Heat Treatment and Surface Hardening (Part–1)

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Lecture Number 23

Variation of Delta G* and r* with Undercooling

So continuing from the previous lecture on the kinetics of phase transformation.

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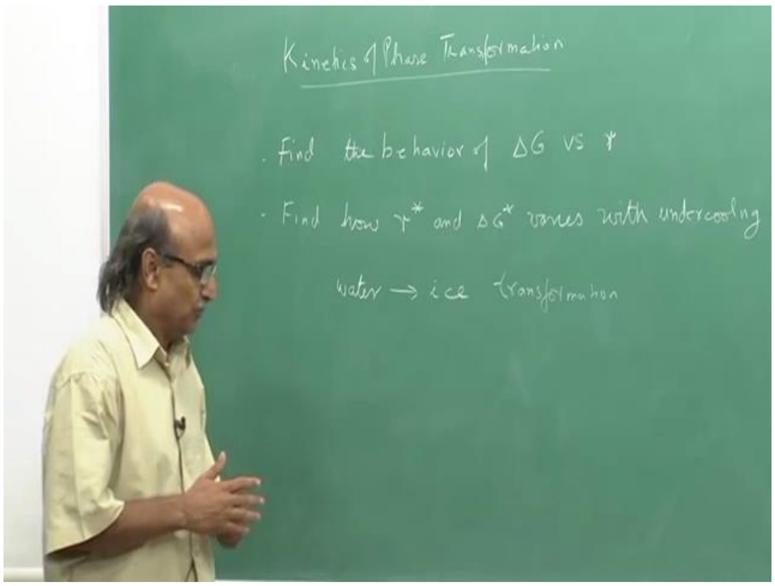

In this lecture we are going to concentrate on the formation of the critical nucleus and in particular we are going to look at or we are going to determine or find the behavior of delta G versus r, the size of the nucleus we also find how r star and delta G star varies with undercooling. And then after doing this after understanding this we will examine and (loo) look at expression for the rate of nucleation.

And for this (fin) finding the behavior of delta G versus r or how r star and delta G star varies with undercooling, we are going to use the water to ice transformation at different undercoolings. So for this purpose as I indicated in the previous lecture, we will use a spreadsheet and you could also follow this lecture by (follo) working with me on a spreadsheet of your own for example like Microsoft excel or any other spreadsheet would do.

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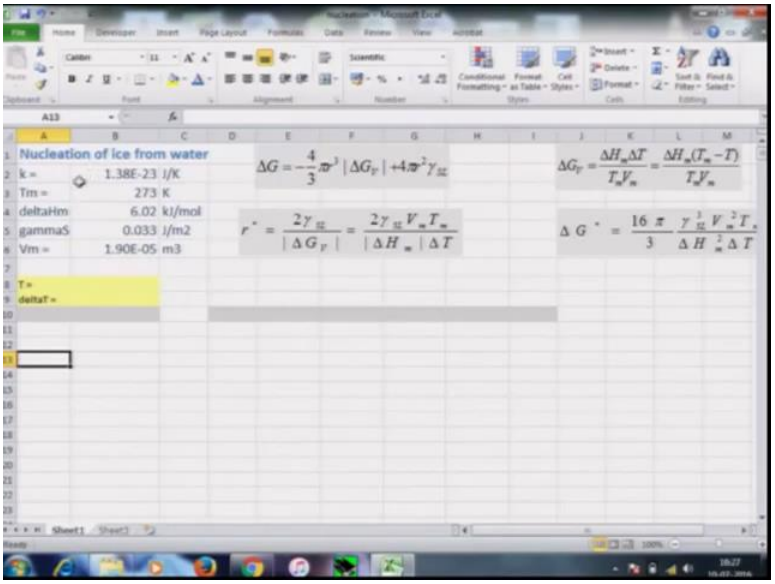

So then let us move on to the spreadsheet and what I have done here, I have put down the data for the ice water system so Tm is the melting point 273 degrees kelvin, the change in enthalpy from water to ice transformation is 6.02 kilo joules per mole, the solid liquid interfacial energy gamma S is 0. 033 joules per meter square, molar volume of ice is 1.9 into 10 to power minus 5 meter cube and k here is the Boltzmann constant. I have also put down for reference the relevant expressions for delta G, delta Gv r star delta G star etc. So what we will first do is look at the curve the characteristic of the curve delta G versus r.

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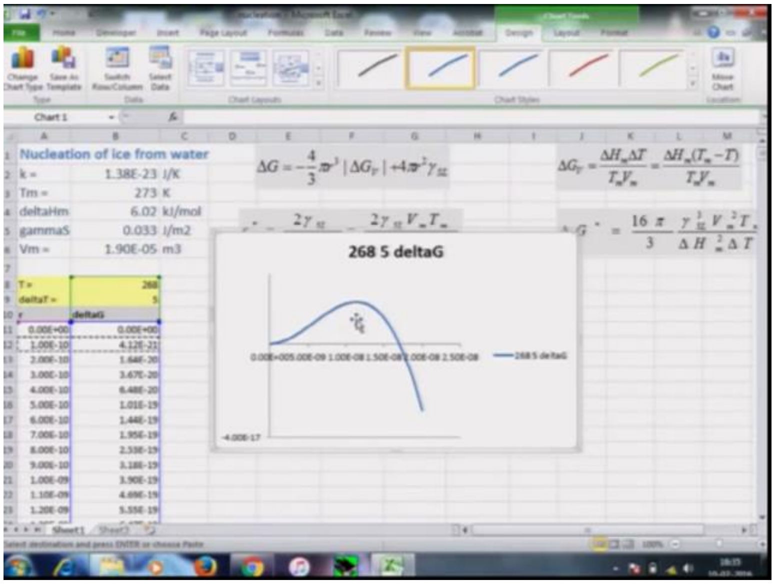

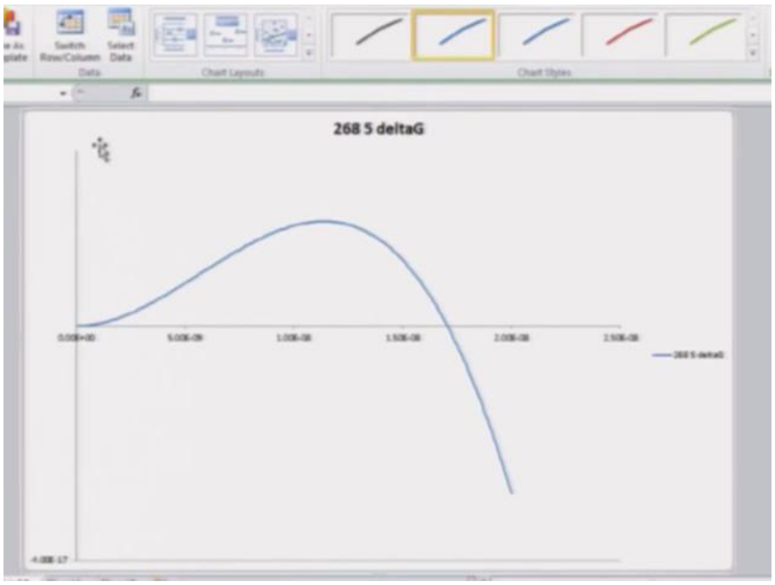

The change in free energy as a function of the size of the nucleus, so in this column I will put r the size of the nucleus, in the second column B I will calculate the value of delta G, and let us say we keep that transformation temperature as that is it 268 degree centigrade, therefore the undercooling that I will have would be I can put down in (sss) cell B9 over here for the undercooling would be Tm which is 273 minus 268 well just put the cell address B8 and that gives me the undercooling of 5, so if I change this temperature the undercooling will automatically change.

We will start, let us say 0 radius and put down the equation for delta G and that let me write it as as it is shown here, so all equations in excel start with an equal to sign as you can see I have a minus four by three multiplied my pi is a function in excel pi with brackets open and close multiplied by delta Gv and instead of delta Gv I will use this expression delta Hm, delta T upon Tm upon Vm. So delta Hm is 6.02 kilo joules convert this to joules, so this is 6020 joules per kelvin multiplied by delta T which is at B9 and I do something different here in the sense that I will put a dollar sign before 9.

And what will happen is, when I copy this formula, this reference will not change and it will remain as the reference for delta T divided by Tm, so first I will open brackets then 273 which is the transformation temperature Tm multiplied by Vm which is 1.9 e minus 5. So 1.9 into 10 to power minus 5 that is the molar volume, then I will close this. So this takes care of the first term over here, second term which has a interfacial energy, so four times pi times r which is in cell A11 and this is squared so let me just put A11 into A11 multiplied by the interfacial energy for the solid liquid interface which is 0.033.

So 0.033 now one mistake I have done which I will correct it, I forgot to put any size of (ra) nucleus here the first term, so bring my cursor back and I have to type pick up this cell A11 cube, so let me just I will do it three times, so that is that will make it r cube. Once I have this I enter I will get the value which is 0 of course because I have radius r if I had different value of r, for example 0.01, then I get a value of 2.4 into 10 to power 1 here.

Now this is in meters and we are going to talk about very small values in meters, so for example I could say this is 1 into 10 to power minus 10 (me) meters which is 0.1 nanometers, then I get a delta G of 4.12 into 10 to power minus 21. So let me come back and make this zero and what I will do is I will put here another (equat) equation which will add an incremental (val) value to r. So I will have a different value of r here and let me increment it by to begin with let us try 0.1 nanometer, that is 10 to power minus 10.

So now what I will do, I will take this copy this function equation that I have written and copy it in the next cell, what happens is the equation gets carried to this and as you will notice the reference to r changes to A12 here as you can see this formulae in the top and so therefore it calculates now the delta G for 1 into 10 to power minus 10 meter radius at this point I can just take this and copy this. So now as you will see my size of the nucleus is increasing and as the size increasing you will notice that delta G is increasing and some point of time it is become negative.

So what we can do is, we can look at the behavior how delta G varies with the one that we have drawn on the board let us see how it looks over here, so I put my cursor at the beginning and I go to insert, I go to this cater plot, click on this and choose to join the points to give me a line graph and as you can see that the shape is as expected that initially delta G goes up and then it starts to come down. So somewhere out here is a critical size nucleus and so you could see that for a transformation temperature of 268 at this five is giving me this is undercooling how delta G is varying with the size of the nucleus.

So these numbers on the x axis are the size of the nucleus which is the meters and on the y axis you have delta G. So somewhere out here you will have the peak and somewhere here you will a (crit) size of the critical nucleus. Now what we can do is go back to the sheet and change the transformation temperature, let us say for an undercooling of 10 degrees which means if I make this 263 as a transformation temperature my undercooling goes to 10…

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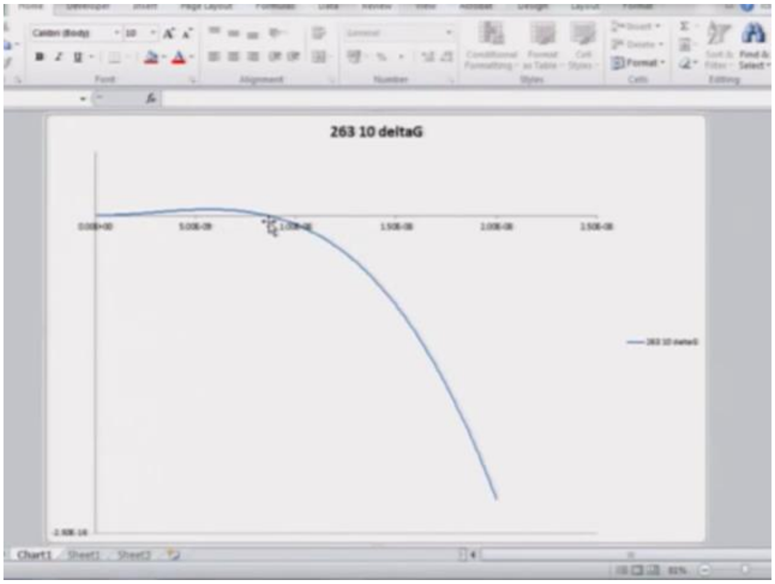

And then if I look the chart, it has changed rather dramatically in the sense the peak has gone down and the peak has shifted to the left to smaller sizes as expected.

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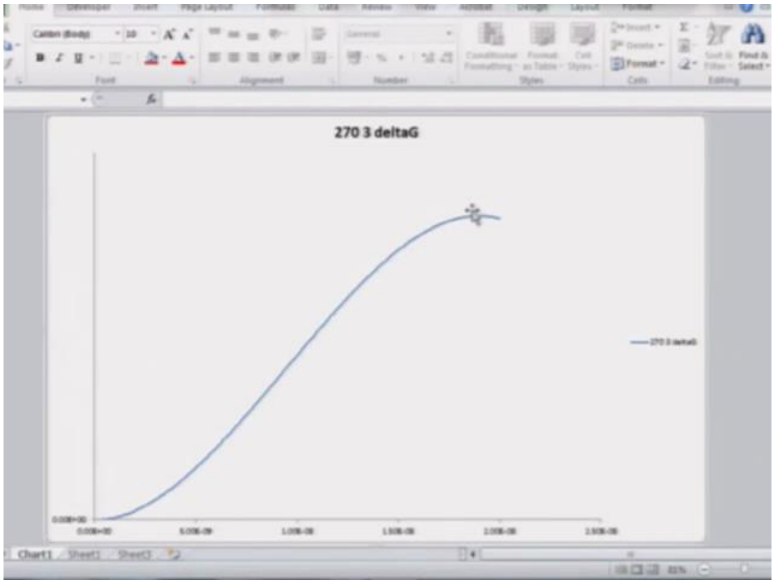

If I make this transformation temperature very close, let us say I make it to 270 so now I have only a 3 degree undercooling if I change this, now I look at the graph well it goes up to much larger sizes and this is somewhere where the peak is and similarly you can now play with these numbers like make it 269.

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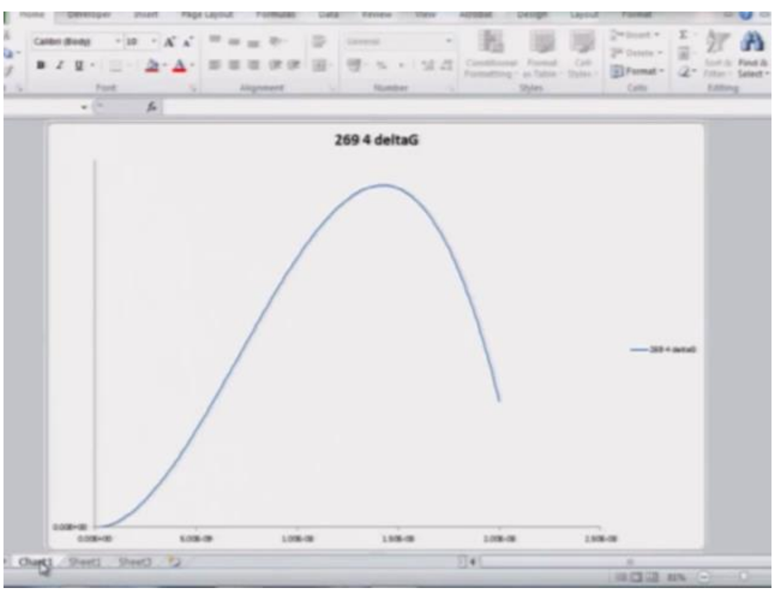

And so there is an undercooling of only 4 degrees, so you will see charts of a or the graphs of various (sha) basically the same shape but the critical size is reducing as the undercooling is increasing the energy hill is reducing as undercooling is increasing.

Using this you can get a good picture of what is going to happen to r star, what is going to happen to delta G star as the undercooling changes. Now the next thing that we want to do after we have analyzed this is to find and draw pictorially or graphically how actually the r star is changing, how actually the delta G star is changing as I change the undercoolings. So what we will do is we do some more calculations on this spreadsheet, so let me write the temperature here, temperature of transformation that this is in kelvin the temperature.

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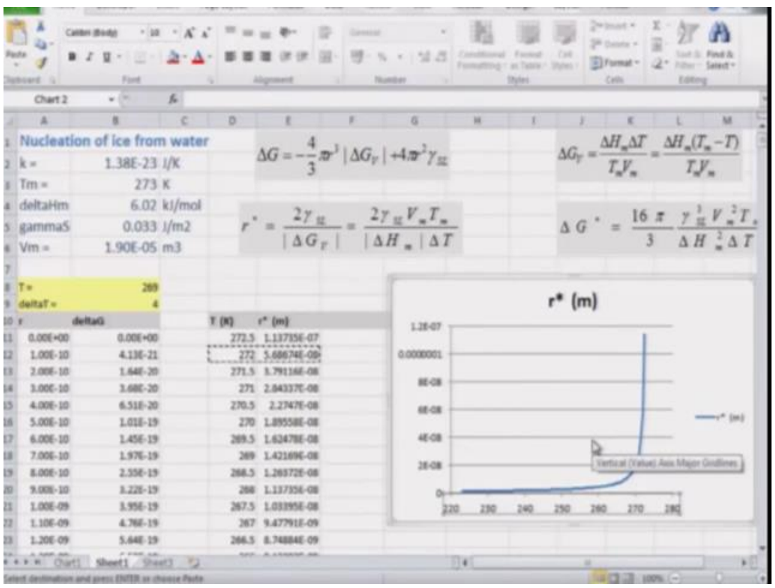

And let me first find out r star whose value will come out in meters, so let us look at let say the first temperature we will look at is just below 273 the transformation temperature, so let me type a number like 272.5 and find out the critical size at this temperature. So for the finding out the critical size I must use this expression of 2 gamma Sl Vm Tm upon delta Hm delta T.

So let me write down the equation is equal to again 2 star the interfacial energy of the solid liquid interface 0.033 into the molar volume 1.9 10 to power minus 5 multiplied by the transformation temperature 273 divided by brackets the change in enthalpy which is 6020 joules, convert kilo joules to joules multiplied by the undercooling, well let me write it the undercooling as 273 minus D11 which is in this cell is 272.5, so the undercooling here in this particular case is 0.5 this bracket close and another bracket close, this should give me the critical size or the nucleus as 1.13 into 10 to power minus 7 meters.

Now what I will do is I will start to increase the undercooling and let us increase the undercooling in intervals of 0.5 degrees, so 272.5 minus 0.5 this becomes 272 copy this formula here (so oops) (co) copy this formula here to and paste it here. So I get a different r star and now what I can do is I simply copy both of these formulae and will get a series of critical radius for different transformation temperatures. So if I just examine as a transformation temperature is reducing here on this column, you will notice that the critical size is reducing.

So as the undercooling is increasing, the critical size is reducing. So let us just graphically look at this data that would be more instructive, so I bring the cursor to the left most point here and go to insert scatter plot and draw a line graph and this is the kind of variation you get. So what I can do is I can change this axis a little bit this we do not need to start all the way from 0 degrees kelvin, rather we can just look at what is the lowest temperature we have gone here so what 223 so let me begin this scale, the x axis scale format axis and I will just change the lower limit to 220.

So I get a variation of the critical size which is this axis, the vertical axis versus this size of the versus temperature. So you can see that at temperatures close to the transformation temperature the critical size starts to increase rapidly, and in fact at the transformation temperature the critical size would be infinite. So this curve is asymptotic with the line at 273 the vertical line at the temperature of 273. And then it reduces as the undercooling is reducing.

Now the undercooling is increasing. Now what I can do is after looking at this, let us see how many molecules how many molecules of H2O are there in this critical size nucleus.

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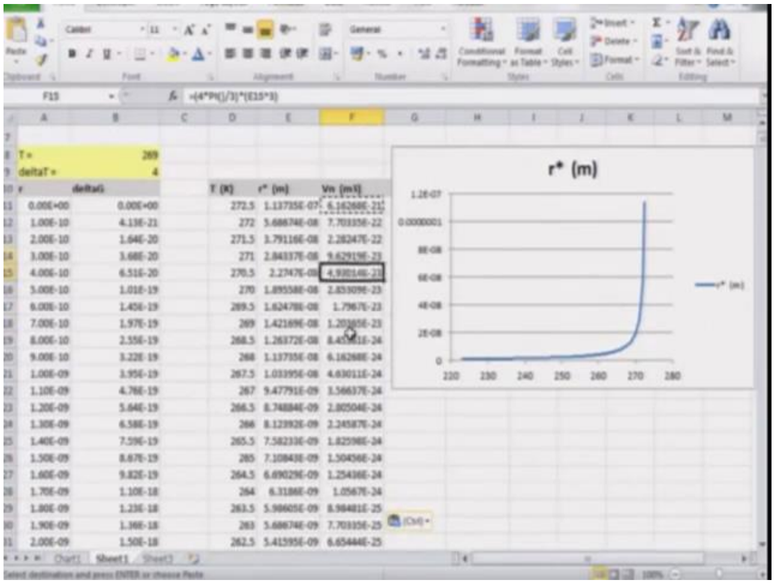

So let us first calculate what is the volume of our nucleus that is easy. This volume will come out in meter cube, I will call it as Vn and that is simply the volume of the sphere, so it is 4 times pi divided by 3 multiplied by r cube brackets and take this value (e) in cell E11 and raise it to power 3.

So instead of writing it three times this time all I have done is E11 hat three, this hat stand stands for power sign in Microsoft excel, close the brackets and this gives me the volume of the critical size nucleus that would be there at a transformation temperature 272.5 degrees centigrade for ice. I copy this formula, so that I get volumes for different sizes. So now in this column I have volume calculated, now let us calculate the number of molecules that would be involved. Now how does one get it number of molecules? Well, for this, once we know the volume of the nucleus, we need to know how many molecules per meter cube should be there in ice.

In order to calculate that, so let me (ca) come here, first let us we calculate that. Number of H2O molecules in H2O how many would be there, this I should be able to calculate from Avogadro number and the molar volume that is given here which is simply the Avogadro number I take it as 6.02 (multipl) 6.02 10 to power 23 multiplied by the molar volume 1.9, let me put in form of numbers only 1.9 10 to power minus 5, no this should not be multiply sorry this we will divide, so 1.9 10 to power minus 5, so Avogadro number divided by the molar volume would give me number of molecules of H20 in 1 meter cube.

So now I know this, so let me call this column heading as Zn number of molecules in a nucleus of a certain size. So I know now for volume of this nucleus, how many molecules should be there. So in one meter cube I have so many so in this I should have, let me put it 3.168 E28 that is the number in one meter cube multiplied by this volume in F11 this gives me so many number of molecules would be there to form a critical size nucleus.

And I will copy this formula again, this gives me as you can see that as now the undercooling is increasing you will notice that the number of molecules are reducing. So in fact at an undercooling of 50 degrees the number of molecules involved is close to 200 as compared to for an undercooling of just a degree, you have 24 million molecules would be required to form a critical size nucleus. So you can clearly see that to get so many molecules together to form a crystalline structure would be far more difficult as compared to just 200 molecules coming together.

At hence it is suggested that the probability of formation of a nucleus at higher undercoolings would be higher, chance of forming a critical size nucleus would be higher and hence the rate of nucleation would be higher.

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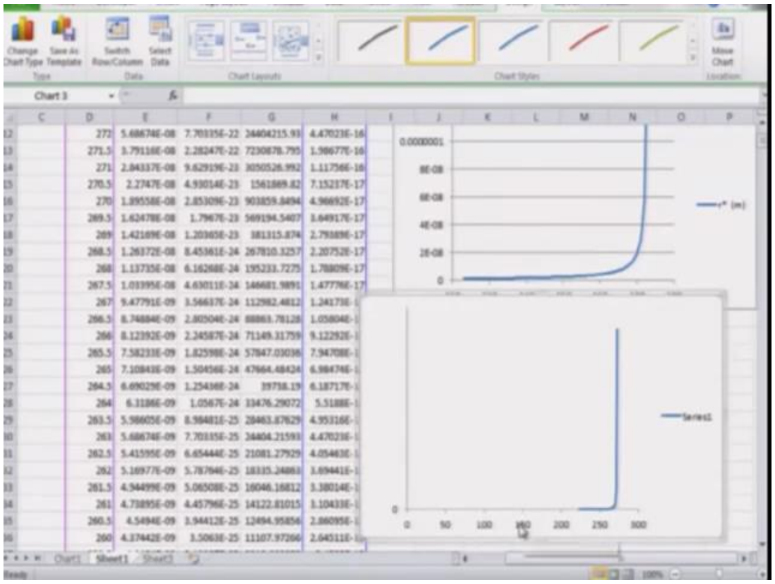

And finally, let us also calculate the critical free energy delta G star. Now this the unit for this would also be joules, now for this we will use this expression here for delta G star, so let me just quickly write this so gamma Sl cube gamma was 0.033 to power 3 multiplied my molar volume square.

So molar volume was 1.9 10 to power minus 5 cap 2 square multiplied by the transformation temperature 273 to power 2, so that takes care of the numerator and then denominator join with enthalpy and if I look at the enthalpy here change in enthalpy is 6.02 kilo joules we will take it as joules so 6020 joules square multiplied by the undercooling delta T again square. So the undercooling is 273 minus transformation temperature square and that should take care of the this thing.

So we get a value of delta G star here, let me just quickly see if I not missed any term 16 pi by 3 then you have the interfacial energy cube, molar volume square, transformation temperature square divided by in the denominator I have the delta Hm square and the undercooling square. So that appears all right and let me just copy this and I get and let us just examine these values as you can see that my delta G star this is reducing as the undercooling is increasing and that is to be expected.

So we are seeing that both r star as well as delta G star are reducing. Now let us just quickly plot this delta G star versus r start as well. So I go to I will just bring my cursor in a empty field this time, insert and make a scatter plot again accept that I am going to get a blank this thing slate on this I will now select the data add so for x values is the temperature, so I will just choose this is my x axis and now I will select my y axis which is delta G star and I will plot this to get this graph and you can see in both cases both r star and delta G star show a similar trend.

So you can see here that in both cases, as the undercooling increases or the transformation temperature decreases r star decreases and delta G star drastically decreases. So conditions for nucleation becomes favorable when the undercooling is increased. So this in this lecture, we saw how r star delta G star varies, how the number of atoms also (re) or the number of molecules are also changing as a critical size is changing or the undercooling is changing. So with this I will stop here and then continue in the next lecture our discussion on nucleation rate, thank you.