Module #01
Lecture #12
Kauzmann paradox, Order of a transformation, Glass forming ability

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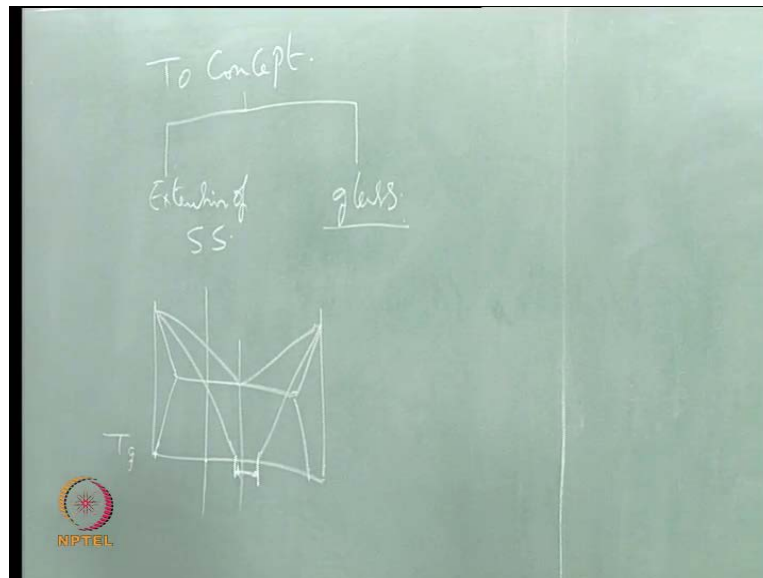
We will continue where we have left last class. And, we were talking about Glass formation. We basically talked about the T naught concept. T naught concept; basically gives two things. One, what is called extension of solid solubility. As we can see, if you choose any composition, for example, if I redraw this T naught and choose a composition of the slot and can bring the liquid below the T naught in such a way that, I take care of even the temperature rise, during decalescence also. That, if I can undercool the liquid sufficiently so that, it can undergo what is called partition less solidification. Then, I have a lag here, which has the same composition as a liquid that with, which with I have started. And, this is the single phase solid solution now. So, I have a single phase solid solution, which has much higher solute contain than it can actually, contain according to the phase diagram.

So, that means, basically what I have done is, I have got extended solid solution. So, this is the most crucial aspect of the T naught concept. And, that is what we get, whenever you undercool. So, undercooling can give you variety of things. One thing is that we have seen earlier, in the beginning itself that undercooling can live to a higher nucleation rate and can give you finer grain sizes. So, fine grain sizes that we usually see at faster cooling rates is basically coming from higher undercooling. But, yesterday if you remember, we talked about it, this particular undercooling and higher nucleation rate; we are only concerned with the upper part of the seeker. When we actually come into the seeker, later, we will look into it. And, if you are below that, then, basically this concept that, higher undercooling leading to higher nucleation rate is actually not right; because it is below the half part of seeker. The bottom half part of seeker, it is a diffusion, which takes a control. And, as a result, just because we have higher undercooling, does not mean that you will have higher nucleation rate.

So, basically, as that top portion of that seeker is concerned, then we are right. We can say that the higher faster cooling rate or higher undercooling will give you fine grain sizes. But, that has nothing to do with that T naught concept. Just, higher undercooling leading to a higher nucleation rate and as a result, finer grain size. The T naught concept, basically tells us that, yes, we can get extended solid solutions. And, if you can choose your composition as an appropriate composition, you may end up in getting a glass; provided, for example, if you have two T naught curve like this and if you are choosing like this alloy composition and in fact, we call this range as a glass forming composition range, wherever the two T naught curves intersect the T g line. More or less, T g is not a strong function of the composition of the alloy in any system. So, as a result, you see it is more or less, as a horizontal. And so, wherever the two T naught intersected the T g that range will give you the range of composition; where liquid is more stable and liquid has no chance to undergo partition less solidification. As a result, this liquid, once it reaches the T g will undergo glass formation. So, that is why we call this as glass forming composition range.

But, all this you have to keep it in the mind; is only we are talking from the Thermodynamics point of view. In principle, you can even have a larger glass formation composition range, if you have used much faster cooling rates. That kinetics takes over that you are somehow preventing the crystal to form. Ultimately a glass will form,

whenever crystal is suppressed. So, if you can suppress the crystal formation from the liquid, you can always get a glass. So, but this gives you tentatively glass. So, just looking at the phase diagram, we will be able to tell, which phase diagram has a higher glass formation ability, which does not; provided, I can plot the T naughts. And, I have also mentioned to you sometime back. We will also talk about it when we continue with glass formation. What is a glass forming criterion? One of glass forming criterion involves the phase diagram itself. How deep the eutectic or how shallow is the eutectic?

So, that you can see from the diagram itself and we have talked about it, a criteria based on that. What is called the deep eutectic criterion? We will come to it, as we go along. So, this glass formation is a second concept that you get from the T naught.

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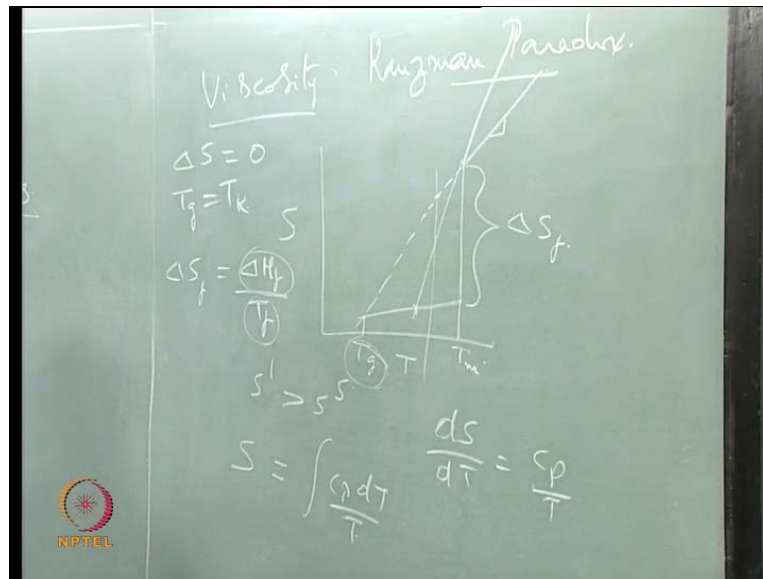
And, yesterday in the last class, we started talking about it and we looked at, how the glass forms as one of the parameter, which is Viscosity. We looked at how Viscosity changes with temperature. And, we said there is a particular temperature at which the Viscosity of the liquid reaches almost to the 10 to the power of 13 or 14. And, that particular temperature defines what is called T g because below that temperature, liquid cannot be undercooled; because by the time, the atomic movements in the liquid freeze and as a result, this liquid become a glass. Now, let us try to understand this glass formation from the Thermodynamics point of view and what we have seen, viscosity is mostly like a kinetic point of view. And, look at it from the Thermodynamics, how do

you understand glass formation? Glass formation, we understand from <mark>Entropic</mark> criterion. If, I look at how the entropy changes function of temperature, we all know that the entropy of liquid is higher than the entropy of the solid. Am I right. So, S of liquid is always higher than S of solid. But, at the same time, we also know that the rate at which the entropy of liquid changes with temperature is also higher than the rate at which the entropy of solid changes with the temperature. Why because we know pretty well, the S is nothing but integral C p d T by T. And, as a result, d S by d T, I can always write as C p by T. And, because of this, and because we know that C p of the liquid is always higher than C p of the solid.

So, I can expect the slope of the entropy versus temperature curve to be steeper for the liquid, when compared to the solid. This is understood. If that is the case, if I plot entropy versus temperature for any metal, for example, I can show that entropy changes something like this. Of course, there is a mistake in this curve. What is it? These are not straight lines. These two portions, which <mark>I have</mark> showed them as straight lines are actually not straight lines. If I say that they are straight lines, basically I am seeing that slope is constant. The slope is constant means C p by T is constant; C p by T is not constant, it varies with temperature.

So, as a result, in principle, that these two portions, this portion and that portion are actually not straight lines. One has to remember that. But, for the present understanding, we do not need to bother about that much. But, what we need to understand is that, this slope is higher than this slope. If that is the case and what is this? That, at the melting point, in the principle at the T m, there is something called delta S f. <mark>That</mark> is called entropy of fusion. Is not it. So, in fact, entropy of fusion is known to be delta S f is actually delta H f by T f; because d S is actually d H by T. If you look at the second law of Thermodynamics, basic definition of entropy, where d S is d H by T; so, you can always write that the delta S f is nothing but delta H f.

So, if I know the heat of fusion and if I know the melting point, in principle, I can find out what is the entropy of fusion. And, this quantity is basically this quantity. So, once I know that now, let us look at the nature of the two curves on the liquid side and on the solid side. Because the slopes are different, if I now undercool the liquid below the melting point; that means, the liquid remains as a liquid below the melting point and its entropy can be treated as nothing but extrapolation of this curve. So, if I want to know

what is the entropy of the liquid at some temperature; below the T m, I simply, basically extrapolate this. And, say that, at a particular temperature here, entropy of liquid is this, if it remains as a liquid. am I right.

If I keep an extrapolation that too at very low temperatures, I will come to a situation, where at some particular temperature, suddenly I start seeing that below that particular temperature, and the entropy of the liquid becomes lower than entropy of the solid. This is, which is an upset. It is like a paradox. And, this particular paradox is what people called it as" Kauzmann paradox". It was Kauzmann in around 1950s, possibly 1954, who pointed out at this paradox; he says that there is a temperature below which the entropy of the liquid actually appears to be below that of the entropy of the solid, as it keeps on undercooling. And, that particular temperature at which you see this happening will be the temperature, where liquid wants to avoid that kind of paradoxical situation. And, the only way it can avoid is to simply become a glass. And, that is what we called it as the ideal glass transition temperature. The Thermodynamic definition of a glass transition is at, where liquid freezes into some structure, some solid structure; in order to just avoid becoming a crystal, of having a situation of lower entropy than that of the solid. So, just to avoid this particular paradoxical situation, liquid becomes a glass. And, that particular temperature is what we call it as the glass transition temperature.

So, this is Thermodynamics definition of glass transition temperature. And, in principle, we can even calculate this glass transition temperature very easily. How do you calculate glass transition temperature? Basically, find out the temperature at which delta S is 0. So, the definition of a glass transition is delta S is 0; delta S between the solid and the liquid. So, calculate the entropy of the solid using this, calculate the entropy of liquid using that, expecting that in one case C p of solid, we will use in another case, we will use C p of the liquid. And, once you know this, to find out that particular temperature, where this entropy of a liquid becomes equivalent to the entropy of the solid and that is the temperature, where you can say, one can call it as Kauzmann temperature.

People also called this T g as T k; Kauzmann temperature or the glass transition temperature, ideal glass temperature. And, so this is how one can, in principle, calculate what is this glass transition temperature. And theoretically, in the number of cases, if you are just simply looking at the pure metals, this temperature is actually is very close to absolute 0. That is the reason why, most of the pure metals you do not see that they

become glasses. But, in case of alloys, yes, you will see that. It is easier to become glass in case of alloys; because in case of alloy, the entropy is still higher; because of the configurational entropy is being added in the liquid. As a result, it is the curve, is much steeper. So, as a result, when you see that the temperature at which it intersects that of the solid is higher; for example, if you imagine this is steeper, you will see that it intersects somewhere here.

So, that means the actual T g is higher. So, you will see that the reason why, you will see most of the bulk metallic glasses, which are very stable glasses, there glass transition temperature are actually higher. So, because that, they form glasses very easily. And, you would also understand that, there are number of parameters to look into that. We will see it, as we go along. So, this is one of the very important concepts, which comes from Thermodynamics.

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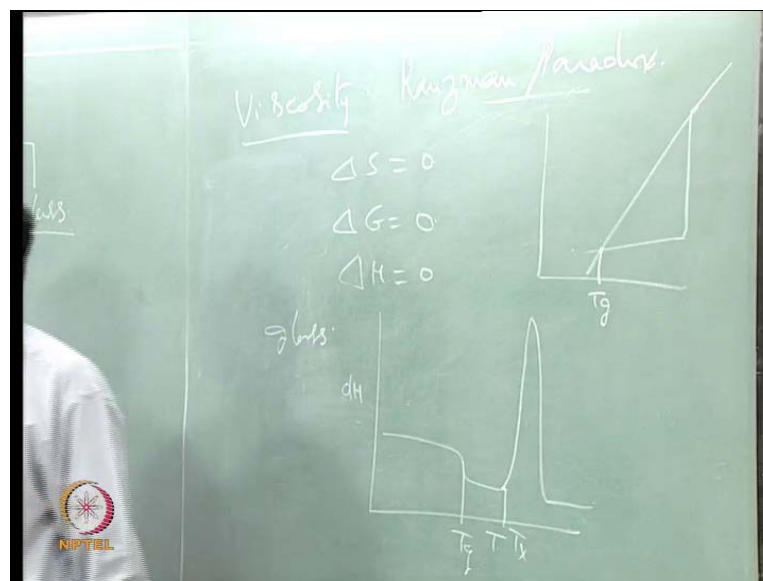
But, if you look at this particular thing a little more carefully, what you see is that, there is a situation; whenever a glass is being formed the delta S is 0 and what about delta G? Delta G, for any phase transformation, in principle has to be 0; otherwise, there is no phase transformation. If you treat liquid and glass as two different phases, at any given phase transformation delta G is 0. Is not it. So, if that is the case, if delta S and delta G are 0, in principle, obviously, delta H is also 0. So, that is a very special transformation. In fact, this is what we called it as a second order transition. Have you ever come cross

first order and second order transitions? First order involves latent heat; second order does not involve latent heat. ==And anybody==, ==yes you partly right== First order transition involves latent heat of fusion.

That means that there is a certain delta H associated with the first order transition. Whereas, the second order transition is the one, where there is no delta H associated with it. That means there is a transition, but there is no delta H associated. For example, if you draw, if you take a sample, let say a metal like this, an aluminum and keep hitting it in a d S C, how do you recognize that it is melting in d S C? ==Endopic==; you will see an ==endopic==, am I right. A solid, when it becomes liquid, obviously it observes heat at a particular temperature. So, you see a peak corresponding to this melting. And, the area under peak actually is what is that related to. Of course, with some cycling factor is related to the delta H of fusion.

So, any melting transformation or any transformation, for example, even a simple example transformation, such as b c c iron changing to an f c c iron or f c c iron changing to b c c iron. All these transitions, they all will have a delta H associated with it. And, we can easily see them. Only thing is solid transformation. Solid transformation will have a smaller delta H; solid to liquid transformation will have larger delta H because the two phases have largely different ==enthalpies==. And, as a result, the delta H is larger. Similarly, when a solid is actually becoming a gas by sublimation, you will see that the delta H is much larger because the enthalpy of the gas is much different from the enthalpy of the solid. So, the enthalpy difference actually is related to how much is the change in the structure; that is taking place from one to other. Particularly, if it is simply an f c c to b c c transformation, the delta H is usually very small.

So, this is how we can see the delta H; whereas in a second order transition, you do not see this happening. That is why, for example, if I take a glass and simply heat a glass in d S C, what we usually see is that, if I heat a glass, I see a plot like this; where here is temperature, where here is some delta H, heat evolved or heat observed, whatever it is; depending on the direction. So, you see, as I heat, you see a step somewhere here and then you will see a peak. What does this step and what does this peak correspond to? Yes, the first one is what is called the glass transition called T g.

And, the second one, where here at this point, you start seeing a peak, we call it as onset of crystallization. Then, what is happening at the glass transition, when I am heating a glass at the glass transition, what is actually happening? And, what is that, that is becoming a crystal later? That means, between this T g and this, if I call it as T x, what exists between the two temperatures, what is it? Something is, see we say, when I say glass transition; that means, glass is changing into something and that something is crystallizing at T x. What is it changing it to? If you remember, what has changed into glass in the previous plot in the graph that we have drawn, in the previous curve that we have drawn, where you see entropy. So, this is what is T g. What is it above that T g? It is liquid, it is supercool liquid. It is supercool liquid, which is transforming into a glass at T g.

So, when we start heating the glass, this glass, will again transform to a supercool liquid. It will transform to a supercool liquid above this temperature, when I start heating the glass. And, this supercool liquid because it is not stable, it is much below its normal melting point. And because of that; liquid is not stable because it start transforming into the crystal. Depending on, whichever crystal can easily nucleate, it can nucleate to some crystal and that is what we call it as crystallization. So, what you have here between these two is a supercool liquid. In fact, that the temperature difference between the T x and T g is one of the measures of how strong is a glass.

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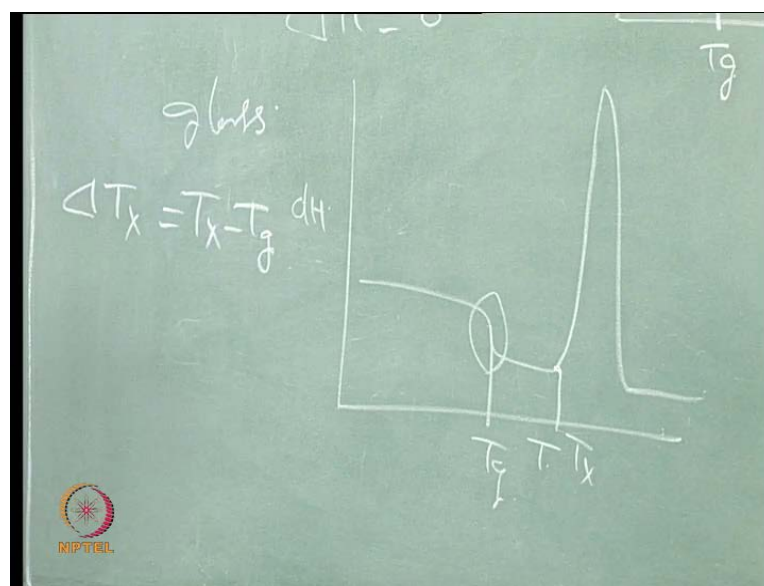
The larger this difference, which we call it as delta T x, which is equivalent to T x minus T g. This delta T x is one of the measures of, how stable the glass is; that means, the glass does not want to crystallize. In fact all, what are called silicate glasses; they do not want to easily crystallize. You will see a large difference between T g and T x. Similarly, all bulk metallic glasses are all like that. That, they can become a supercool liquid and they do not to want to become…. because the viscosity of the liquid, the atomic movement in the liquid is so difficult.

Imagine a bulk metallic glass with some six elements in it, the atomic movement, the diffusion is so difficult. So, this atoms which are present in this liquid, do not want to crystallize to form a unit self. So, formation of a nucleus and its growth is so difficult in such liquids. As a result, they remain as liquid for a longer time or a higher temperature. That is the reason, why you see this difference can be as high as about 100 Kelvin. Most of the bulk metallic glasses have a large delta T x. This is one of them. So, we can easily see, whether the glass is stable glass or not, based on this. But, what is more important for us for the discussion at the moment, you see that, you see a step there. The moment you see a step there; that means, it does not, it is not associated with any delta H. You do not see either an exothermic or an endothermic peak there. So, you will only see a step and that step indicates that the delta H is 0.

And, if the delta H is 0, then what is that, that is happening, what is the change that takes place there. To understand that, we need to understand what is the meaning of first order and second order. Let us look at that. We call something as a first order transition, when the first differential of the free energy is discontinuous at the transformation temperature.
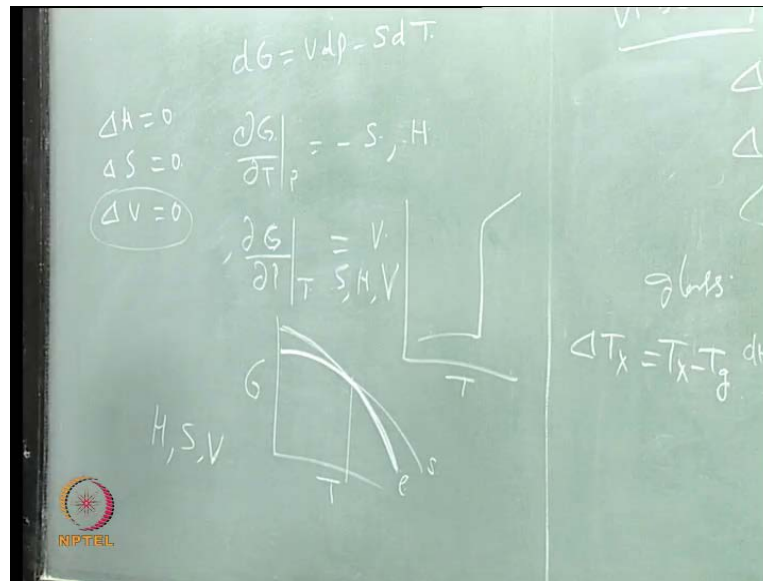
What do I mean by first differential of free energy? If you look at free energy, and look at d G is V d p minus S d T. If I write this Maxwell's <mark>equation</mark>; so, the first differential of free energy with respect to temperature at constant pressure is minus S. Am I right.

Similarly, the first differential of free energy, with respect to pressure at constant temperature is nothing but V. So, these two will be discontinuous at the transformation temperature; that means, if I plot S versus T, you will see a situation like this. At the transformation temperature, there is a discontinuity between the entropy of the liquid and the entropy of the solid. I mean, I am talking of liquid and solid as transformation; any transmission, you take product and parent phase. So, between the product and the parent phase, there will be an entropy difference. But, if I plot the G versus T, you do not see such a discontinuity.

For example, if I plot, you remember this, this plot we already done. We say that this is the liquid portion and <mark>this is,</mark> this is the liquid free energy curve and this is the solid free energy curve. And, if I want to see what is the stable states beyond this temperature, it is the liquid that is stable; below this temperature, it is the solid that is stable. So, if I look at the free energy of the stable states, you see that, this is the free energy of the stable state below the melting point; this is the free energy of the stable state above the melting point. So, if I simply look at the free energy curves of the two stable states and at the <mark>transmission</mark> temperature, there is no discontinuity. There is only a change in the slope.

So, you will see the curve is continuous; curve is actually continuous; expecting that, at the transition temperature, the slope of this and slope of this are different and the slope actually is this. This is entropy. That is the reason, why you will see, at the transformation temperature there is a step because there is a slope change here. The step that you see here is because of the slope change. So, you can see the first differential of the free energy. Free energy itself is continuous at the transformation temperature, but the first differential of the free energy is discontinuous. And similarly, because if S is discontinuous because S is related to H. S is a H by T. So, H also becomes discontinuous. That is the reason why, if I plot H versus T, I will again see this same discontinuity. So, because entropy is discontinuous, automatically enthalpy becomes discontinuous.

And similarly, If I plot V versus T, you will also see a discontinuity of V versus T. Something like, what we have seen just for the, yes I can say, V H V also at the transition temperature, you will see suddenly it is discontinuous. That is the reason why, we always talk about a volume extension or volume contraction during the solidification. Why is that because the volume of the liquid is different from the volume of the solid at the transformation temperature. This volume can change with temperature because we talk about volume expansion. So, there is a volume expansion that can occur in the solid state, there is a volume expansion that can occur in the liquid state. But, at the transformation temperature, if I look at it, there is a difference in the volume. And, that is why we talk about shrinkage during in a foundry. For example, we talk about shrinkage allowance of all that. So, this all are because of this.

So, if I plot S, H, V, all three of them have discontinuity. So that, those are all the first differentials. Now, if I say a second different, a second order transition; second order transition is that transition where the first differential is continuous, while the second differential becomes discontinuous; that means what? That means, the first differential is continuous; that means H, S and V, all of them are continuous; that means, delta H should be 0 for the transformation; delta S should be 0 for the transformation; delta V should be 0 for the transformation.

In fact, this last one is a very important property which people are using in bulk metallic glasses. To make any shapes that you want, people are making what are called micro gear the world's smallest gear, if you can go to the Google and see, which the order of

hundred microns size has been made by bulk metallic glass. The basic reason that the delta V is 0. Once the delta V is 0, when a liquid is transforming into a glass, there is no volume expansion or volume contraction. So, as a result there is no actually the shrinkage or the expansion that we talk about. So, whatever is the mould that you create exactly the liquid will fit into that. So, what if you can create a small mould by whatever means that you want; for example, Lithography you can use, there are variety of techniques are available nowadays to make very small moulds. And, you put liquid into it and allow that liquid to solidify into a glass, you will know that exactly it comes with that. So, people are making very précised dimensions of glasses using this particular, one single property that the delta V is 0.

The delta V is 0 because it is a second order transition. So, all second order transition will have delta V being 0. And if, delta V is 0, then what is the second differential? Look at what is second differential, from this. If this is the first differential of free energy versus temperature what is the second differential? C p by T.

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So, dou square G divided by dou T square, if I put, it is actually C p by T. So, it is C p which becomes actually discontinuous. So, the C p of a glass is different from the C p of the liquid at the transition temperature. If you really want to find out that what is this glass transition, what property I should measure to see that, actually there is a transition that is taking place. For example, whenever you want to use Thermo analysis to find out

solid transmission, you find it very difficult. Why because the enthalpy that is released or observed so small that you actually do not see in the cooling curve, a major slope changes.

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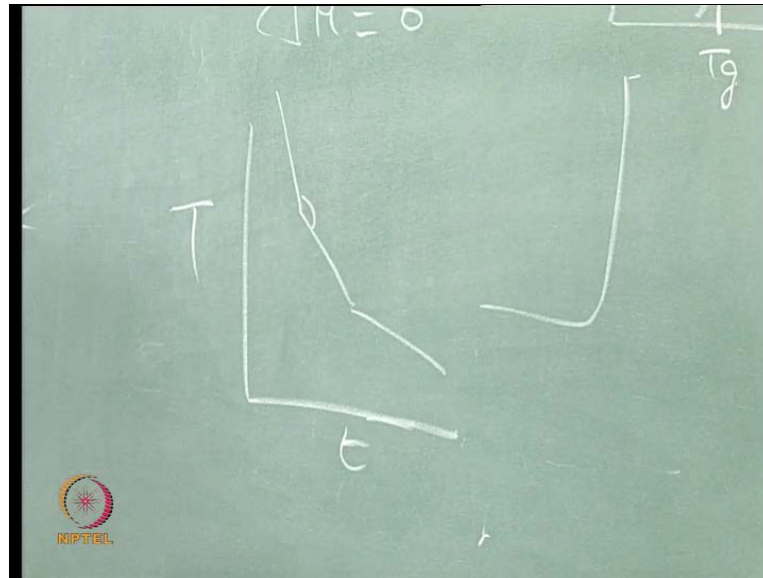
Whereas, when a liquid to solid is taking place, for example, if I plot a cooling curve, all of you aware of this cooling curve. For example, if I plot T verses t for an alloy, you see that, it shows something like this. Am I right. This is for a typical solid solution formation from a liquid. But, these slope changes that you have seen are only because of delta is differences. I mean enthalpy differences that the moment this liquid is starts forming the solid, suddenly the slope becomes shallower. Why because heat is evolved. When a solid forms out of the liquid, the heat is evolved.

So, there is an excess heat for it to be removed. As a result, cooling rate becomes lower. Almost, the cooling rate become lower, the cooling curve becomes shallower. And, that is why you see; and if the delta, which is very small and you do not see a small difference here. So, a typical cooling curve we, that is why a normal Thermo analysis, we do not use to simply find out the solid state transmission. That is why we use what is called differential Thermo analysis because we are going to, looking at difference between a reference and a sample, where the reference does not undergo any transition at the temperature, whereas the sample is undergoing. So, because the differences we are observing, then that is why you start seeing peaks. So, if you do not use d t a or d S C,

simply using a normal thermo analysis, putting a thermocouple inside the sample and seeing, how this thermocouple is responding as a function of time.

You will not be able to really see solid transformation because the delta H is very small. So, similarly if you want to see a liquid to glass transition, the only way to see is that there is a small step, that you see; very small step. Unless, your d S C is very sensitive, you will not be able to see that small step ==anyway.== There is a small step and that step indicates that there is and if you can measure the C p as a function of temperature, then you will actually see, there will be a discontinuity in the C p; suddenly, the C p will jump from a glass to supercool liquid; the C p will jump. And, that jump will give you an indication that, yes, there is a transition. So, second order transition, always will have a C p change. For example, order, disorder transitions are, most of the order, disorder transitions are second order transition. In fact, people, some of them, call them as ==lambda== transitions.

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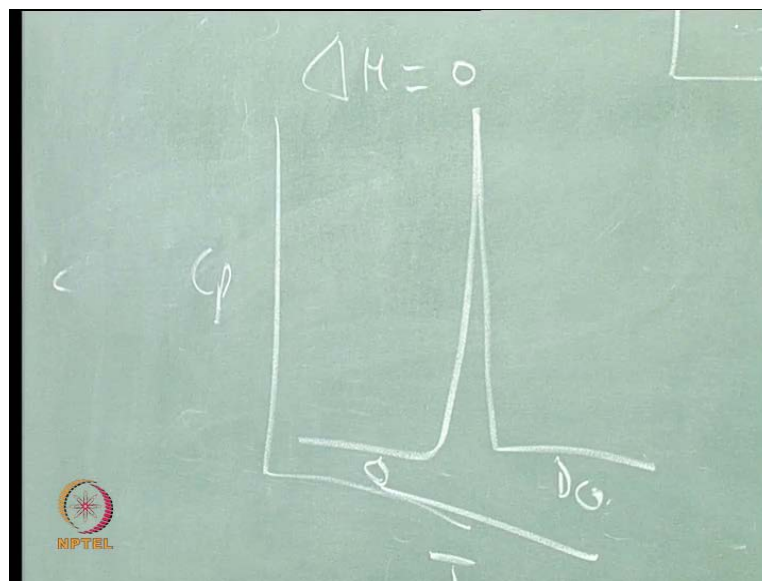
Because there C p, if you look at it, plot C p versus temperature, you will see something like this. So, this is a disordered state, this is an ordered state. From an order state, when you are going to a disorder state, you suddenly see a C p change. And, that is what usually people call them as lambda transition. So, there are number of order, disorder transition that are second order transitions; where you will see C p change. Similarly, if you look at, as a function of pressure, the second differential of free energy with

pressure, will be what? Dou square G by dou T square, what will it be? What is that parameter, if you ever heard of it.

Dou G by dou P is V. So, dou square G by dou P square should be basically nothing but d V by d p. Am I right. Second differential of this is the first differential of this. So, d V by d p is what? Rate of change of volume with pressure; what do you call that? It is called compressibility. How, a phase changes its volume as a function of pressure.

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So, the compressibility; this is the parameter, which is very important for liquids. Particularly when people talk about liquids, liquid compressibility is one of the important parameters. Solids have very small compressibility, they do not change their volume much with pressure. But, liquids change and gasses, more importantly, they change their volume in a large extent with pressure.

So, the d V by d p is very large for the gasses and smaller quantity for liquids and for solids is much smaller. So, wherever there is a second order transition, if you really look at the compressibility values, you will see a peak. I mean, you will see a discontinuity in the compressibility. So, that is how we can talk about second order transition. So, glass transition is, one such second order transition. Correct. That is why, is in change in structure, most of the time change in the structure are simply first order transitions. So, that is why you do not see. In a first order transition, you do not see any phase. C p also, you will not see because delta H itself, there is a major change you will see. Then, order,

disorder also. If you really, if it is second order transition and if you measure the compressibility from the ordered structure to disordered structure, you will see a small change. The small change; change could be small. But, may not be like liquid to glass transition, but you would see that there is a change; it depends on how sensitive your instrument is, but you definitely see this theoretically.

We are only saying that there is a discontinuity; we are not talking about the magnitude of the discontinuity. So, that has to be remembered. So, the magnitude depends on the particular system. Similarly, delta H also; delta H also, when we say delta H is there or if there is a discontinuity in the H, when we are talking about first order transition, the discontinuity can be very small. The delta, for example, solid to solid transformation, still it is first order, there f c c to b c c transition of a pure iron is also first order transition. But, delta H is very small. So, it depends on how sensitivity your instrument is. So, we are not talking about quantity, but we are only talking about the possibility of discontinuity.

So, this is how order of a transformation can be talked about, first order. Though, it may not have any practical significance, but theoretically one should understand how the transformation is taking place. Particularly, physicists are very concerned about what is the order of transition. Particularly, whenever they talked about order, disorder transition, many of the order, disorder transitions are all second order transitions. So, one has to remember. Why glasses are brittle? Basically, it is because they are very hot, the molecules are very high. So, when I, is a question is not that. You know, the moment you talk about even, diamond also is brittle. I do not think diamond is ductile because first of all the bonding itself is, call on bonding there.

So, once I crack nucleus, when you say a material is brittle; that means crack propagation is very easy. Is not it. So, similarly any brittle material from the girdle criterion, if you look at it, as long as the crack propagation becomes very easy. In a glass, whenever a crack is nucleated, then there is nothing to obstruct the crack. In a normal poly crystal material, grain boundary is an obstacle. There can be precipitate, which can be obstacle; there can be lot of obstacles. Whereas in the glass, no. That is the reason why, in fact, people now are trying to have a small amount of nanoparticles; into the glass by, actually in fact, this is very interesting experiment people have done. That, you think of windshield of the car, the moment there is a crash, it just shatters into pieces. Is not it.

So, people are now, trying to put the nanoparticles into the windshield. So, whenever there is a crash the windshield actually bends and goes back. So, we are making a glass into a tough material. In fact, nowadays people talk about tough glasses. There are number of tough glasses. This tough glass concept is all coming basically because of the presence of the nanoparticles; that means, if you take a glass, crystallize it and do not crystallize it at higher temperatures. Crystallize it at very close to the crystallization temperature, control the temperature and time of crystallization in such a way that, where you find nanoparticles are dispersed inside the liquid. Then, whenever the crack is propagating, this nanoparticles can be an obstacle for it. there, what is called shear bond formation. That occurs, in every shear bond gets stop by one of these nanoparticles. That is one of the reason why many of this bulk metallic glasses, for say bulk metallic glasses may not be of great use for structural applications because they are brittle, but if you can nano crystallize them, then I can make a rod of bulk metallic glass like this very easily and then crystallize it, and get nano crystals in it; so that, it is like a composite now. It is a glass nano crystal composite and such a nano composite can be of great use.

So, when I say, see that is, I think, we have been talking about it for quiet sometime. When, you look at how glasses are first made, glass was first made by what we call it as a Gun quenching technique. You remember. Where we have taken a liquid, cooled it rapidly to get, when the liquid suppressed, liquid to crystal transformation we suppress to get a glass. Why we have to really suppress the liquid to crystal transformation is because the crystal formation is very easy and most of the metals and alloys; because most of the metals and alloys are simple structure such as f c c, b c c. And, as a result, so liquid to crystal into those structures is very easy.

So, to suppress that, you need really very high cooling rates. So, that atom is not able to move to form that particular nucleus and the nucleus for it to grow. As a result, you need very high cooling rates. Whereas, in silicate glass, you do not need high cooling rates, why because crystal formation is more difficult there. We know that the crystals are more complicated structure. So, from that concept, what people are now… is that, if I can somehow make crystallization more difficult, then I can form glass very easily. So, what they have done in these bulk metallic glasses is they have added a large number of elements. Instead of just a binary alloy, they made a five component or a six component alloy. Once, you have these many elements inside this, inside the liquid, for a unit cell to

form and for nucleus of an r star size to form and grow, you see that, all these six elements have to sit inside the unit cell itself. This is what we called it as confusion principle.

So, because of that, the liquid for it to nucleate a solid becomes more difficult. So, in other result, you can easily undercool the liquid. Earlier, undercooling the liquid is more difficult because crystal tries to form at the melting point itself. So, here because crystal is not forming, you can keep on cooling the liquid without the crystal forming, so that you can bring that liquid to the glass transition temperature; so that, this liquid becomes a glass. So, such glasses are called bulk metallic glasses because they are able to be cooled to a glassy state at very slow cooling rates.

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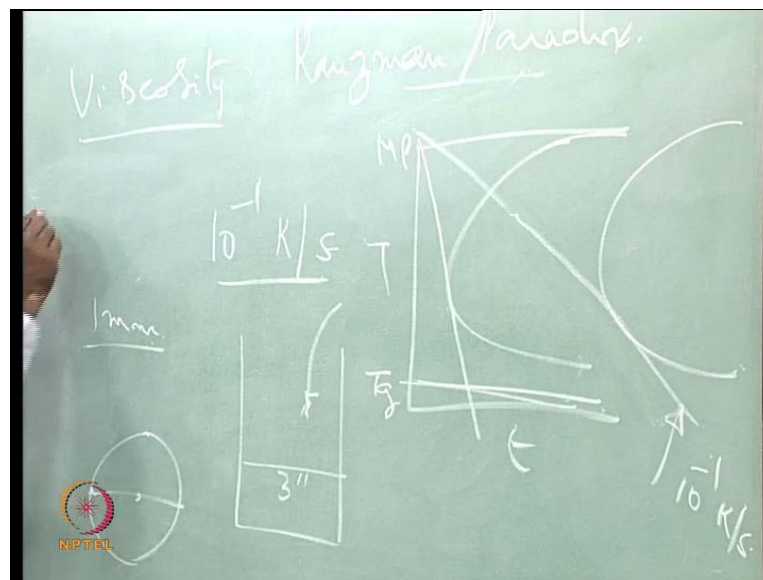
 For example, as slow as cooling rate as 10 to the power minus 1 Kelvin per second. So, what people have simply done is, they have taken liquids of such glasses, glassy compositions and poured into a mould of almost three inch thickness.

And then, basically cut this cross section and then took that in the microscope and then they saw that, throughout this cross section from the center to the surface, it is all glass. It is almost similar to your harden ability parameter. When you talk about harden ability in steels, we talk about a critical diameter. What is this critical diameter? The minimum diameter in which, the center and the surface, both of them will have martensite. Why because the center cooling rate is different from the surface cooling rate. As a result, you

may have a situation where the surface may give you martensite, but the center is not giving a martensite. So that, that particular diameter, where you will get martensite even at the center, is what we actually call it as a critical diameter.

Similarly, when I pour a liquid metal into a mould like this, the surface cooling rate and the center cooling rate is different. So, if I have the center also having a cooling rate, which is higher than the critical cooling rate. How do I talk about critical cooling rate in this particular case? For understanding that, I can draw aT t diagram for a liquid to solid. The way you drawT t diagram for the austenite to perlite transformation, one can always draw a T t diagram for a liquid to solid. And here, what was the temperature that we put in case of austenite to perlite? That, what is called your… temperature. Here, we put melting point there. That is how melting point in this case. So, you will have T t curve like this, where I can now talk about what is called critical cooling rate.

The way I talk about critical cooling rate in austenite to martensite, is exactly the same way I can talk about critical cooling rate. And, this critical cooling rate for a normal metal or a normal binary alloy such as a steel let us say, is so high that I need to use a cooling rate as high as something like 10 to the power 6 Kelvin per second or 10 to the power 8 Kelvin per second. And, if it is the pure metal, I may even have to use to 10 to the power 12 Kelvin per second to be able to avoid the crystallization. And, if I use such cooling rates, I can get a glass. In principle, for any material, as long as I have T t diagram generated like this, for a liquid to solid transformation, I can always find out, what is that cooling rate that is sufficient for me to suppress the crystal to formation; so that, I can get that liquid. Remained as liquid, until you reach a temperature here, which we call it as m S, there in case of martensite transformations and we call here as T g.

You see the concept is exactly more or less similar. So, the moment that liquid, this brought below the T g the liquid becomes a glass. So, this particular critical cooling rate for a pure metal is very high. Similarly, you see, even in the martensite also, we say, when you add an alloy element, the curve shifts. Why does it shift? because diffusion is made more difficult; the perlite formation is made more difficult. Whenever, you add chromium or any other alloy elements, you see that T t diagram shifts. The reason it shifts basically, is because the diffusion is more difficult; that means the time required for the perlite to nucleate is longer. And, if the time required for the perlite to nucleate is

longer it takes, similarly, if I had more and more alloy elements into liquid, this curve shifts like that.

To an extent that this cooling rate is, now of the order of 10 to the power 5 minus 1 Kelvin per second in most of the bulk metallic glasses. And, in silicate glasses, are also almost like that. So, just 0.1 degree per second is good enough for you to be able to get a glass. And, that means that you can get a glass, even simply just by pouring the liquid metal into a metallic mould, so that in the center also you can get a glass. And now, people call a metal a bulk metallic glass are those, where the glass forming ability is such that, you get a critical diameter of 1 millimeter. If you have a critical diameter of greater than 1 millimeter, we usually call them as bulk metallic glasses.

In comparison, if you remember the earlier cases of the what is called gun quenching technique or melt-spinning technique; the thickness was only of the order of 30 to 40 microns. The first metallic glass that people have made… what was the system? Gold silicon. So, the gold silicon, the metallic glass had its thickness of the order of 30 to 40 microns. So, melt-spinning technique does not really give you thicker than this. The moment it is thicker, then you lose cooling rate. The moment it is thicker, it will not have a high cooling rate. So, that is why, only by reducing the thickness. That is the reason why most of the old systems, where this concept of bulk metallic glass did not exist, people were forced to use high cooling rates to get good glass.

And, because they were forced to use high cooling rates, they were forced to have thinner sections because thicker sections, you cannot get high cooling rate. So, that is why people had only just thin film sheets of the order of that kind of thickness. But, such materials, such components are not really useful in all applications. I cannot use the thin foil for all applications. But, if particularly, if I want to make a structural material, so I would like to have thicker samples and as result, now bulk metallic glasses promise you, thicker sample.
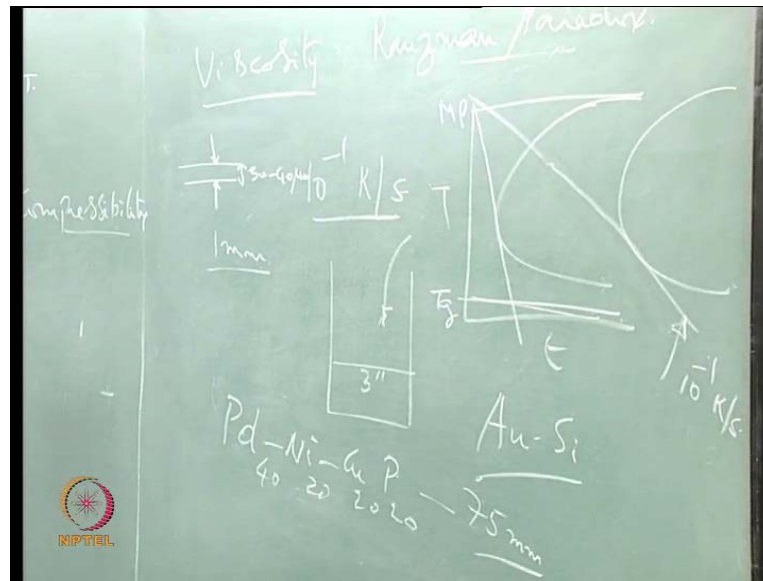
The glass for example, the one which has the highest glass forming ability is a Palladium, Nickel, Copper, Phosphorous alloy with the about 20, 20, 20 and this has 40. This as given almost 75 millimeter thickness; that is the best glass forming, glass forming alloy so far.

And, there are so many others with the different thickness of the order of 30 most of the zirconium base alloy have very high glass forming ability of 30 and 30 millimeters critical diameter. So, like that, we have number of systems. So, you can see the whole concept of glass forming ability comes from the same T t diagram, which we are familiar in case of T C. We will stop here. Yes. To a large extent, diffusivity… the elements.

That is the reason why we, when we take a metal, of course there are many concept. One is diffusivity, where you tend to add metals with a higher melting point. So, that the diffusion is slower. You take, let us say an aluminum, add an iron to it or at the titanium to it or add vanadium to it, which are all high melting metals or add to aluminum, the tendency is that the diffusion becomes slower.

The second concept, which is also important, is the delta H. You should add those elements, which have a large delta H because when you stabilize the liquid, then only a glass gets stabilized. Stabilizing a liquid means that delta H of the liquid should be highly negative. We will talk about it possibly in the next class. Yes. you see this. We will talk about it. They are not really; need not be very high entropy. Structurally, yes.

There entropy is very high, but consecrationally, the entropy did not be very high. The reason is, for example, if I take a bulk metallic glass, for example, with this particular composition, which I have told you 40, 20, 20, 20 obviously, can have higher entropy.

But, there are number of systems, where one of the elements has very large quantity. This is 70 percentages remaining. All elements put together or about 30, you do not except very high entropy because consecration entropy, all of you know goes to a maximum at the center of the phase diagram. So, high entropy alloys are those alloys, where you take equal atomic compositions. Let us say a five component system is 20 percentage of each of the element; that way, it really gives you very high entropy. A glass.., as those again like nano composites, where you try to crystallize a little bit and get a crystal inside the glass; so that, it is like a composite. So, that is again basically, particularly for the kind of applications that I was talking about that, where you want to make a tough glasses.