Heat Treatment and Surface Hardening (Part–1)

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Lecture Number 06

Thermodynamics of Phase Transformation Driving force for Phase Transformation

Let us start our sixth lecture and the topic of sixth lecture would be same as before because we have discussed that, we have already discussed that these driving force calculation would continue for next couple of lectures.

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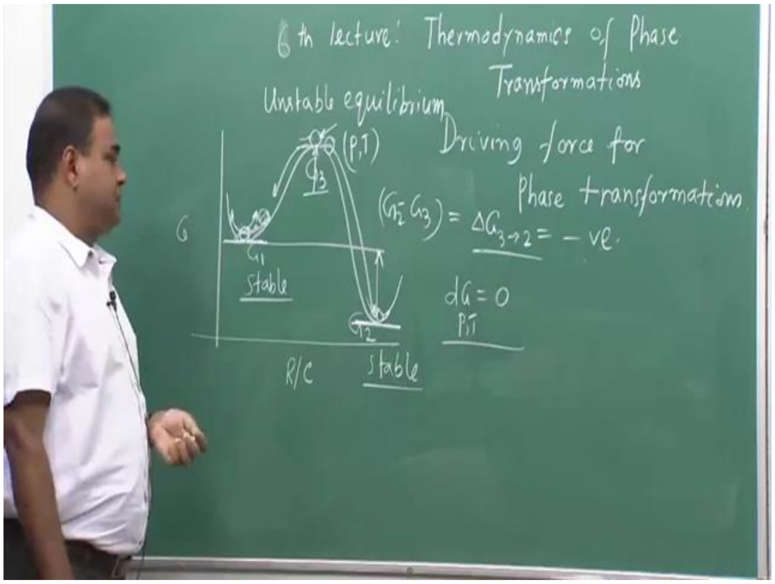

Now we were discussing this particular graph and where we have seen that this is unstable equilibrium, this is stable, this is stable and we wanted to see what happens if we try to see the difference between G1 and G2. Let us say a particular this ball wants to go to this particular position, then I see that G2 is lower than G1.

So there is a possibility that the ball can go from G1 to G2. Now can it go the way this ball went to this position? Now there is a barrier, there is a barrier it has to be taken to this point and then it is to be given little push, then the ball can go spontaneously to this. Now in this situation, though there is a spontaneity, that means though G2 – G1 is negative, so that means there is a spontaneity but this spontaneity is not a complete spontaneity what we had here, rather in order to meet the process, whether the process would take place or not.

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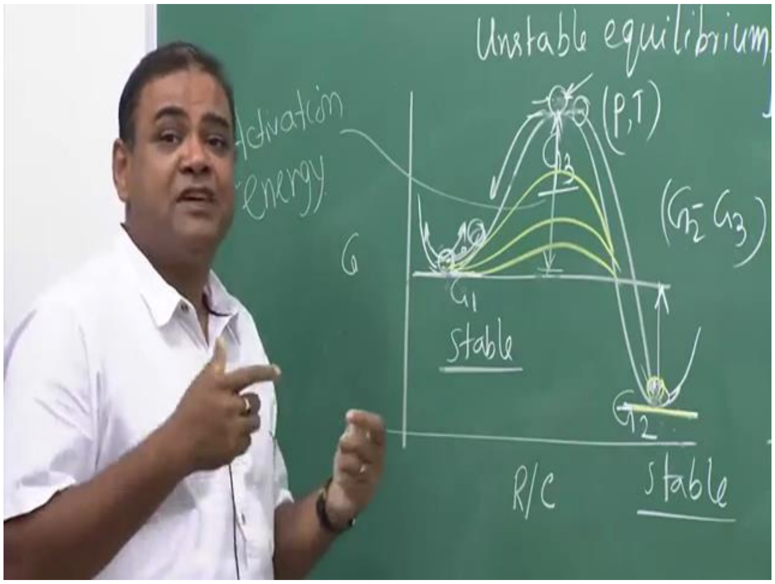

That means process means the ball goes to this point from this point to this point. This ball has to be taken to this, that means it has to be given sufficient energy to go to this particular point, that means it has to from G1 to G3 first and then we can give a little push and then from G3 to the G2 it can go on its own. So that means spontaneously it can go. So there is a spontaneity from G1 to G2, but we need to provide sufficient excitation to that particular ball. And this excitation part is coming in the form of activation energy and this is basically my activation energy.

This is my activation energy, so this is the energy barrier and now though we have a spontaneity, whether the process would take place or not, that would be decided by the value of this activation energy, the (deg) the amount of activation energy this ball has to acquire in order to jump over this barrier. So if this particular barrier is smaller and smaller, let us say I started reducing this activation energy, what happens? I have a smaller and smaller barriers to cross, it is like just like kind of a huddles if we have a big huddle, it is difficult to cross, rather if we have a small huddle it is very easy to cross.

So this easiness or toughness that is coming from the degree of the value of activation energy and this activation energy would guide whether that particular spontaneous process actually takes place or not. So if some process is spontaneous that does not mean that the process would take place, that means a process can be spontaneous, that means there is a negative free energy change, but in order to have that particular process in practically, practically if we have that if we want to have that particular process, we need to cross a barrier, okay.

Now similarly, if we try to see the ball wants to go to this point to this point, it is not a spontaneous process, because the ball cannot go on its own from here to there, but it can go if we give sufficient excitement, it can cross this barrier and can come here. But now let us see this and this, can the ball go to this point on its own? It cannot, why? Because the ball the, the natural process would be the ball can roll down against the potential energy in towards that potential energy lowering, rather it cannot go spontaneously up the hill rather up the potential energy.

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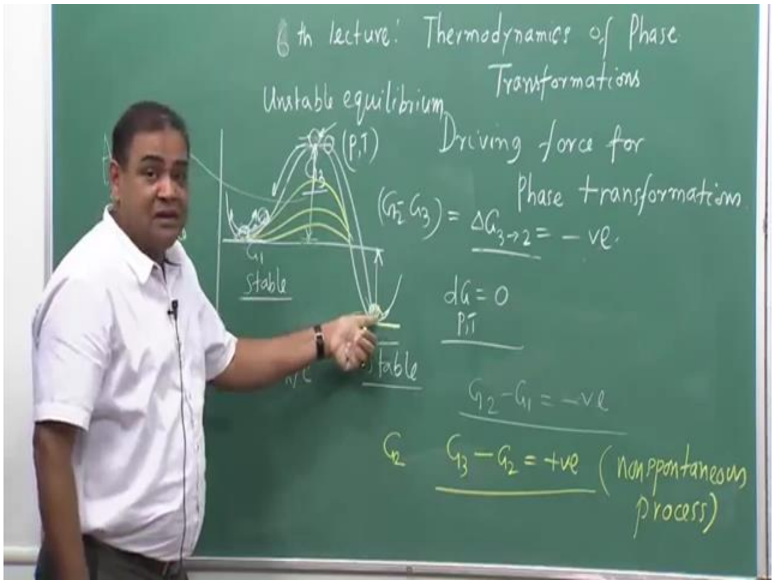

Now if I try to see this is the starting point and this is the final point, now this is my starting point that means G2 is my starting point and G3 is my final point. So now if I try to find out what is the energy difference if that ball wants to go from G2 to G3, so G3 – G2 this is a positive quantity. If the free energy change is positive, then on its own the system cannot move. So that particular process is called non-spontaneous process, non-spontaneous process.

So from this information it is very clear the ball can move from here to there spontaneously without giving any sort of excitement, but if this ball cannot go to this point on its own. So if the free energy change is positive, that is a (spont) non-spontaneous process and we can immediately say that this process is impossible on its own. But if we take this to this, then the process is possible and spontaneously possible. But if I try to see this to this, the process is possible with a bar that it has to cross this particular barrier.

That means I have to give sufficient excitement. So if some process is spontaneous that does not mean that the process will take place, we will come to that we will come, we will take this example while talking about the transformation of solid from liquid, okay. Let us come back to this particular diagram, we have seen that at this point free energy change is zero, that means it is an equilibrium and that equilibrium point is nothing but the melting point.

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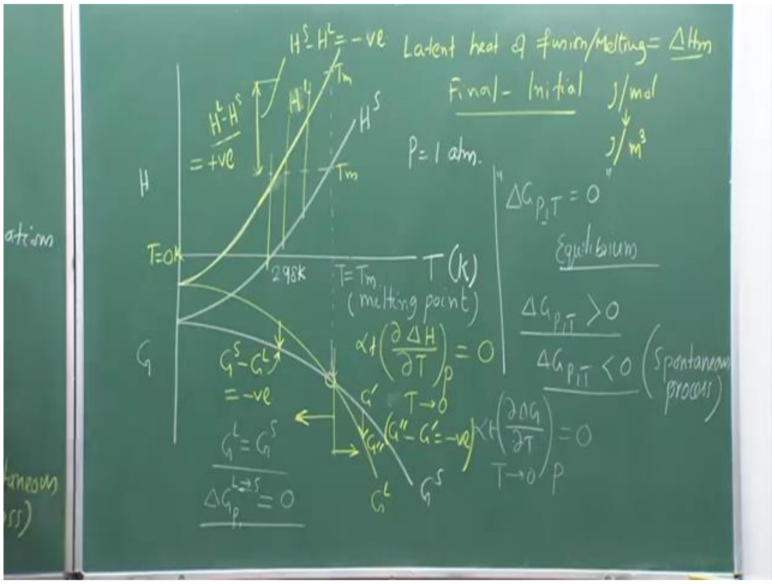

Now if we extend it, if we extend it now this is also Tm this is also Tm because of the same temperature. And this is my Hl, this is Hs, now at this temperature, the difference is Hl – Hs, now Hs – Hl in case of thermodynamics state function this are all thermodynamic state functions. Now whichever I am writing wherever I am trying to reach, let us say I am reaching I am trying to reach from liquid to solid, so then solid would be my final state. So it should be final minus initial. In this case, I am subtracting liquid enthalpy I am subtracting solid enthalpy from liquid enthalpy. That means my final state is liquid. So that case, what is this value? This value becomes positive, means this is higher than this, so this becomes positive.

But if try to subtract same thing, if I try to do Hs – Hl which becomes negative, now interesting, here things (beco) things are becoming interesting. Now if we get liquid out of solid we see that it is a positive quantity and if we get solid from a liquid, then we get negative value. Now as per our understanding, when we have a melting, we absorb heat, okay. So that means solid has to absorb heat and when system absorbs heat, that means the liquid is forming from a solid it has to take heat, so that whenever a system absorbs heat we call it endothermic process, okay.

Now in our sign convention, endothermic process the state function change is a positive quantity. Now you see solid going to liquid, the value becomes positive, that means a liquid solid has to absorb heat, okay, and then it can go to liquid at that particular temperature. But if I try to find whether solid forms from liquid, then it is an exothermic process because it has to release heat, okay you see there is a negative quantity, it releases heat, okay. So again the convention is right, fine. So that means this is my exothermic process, this is my endothermic process.

And interestingly, I see that there is a huge change in enthalpy if it is liquid to solid I am seeing that the enthalpy reduces from this point to this point and if I see solid to liquid enthalpy increases from this point to this point and that time even though there is lot of heat capacity change or enthalpy change, I do not see any change in temperature and where this is possible? This is possible at melting point, and that time that particular difference we all know that is called Latent heat of fusion or melting or melting if solid goes to liquid.

So that means my, this is my this difference is a Latent heat of fusion or melting. In our sign convention we would consider this as del Hm and the here m is melting, here also Tm m is melting. So that means that is melting enthalpy or Latent heat of fusion or melting. And now this latent heat of fusion or melting, we have to quantify what is the amount of material, we come we measure in the form of latent heat of fusion or melting per unit mass or per unit mole or it can also be converted into per unit volume and you would see that in our purpose, later on you will see initially this value is given a energy joule per mole and later on we will convert this particular unit to joule per meter cube. We can convert this in many form. So if it is mole we will just divide it by mole or volume that time it will become per volume, okay.

So now we will come back to this particular term because this particular term would be very very crucial. Since this is a constant term for a particular metal at a constant pressure, okay whenever the solid goes to liquid. So this we can call it as a reference data. And this reference data will be used to find out the enthalpy change at any other temperature, at any other temperature, okay how would you do it? Okay and before going to that particular calculations, now let us see what happens if we change this particular point if we take this (par) if I go this is my temperature, if I go this way or if I go this way, what happens?

Now if I go this way, what would be the spontaneous process and in order to find spontaneous process, I need to see which way the free energy is redution, that means which way the change in free energy would go to negative. Now here, if I try to see, if I see that this way the free energy goes negative. That means the change in free energy, if I try to see this is G prime and this is G double prime. So G double prime minus G prime is equal to is a negative quantity.

So that means, this is a spontaneous process and now this G double prime is a free energy of what? It is a liquid, so that means temperature greater than Tm, that means the melting point I would always get a liquid because solid to liquid transformation would become spontaneous process because the free energy change is negative. Now if I try to go this way, then I would see that this, that means Gs – Gl at this temperature, okay this becomes negative. So again it becomes a spontaneous process, that means this transformation is possible, this transformation is possible wherever I see there is a decrease in free energy.

But from liquid to solid, temperature less than Tm is not a spontaneous process because that time free energy change is positive quantity. So on its own it cannot transform, okay. So now we will come back to this that would there will be possibility that even if there is a delta T change, that means even if there is a delta T change (())(16:40) actually have solidification. That means (woul) we actually have solid formation from liquid. That particular information would be critical to analyze, but at least from this information it is very clear that this becomes my driving force.

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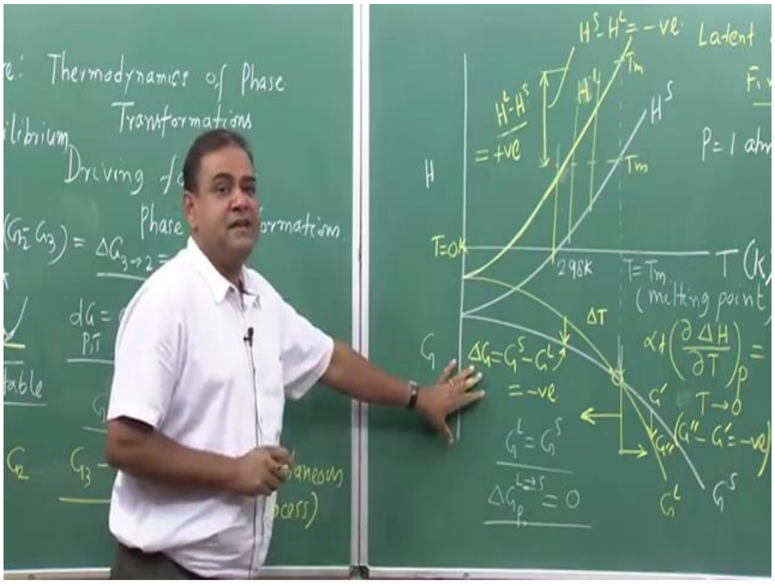

And the driving force is nothing but the change in free energy. Now I am to that part the driving force for phase transformation, here I am seeing the solid is forming from liquid and that driving force is nothing but the change in free energy, okay. And that change in free energy is negative quantity. Now our main interest would be how to quantify this particular value, okay. Let us get to the quantification of this value and this quantification of this value would require little bit of thermodynamic understanding we will discuss that thermodynamic understanding in the next part, okay.

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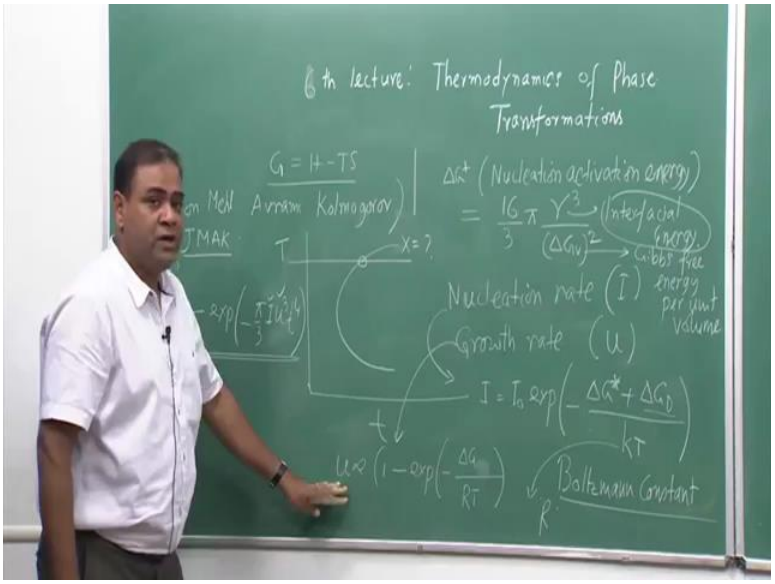

Let us go to the thermodynamic understanding in order to quantify this value. Now we know G equal to H minus Ts now at the same time, our understanding says that absolute value of this state function would be very difficult would be not be possible to find out. So we find out change in values, either del H, del S or del G and at the same time you see that we are not bothered about finding Gs or Gl, we are bothered about finding del G. Now why this del G would be required? First we should understand why should it be required then we should crack our mind we should, we should break our mind to see how we can quantify this.

Now in order to know that part, I am just going little ahead in this, little ahead what the part what professor Sangal will be taking. You will be seeing that in most of the cases, for example in case of steel or in case of aluminum alloys precipitation hardening you would be coming across a TTT diagram. Whenever we come across this TTT diagram, you will be seeing that he will show all the calculations how to find out TTT diagram. TTT diagram we can find out experimentally, we can do raw experiments and find out what is the TTT diagram these points over a temperature and time axis.

At the same time we can do simple calculation from simple thermodynamic (pa) data, for example the data would be require in which is del Hl, data which will require is T, data which we require is viscosity value, so those are measureable quantity, okay. So those parameters if we use we can get this TTT diagram and in most of the cases, this TTT diagram experimentally found out values and theoretically found out values they match with some little adjustment, okay.

But, the nature of the graph remains like this which is a c curve is a TTT diagram and while considering this while calculating this TTT diagram, we would be requiring information about nucleation rate as well as growth rate. And interestingly and this are called you will see the notation would be u and v, u is basically the growth rate and nucleation rate is denoted by I. Now, this nucleation rate it would have is o its own expression. And the nucleation rate expression is if I try to see nucleation rate expression I am just writing the expression, the expression is I = I0 exponential (- del G star + del Gd by Kt) this temperature is in kelvin scale, this k is Boltzmann constant, Boltzmann constant.

If it is per atom, then k, if it is per mole then this particular Boltzmann (con) (con) constant would go to universal gas constant which is R. Now in this, we are seeing that there is a term called G star, there is a term called del Gd. Now this del Gd as well as del G star are called this is called nucleation activation energy, nucleation activation energy and now since I have used activation energy, it immediately tells me that it is talking about some barrier in the energy axis energy distribution graph as what we did in the just before just ten minutes before, okay.

So now this is also express in the form of if it is simple homogeneous nucleation that is called 3 pi square. Now this term is interfacial energy and this is Gibbs free energy per unit volume and this Gibbs free energy per unit volume is nothing but this. So that means, in order to find out del G star we need to find out what is the value of del G star del G and if it is given in mole, so we will just divide it by the mole of volume of that particular substance and we get del Gv.

So that means, in order to find out I, we need to find out del Gv and this del Gd is another activation barrier and this activation barrier is nothing but the barrier for diffusion to take place in the material because whenever we try to find out some phase formation out of another phase, if it is a thermally activated process, then we need atom migration and this atom migration does not take place just like that. It has to cross a barrier, and that barrier is nothing but del Gd, okay.

Is a diffusional activation barrier and this I is to be calculated. So this I0 is another constant and this is the temperature where I would like to find out I, okay I is a nucleation rate, that means the number of nuclei appearing per unit volume, per unit time, okay. So that is basically decided by del G star as well as del Gd, we have ways to find out del Gd but when we try to find out del G star we need to know what is del Gv, that means I need to find out the driving force.

The driving force for the transformation which is negative and this particular term which is interfacial free energy, okay or interfacial energy this is another important term we will (ta) we will try to see what it exactly means, we will try to see. But why I am telling that this particular term is to be quantified? Because this is needed in order to find out I. Similarly, if I try to find out growth rate, it's the expression u proportional to one minus exponential minus delta Gm, I would say m, m means or let me put only del G in the molar quantity T. So this is the term, so here this term is also this term.

So we need to find out this term also. Now we are wondering that this we said that this for finding this TTT diagram we need to know nucleation rate, we need to know growth rate and overall this particular graph says the overall transformation kinetics.

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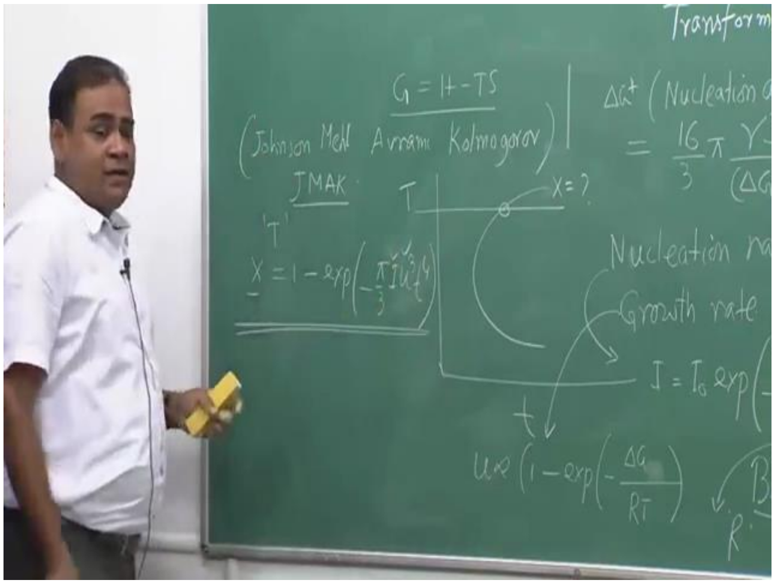

And this overall transformation kinetics is given in the form of Johnson Mehl Avrami Kolmogorov which is popularly known as JMAK equation which is given in the form of x which is the fraction transform, that means the product phase when it is appearing in the parent phase, the fraction of that particular product phase is given by x equal 1 – exponential – pi by 3 I u cube T to the power 4.

So this is the expression, so where I need and this particular graph is plotted with some x value, some x value and then where I need to know what is my I, what is my u and this time is basically this time axis and this is at some particular temperature T. So now if I try to find out at this temperature, this point where when this point would appear, that would be decided by u and I. So this is overall kinetics, that means in order to find this, we need to know I, we need to know u and in order to know I and u, we need to know del G.

So that is the reason why we should try to see first how we quantify del G. This is extremely important because otherwise we will not be able to calculate this graph, okay. So now let us come to finding this value, okay since we have understood what is the importance of finding this particular parameter which is the free energy difference or which is the driving force for that transformation. Let us stop here, we will take it up in our next lecture, thank you very much.