Heat Treatment and Surface Hardening (Part–1)
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Lecture Number 09
Nucleation Treatment Single Component (Solid-Liquid)

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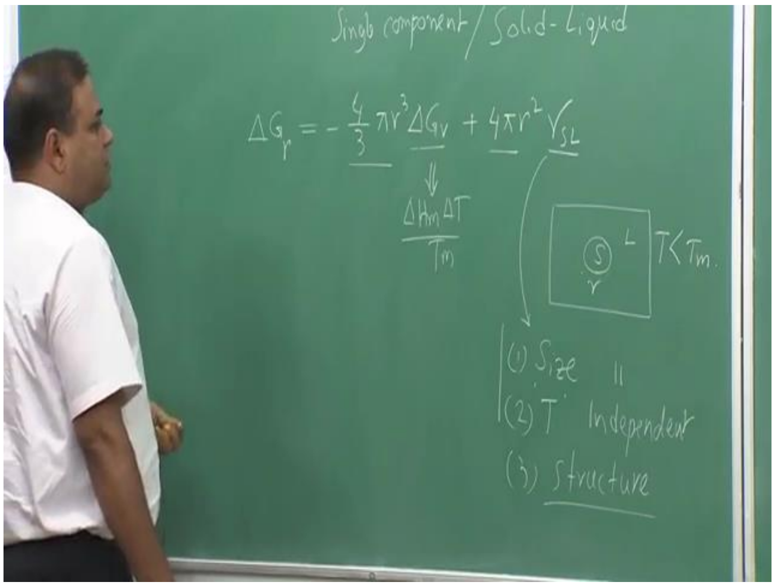

Hello everyone, we will start ninth lecture today and the topic of the lecture, we will continue our nucleation treatment in single component system and that two we will take solid-liquid transformation. Now the last lecture, we came across this equation which is del G is equal to - 4 by 3 pi r cube del Gv + 4 pi r square gamma Sl. Now this particular equation we came across considering that in a closed volume I have a spherical solid forming inside the liquid, so this is solid, this is liquid and this is of radius r and this is at temperature T less than Tm.

Now when we have this, that time since it is a spherical radius, spherical particle and we are considering in terms of r. So this is the volume term, this is the surface term and this is the total surface energy that is the positive energy contribution for the solid formation and this is the volumetric energy consideration which is giving a volumetric free energy and that has a negative sense, that is what we have put negative, so we can also incorporate this negative term within this, but that time we will be calculating critical radius from this equation.

So that critical radius, there would be a negative sign but that negative sign is does not mean that the radius becomes negative. So is actually meaning that that negative term is coming from this negative free energy for the formation of liquid to solid. Now since it is r, so we can consider it to be r, del Gr. Now whether this nucleus will form or not, this is we consider this is, this is consider to be kind of nucleus, okay. Now if it does not grow, that time we cannot call it as nucleus, rather we call it as cluster or Embraer, we can we can see later on what happens to that, but at least we can say for the time being solid sphere is formed.

Now once we have this, now there are terms, for example del Gv term and gamma Sl term, this gamma Sl which is surface energy or the interfacial energy for the solid-liquid interface, this can depend on various factors. So those factors are, for example the dependencies, it can depend on size that means if radius increases or decreases this can change, it can depend on temperature because the interface is always a kind of entropy term. So that entropy term also would depend on temperature, now mainly if we consider this two, also it depends on structure, structure of interface.

So there are several factors with these are the major ones. Now we assume that this is independent of temperature, independent of temperature, it (ca) it is also independent of temperature and now in the beginning we are not considering any structure affect. So now if it is independent, this is also dependent on temperature because we have seen that the relation of del Gv is del Hm del T by Tm. Now since we are considering at a particular temperature, this does not vary at a particular temperature.

And since we are considering this is to be independent of size even if this particular thing grows or decreases this does not change. Now in addition to this, this one does not vary with temperature, so it is a constant term. Now this is the expression for del Gv, now in order to find so this equation, this is a negative term, this is a positive term. So that means, d del Gr del r we can find and that time if we plot this one and this one gives a critical point of a particular curve.

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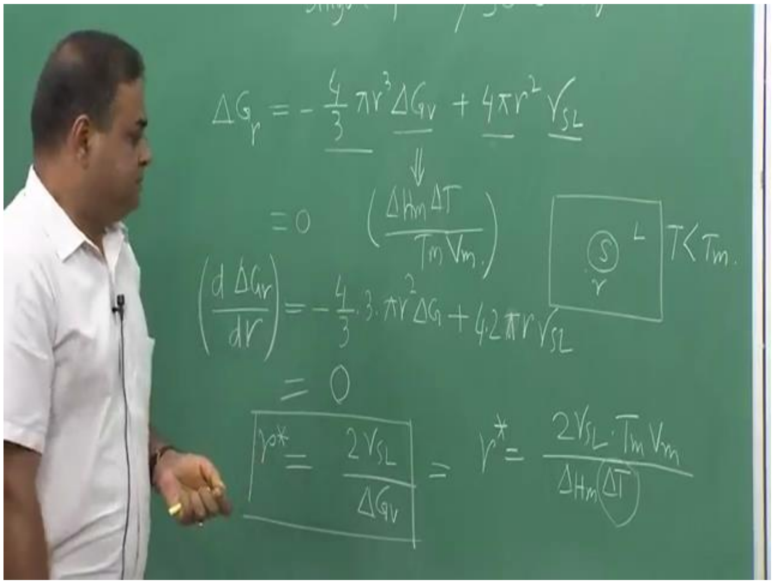

So now if we do this, then we would get gamma Sl. So this at critical point, this slope becomes zero, slope becomes zero and that time when slope becomes zero, so r so that means when the slope becomes that we consider as r star would go to delta Gv. Now if we see this expression, this expression for del Gv there is small problem, the problem is this term is molar term but this term is a volume term. So now in order to make it volume term, so we have to divide it with Vm we have already seen that, we have already we have already done this particular treatment in order to convert molar to volumetric.

Now this is a critical expression, now if we try to see the variation of r star with temperature or undercooling, so this would become 2 gamma Sl divided by del Hm del T Tm Vm what we have done, we have just replaced these particular expression in the place of delta Gv. Now it is pretty clear that as we increase del T, that suggests that as we go down the temperature axis below Tm this are still keeps on decreasing since this is a constant term, this is a constant term, this is also constant, this is also constant because for a particular solid-liquid transformation molar volume of that particular single component system it is constant.

So there is inverse proportionality between r star and del T or other way in other way r star decreases with increase in undercooling or decrease in temperature.

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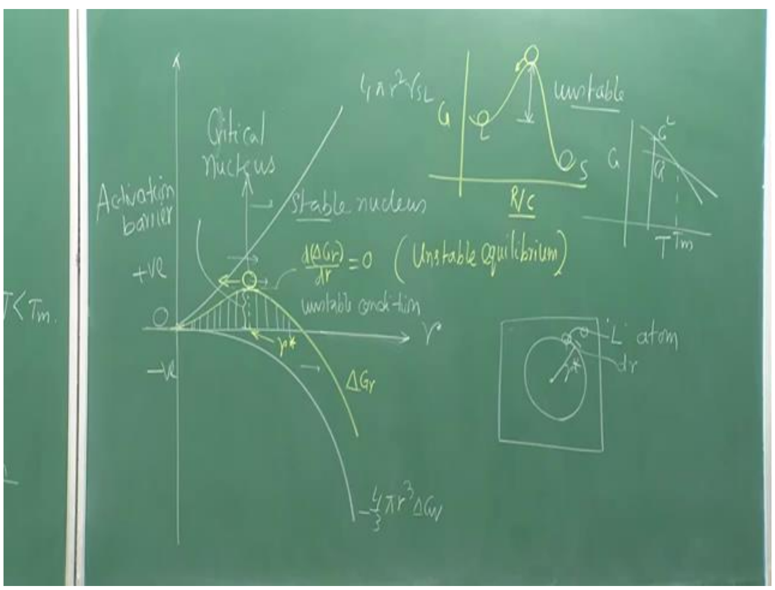

Now if I try to see individually, if I try to plot this particular term and this particular term, let us see what happens, since this is a negative term, so we will put it this one to be zero and this one would be on the negative side and this one would be on the positive side this one. So now if we consider this, if we come to this particular expression, if we consider this its varies as if square of r.

So it would vary like this, now this term is this is basically 4 pi r square gamma Sl. Now similarly, I can also have a plot between this particular term as a function of r, so this is as a function of r, so this term would vary like this. So now since it is 4 by pi by 3 pi r cube delta Gv and there is a negative sign so that is what we have taken it to the negative side, this is positive side at the same time this is a positive energy this is a negative energy, so and also this varies to the power r to the power cube.

So its variation would be like this, now if we try to see the variation of delta Gr as a function of r, it would look like this. So now there is interesting thing, so this is my delta Gr variation and at this point the slope equal to zero. So now corresponding to that point, this would be my r star. Now if I take a (situa) if I place that particular sphere here, that means this is the size of r star, this is the size of r star if it stays there, this is a situation a typical situation unstable equilibrium.

It suggest that if we do not disturb it, it can either go this way, or it can either it can go this way. And this is the zero value of r, now zero value of r means there is no existence of solid. Now if it goes this way, then I am seeing that the spontaneously this particular thing can go to this particular level because as per our energy distribution, we have seen this particular thing if you recall reaction coordinate and that reaction coordinate here it is r. So now there if the ball rolls down from here to this place, it will spontaneously go without stopping because it has it will go in the, it will go as per this energy lowering process and finally it will stay here.

So that means, if I can take it, if I can give a little push from this side, so then it can roll over and come there, what does it mean? It means that the solid would lose solid atom that means the atom of that particular metal from the solid phase it will go to the liquid because gradually it will lose its radius and finally reach there. That means gradually it will (re) it will reduce its radius, how can it reduce its radius? The atom which are, atoms which are part of solid now they will start dislodging from the solid phase and go to the liquid phase.

So that times this becomes unstable once it goes to the left side, okay. So that is unstable system we have seen that this is unstable system, unstable. So that means this particular sphere becomes unstable and it goes to the zero point, but the interestingly part would be, if we take a push this way, now how can we give push this way? The one possibility is if I can say if a situation if you have a situation like this is a sphere, this is a sphere of radius r star.

Now by any means, because of let us say thermal fluctuation, one liquid atom let us say this is liquid atom come and join the solid phase. So once its joins the solid phase, the solid radius increases by del r, okay. So it is a small radius increase, which is del r, now if it increases this radius by del r, it goes to the other side of this slope, other side of this slope. So then another unstable condition setting up, another unstable condition setting up and this unstable condition is always preferred because that time this solid can only grow it size because it always goes to the right side.

So that means, it can only increase its size, what does it mean? It means, that the solid becomes a stable particle or the stable particle inside the liquid, the solid cannot go back and melt. So this, from this to this way it melts again and this to this way it actually takes more liquid atom and becomes solid and solid so the solid grows in size. So this unstability as per this model is always good because that time the solid can go and increase its size.

So that time we call it as a stable nucleus, okay. So that means this is critical nucleus we call it critical nucleus, critical nucleus and this is once it goes to the other side, it becomes stable. So this side is stable nucleus, stable nucleus. Now since this is staying on top of it, which is unstable equilibrium and this is also another interesting part, that means if I try to see this, this is my activation barrier. So now if this is my liquid, this is my solid, this is as per our understanding, so this is G, this is temperature, so this is my Tm at any temperature T Gl is more than Gs.

So this is Gl, this is Gs. So Gl to Gs though there is a spontaneity possible, that means the reaction is possible because there is always a reduction in free energy but that does not go the way it moves from here to there because there is an activation barrier, okay. So this activation barrier is this one, okay so this barrier is called activation barrier, activation barrier. So this activation barrier whenever liquid atom goes to the solid phase, it has to cross an activation barrier and interestingly this activation barrier is evolving due to this term.

Which is interfacial energy term which is a positive energy, okay. So this positive energy does not allow that solid that liquid to go to solid immediately it has to acquire sufficient negative energy before it convert from solid liquid to solid, okay. So this (acive) activation energy has to be crossed, that suggests that this liquid atom has to gain sufficient energy has to get sufficient excitement to cross this barrier and go to the other end. So that time we have nucleation, okay. So that means this is critical nucleus, this is activation energy, okay and the other side is stable nucleus formation and the left side is unstable cluster because it always goes and melts, okay.

So that means liquid will again form, so we are if we would like to find whether the solidification would take place or not, our interest would be to cross this barrier and go to the other end. So now whenever I am trying to cross this barrier there are two events, 1) is has to get sufficient excitement to cross this barrier, okay the other one is, another atom should join, the another atom liquid atom should join to the solid surface, okay.

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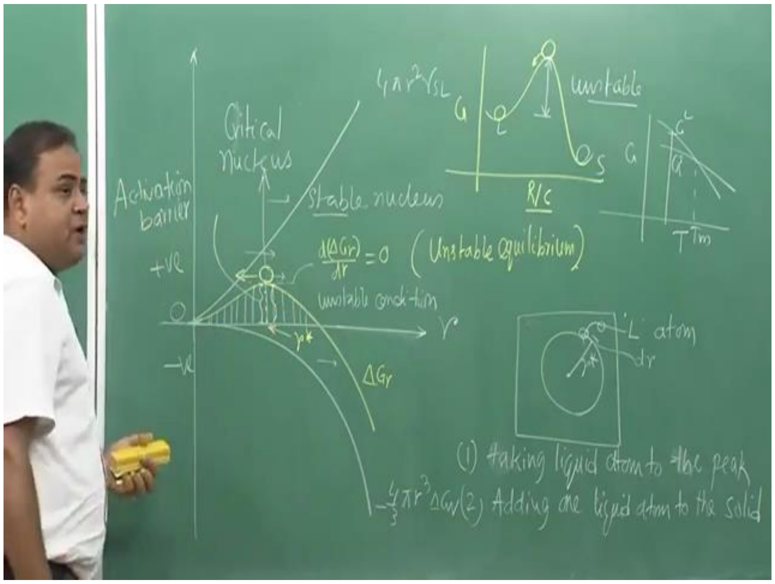

So that means two event, first is crossing taking liquid atom to the peak, peak point and the second is one is adding one liquid atom to the solid. So these two events are taking place, so this particular event we call it nucleation event and this is a part of growth event, because the critical nucleus is growing because of one liquid atom is joining the solid atom and making it going to the other end of this this end of this particular nucleation barrier. Now if we consider that, then we would get what would be the rate at which this solid is becoming the critical nucleus is becoming stable nucleus, okay.

So before we go to that, we have to also quantify this particular value. So that quantification becomes easy because already we have calculated r star, if we have calculated r star, so that means this is del Gr, del Gr value at r equal to r star if we convert, then it becomes the activation barrier.

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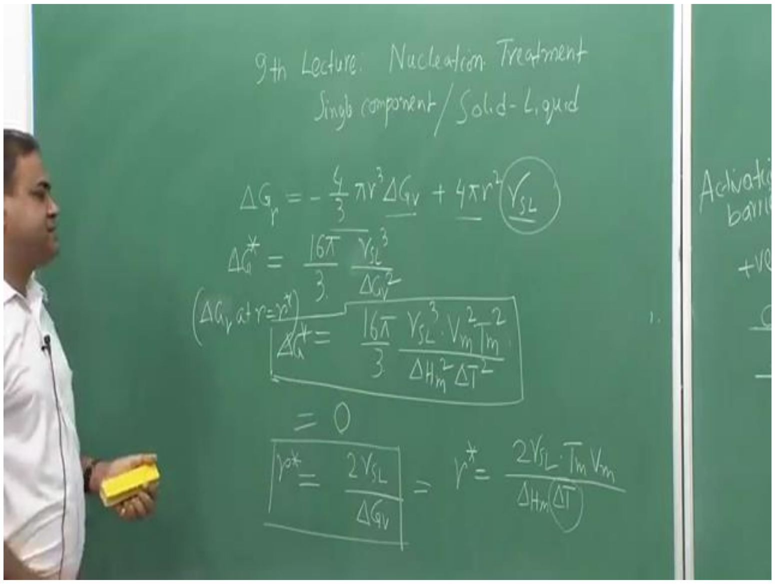

So if we do that particular operation we just replace r value with this, first let us replace with this, so if we replace it, you would get you try to do that particular operation so then you will get 16 pi by 3 r cube, sorry gamma Sl cube by delta Gv square.

So now that time this becomes delta G star, and this delta G star is basically calculated is basically nothing but delta Gr at r equal to r star. Now if we try to replace delta Gv, we can get 16 pi by 3 gamma Sl cube Vm square Tm square delta Hm square delta T square. So this is another important expression, in the next lecture we will solve some problems using this two equations, okay. Now coming to the rate at which this solid will form, solid will go to the other end, I am just talking about the solid going to the other end, my operation is over.

For example let us say there is a possibility of a 100 of such critical nucleus to go to the next layer, next layer if we consider this particular zone to be the increase in size which is del r, if we consider this to be del r and this del r is becoming this due to the addition of one liquid atom to the critical nucleus, okay. So how many of those critical nucleus can increase its size by del r, that number if we calculate that number becomes my nucleation rate, that becomes my nucleation rate, okay.

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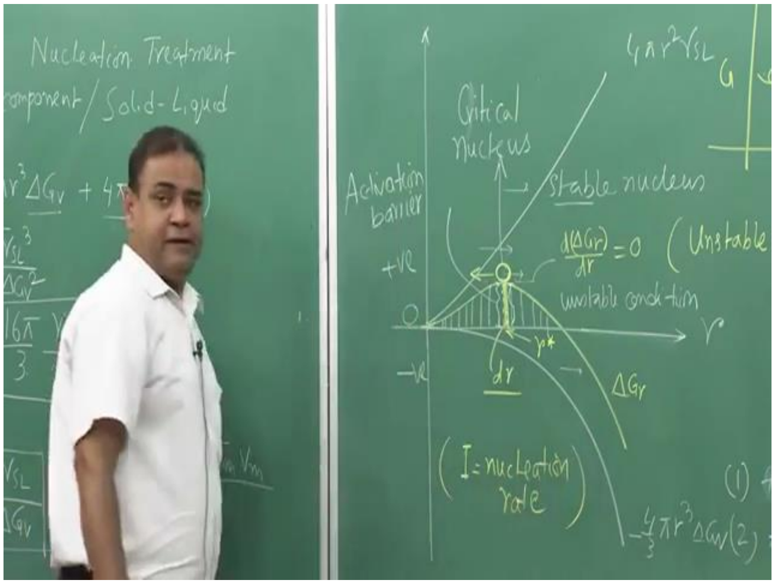

So now, if we try to see this particular nucleation rate, it has two events now, first is taking liquid atom to the peak and second one is adding one liquid atom to the solid and this nucleation treatment it will be elaborately explain by professor Sangal but we will just see the expression and try to see its graphical (inter) implication and also we try to see that it has got any relation to heat treatment, heat treatment of materials, okay we will see that.

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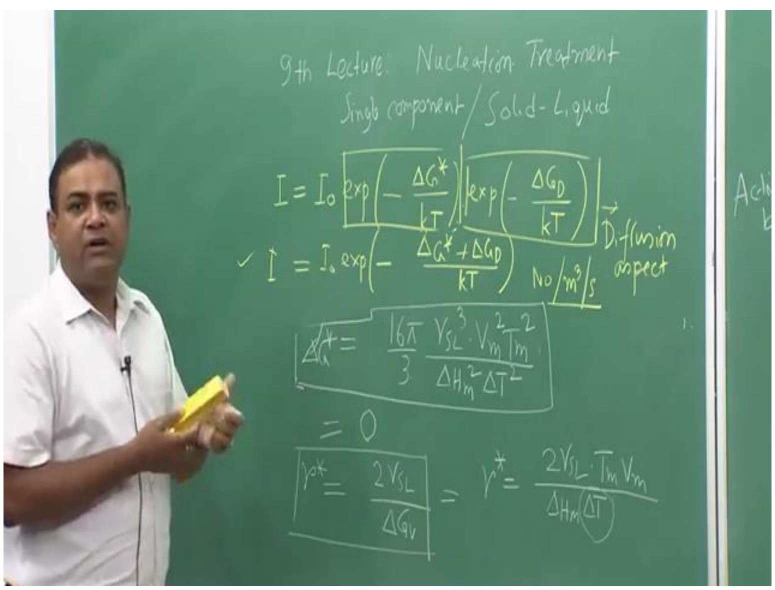

Now if we try to see the expression for I, considering this two events, you will see that expression becomes kT this is their expression. Now in this expression I can also write in terms of exponential minus delta G star plus delta Gd by kT, this is a very very popular expression and this considers delta G star which in can be calculated from this, this consider delta Gd, now what is delta Gd? This term is coming from the first consideration where taking the solid to the peak of that particular graph, this peak of this particular graph, okay.

So that is considered by that, that is taken care of this particular term which is exponential term and the second part is coming from addition of one liquid atom to the solid surface once it reaches to the top of that particular peak, okay. So that means this is coming from diffusion aspect, diffusion aspect. So the diffusion aspect is coming from liquid atom has to diffuse through the liquid phase and it should get added to the surface of the solid. So that means this is the diffusional aspect and this is the activation aspect, okay.

But if you see the exponential term, since there is an exponential term you will see later on that it has, it follows Boltzmann statistics because when I it will be consider by professor Sangal that he would say that it actually follows the Boltzmann statistics. So that is what you get exponential term, now this is the rate at which stable nuclei forms from in a particular volume of liquid. That means the stable solid particle form in a liquid volume per unit time.

So this unit becomes the number per meter cube per second, okay. So that means we have critical nucleus size, we have critical activation energy and then from there we get nucleation rate, the rate at which the stable nuclei forms in a particular volume of liquid, okay per unit time. So with this three expression we will try to see some of those we will do some problems solving in our next lecture so just to make it more clear, okay. So let us stop here thank you very much.