delta V \cdot T_p}}$$

Clausius-Clapeyron

So, therefore, delta G is nothing but delta H minus T delta S at transformation temperature at T equal to T p transformation temperature, delta G is must be G of any phase, otherwise, it will not transform. So, therefore, I get delta H minus T p delta S is equal to 0 . So, therefore, I get delta S is nothing but delta H by T p. So, if in plug, in there I get d p by d T, I can get equation, use this equation and write down delta H, delta S. We can replace delta H divide by delta p multiplied by T p and this equation is known as Clausius-Clapeyrons equation. This tells you the effect of pressure on temperature. So, if I know the delta H that is the heat of transformations. If I know the volume change, delta V, we can calculate, what is the temperature change of this phase boundaries as a function of pressure.

And this is used wherever for pure iron. So, let us for the take, for the water, we know that when ice forms from water to ice volume, actually increases. So, if the volume increases, volume probably, product minus volume of the front phase that is volume of ice minus volume of water that is positive, but on the other hand when you have ice transforming to water, this delta V is negative, because volume of water minus volume of ice is always negative. Volume of ice is small and this, because it is negative, therefore, if I have pressure, the moderate temperature of water will go down that is what happens if you apply pressure, pressure application. Pressure will have a strong effect on the moderate temperature, going down, because this slope is negative and that is why in the water phase diagram, we will find the solids. Liquid transformation curve is always be negative slopes, but metals is not metal is the, because delta V is always positive for the most of the metal transformations.

So, if you want once to use the effect of pressure basically, on the transformation temperature then, this is the equation 1, is to use, is to show you that. So, in the next lecture, I am going to talk about, what is the effect of anyone, effect of basically, curvature on the transformation temperature and how even that solubility of these phases can be again mathematically proven as a function of temperature. These two effects will look at it, because these mathematical formulations are required for you to do different calculations.