Heat Treatment and Surface Hardening (Part–1)

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Lecture Number 27

Maximum nucleation rate for homogeneous nucleation

In the last lecture we talked about critical undercooling and we had estimated the critical undercooling for nucleation of ice and water to be of the order of 42 degrees. Now I want to explore that is there a temperature or an undercooling at which one would get the maximum undercoolings or maximum nucleation rate.

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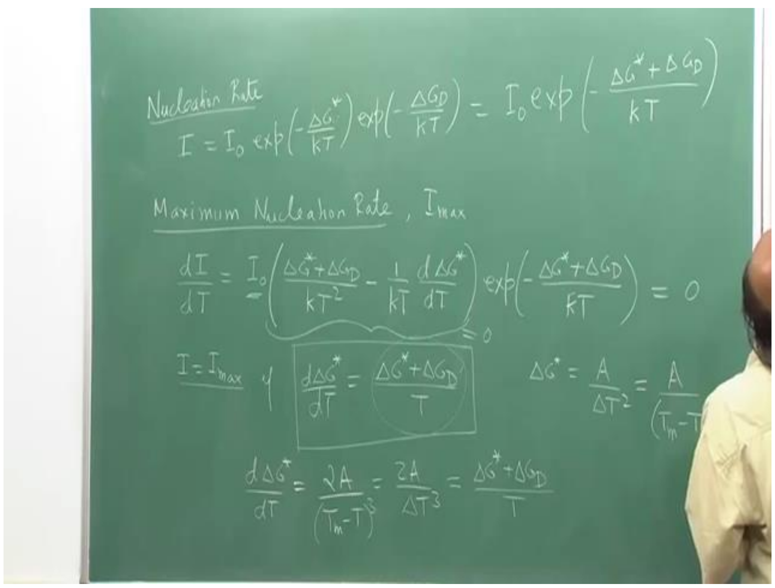

So let us try and look at this problem, so we have the nucleation rate, it is already written on the board and I want to see that is there a temperature at which I would get maximum nucleation rate. So how do we do this? Well, all we had to do is differentiate the nucleation rate relationship and set that to 0.

So dI by dT if I differentiate this will become I0 and then one will have to differentiate this because one knows that delta G star itself is the function of temperature, but here we will assume that delta Gd is more or less constant independent of temperature. So by doing this simplification, dI by dT will become I not delta G star plus delta Gd upon kT square minus 1 upon kT d delta G star upon dT times exponential minus delta G star plus delta Gd upon kT.

I think you can see that easily from here we can reach this step just to make things easy you can start with this expression I not exponential minus put both the delta G star and then delta Gd term in the same exponential. So start from here and you will easily reach this step. And in order to get at I max, this will be 0. Now let us examine this, this exponential term will never be 0, I not is again another constant non-zero, therefore dI by dT will be zero only when this term goes to zero, which means that I the nucleation rate would reach the maximum nucleation rate I max if this term goes to zero. In other words this can be written as d delta G star by dT should be equal to delta G star plus delta Gd upon T.

So this is the condition for obtaining the maximum nucleation rate. Now let us look at delta G star, we have already seen that delta G star can be written as A upon delta dT square where A is a function of delta Hm, Vm, Tm so on all constants. So delta G star is A upon delta T square, which means I can write d delta G star upon dT to be well I can write this first instead of (de) in terms of delta T I can write Tm minus T for delta T square and then differentiate. So (de) d delta G star upon dT would be equal to 2A upon Tm minus T cube or it is simply 2A upon delta T cube. So this 2A upon delta T cube I can should be equal to this quantity, so this can be written to delta G star plus delta Gd upon T.

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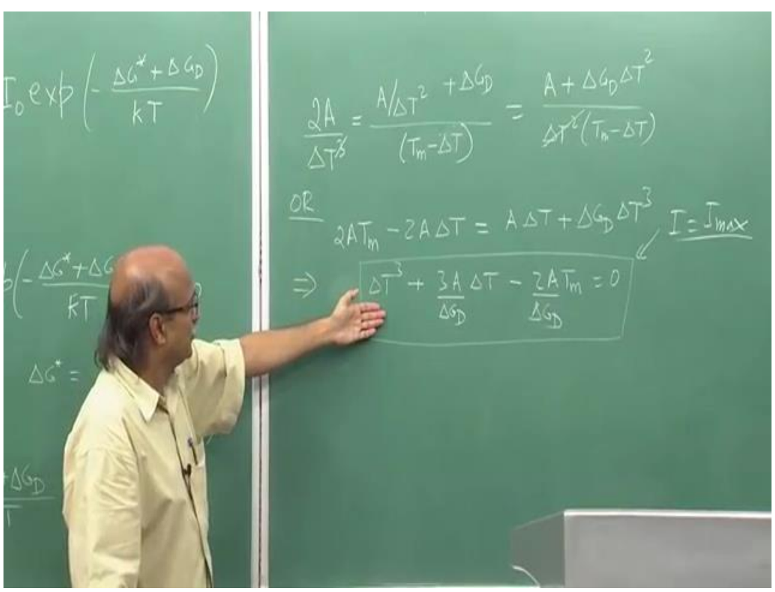

So let us substitute for delta G star, so I can write 2A upon delta T cube instead of delta G star I write A upon delta T square plus delta Gd which is assumed to be constant independent of temperature upon T (aa) now instead of writing T let me write it in terms of delta T, so this would be Tm minus delta T, rearrange the terms this would become A plus delta Gd delta T square upon delta T square times Tm minus delta T.

Or let me bring rearrange a little bit more and I will get that means between this and this I will get 2A Tm minus 2A delta T equals because I can actually delete this delta T square and delete this cube, so here it becomes 2A upon delta T is equal to A plus delta Gd delta T square upon Tm minus delta T and now I am rearranging, so I will get 2A Tm minus 2A delta T equal to A delta T plus delta Gd delta T cube. This will lead to delta Gd delta T cube collecting all the terms on one side delta Gd delta T cube plus 3A delta T minus 2A Tm equals 0.

Let me also change this slightly, divide everything by delta Gd so I have no coefficient for delta T cube, so I will get a equation of this kind and if I solve for delta T here, this will give me the undercooling required for obtaining the maximum nucleation rate. So this is a condition for I is equal to I max, if I look at this equation this is again another cubic like we got in the last lecture the cubic in delta T and in fact this is a similar cubic that we had obtained what I had called is a depressed cubic with no squared terms.

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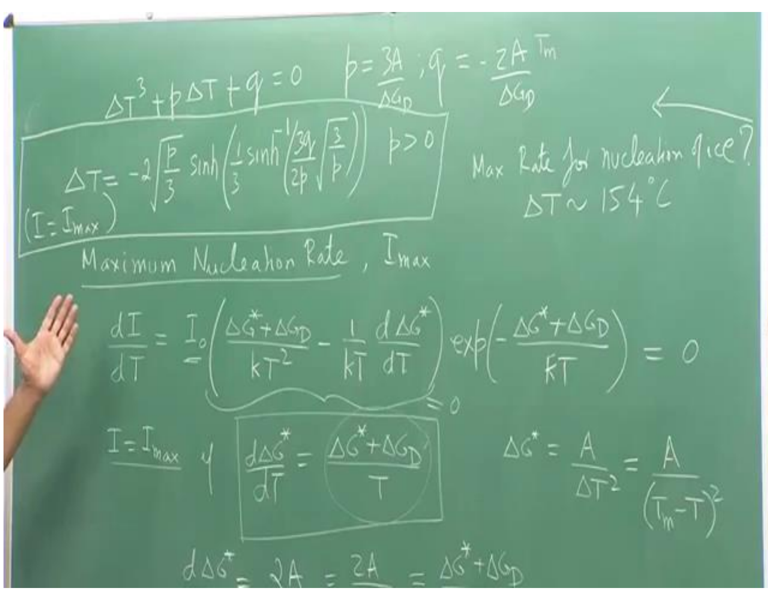

So the solution to this can be written like this if I write this relation in this form delta T cube plus p delta T minus or plus q equals zero, where p equals 3A upon delta Gd and q equals minus 2A Tm upon delta Gd, then the solution for this equation is if I look at the sign of p, A is positive, delta Gd is positive hence p is greater than 0 while the cubic equation I had solves in the last lecture the coefficient for delta well it was not delta T it was x was less than 0.

So the solution for this particular cubic is given as delta T equals minus 2 square root p by 3 sine hyperbolic 1 upon 3 inverse sine hyperbolic 3q upon 2p square root of 3 upon p. So you are taking sine hyperbolic inverse of this quantity and then for this overall quantity I am taking sine hyperbolic multiplied by square root of p by 3 multiplied by 2 and there is a you can also note the sine here. So this will give me the undercooling for the maximum nucleation rate. If I do an estimation again for what is the maximum rate for nucleation of ice, well again the values for A delta Gd into this equations solving it we get delta T to be the order of 154 degrees below 0 below the melting point.

So the nucleation that means we can assume that (af) beyond the critical undercooling, beyond the critical undercooling which we had obtained in the last lecture was of the order of about 42 the nucleation rate should continue to increase until you reach a undercooling of about 154 and since this is the maximum that means beyond that the nucleation rate should start going down. So (heh) hence from this it appears that the nucleation rate will go through a peak as the undercooling is increased. So what I will do next is let me quickly using a spreadsheet calculate what is the how does this function look like.

The nucleation rate function that how the nucleation rate changes with the undercooling and it is very easy to do using a spreadsheet like Microsoft excel, so let me take up this.

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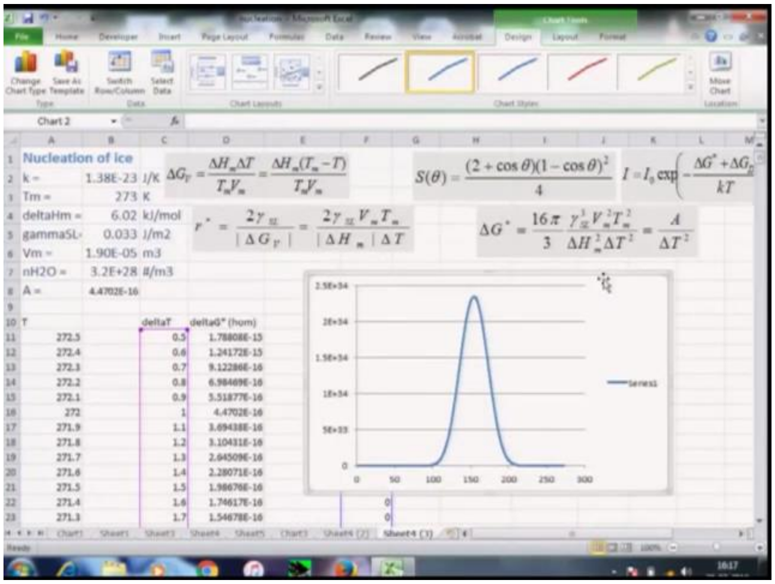

So here I have spreadsheet open I already for again nucleation of ice we will continue to do solve a for this system ice water system, I already have Boltzmann constant, the melting point, what is the change in enthalpy per mole when ice nucleates 6.02 kilo joules per mole, what is a interface energy 0.033, what is a molar volume 1.9 10 to power minus 5 meter cube and so on.

And I already have calculated the value of the constant A in the expression for delta G star as you can see here. So this was expression which is equal to A upon delta T square where this all of these terms comprise the quantity A, so A already calculated here in this particular cell B8. Now to calculate and I have already put down in the cells different values of undercooling and corresponding to the undercooling at what temperature we are looking at below the melting point of 273 degrees kelvin.

So the first temperature we look at is 272.5 which gives me an undercooling of 0.5. So let me calculate what is delta G star and here I have put this term hom to stand for homogenous, just to remind you that we are still dealing with homogenous nucleation. So this is very straight forward I can put the formula, I put down the value of A which is 4.4702 10 to power minus 16 divided by delta T square. So this is my delta T and I square it by putting a hat sign to represent that this is being raised to power 2. So with this I get that at an undercooling of 0.5 my value of the critical free energy is 1.788 into 10 to power minus 15 joules.

Corresponding to this, let me calculate the homogenous or let me calculate the homogenous nucleation rate which is given by this expression here, I is equal to I not and I not I have taken as 10 to power 42 exponential minus delta G star plus delta Gd order of magnitude estimate is 10 to power minus 20 joules, so that is taken here.

So we will put down this formula in here I0 which is 10 to power 42 multiplied by exponential minus brackets and I want to put delta G star here which the value is residing at D11 cells, so I click on D11 to get my D11 here plus delta Gd I am taking at 10 to power minus 20 put this divide it by the Boltzmann constant which is 1.38e or 10 to power minus 23 multiplied by the temperature at which I want to calculate the nucleation rate.

So this is this value is residing at cell A11 which is 272.5 in this case, then I close the bracket for the exponential and enter. Well I get a value which showing a 0 which means that at this small undercooling the nucleation rate is essentially 0 it is a very **very** small number and it is not able to show. Now all I have to do is copy these two formulae (at) downwards to get nucleation rate as a function of various undercooling and paste it here. So here correspondingly I have now many values for delta G star and nucleation rate for different values of delta T.

So as we keep going down initially up to about 13 degrees it is essentially a very small number in fact even beyond 13 you can see these numbers are very **very** small. Let me see at what temperature or at what undercooling the nucleation rate is becoming equal to the critical nucleation rate that I have assumed in the last lecture of 10 to power 6 per meter cube per second. So let us go down and see where nucleation rates reaches to the order of 10 to power 6. So there around here, if you look at it between these two values here, if I just highlight this between 41.9 and 42 lies exactly 10 to power 6 per meter cube per second as a nucleation rate.

And in fact that is what we had calculated in the last lecture. For the critical undercooling to obtain the critical (coo) nucleation rate of 10 to power 6 per meter cube per second to be 41.9, so there we are that this is showing this. Now let me try and look at it how this nucleation rate varies with undercooling delta T how does this function look like. So let us plot this function insert go to scatter plot, so I get an empty plot and I will select the values now for the x and the y axis.

So select data, so I right click on the plot, select data and add. So I add what are the x value so x values are my delta T. So press shift and down arrow key and I will select the entire column and I brought the x data chosen, similarly I will select the y data now which is the nucleation rate, again I select this and I click ok again ok and I should have the plot for the nucleation rate. So this is how let me enlarge this plot so I will move this to a new sheet so that I can see this plot in enlarged manner.

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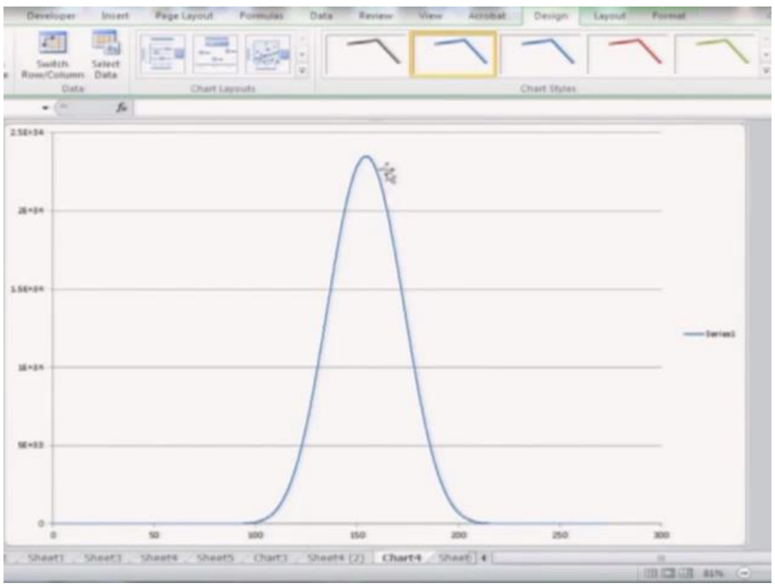

So here you can see where is the peak coming, the peak is coming around 153 one and if you recall just now by solving that cubic polynomial in delta T the undercooling we had calculated was of the order of 154 degrees and that is where we are closed by here. And similarly the critical undercooling you cannot see in this graph because of the large scale involved would be around 42 over here it cannot show this because this scale is very large. So the critical undercooling is somewhere here and this is the peak in the undercool peak in the nucleation rate at about 153 154 degrees and then beyond which the nucleation rates starts to go down.

So what we have here is that there is a critical undercooling beyond which the nucleation rates starts to increase rapidly, it goes through a peak and then after that further undercooling the nucleation rate goes down. Now why does that happen? Well, this increase can be explained on the basis of that as the temperature is going down the nucleation rate equation if you see and I can show it right here, delta G star starts to drop the barrier to nucleation is going down and hence the nucleation rate is going up.

But at the same time the temperature is going down and if the temperature goes down too much, then a critical nuclei for it to become super critical an atom has to jump across the liquid solid interface, the jump frequency of that will go down as the temperature goes down simply a because the barrier or other atoms do not have enough energy at very low temperatures for them to jump.

So the probability of the jump successful jump goes down, so number of critical nuclei forming becoming super critical they start to drop. So there is a trade of as a temperature goes down, the mobility of the atoms goes down but the driving force for the nucleation is (go) is increasing. So these two opposing forces initially lead to an increase in the nucleation rate goes to a peak and then it starts to drop again. Now we have what we have done is in this lecture and until now we have looked at the critical undercooling, we have looked at the maximum nucleation rate and we have kind of understood how the nucleation rate in a system where homogenous nucleation is taking place, how this nucleation rate is going to vary with the undercooling.

And this is going to become very important when we try to model at what rate transformations will be taking place. So this is just one aspect of the transformation which is the nucleation rate, once a nuclei form they have to grow, so we will be looking at how fast they will grow by taking the nucleation rate and the growth rate putting them together we would get the overall transformation kinetics. But before we go into the growth kinetics, what we saw here was the critical undercooling that is the undercooling required for homogenous nucleation of ice to take place was of the order of 42 degrees.

Now how does this happen that we are easily able to form ice in a refrigerator where the undercoolings are very small, maybe just 5 degrees 6 degrees, maybe in some refrigerators it may be 15 degrees. But we get ice formation very easily, how does this happen? I leave this question to you to ponder and we will look at it in the next lecture, thank you.