Heat Treatment and Surface Hardening (Part–1)

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Lecture Number 10

Nucleation Treatment single Component (Solid-Liquid)

Hello, we shall start 10th lecture, this will continue discussion on nucleation treatment single component system, solid liquid transformation.

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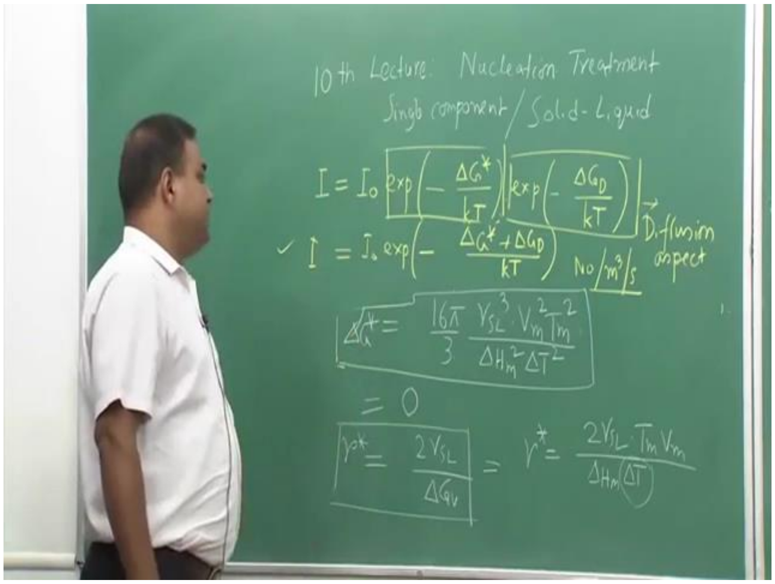

10 th Lecture: Nucleation Treatment
Single component / Solid-Liquid

$$I = I_0 \boxed{\exp\left(-\frac{\Delta G^*}{kT}\right)} \boxed{\exp\left(-\frac{\Delta G_D}{kT}\right)} \rightarrow \text{Diffusion aspect}$$

$$✓\; I = I_0 \exp\left(-\frac{\Delta G^* + \Delta G_D}{kT}\right) \quad \text{No}/m^3/s$$

$$\boxed{\Delta G^* = \frac{16\pi}{3} \frac{\gamma_{SL}^3 \cdot V_m^2 T_m^2}{\Delta H_m^2 \Delta T^2}}$$

$$= 0$$

$$\boxed{r^* = \frac{2\gamma_{SL}}{\Delta G_v}} \Rightarrow r^* = \frac{2\gamma_{SL} \cdot T_m V_m}{\Delta H_m (\Delta T)}$$

And if we see in the last lecture we have found out this expression and where this is uhh critical nucleation barrier or activation energy. This is critical size, this is nucleation rate where this term is taking care of taking the liquid atoms in the form of solid sphere to the top of that particular hill.

And this part is taking care of the second event where one liquid atom is added to the solid surface in order to make it stable. Now this is the diffusion aspect what we have expressed and this term is also called diffusional activation energy for liquid atom going to the solid surface. Now if we try to see its evolution so this is let us say this is my solid surface and this is my liquid surface let us say. Let us assume that they are having interface like this.

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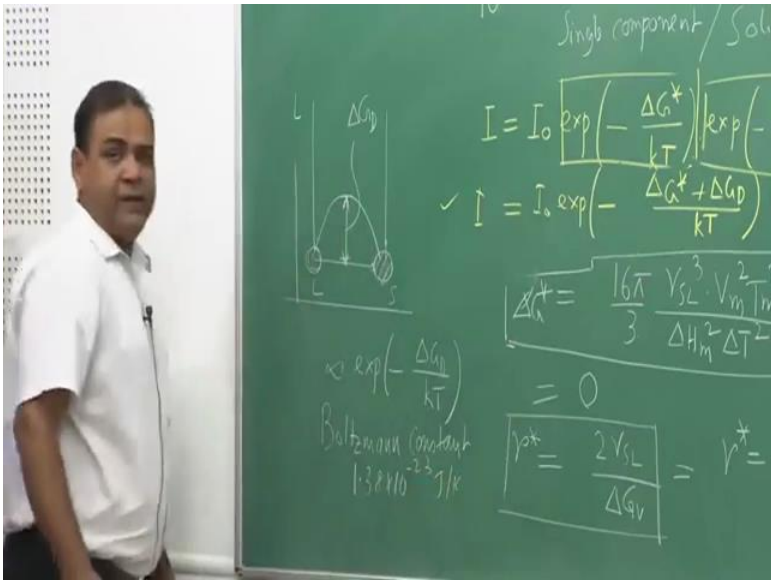

Now, liquid atom if liquid atom position is this and solid atom position is this. Now this atom let us say this solid atom position is vacant and this liquid atom takes the solid atom position so it cannot go like this. It always takes a path like this which is governed by a kind of activation energy. So this activation energy is nothing but delta GD. So again this is also call taking talking of some jump.

And that time this should be the rate is proportional to exponential minus delta GD by KT. And this K is Boltzmann Constant, Boltzmann Constant its value is 1.38 into 10 to the power -23 joule per kelvin. So now this particular term is sitting there because it talks about jump of liquid atom and going to the solid surface. Now if we try to see the variation of R star and variation of I, we can get some interesting information, ok.

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Let us see that information in the form of graph, if I try to plot R star as a function of del T, so now if we see that R star is inversely proportional to del T. So that means R star would have a very high value and then gradually it will decrease like this, ok. So this star is R star variation. Now if we try to plot I variation as a function of, this is I as a function of temperature. Let us say this is my Tm which is the melting temperature at Tm what would be the value of R star.

So, now at Tm del T is 0, R STAR is infinite, ok. So now at the same time if I try to plot if I try to see del T G Star value, ok. Delta T0 delta G star value would be very high, ok. So now another thing if I try to plot at different temperature what would be the variation of R star, we can also have a plot like that.

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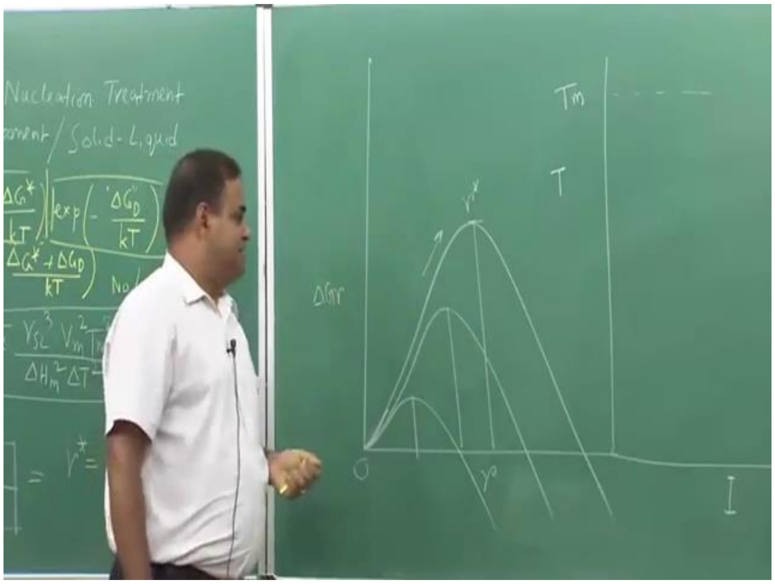

For example if I try to see the variation of delta Gr as a function of r you will see that, that plot would be look like this. So all will emit from this particular 0 point and you will see that the R star is gradually increasing. Now, interestingly we have to see what would be the temperature of those GNTG, delta Gr plot. Because delta Gr plot is at a particular temperature. Now if I try to see that temperature, now as we see that R star is inversely proportional to del T, if we decrease the temperature R star would decrease as we have seen in the last graph.

So that means as we are going from here to there that suggest that delta T small that means we have we are going closer to melting temperature. And R star is also increasing, so at Tm, R star would go to infinite. So that means smaller and smaller r value that means the critical nucleus that we are getting, if del T is small.

This is interesting conversation, because we have seen from our normalizing and annealing consideration, we have seen that if we increase cooling rate. Increasing cooling rate means that we are taking del T more higher and higher. So that means that we can achieve del T higher del T in the same time duration.

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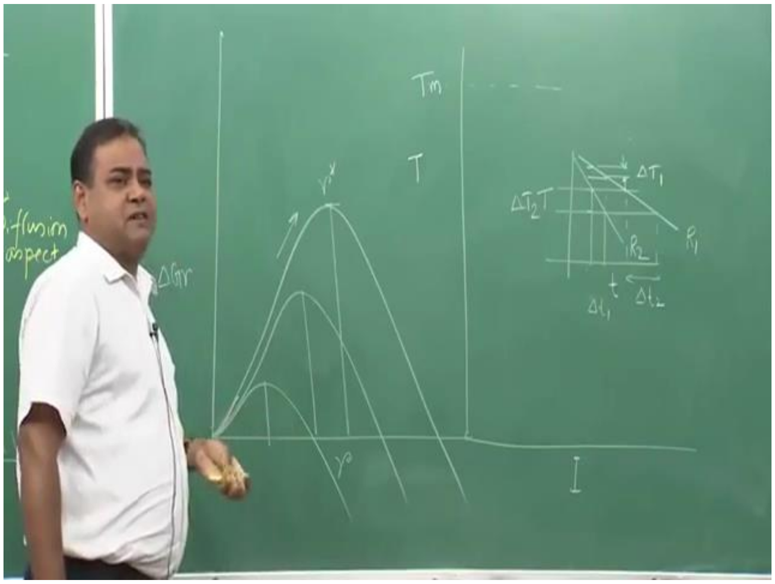

Let us analyze that, for example if I see the cooling rate this is T (minu) and t. If, I see the cooling rate is this and the cooling rate is this, so this is cooling rate R1, this is cooling rate r2. If I try to see a particular temperature drop, ok. So that means within this (tem) temperature time duration which is let us say uhh del t1 and if I try to see this duration which is del t2, now we are going by the same del T same del T but if the cooling rate is fast we can achieve that del t much quicker than when the cooling rate is slow.

So that mean in other way let say I fix my delta t1, let us say this one I am this one I have fixed. So I would like to see in a similar time duration, how much del t I can achieve. So now if I go there, so here I am achieving this much but here I am achieving this much. So this del t is this one, if I try to follow the same duration this much is the del T1 and this is del T2, delta T2 where in case of higher cooling rate.

So that means higher cooling rate gets me higher del T. that means higher under cooling. Now, if I get higher cooling rate I am getting higher del T that means my R star would also decrease it suggest that I might get fine structure, ok. The size of the sphere would be finer and finer and I would get very very fine structure, ok. So that also gives little idea that why increase in cooling rate during steel heat treatment gets me very very fine per rate.

That means or very fine grain size that means I am reducing the critical radius. Because of higher under cooling and that is because of higher cooling rate, ok. So now this gives a little idea that yes if we go for a higher cooling rate, higher under cooling I would get very fine structures. Now let us see the plot of I, now if I try to plot I, I have two parts one is this part, one is this part.

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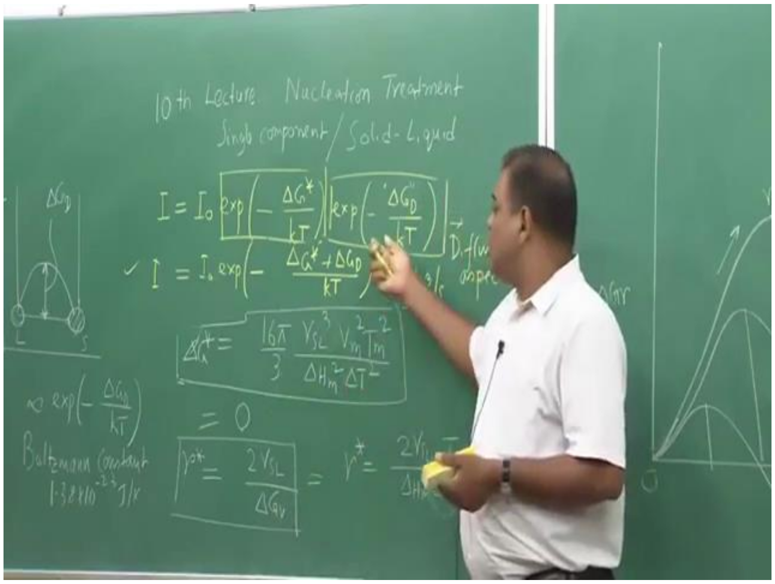

And interestingly if we did not mention this part this I0 is a constant, ok. This I0, the detail expression of this I0 will be again covered by process angel, will not talk detail about this our entire thing will be govern by how we can find out del TGV. And at the same time consequently how those expression would look like if we consider if we if we take those delta GV value.

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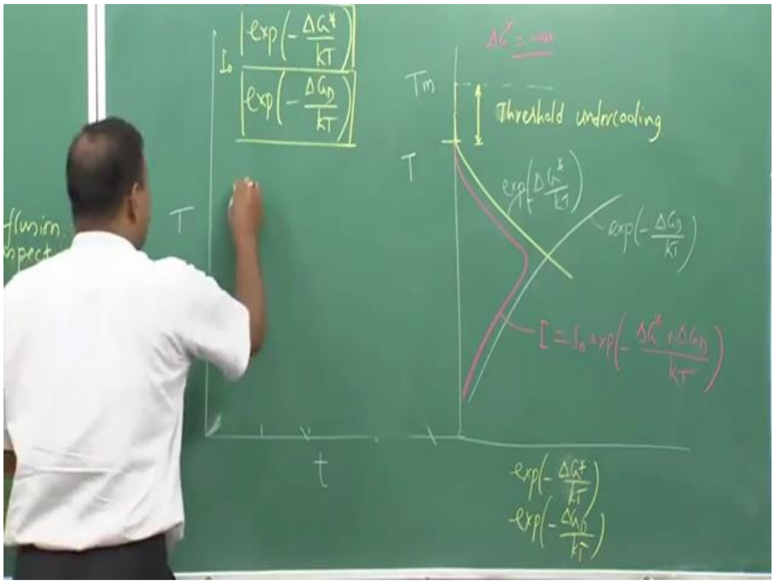

Now if we plot this two expressions, so let us write that two expression. Exponential minus delta G star by KT and the another one is exponential minus delta Gd by KT, ok. Now I is common, I is common, now if I try to see this variation and if I try to see this variation let us see how this two variations would look like in the temperature access. Now I am plotting first I am plotting exponential minus delta G star by KT.

Now at T equal to Tm, so that means at T equal to Tm would we get any, would we get any r on the solid. Because at T equal to Tm, I do not have any under cooling so that means if order to get r it has to be very very large which is not possible, ok. So it cannot go immediately to that particular big r. so initially it will not be, there will not be any uhh uhh existence of this particular term.

Now as we are going lower and lower temperature and this particular nucleation event happens, that means going to the top of this particular peak, ok. It takes thermal fluctuation, so that thermal fluctuation will not be sufficient to form a very large crystal or very large solid. So that means we need a (mmm) uhh little under cooling. So even if we have a sufficient under cooling we will see that still the R star would be very large, still it is not possible, ok.

But at some point of time I would be able to see that the thermal fluctuation is able to give me a sufficient number of R star, ok. And which would be feasible and which would be able to uhh experience through this (experie) through this expression. So now it would look like initially there will be no nothing and then finally it will increase like this, ok. So till the point I do not see any expression then any existence of this particular term that means I do not have critical nucleus, ok.

So now this particular section we call it under cooling, threshold under cooling, threshold under cooling. Now then if we consider the second term exponential minus delta Gd by KT. Now as we increase temperature, I have more and more (ex) excitation of atoms. The atom can move easily so that means I must this particular barrier term would decrease gradually with the increase in temperature so that times it would always increase.

It is always increasing, ok. So now this is my exponential minus delta Gd by KT and this is delta G star by KT exponential minus, fine. Now what is r what is I, I is combination of this two, the product of this two. So the I would experience, I would be found out between these two lines. So this is my I which is I0 KT. Now before we go and do some calculations let us see the uhh practical existence of this threshold under cooling.

Now what does it mean this threshold under cooling means that until unless we go till certain temperature range, temperature down temperature we cannot come cannot get rid of this surface energy, cannot sorry rather we would say that cannot super seed or the exceed that surface energy contribution and make this delta Gr term negative, ok. So then until unless this volume free energy term exceeds the value of surface free energy term the nucleation is not possible.

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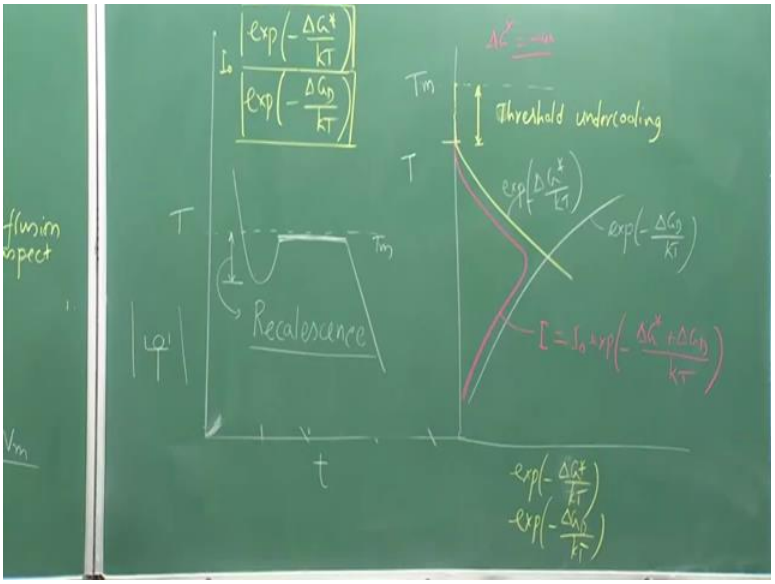

Now this particular thing we see when we solidify pure metal, we try to see cooling curve of the solid liquid metal. If we try to see the cooling curve that means the cooling curve is nothing but temperature time plot. If it is a pure metal, we some time see this kind of variation. So the (exp) experiment is pretty simple I have a furnace, I have a furnace and in the furnace you keep a liquid metal and I put a thermal couple here and starts measuring the temperature as we cool down the metal temperature, liquid metal temperature.

As we cool down we see that the melting point at melting point this is if this is the melting point it never solidifies at melting point. Rather the temperature of the liquid drops to a certain extent before the solid start appearing, ok. And then once the solid starts appearing it will go to it will take a flat line till all the solid transforms, all the liquid transforms to solid and it will be little below Tm, because at Tm it is all equilibrium. So we cannot say the whether the transformation would take place or not.

Equilibrium cannot be said to uhh cannot be cannot be uhh experienced this phase transformation cannot be experienced at equilibrium point, we have to go little away from the equilibrium point, ok. So now that is why this particular thing has to occur little below the Tm. But if we see this drop this drop, so that means the liquid temperature drops far below the melting point before the solid appear and this happens because of the interface energy term.

This interface energy which is the positive contribution does not allow the total system energy to go down, down the hill, ok. So that is why this particular thing we call it Recalescence. So this particular thing is nothing but this, ok. So now if we see that I variation the I variation is like this. So that means until unless we go for uhh little below the melting point we cannot have any existence of nucleus, ok. So, let us stop the discussion here, let us do some problem solving, so then things will be very clear.

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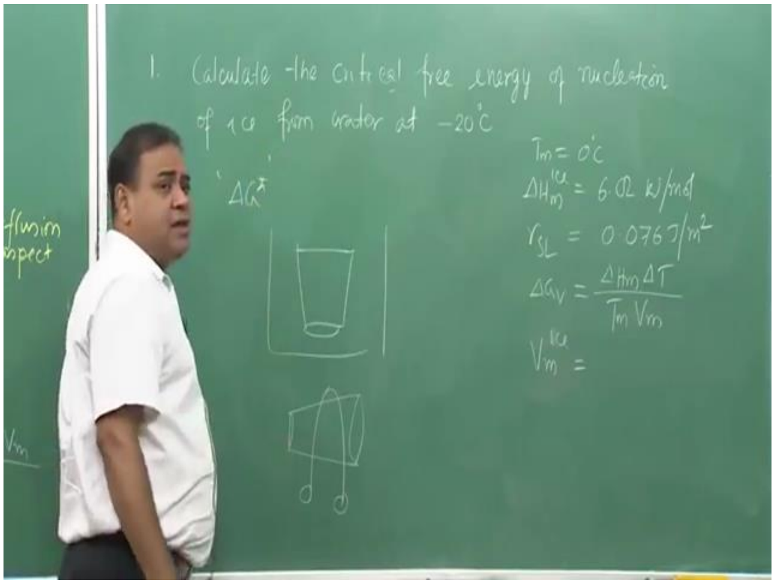

Let us take a simple problem first then will solve a complicated problem uhh calculate critical free energy of nucleation of ice from water definitely at minus 20 degree Celsius and where Tm is 0 degree Celsius, delta Hm ice is equal to 6.02 kilojoule per mole and gamma Sl which is ice water interface is 0.076 joule per meter square.

And also while calculating this critical free energy, so we have to calculate delta D star delta G star. So if I try to calculate delta G star we need not delta Gm rather we need delta Gv which is delta Hm delta T Tm Vm. So now one data is missing the Vm solid that means ice is equal to or liquid because we are considering that there is no volume difference when we go from liquid to solid but actually it does not happen.

Because the liquid to solid when it transforms it has a positive volume expansion. So that means uhh solid when solid forms the volume expands and because of this volume expansion some interesting thing happens in liquid, ok. If you have noticed for example if you can you can do one experiment let us say you take a small uhh you take a water in uhh uhh glass open uhh this one one steel glass take it to refrigerator freeze it.

Take that particular block out, ok. So let us say you have uhh have a glass and you have taken water and let this thing to be taken into a refrigerator so that means you have now you form total ice. So that means once you take the ice that means after that you take it out try to (wai) wait for some few minutes. You will see that this ice becoming little free from this ah glass then you take that ice out.

So, uhh this ice is taken out taken out. Now you put a wire around that and have little weight you will see that gradually this wire will cut through the ice but the this particular ice block will not be separated into hubs, ok. So this particular thing is coming from that volume expansion also the pressure effect. So we call it Clausius Clapeyron effect but we will not consider this particular Clausius Clapeyron effect right now.

When you talk about steel uhh heat treatment it might come across, ok the Clausius Clapeyron effect. So right now we are not considering because our basic assumption while coming to this value was liquid to solid transformation does not have any volume change. So this Vm is 19 meter centimeter cube per mole this is per mole. So now we can convert into uhh uhh meter cube so 19 into 10 to the power -6 meter cube per mole.

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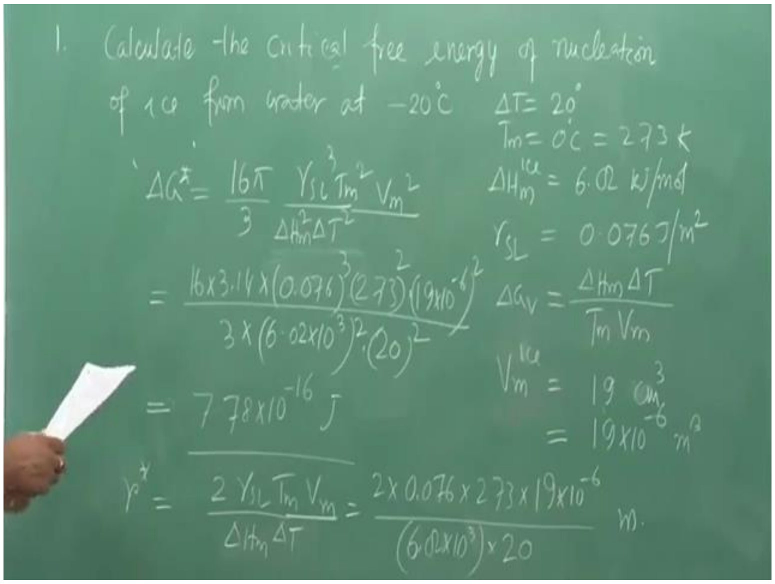

1. Calculate the critical free energy of nucleation of ice from water at $-20^\circ C$

$\Delta T = 20^\circ$

$T_m = 0^\circ C = 273\ K$

$\Delta H_m^{ice} = 6.02\ kJ/mol$

$\gamma_{SL} = 0.076\ J/m^2$

$\Delta G_V = \frac{\Delta H_m \Delta T}{T_m V_m}$

$V_m^{ice} = 19\ cm^3$

$= 19 \times 10^{-6}\ m^3$

$$\Delta G^* = \frac{16\pi}{3} \frac{\gamma_{SL}^3 T_m^2 V_m^2}{\Delta H_m^2 \Delta T^2}$$

$$= \frac{16 \times 3.14 \times (0.076)^3 (273)^2 (19 \times 10^{-6})^2}{3 \times (6.02 \times 10^3)^2 \cdot (20)^2}$$

$$= 7.78 \times 10^{-16}\ J$$

$$r^* = \frac{2 \gamma_{SL} T_m V_m}{\Delta H_m \Delta T} = \frac{2 \times 0.076 \times 273 \times 19 \times 10^{-6}}{(6.02 \times 10^3) \times 20}\ m.$$

Now, this one is 16 pi 3 gamma Sl cube delta Hm delta T Tm Tm this will be all square Vm square this would be the expression. And now I just put those values 16 into 3.14 into 0.076 cube, 0 degree Celsius that means 273 kelvin, 273 square Vm is this 19 into 10 to the power -6 square 3 into 6.02 into 10 to the power 3 since is kilojoule where and here I am saying that -20 degree Celsius.

So my del T would be 20 degree. So that means 20 kelvin this square. So (nn), if you do this simple calculation you would get 7.7810 to the power -16 joule, so this is the expression. Now you can also find out R star you can find out by 2 gamma Sl by delta JHm delta T Tm Vm so it would be 2 into 0.076 into 273 into 19 into 10 to the power -6 divided by you can get r. So that time this will be in meter. So this was one simple (ex) example we can calculate delta G star using that simple expression.

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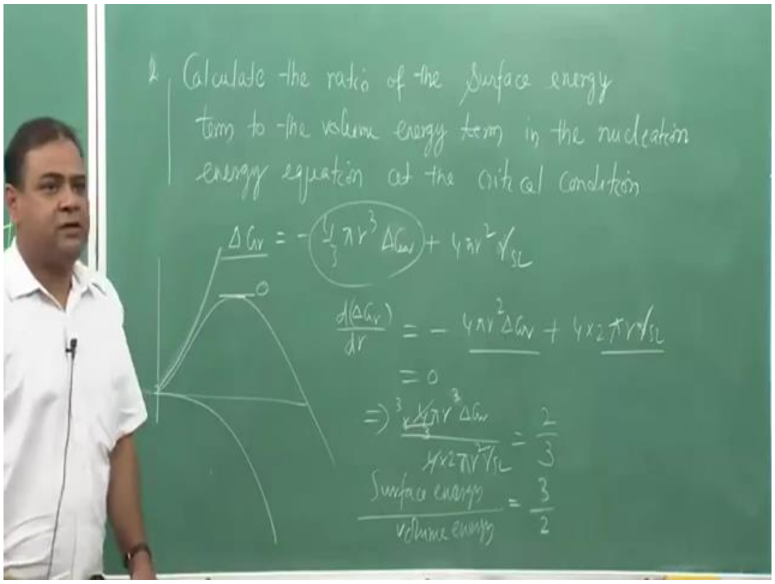

2. Calculate the ratio of the Surface energy term to the volume energy term in the nucleation energy equation at the critical condition

$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}$$

$$\frac{d(\Delta G_r)}{dr} = -\underline{4\pi r^2 \Delta G_v} + 4\times 2\underline{\pi r \gamma_{SL}} = 0$$

$$\Rightarrow \frac{3\times\frac{4}{3}\pi r^3 \Delta G_v}{4\times 2\pi r^2 \gamma_{SL}} = \frac{2}{3}$$

$$\frac{\text{Surface energy}}{\text{volume energy}} = \frac{3}{2}$$

Now let us consider a bit uhh typical problem. That time I can write this delta Gr term which is 4 pi r cube gamma SL sorry delta Gv + 4 pi r square gamma SL. Now during that case I need to find out the critical condition we have seen the expression or variation of delta Gr, which is like this which is like this where this is my this is by surface energy term, this is the volume energy term.

And this is my delta Gr and at critical point which is this delta Gr becomes maximum and the slope becomes 0 so that means unstable equilibrium. And that time I just find out what is the condition there so that means delta Gr dr is basically my critical condition or the nucleation condition, critical nucleation condition which would be -4 pi r square delta Gv + 4 into 2 uhh pi r gamma SL, gamma SL so this case this case so this becomes 0, the slope become 0. So from there I can say that 4 pi r square delta Gv by 4 into 2 pi r gamma SL equal to 1.

Now I have to convert it into this so in order to convert this, if I divide it by 3 and multiply with 3 and also I multiply with r so this is r square. So that time it becomes, so this 4, 4, 2, so it becomes 2 by 3, ok. So now if I try to see the surface energy is saying that surface energy to the volume energy term it just reverses so uhh this term surface energy is equal to 3 by 2, ok this is the answer, ok. So let us stop here uhh will go to the next topic in our next lecture, thank you for listening, thank you.