Advanced Metallurgical Thermodynamics

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Module #01

Lecture #16

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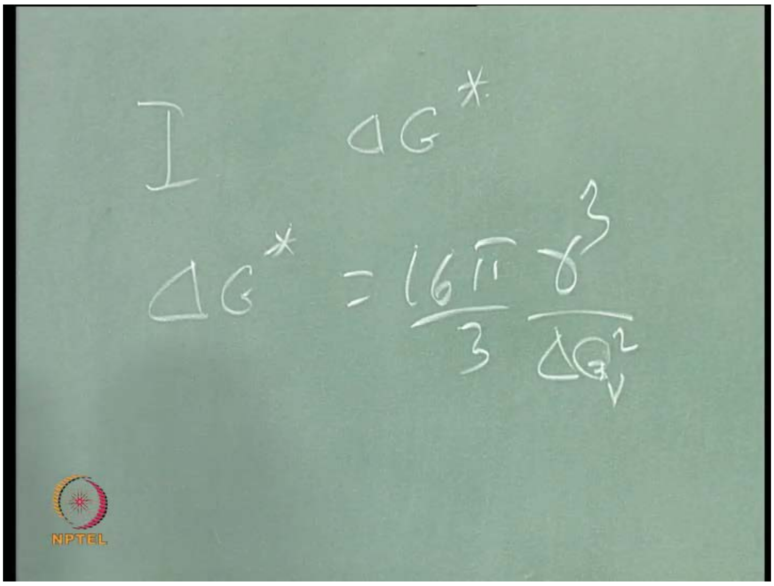

We will take up today, one aspect, which was related to the free energy associated with under cooled melt. We talked earlier that the, "I" which is the nucleation rate is basically, related to, I could say, I will not even put equation there, it is related to delta G star. All of you know the equation. So, I will not put the equation; of course, there is also, another term, which we always remember, which is the delta G d term, which one has to consider and delta G star is related to delta G v. Am I right. That are, expression also many of you know, for a spherical nucleus. We can talk about it.

And if, that is what controls, delta G star, for example, I can put the equation for this case. Let us say, 16pi by 3, gamma cube by delta G v square, let us say. So, that means this controls this, which to a large extent controls this, at least, at the temperatures above the nose of the T t diagram. At all temperatures above the nose what controls the nucleation rate is, only this. Am I right?

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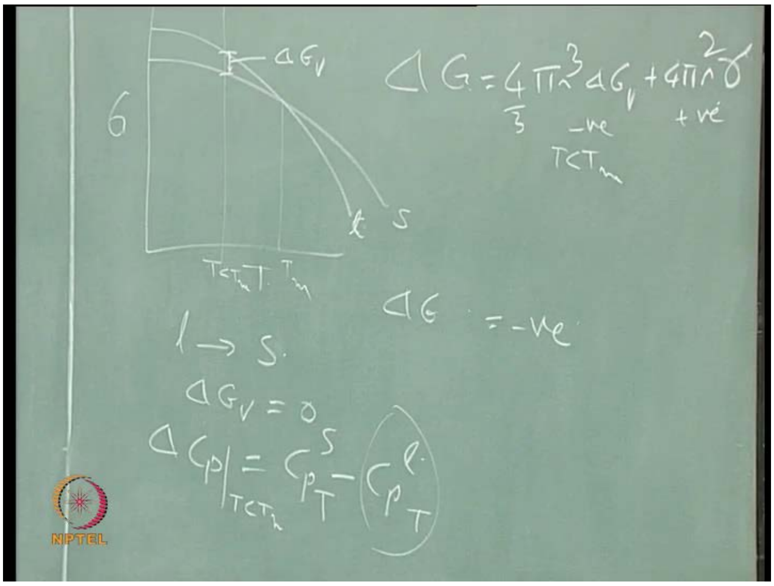

So, if that is the case then, the nucleation rate, to a large extent is, dependent on this and how do I know that value? What is delta Gv? Delta Gv is a driving force for solidification. If I draw this G verses T, so this is, let us say solid; this is let us say liquid. And this is our melting point Tm. And, at any temperature below the T m, T less than the T m, liquid has a higher free energy than the solid. Am I right. And, this differences in the free energy between the liquid and solid, which is, what we call it as delta G v. That is our delta Gv and that is, what drives the liquid to become a solid.

And, the higher the under cooling, usually this is higher, as you can see from that curve itself. This two, start deviating more and more, as you approach lower and lower temperatures and at T m the delta Gv is 0. That is why, in principle at the melting point, there is no transformation. You do not have any transformation at all and you need the liquid to be under cooled. You may say that even for heterogeneous nucleation for that matter, you need a small under cooling; however, small that could be, you need a small under cooling for the liquid to transform to solid. We are not simply talking in terms of the barrier for nucleation. Barrier for nucleation is any way there that is the surface energy.

I may say that I am providing you the surface energy, why not the transformation occurs at the melting point? Because there is because when a surface is already provided, what is the problem? Then, we say, if I want the transformation to occur at the melting point delta Gv is 0. And, if the delta Gv is 0, there is no driving force at all. So, even if you provide a surface, which is a perfect wetting surface, let that say the theta is 0 contact angle is 0, even then you need an under cooling.

But, usually because such surfaces are not available, you need a higher under cooling. One, to give you a driving force; second to take care of the surface energy problem. If you have certain driving force that is available, part of this driving force can be spent to create the surface, so that the surface energy problem can be taken care. So, that is why, we always write this expression delta G, which is the overall change in free energy, for liquid to solid transformation is given by 4 by 3pi, r cube into delta G v plus 4pi, r square into gamma. Remember, assuming that gamma is 0; delta g is actually this.

So, the driving force for the nucleation for the solid to form, if you assume that there is no surface energy at all; that means, there is a perfect nucleating sight available and the surface energy is very small. So, even if you assume that then this is equal to this and at T m, this is 0. So, this is 0. Is not it? So, in principle, you need a higher driving force. So, that this takes care, of the necessary driving force. So, only when delta G, this delta g is negative, a transformation will occur. Am I right? Any transformation, for it to occur, the driving force has to be negative. This is the overall driving force, which takes care of both surface energy. And in these two terms, we know pretty well that this is, at T less than T m, this is negative term whereas and this is positive term. This also we know.

And, as a result, this has to be higher enough, to take care of this. This is what, we are talking about. So, you can see that from all these arguments, we come to one conclusion that this it is this, to a large extent decides this. Of course, gamma is also very important. But, gamma is not in my hands. Gamma is an interfacial energy between solid and liquid and once, I say, define a particular metal that I am solidifying its gamma is fixed. So, that is not in hand, but this is in my hand; this delta Gv, I can change it.

So, many people have tried to understand, how to calculate, this delta G v, and if, you want to calculate that delta Gv basically, it can be broken into two parts. One is delta H; we will not talk about v any more now because whenever, we say delta G, it is basically the volume free energy that we are talking because the moment, it is surface we use actually a different term gamma. So, the moment, I say delta G it is always the volume. So, if I assume that this is, I can say that this is this.

I want to know, delta G at a temperature; T less than the melting point. This is what, I want to know. And if, I want to know that what I need to know? I need to know what is delta H at temperature T. What is delta S at temperature T less than the melting point? If I know these two, I can calculate this. How do I know these two. To know that that is where we see that delta H at any temperature T, can be expressed as an expression, in terms of delta H f. I need to have a reference point. What is the reference point? That I know is the melting point. At the melting point, I know, what is the delta H. Any standard hand book, will give you, what is the heat of fusion at the melting point. But, I do not know, what is this heat released between liquid, whenever I say delta. Delta means liquid to solid. In our case it is liquid to solid, some other it can be, some solid to another solid.

So, whatever I am talking is a change of enthalpy, when a liquid is changing to solid that change is what, we are talking. And, that change at the melting point is known to us at the melting point, it is nothing, but delta H of fusion, latent heat of fusion and if, I know that then I can say, it is "delta H minus, integral delta Cp into dT, T to Tf", this I can say. So, delta H, at any temperature can be found out, if I know the delta C p. What is a delta C p? Heat capacity difference between liquid and solid; that means, if I can have an expression of heat capacity, in terms of Cp equal to a, plus b T, plus c T to the power minus two.

And, if I know these a, b, c constants for both liquid and solid, in principle, I can plug that into this and I simply do the integration, get this value and this is known to us and I can find out this. Similarly, I can say delta S at T, can also be written as, "delta Sf minus T, integral delta Cp into dT by T, within the limits to T f". Am I right. This appears to be such an easy thing. But, in practice, it is not easy. Where is the catch here? The catch here is trying to find out, when I want delta Cp, what is delta C p? Delta C p is," C p of solid minus C p of liquid". Remember, whenever I say delta, I always write product minus the reactant.

The product for us is the solid, the reactant is the liquid. So, C p of solid minus C p of liquid. And, if I want delta C p, at temperature T less than T m, I need to know the C p at the temperature T,C p of solid at temperature T, C p of liquid at solid at temperature T, then, I can find out delta C p. Am I right. Now, the question that comes is to, find out Cp at temperature T, is not very difficult. I have aluminum; I want to find out the melt heat capacity of that aluminum at temperature 600 degrees, which is below the melting point. Melting point is 660 degrees, measuring this heat capacity of aluminum solid, at 600 degrees, is not a problem. I can put into a dsc and happily measure the heat capacity.

But, if I want to measure the heat capacity of the liquid at 600 degree centigrade, how do I measure? I want to know the heat capacity of liquid aluminum, at 600 degrees. To know the heat capacity of liquid aluminum, at seven hundred degrees, is not a problem. For me no problem, but at 600degrees, liquid does not exist and if, I somehow bring the liquid aluminum to 600degree centigrade and start measuring, by the time you measure it may not be liquid, it will become a solid.

So, practically, it is very difficult to measure the heat capacity of the liquid, at temperatures below the melting point. That is why, if you have ever seen a hand book such as, Smithal's hand book, they give you, Cp data in the form of, Cp equal to a, plus bT and things like that. And, they say that this particular thing the a,b, c values, that they are giving are valid, only in this temperature range, they say. For a liquid, they say above 660 degrees. For aluminum, it is valid below 660 degrees that, particular a, b, c are not valid because nobody can measure them, unless there is a liquid, which can be easily under cooled.

And, still kept as liquid before it actually, crystallizes something like a glass forming. Liquid like a silicate glass, you can happily under cool. Nano aluminum actually, melts at lower temperature. Is not it. We are not measuring the heat capacity of the solid. We are talking of heat capacity of the liquid. So, but then, but then the question is that for that particular Nano aluminum, the melting point you have already crossed. So, you cannot see. You cannot compare apples with your bananas.

So, the moment, I say Nano aluminum and its melting point, let us say is 600 degree centigrade, if I say, I am measuring the heat capacity at 600 degree centigrade, for the liquid, but that is, the stable liquid already, it is not a metastable liquid. It is not a under cooled liquid. Is it a under cooled liquid? And then, if you are measuring of that is of no use to you because that is of a different type of material. I am talking of a bulk liquid, under cooled to below the melting point. And, I am measuring the liquid, what is called the Cp below the melting point and maintain that liquid as a liquid, during this measurement.

And, this is possible only, when the solidification of the liquid into a crystal, is very difficult that liquid can remain. There are, so many, you know polymer liquids, which do not want to crystallize easily. All, that is why, if you go to any, you know modeling fellow for solidification. They all do modeling on polymers. You, if you have ever read a book on solidification like a “Bruce Chalmers” or if you have read a book “Mallin Zacatecas” book or any other books, you will see that, all the modeling works that they have done Physical modeling, not really Mathematical modeling. ah.

Physical modeling works are all under cooling experiments, for example, how do I know the material has under cooled? I say that under cooling and micro structure is related, why “under cooling” and “I “are related. So, I can actually, measure the I. How do I measure the I? I need to be able to see, how many nuclei are forming? And if I want to physically see then, these nuclei forming I, should have something, which is a transparent a liquid in, which actually nuclei are coming.

So, people have done a large number of experiments on transparent liquids, which are polymer kind of liquids, Cecilio Nitrate and there are so many such things, where people take such liquids, which are more difficult to actually crystallize. And, in such liquids one can do this. In a normal metal this is very difficult. You cannot under cool a metallic liquid and then, retain it to be liquid and that is where, the problem comes is measurement of this and that is where, many people started making assumptions.

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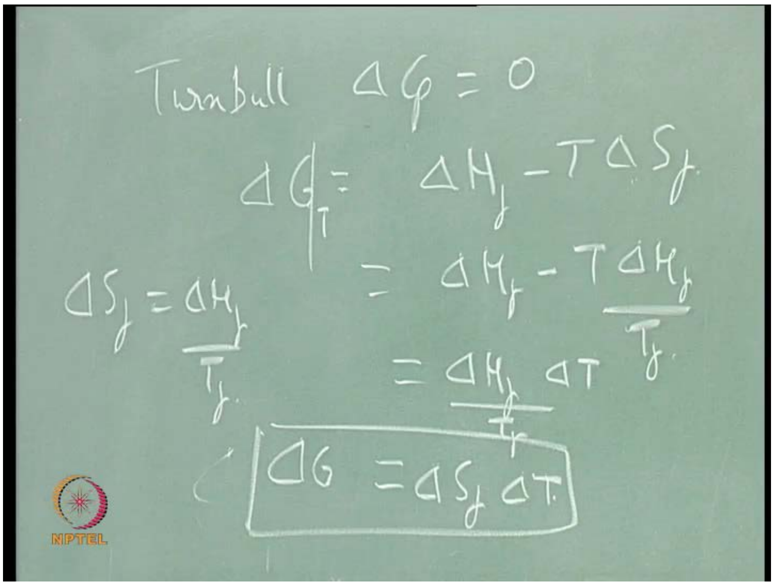

The first fellow to assume, something is a person by name" Turnbull". Turnbull said, "let us assume, delta C p is 0".As there is a crudest assumption, one can think of and we know, definitely it is not a close to reality. But, there are so many things. We assume for example, Ideal solution Thermodynamics is not close to reality, but we still assume. So, assumptions are one can assume anything that he wants.

So, he assumed delta C p is to be 0; that means, difference between the heat capacity of solid and liquid is, the same. Once, you assume that what happens this whole two? These two terms vanish. Is not it. These two are 0. Once, they are 0 then, this term vanishes. Then, I can say delta H at, I mean, delta G at any temperature T, at any temperature T, is nothing but, "delta Hf minus T into delta Sf ".Why because delta H becomes equal to delta H f, delta S becomes equal to delta Sf. Am I right. And, that is where; you see a typical expression that you see in all standard text books, where you see that this is equal to. And, delta Hf, Sf can always, to written as delta Sf equal to delta Hf by Tf. Only, at T f it is valid. Is not it. So, because from the basic definition of ds itself, ds equal to dH by t.

So, if I use that then I can simply say that this is delta Hf by T into delta Hf by Tf and that brings you to a and that leads you to a formula, which is delta Sf into delta T or to do this, simply you can multiply this and then say, you can convert this into delta Sf into Tf. You take it as delta S into Tf, take out delta Sf common and you see, Tf minus T is delta T.

So, you can now, say delta G is this. And, this is what all standard text books talk about it, but this, you would not have known, it has come from such a, you know easy assumptions and such an assumption, which is actually not valid. So, but this is what, all text books talk about and then, after that, there are large number of people, who have tried to make various assumptions because measurements are difficult and after assuming bring out an expression, for delta G.

And then, try to take certain, you know experiments try to conduct certain experiments on those systems, where you can actually under cool the liquid and still, measure the C p of the liquid, which are not definitely metallic systems, but other type of systems. And see if that that delta G that you have calculated, based on that particular formula are derived, based on the assumption matches with the actual delta G, that is measured. How do you measure the delta G? By measuring this delta C p, I can get this delta H and I can measure this and I can get the delta S. Once this two can be measured, I can actually measure the, find out what is the delta G, at any given temperature.

And that if it matches with whatever assumptions that we have made. And what are the various assumptions? One assumption, where people have said, let us assume delta Cp is not 0, but it is constant and its value is equal to delta C p, at freezing point. This is one of the assumptions made, which is what we call it as, Thompson and Spapen. So that that is what, one possibility could be if, I know how Cp is changing or the liquid you extrapolate it. That is one way, but the thing is, we, for us to know, whether the extrapolation is valid or not, you need some experimental. You know, any extrapolation somewhere, you need to have some, you know Experimental validity.

And, the experimental validity is actually, coming from nonmetallic systems. So, just because this extrapolation, is working in nonmetallic systems, can I assume that it would work in metallic systems, is another thing. So, one can always argue, but people are trying to do that. So, people are trying to do that and this is one such assumption. And, once you take that this is constant then; again this integration becomes easy for me. I can take the constant out. So, and then, there are a variety of, if you are interested there are some recent papers on this. a paper by acre we have done a lot of work on this.

In Applied Physics, let us two thousand three, by the first author is K. Mondal. you can see Mondal and Murty, where we have a try to do certain other ways of doing the same thing. I do not want to go deeper, unless you are really serious about it, to find out an expression, which would fit for variety of liquids because most of the assumptions that people have done

Each of them have certain limitations, it would fit for, you know binary liquids, but it would not fit for ternary and quaternary because now, we are talking about bulk metallic glasses. Luckily, in case of bulk metallic glasses, people are able to do certain experiments because bulk metallic glasses, one of the advantages is that liquid does not want to crystallize easily because the T, t curve is shifted to the right, to a great extent; that means, the nucleation is more difficult in such liquids because the liquids are viscous.

So, in such liquids, there is a possibility of making measurements. So, in such cases, people are able to measure and see that whatever long back people, I can tell you there was the major assumption. One must, by this man Hoffman. If you read this paper, you will get all this details. Then Thompson and Spapen, I have already given and Jones and Chadwick. One has said let us assume the Cp as that Cp where delta H is 0.

So, Hoffman's assumption is that so, delta C p is that at delta H goes to 0. In principle, this delta H which is delta H of minus T, integrals delta Cp into dT within the limits of T to Tf. In principle, at some particular temperature that delta H actually goes to 0.

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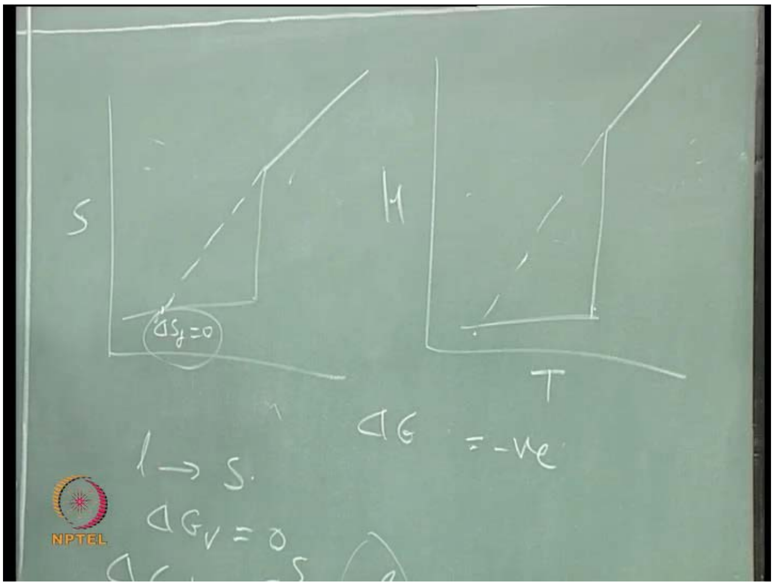

It could be a theoretical temperature. The way I have, should you earlier, if you remember this. When, you plot at delta Sf or simply S entropy itself. You remember there is, this kind of a thing and we said if I extrapolate this, at some time it intersects that, and at that temperature delta Sf is 0. Is not it. Similarly, if I draw H verses temperature, I will again see a similar situation and that H also, if I extrapolate at some stage it would go to 0.

And, in principle, actually if delta Sf goes to 0 and delta G is also 0, automatically at the same temperature, delta H also goes to 0 because delta G is finally, nothing but, delta H minus T into delta S. Is not it. So, if delta G is 0, delta S is 0 and automatically, you will see delta H goes to 0. So, there is lot of theoretical calculations to see, whether this and this are exactly the same or not. And, to a large extent, they come closer to 0. So, whereas, when Hoffman talked about it, he does not bother about this. He says,” let us assume that delta Cp and take the delta Cp absolute value of it as that that you get when delta H goes to 0. At that value, find out, what is the Cp of the liquid, what is the C p of the solid and that you can”.

And, in principle, one can calculate if you assume that this is going to 0 then, extrapolate H as integral Cp, dT. And if, you put this as delta H integral Cp, dT and which is nothing but, delta Hf minus integral Cp, dt.And take this as 0 and if, this is 0 what is this delta C p? Where this is 0 and you can get in terms of the expressions of delta Hf. So, you will get some value of delta Cp, in terms of delta Hf. And, that value, you plug it into that particular equation and then, try to do it. That is one way of doing. Jones and Chadwick said, “let us assume that delta S, the C p is that value, where delta Sf goes to 0”. This is another assumption. A variety of assumptions, I want you to actually go through because there are lots of derivations I do not want to really go into these derivations, but for those who are interested, if you read this paper, you will know most of them.

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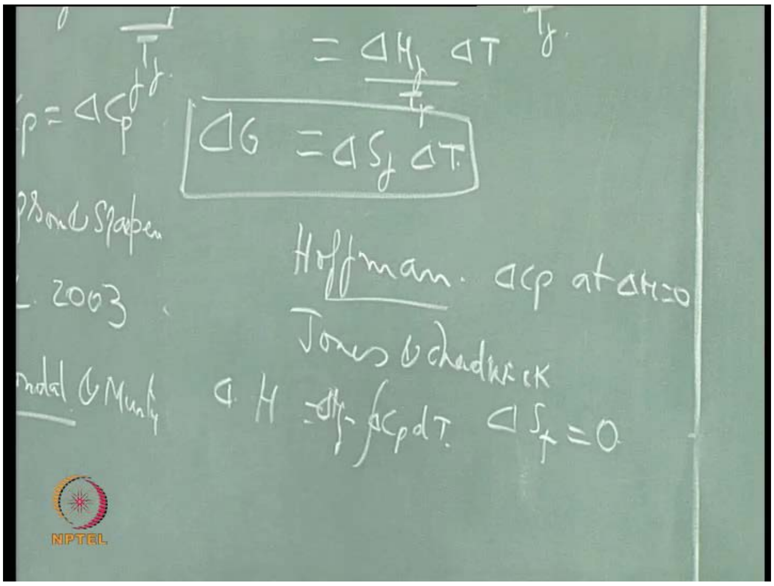

So, this is one problem that all of us face when you talk about under cooling. So, we do not really know. And to a large extent, everybody uses this because it is a very easy expression. And in fact, I should also tell you that in this connection, there is a professor by name professor P Ramachanda Rao. How many of you have heard of him? Who is this man? He was a former Vice Chancellor of BHU; he is man who did a lot of work on under cooling under cooled melts.

And, he has two theories credited to him. On the same thing, one he tried to expand the delta G by a Taylor series expansion. He simply took it as a mathematical expansion and when you tried to expand delta G, as a function of Taylor series, then you will get different series order the First order, Second order, Third order and at some stage, you truncate it and try to calculate the delta G, that is another way. Again, in this paper you will see that also.

So, there again, another thing called Hole theory. Assume that the liquids are composed of a free volume that there is always certain holes as if because definitely, there is much more free volume, in a liquid than a solid because solid has definite crystalline structure. Crystalline solids only I am talking about. And, there you talk about, tetrahedral voids and octahedral voids and things like that. Whereas, in a liquid, you have much bigger voids that we can talk about.

And, that is what, Hole theory talks about it. And, from that they tried to derive, what would be the C p of a liquid at various temperatures? Assuming, that these holes kind of change their dimensions as a function of temperature and so, there are certain theoretical assumptions there again. So, when they tried to do it, they got one expression, which is based on that that is again another expression that is used.

So, there are variety of these expressions, which are available in the literature and people depending on, what suits a particular system. In all the cases, they suit a particular system, but they may not really suit because that is where, each liquid behaves differently, like the each of us behave differently. So, each liquid would be a different because of its nature. Though, we can more or less assume that liquids are all similar because there structure is similar, but if I take an iron based liquid and an Aluminum based liquid, both of them, though, we say it is liquid, this Iron, when it solidified it gives you BCC, Aluminum when it solidifies it gives you FCC. Is not it.

So; that means, there must be something different in these two liquids. Though, we say they both are liquid that is where you know, you would see the clusters are different, in both of them. And based on these clusters, its behavior would be different. So, that is how people see that some of these expressions are valid, for certain things. In some cases, they do not. So, now, let us see, how we do. Yes. Another question, Validation. How do we do validation? Is again based on those glass forming, the reason why people bothered about, all this to a large extent is, after 1959.

After 1958, when Paul due showed that it is possible to get a glass from metallic liquids, that is the first time somebody talked about a metallic glass. Till then, people knew about glasses, but they are all silicate glasses that we know as, silicate can be easily made into a glass. But, a metal can be made into a glass is something, which for the first time people have seen in 1959, and then they are able to make. So, people wanted to know, what was the under cooling, that is necessary for making a liquid into a glass.

So, that is where, the lot of calculations took place to find out, what is that delta G, how does it change the driving force for solidification, how does it change as a function of the temperature. And there, they tried to always take the glass forming liquids. The advantage of glass forming liquids is, glass forming liquids, the liquid is a stable liquid. It does not want to crystallize easily that characterizes a glass forming liquid, from another liquid. That is why, when I said, if you take Eutectics, we talk about a deep eutectic and a shallow eutectic. In one of the classes, I think we talked about it.

And, In fact, we even, tried to give, how we measure this depth, in terms of a certain expression. We basically, take the melting points of the two metals. Consider a kind of a linear relation between the two, for a particular alloy and differentiate that temperature. I mean, take the difference of that temperature, with respect to the eutectic temperature. And, we call it as delta Tl, mixing something like that. And we said if it is smaller than certain number, it is a shallow eutectic; if it is greater than a certain number, it is a deep eutectic.

And, these all more of empirical because they have seen that wherever this crosses certain number they saw a glass formation, in that particular eutectic. Wherever it is less than a particular number, this did not see a glass formation. So, from that people started talking about shallow and deep eutectic and in all this deep eutectics, where glass is easy to form. And, in such cases, people were able to make those measurements. So, when you say, how you do validate, people who are able to validate in those cases, where it is easy to; that means, you can under cool the liquid and still this liquid is not able to become a solid crystal.

And, during that whatever little time that is available, you know for example, if you have heard about you know, what is called micro gravity solidification. Interested, I could like to tell you, all those who are interest in solidification, November twentieth to twenty third; here we have an International Conference, which we are organizing, where all the people who have been working on solidification, who are working on solidification, the top grass people come. It is a conference, which we organize once in three years and bring everyone, who does modeling on solidification, who does experiments on solidification.

So, that is where, you will see a lot of people are the best person, who works on glasses is one person in ova he is coming. So, there are lot of people who come it is a small conference, about 100 peoples is 80, 90 people and, but it is a much focused conference everything on solidification and we have been doing it this is the fourth conference. We are doing last 210 to 12 years we have been doing this.

So, what I wanted to tell you is that you will see that all those people which have been doing this under cooling, is one branch of this under cooling, which people call it, as you know solidification under micro gravity. When, I tried to solidify liquids without gravity or at very small gravities, how does how does this liquid solidified? Whether the micro structure, that evolves is going to be same, as what you get under gravity or not we are all compelled to have gravity on the earth.

So, whatever micro structure that is coming, we accept it that this is possibly the type of micro structure because there is always, we are aware of what is called you know, gravity segregation in most of the alloy solidification. But, this segregation is something, which we have to accept because gravity is there. So, in case, there is no gravity; obviously, you would not see this gravity segregation takes place. Similarly, dendrite growth, dendrite nucleation, is it a function of the gravity.

So, there are lots of people, who do experiments. There are people who have been doing experiments on ISS, the International Space Station. In fact, Kalpana Chawla, who died, many of you have possible are aware. In one of the Space Shuttle, they were doing at that time, experiment on solidification, and an incidental. Again, this is a experiment designed by another Indian professor from IIT Kharagpur, there is a professor by name

Hinda, who does a lot of work on micro gravity solidification. This was an experiment that was going on there.

Basically, they want to do, see if you want to take a composite, let us say Aluminum Silicon Carbide composite, you want to know, where these silicon carbide particles segregate. Do, they go to the grained boundaries of aluminum or they are inside this Aluminum. That depends on whether the growing front, will push the silicon carbide particles or will it engulf. Once it engulfs, then you will see it curves inside. This engulfment are pushing, there are lot of theories that are available. People wanted to prove it in a micro gravity. So, they are doing experiments on that.

So, there is lot of people, who do micro gravity experiments, who will come here and make their presentations. You will see them. So, what is important there again is, how various forces influence the solidification. We have been only talking about, only temperature as one of the force. We even, do not consider pressure at all. So, the moment you bring in the pressure aspect, how does it influence? So, this is pressure, can be just a vacuum, you can talk about it. And, the other thing that you can think is that if how the micro gravity brings in pressure? That is, another area lot of people are interested in that.

So, the point that I want to make here is that many people who are interested in under cool liquids, whether this under cooling is achieved because of micro gravity because when you do it under gravity. Many people have observed the liquid does not become a solid immediately at the melting point. But, it under cools and then, becomes a liquid, solid. So, they were able to see that this extent of under cooling is a function of the extent of micro gravities that you provide. But, in a normal earth, it is very difficult to provide a micro gravity accepting under cases, where people have designed for example, in Germany there is, what is called a drop tower. You take a liquid drop, let and from a hundred feet, you drop that liquid drop.

Let us say, a furnace, a small furnace, you keep it liquid is you know metal is liquefied and this liquid, through an orifice, it comes out and then simply falls in a drop tower, which is evacuated and kept in high vacuum. So, that there is no oxidation and things like that. And, such liquids, when they took after, it solidified, took that solid piece and then tried to solid, when say solid piece, it is just like a flake because what you are dropping is one millimeter drop let possibly. And, they have seen that from the micro structure, it is all indirect. You see the micro structure and from the refinement that you have seen in the micro structure, you quantify, what would have been the nucleation rate.

And, from the nucleation rate, that calculate what would have been the delta Gv and from the delta Gv again, back calculate and say this could be the under cooling. So, this is how people go because there is no way directly, for you to measure the under cooling. Accepting, if there is a way, that it is a transparent liquid, that I am under cooling and I can see with a with a video, very fast video that as I under cool, I can for example, professor Phani Kumar does experiments on Levitation.

If I can levitate a liquid, and then, where there is no surface available now, this liquid is now, being allowed to solidify and I keep on reducing the temperature and then, catch up if it can show where the nucleation is coming. And, in a normal metallic material, they are all opaque. So, I cannot really see, if the nucleus is coming inside the liquid somewhere, at some particular temperature, catching that temperate is not very easy. But, in other organic liquids, where there is a possibility of under cooling, people have done this experiment and to see, where exactly, what is the temperature at which, the nucleation is solidification.

Of course, again the problem is, nucleus is very small or the order of few Nanometers how do I catch that? Because my camera, may not have that resolution. Obviously, it is an optical camera it would not have a resolution of an Electronic microscope. So, it has to grow to a few micron sizes, for you to be able to be actually catching it. So, these limitations are there. Within these limitations, there are lots of people, who are trying to do those and find out that temperature, where they have seen the first solid. And, that calculate that if this is my resolution of, let us say ten microns are so.

And, for if it, I visualize it at this particular temperature, at what temperature it could have nucleated? Again with certain assumptions, one can, there calculate it all this. There are lots of people, I mean, say wonderful field solidification, lot of people are working on it. So, again all of them are driven by this simple thing that how do I actually predict? Before even, doing the experiment before, can I predict that if I cool this liquid at this rate, this is will be the grain size that I will get. Is not it. That is what; everybody wants to know that can I predict the grain size that I get or a micro structural refinement that I can get.

And, or what should be the cooling rate that I should use to get a glass in this particular liquid. So, for all this, you need to have an under cool models, that are available, where you have a relation between the cooling rate and the under cooling. Cooling rate and under cooling to some extent we can understand. So, relations between cooling rate, under cooling and the delta G, so that delta G to I, again the relations are more or less clear to us. Delta G to I relations are clear.

But, the delta T to delta G relations, need to be established. And, that is where, all these modeling has been happening. And, if you are interested, I can give you a large number of papers, but any way, we will close that discussion. And that there is another aspect, which I thought, I will tell you again because we are talking of again nucleation. We started it, but we did not go to a large extent on that. Earlier, what is the shape of the nucleus? You asked me this question some time back. What should be the shape? We always easily assume sphere.

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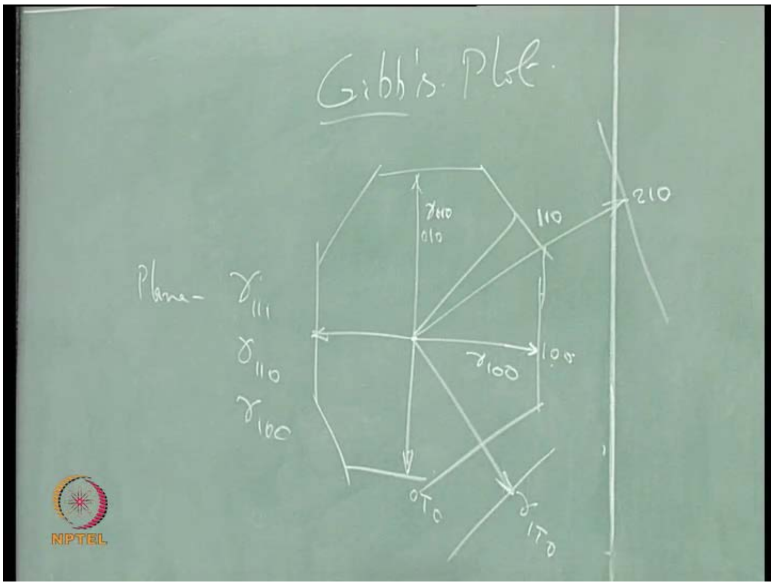

And, we talk about, four- third pi, r cube, four pi, r square gamma all that. So, what is the shape of that? So, I was telling you that each plane in a crystal because when I say, a solid, I am not talking of a glass here, I am talking of a crystalline solid, that is coming out of a liquid and if, it is crystalline solid that is coming out of a liquid, it has a unit cells. It has planes and different planes have different surface energies. If different planes have different surface energies then, and how do I assume that a liquid will have a spherical particle because the moment, I say spherical, what kind of a crystal structure that I can imagine, which would give me a spherical particle.

Because basically, what is a nucleus? Nucleus is nothing but, a bunch of unit cells. Is not it. There are a number of unit cells so; that means, I take a unit cell, I extend this unit cell, with a number of other bricks. It is like a wall, with a number of bricks in all the three dimensions that becomes a nucleus. And if, I take a brick with certain shape, we have seven shapes that are known to us, which are crystal systems and 14 braveletes. Out of this 14 braveletes, I chose any one of the braveletes and that unit cell, I add number of those bricks, in all the three directions, can I ever get a sphere out of it. It is not possible.

It is not possible that I can think of a nucleus which is composed of unit cells and the unit cells, none of the unit cell is a sphere. If the unit cells are not spheres then; obviously, this nucleus cannot be a sphere then, what should be the shape of it then. What people said is now; let us assume that the unit cell, that the nucleus is composed of certain planes. The moment, you think of the outside planes, at this moment, we are thinking that this sphere, it is curved. It is not possible that atomic planes are curved atomic planes are not curved. So, as a result, an actual nucleus would be something like this, with certain planes on the outer surfaces in a two d, it is like this in a three d, it will have other phases.

Now, if that is the case, then the actual shape of the nucleus is that which minimizes the overall surface energy. It chooses those planes, for its enclosure in such a way that the overall surface is energy is minimized, for that wool, there is a Gibbs plot. People talk it Gibbs long back talked about it, what people call it as Gibbs plot. What he has done is, let us assume, a crystal structure. Let us say, a cubic, let us say, FCC aluminum is solidifying, a liquid aluminum is solidifying into FCC aluminum, what should be the shape of the nucleus for the FCC aluminum that is coming out.

If, I want to know, let’s simply think that every plane has a certain surface energy. There is a gamma of 111 planes, there is a gamma of 110 planes, and there is a gamma of 100, and so on. Am I right. And, this surface energy depends on what? It depends on the number of broken bonds. And, one can easily calculate this, in principle and so, these surface energies are there. And, if I try to find out a polar plot, where if I draw take a dot and then, draw a direction and call this as 100 a perpendicular direction, I call this as 010 and this is 001.

Let us say, and I say in this direction, I know these values. Let us say gamma's and in each direction the length of this particular vector, I take it as a scaling of one of the surface energy, let us say and so, let us say, if I take a vector like this; that means, this represents gamma of 100, let us say and this is gamma 010; that means, every surface energy, for every surface I show it in the form of a vectors. And then, once I show that I can talk about gamma of this is 100 and if this is 0bar10, this will be 1bar1 0. Am I right.

And, this will be 110. And, the value of this gamma, if I take, any scaling factor. And once, I take this scaling factor, I can talk about this is the value. And, once I put all those vectors then, what you do is you simply draw perpendicular to those vectors and this perpendicular now, represents that plane. Any vector, for a particular plane perpendicular to that is actually, that particular plane.

If I assume for example, if I draw a perpendicular surface like this, that surface actually is 100 surfaces. And similarly if I draw a surface here, I can think of that, as a surface of 110 surface now, what you do is, there can be some plane, some plane which could be if this is 110, this could be 210 and its surface energy is so high. Let us say that it is this vector, goes out to a large extent and now, I draw a perpendicular to that also. And for, each of these vectors, you draw perpendiculars in a 2d. We are doing in a 3d basically; you are drawing surfaces, which are perpendicular to that. And if, you do this, find out that particular enclosure, which has a minimum area in a 2d, 3d the minimum volume.

That will be minimization of the surface energy, for that particular structure. If, I know for a particular structure and this gamma of 111 for an fcc, will be different from gamma of 111 for a bcc. See, for a given structure, I need to calculate these values because 111 plane in an fcc is different, from 111 plane in a bcc. Their packing factors are different. So, as a result, for a given structure, if I can calculate these things and do this and then find out a particular a shape, which gets formed, which has a minimum area is the one that actually has.

The moment, a plane, one of the plane, the vector is going out; that means, it has a large surface energy, I am avoiding all those large surface energies and taking only that particular area, that is the system would choose that particular shape, in such a way that it is, it need to spend minimum energy because surface energy is something, which you need to spend. And, where from your spending? It is from the delta Gv that is available. So, it would like to spend the minimum energy, before it actually solidifies into a shape.

So, it would choose that particular shape. This is what is called Gibbs plot. Which is, what has been used to, find out for various. And people have done this kind of calculations, to find out, what should be the…That is what, people talk about tetrahedron, octahedron is the shape, that comes out and variety of the names are given, to such shapes depending on, which structure that I have. If, I say bcc, I can actually, in principle, calculate what should be, but will that remain, after it grows, is another question.

A point is, once it grows, the shape could be different. Why? Now, if I take this particular shape, I will continue a few more minutes, when it grows the rate, at which this plane grows and the rate, at which this plane grows is different. Why because the packing density of this plane is different from, packing density of this plane, whenever, this has to grow the rate at which, it grows, depends on how many atoms, this plane needs to fill up that plane. When that plane is filled, it grows by a small delta x. So, if a 110 plane needs, lees number of atoms than 100 plane. 110 plane will move faster than 100.

The plane which is loosely packed, plane will always move faster than the plane, which is close pack. And, as a result, as a after sometime, you may see that this is not growing faster. If, this is growing faster and these four are growing faster, slowly you will see that the final shape, later after the growth, you will see the shape would have changed, if these planes will not exist there. So, you will see a different.

So, the nuclear shape is possibly, is a why possibly? I should say, it is definitely different from the shape after grown. But, the problem is, we can only see the shape, after it has actually grown. We will not be able to see the shape of the nucleus, unless you freeze the nuclei somehow and put it into an Electronic microscope and be able to see it. So, that is another problem. With all these calculations, though, we are able to calculate, what is the shape of the nucleus? We do not know, whether this is going to remain and the actual shape that I am seeing is a growth, shape modified by the growth.

That is the reason, why you will always see, for example, in Aluminum Silicon alloy, you see Silicon needle. In an Iron Carbon alloy, the cementite is like chunky particles. Why does this happen because certain directions have a faster growth rate in silicon. So, it grows faster there. So, this is another issue that one needs to consider. But, for the sake of academics, one can calculate the shapes like this. That is why, this you do not see in every text book this information. Because this has its own limitation because the shape, this shape, that it can predict. You may not be able to actually, seeing this shape after it as gown. So, it has; obviously, certain limitations we will stop.