Heat Treatment and Surface Hardening (Part–1)

Professor Kallol Mondal
Professor Sandeep Sangal
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture Number 5

Thermodynamics of Phase Transformation Driving force for Phase Transformation

Hello, today we will start our fifth lecture.

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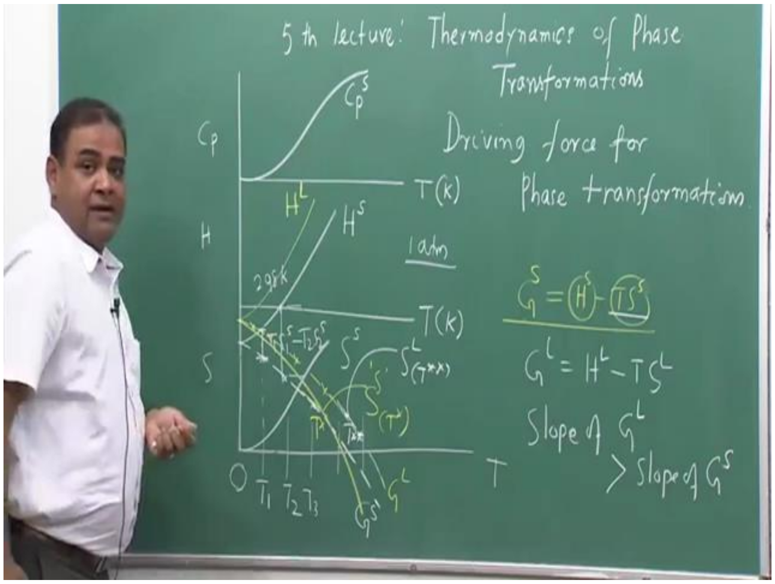

It will be on Thermodynamics of Phase Transformations and mainly our interest would be to quantify the driving force for phase transformations. So this entire lecture in next couple of lectures also we would mainly concentrate on how we can calculate the magnitude of driving force for phase transformations. And in the last lecture we started with a finding enthalpy entropy from the Cp value because Cp is the measureable quantity which can give a some sort of quantification of enthalpy variation as well as entropy variation.

And once we know the enthalpy as well as entropy variation, we can easily find out what is going to be my free energy variation and that free energy variation would let me know would would let us would would let would would know would allow us to know that what would be the driving force for that particular phase transformation. Now last class we started with a the pictorial change of enthalpy as well as entropy as well as Cp as a function of temperature for a condense system and we have taken a single component system that means is a pure substance we have taken pure metal actually and we have try to see how Cp, enthalpy, as well as entropy varies as a function of temperature.

So we have seen that the Cp varies like this as a function of temperature this is, this is in kelvin scale and then enthalpy varies like this and entropy varies like this again. Now also we have seen that if the substance is in most stable condition and in case of metal we have seen that the solid is the most stable condition. That time we find out, rather we impose some particular condition with reference to that condition we tried to measure the change in those parameters. These functions enthalpy, entropy we try to measure with reference to that particular value.

And in case of solid metal, we if the atmospheric pressure is 1 atmosphere, that time at 298 kelvin the value of enthalpy of that particular pure substance in solid state is zero. So now, this is also in kelvin so this value is zero, that means this is enthalpy of solid, this superscript s means it is solid condition. Now this entropy of a pure substance as per the third law of thermodynamics, we know that if it is absolutely pure, if there is no contribution of mixing enthalpy entropy to that particular total entropy (contri) entropy of that substance then if it is a condense state, okay, that time at a constant pressure this value at zero kelvin is zero.

Now once we have this information, so now if this is for solid, this also we can say that this is entropy of solid and this is also Cp of solid. Now for solid phase, we have found out these values. Now accordingly, if we have a condition which is liquid, we can immediately find out what would be the entropy as well as enthalpy values. Because in case of liquid also, we have the information of Cp for the liquid, okay. So now in that case, the Cp of liquid is little higher, is higher than the solid enthalpy Cp.

So if the Cp of liquid is higher than solid Cp, then the enthalpy of that liquid, of that pure substance would also be higher over the entire temperature range. So now, I can draw the enthalpy of liquid as the yellow line which tells me the enthalpy of liquid. Now here, interestingly it is also going through a zero value, but that zero value does not cross the temperature axis at 298 kelvin because the standard state which is 1 atmosphere pressure and 298 kelvin, that time this enthalpy of solid is taken is assume to be zero, okay.

So now, then away other than that particular temperature for other phases this zero would appear at different points, different temperatures. So it is appearing at this temperature because the enthalpy of liquid is higher than the enthalpy of solid. Now entropy of solid liquid also would be higher than the entropy of solid because the Cp of liquid is higher than the Cp of solid. Now our primary interest to is to find out G, now G can be related to which is TS, this is the relation. Now if I find out the enthalpy of solid as well as liquid separately and at the same time if I find out what would be the entropy of solid and the liquid separately from the Cp data I can get these two values. For solid I can get solid, and for liquid I can get liquid. Now once we have this information we can also accommodate this TS term in this along this line with a negative sign we can accommodate that.

Now at each temperature if I take each temperature, I would be able to find out what is my TS term with just temperature I know, s I have calculated from Cp data. Now that TS term if we subtract from H value, then I will get point at each temperature. Now let us say at this temperature which is T1 I try to find out what is my TS solid, which is T1 s solid, so then that particular thing I let say I plot it here, so this is that locus so let us say this is that point. Similarly, at little higher temperature which is T2 I can also get another point.

Then T3 I can get another point, okay. So like that I will get a information where this particular value is nothing but T1s1s, this particular value is T2s2s. So gradually it would go like this, then if I connect those locus point because those locus points are telling me the G of that particular solid at different temperature. So now, if I connect them, if I connect them, so this dash lines is actually giving me the information of G solid at different temperature. Now similarly, I can have those locus points for the G of liquid at different temperatures since I have the value of Hl as well as sl.

Now that case also, I will get another point like this, another point like this let me put it in a yellow color because now the question is and those every point on this point on this particular line would be the minus Ts liquid term. So now point is whether this line will go parallel to this? Or the G of solid or it might cross at some point, okay. So now this is Gl, now if I have this particular plot if I try to see what is the slope at each point, okay, that slope is nothing but the entropy of that particular material at that particular point of that particular phase also.

So that means if I trying to find out the slope here or that means this slope is nothing but for solid. And similarly, if I try to see from this diagram that slope is nothing but the entropy at that particular point. So this is nothing but entropy of solid and if I take this temperature to be T star, so this is at T star. Similarly, if I try to find out entropy of liquid at this point, then that would be my s of liquid at T double star let us say, this is my temperature T double star.

Now we have already seen that entropy of liquid is higher than the entropy of solid. That means a slope change for the solid free energy line is much higher than the is higher than it could be high very high, it could be slightly high but it will be higher than the slope of the Gs line. So if that is the condition, that means slope of Gl line and that means is greater than slope of Gs line. So and also there is a negative term because these points are obtained after putting a negative sign with this because this minus this we are getting this G term because G is nothing but H minus TS.

So that means if the slope of Gl is higher than the slope of Gs, that suggest that they cannot go without touching rather they cannot go without crossing. So they would cross at some point, okay because this slope is higher than the slope of this. So that means they will cross at some point, okay. Now interestingly, wherever it crosses, let us see what is the condition there, okay. Now I would like to draw this particular diagram separately only this part because I know how this diagrams are coming, okay.

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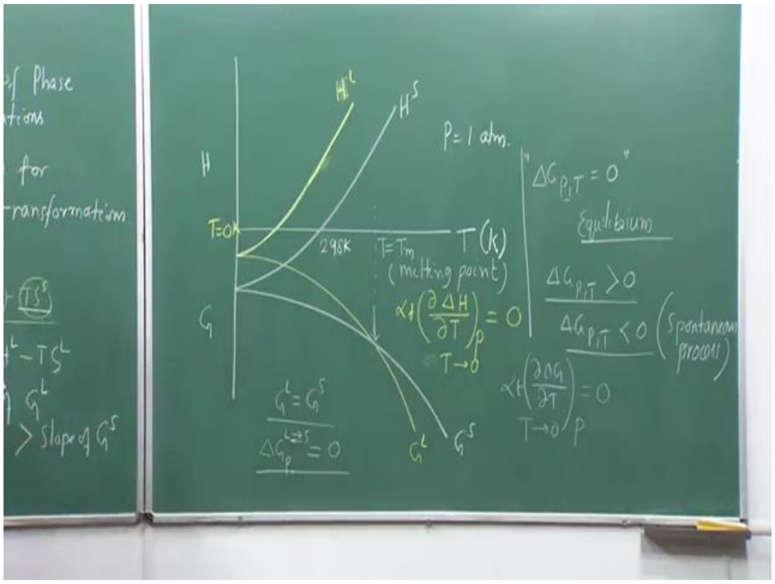

So if I try to draw that, so now as per this diagram it is very clear this is my Gl, this is my, sorry this is Hl, this is Hs, this is 298 kelvin and pressure is 1 atmosphere this is in kelvin scale. So this becomes my Gs, this becomes my Gl and interestingly one more information because both this lines are actually emitting from T = 0 kelvin and if we see the slope variation it is basically if we try to see the slope, you will see that it is, it is zero. Similarly, limit zero with a constant pressure.

Why they are actually gradually becoming (ma) asymptotic and then becoming meeting them at zt = 0 kelvin because this concept is arriving from the nerst postulate which says that for a condense matter at constant pressure these change in enthalpy values of a particular condense phase goes to zero if T tends to zero kelvin. So this is a kind of statement for third law of thermodynamics in a nutshell, okay. But we will not go in depth in that particular third law of thermodynamics, we will concentrate on these two curves, okay.

And according to this two curve graphs, it is very clear the slope of liquid line is higher than the slope of solid line and that is why they are crossing. Now some interesting phenomenon is taking place at this point where both the lines are crossing. So at this point Gl equal to Gs and if Gl is equal to Gs it see means that del Gls or S to liquid, that means if liquid transforms to solid or solid transforms to liquid at this point both are equal. And now we have to see what is this condition and if we consider p to be constant and this is appearing at some temperature, okay, these two these difference value is zero, then that particular point we call it an equilibrium point.

And every we all know that when metal melts from solid to liquid or metal freezes from liquid to solid at the equilibrium point which is the melting point or freezing point free energy change goes to zero. And that is why that is called equilibrium, okay. So that means that point is nothing but T = Tm, and this small m is nothing but the melting point, so this is melting point, melting point. And as per thermodynamic, perception or concept whenever del G pt goes to zero that means at constant pressure and temperature, if these difference value goes to zero we say that this has reached equilibrium, this has reached equilibrium.

And at equilibrium, we do not have any energy available to do work and if there is nothing available for doing work, so no work will be done there and the system will remain fixed there, okay and at the same time we will not be able to tell whether liquid will transform to solid or solid will transform to liquid, we will not be able to tell. Now anything we can see any change we can see that time this value would take some non-zero value. It can either go to greater than zero or it can either go to less than zero. Now if it is less than zero, that means I have some energy which is freely available to do work, useful work output I can get some work output.

So that time, we call it as a spontaneous process, spontaneous process means that transformation is possible, okay. But if this is greater than zero, we would say that that process it is non-spontaneous, that means it is not possible, okay. Now when we are saying that it is not possible it is possible, we are not incorporating any other external stimulates, okay we will come to that k what are those external stimulates. Now in order to understand these three concepts, let us just discuss a bit on this concept, okay or short while and then we will get back to this information again, this particular situation.

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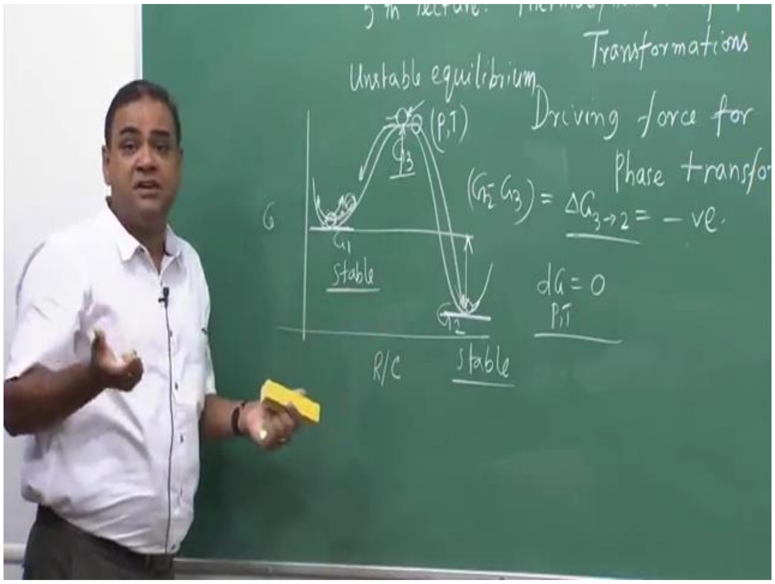

Now in order to discuss that, let us do it here. Now if I try to see a energy distribution curve as a function of reaction coordinate if this is G, we can have we have seen this particular information all the time in our text books. Now this we call it as G1, this we call it as G2, now as per our concept if dG equal to 0 and this is at particular temperature and pressure let us say if this is zero, we call it equilibrium. Now I see that there are three points where I can have this particular situation where slope becomes a flat these three points.

Does it mean that equilibrium is there everywhere at this three points? Yes as per the theory, as per the concept we can say that they have reached equilibrium. But that equilibrium can have a different nature, okay for example¸ at these two cases, if I try to see a ball, okay and if I try to give a little movement to this ball little displacement to this ball, it will try to roll over if it comes here and then again we release it and that releasing it will go like this, it will again go like this like this and gradually the temperature would reduce and finally again it comes back to this.

So that means we can say that the system tries to maintain that particular position if we do not have much of disturbance to this system. So that case, we can call it as stable. And here the same situation persist, so we can call it as stable. Now at this point, if I have the ball and if I give a little displacement to this, very little displacement, immediately it will come to the down slope, then it cannot go back to this position on its own, rather it will try to fall down here, okay. So even if I try to give another small disturbance to this, it will try to move and fall, fall down and come backs, comes to this.

And if I consider this is to be G3, okay. So at this point this condition is there and we can say that this is equilibrium, but since it even if we the slight disturbance, it does not try to maintain that position rather it dislodges from its position and goes to the next stable position, okay. So that time that is what it is not a stable equilibrium, we call it unstable equilibrium, unstable equilibrium. If I do not do anything to this, it will try to maintain that but it maintains its unstability whenever I have little disturbance it will start dislodging, okay. And whether in this two position they will not try to go out of the system, rather if it is a small disturbance they will start going back to this position and stays there, okay.

So that is why these are called stable positions, but now are they same stability? Are they having same stability? We will discuss that, but let us come to this point, once we have little dislodge from this particular point, we see that G3 to G2 it can immediately go, okay. So that means if I try to see what is the difference G2 – G3 that means final minus initial would be del G we can say three to two, this has a negative value because this has lower value than this, so that goes to negative and whenever this is a negative, that means I see that the system goes spontaneously from this point to this point.

So that means the spontaneity is decided by the negative value of the difference of free energy. Similarly if I go from here to there, there is also a spontaneity G1 – G3 it becomes negative value, okay. So that means if this free energy change is negative, it is a spontaneous value and spontaneous process that means that process can take place, okay. Now we will try to discuss these two stability as well as what happens if we try to see this difference, here also if we try to see G2 – G1 we see that is also a negative value, that means that process should have been spontaneous.

But the spontaneity what exist here and the spontaneity what exist here, these two spontaneities are different. So we will try to discuss these informations in our next lecture. Thank you very much.