Advanced Materials and Processes
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Lecture - 8
Amorphous Materials Part – II

In this class, let us start talking about Amorphous Material. I specifically would like to call them as amorphous materials rather than, glasses. Because, we know glasses are only one set of amorphous materials. One class of amorphous materials, which show a glass translation temperature. Otherwise, what is an amorphous material? An amorphous material is anything, which is not having any periodicity, as far as the atomic arrangement is concerned. We know how we define crystal.

Crystal is something, which has both rotational symmetry and translation symmetry. That is how we define a crystal. So, it has periodicity at the same time, at any localized point it has a rotational symmetry. We talk about 2-fold symmetry, 3-fold symmetry, 4-fold symmetry, 6-fold symmetry. All these symmetries, which are called the crystallographic symmetries, in any crystal.

And there are also another class of materials, which look like crystals. But, have some special type of symmetries, which are called quasi crystals, which are 5-fold symmetries and 8-fold symmetry, 10-fold symmetry, this kind of symmetries, which are called forbidden symmetry as for as a crystal structure is concerned. So, in fact for quite some time people never used to treat quasi crystal, as on par with crystals.

Because the definition of a crystal structure, always used to be something which has both rotational symmetry and translation symmetry, which has a translation symmetry. So, because periodicity was an inherent definition into a crystal, because from the beginning we always even from your secondary B. Tech metallurgy. Or even earlier in school, when you read about crystal structure, how do we define a crystal structure? We say three dimensional periodic arrangement of atoms, that is what is a crystal structure.

So, once we talk about that that means, we are talking of translation symmetry. So, if a translate symmetry is not there, which is not there in a quasi crystal. In a quasi crystal what you have is only, a quasi periodic symmetry. So, that kind of a crystal was never

accepted by crystallographer as a crystal. But, recently with so many materials showing that kind of a 5-fold symmetries, the crystallographers have in 1991 have introduced this, as a class of crystal.

And they have redefined the definition for a crystal. The definition a for a crystal, which is accepted by crystallographers today is that, anything that gives you a discrete diffraction pattern. That means, if you take a material and send an x-rays through that. It should gives you clear cut peaks, without giving you a broad peak. If it gives you sharp peaks or a sharp diffraction spots, if it is a electron diffraction or a pin whole diffraction in x-ray.

So, if it gives you sharps spots or sharp peaks, that is a crystal. So, that is how people define a crystals now. So, there quasi crystals can enter into that kind of a class. But, a amorphous material is that, which does not have any sharp diffraction pattern. Because, it does not have any periodicity, whether it is a quasi periodicity or a true periodicity, it does not possess both. The only thing that it has, is what is called short range order.

We can say that, it can have that in a very small range, the atoms probably are arranged in such a way. That probably some kinds of an order exist there. And one can probably talk about, some kind of clusters. For example, even liquids we know have this clusters, otherwise how do you know that when you take a liquid of let us say nickel liquid. And if you try to solidify this liquid, always nickel became FCC.

If I take a aluminum liquid and then solidify at the melting point. And once I come below the melting point, I have always get a FCC. I never get a BCC, I never get a HCP, why is that, how does the liquid know, that it has to become only FCC crystal. It is because, there are clusters in the liquid, near the melting point particularly with these FCC structure. And if you look at a number of such clusters with different atomic arrangement.

Whether, it is a FCC, BCC, HCP. And you will see that for aluminum, the FCC clusters will have the lowest free energy. And people have done such calculations, which is called lattice stability a phenomena. The number of first principal calculation, that have been taken place, where people talk about what phase can come out from a liquid. And in principle calculate the free energy of BCC iron, FCC iron, HCP iron. And some may be tetragonal iron, whatever it is.

And you will find that at the melting point, near the melting point, the free energy of the BCC iron is a lowest. And that is why liquid gives you that BCC iron, under equilibrium condition. And people have shown that, if one can use non equilibrium conditions. One can generate different crystal structures, which are other than what is under equilibrium conditions, one can achieve. This is because, the other structures also can exist, but have a different free energy.

And if somehow the kinetic surface that the activation barrier, for the second phase to form. If that is lower, it is possible for the liquid to transform into such a phase, if you cool it rapidly. So, there are some examples where people have shown, that on fast cooling the liquid. And instead of the equilibrium crystal structure forming, some other non-equilibrium crystal structure can form.

So, that is basically, because liquid has short range order. And that is how in fact, we define solid liquid and a gas. A solid is that, which has both short range order and a long range periodicity. A liquid is that, which does not have a long range periodicity, but only has a short range order. And a gas is that, which does not even have a short range order; that is how we define. So, an amorphous phase is in the middle. It has a structure, which is similar to that of the liquid.

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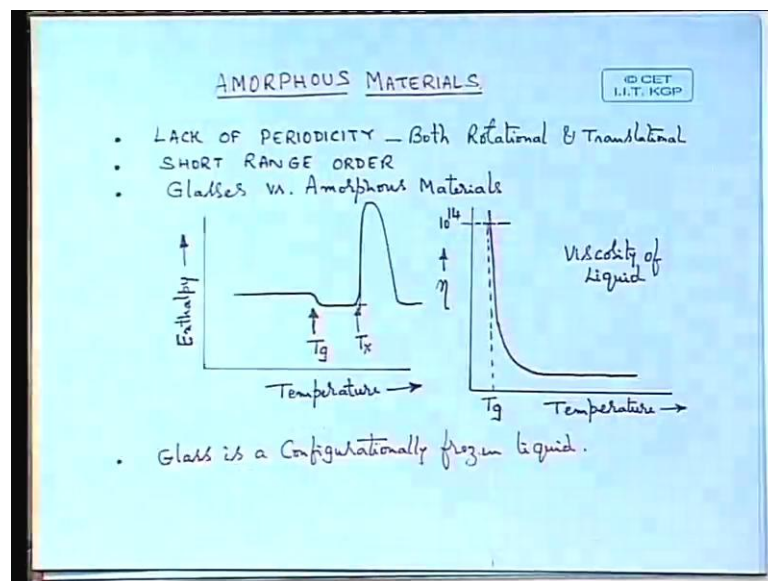
And in fact, most of these amorphous materials, so far have been made particularly from the liquid. In fact, if we talk about the classical amorphous materials. What are the

classical amorphous materials? They are the silicate glasses, everybody knows this silicate glass. We use it for so many applications, we cannot imagine living without a silicate glass.

So, all these silicate glasses are nothing but obtained from the liquid. And these are what are called the configurationally frozen liquids. And they are called glasses. So, a glass is a term, which is used for all those amorphous materials, which are obtain from the liquid. Because, such a glass shows, what is called a glass translation temperature. If I take a glass, heat it in a differential scanning calorie meter, what I see is this type of a picture, this type of a DSC trace.

That initially the enthalpy is constant. In fact, it will slightly increase, I should say this. Because, we know enthalpy has to increase with increase in temperature. Why, because of the CP, enthalpy is what, integral CPDT, because it is integral CPDT, even if I assume CP as constant. Then also the enthalpy is nothing but CP into delta T. And because, it is CP into delta T, the enthalpy has to increase.

But, because this is a differential scanning calorie meter, where we are trying to find out the difference between a reference and a sample. Usually you will see a stable base line, this is called a base line. You try to calibrate the system in such way, that you get a flat base line. And then you get a step there and that step is called a T g. We will come to it in a minute later, that T g being a second order transition. It will never give you a peak, in a enthalpy versus temperature plot. But, it will only give you a step, because in a second order transition the situation is such that, the enthalpy does not change much. We will show you it in the next transparency, later. That what you see is that, there is step there which is a T g glass transition temperature and then you get a peak. And that peak is for the crystallization of the glass, because a glass is a meta stable. So, meta stable phase has to crystallize, when you heat it.

So, an equilibrium crystal comes out. And T x is usually defined as the temperature, at which either the crystallization starts. That means, what is called onset of crystallization. For example, here how do you get the onset of crystallization. You take the flat portion, and extrapolate it and take the linear portion of the crystal in peak. And then extrapolate it and find out where they intersect and that is a T x. This is called onset of crystallization.

And some people take the peak temperature also. But, the peak temperature is not really the T x, though many people use it. Because, what does peak temperature represent, can somebody tell me, what does the peak temperature represent?

Student: ((Refer Time: 11:45))

It is not complete crystallization no

Student: ((Refer Time: 11:49))

It is related to activation barrier fine, but that is not a the final answer. It is the temperature at which, the rate of the reaction is maximum, rate of the transformation, whatever transformation it is. It can be for any transformation, the peak temperature is the temperature, where the kinetics are the fastest. And the onset temperature is a temperature, where the reactions starts?

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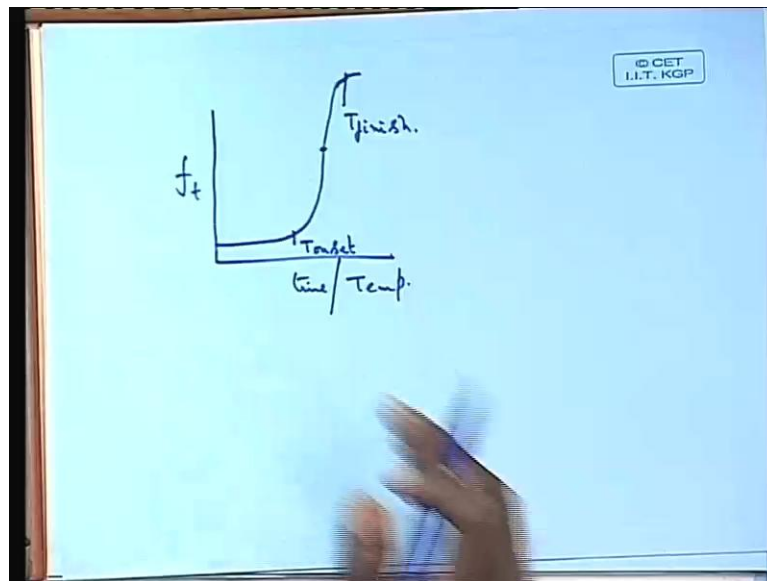
For example, if I show you a percentage fraction transformed, as a function of time if I show you. If I translate this to temperature, for example instead of time, this temperature the onset temperature, is the onset temperature, T onset. And you take the temperature which is somewhere in the middle of this is the one, which is the rate of reaction is highest. And then later it again saturates. That means, transformation is more or less complete, this is the finish temperature T finish, you can say.

And in the middle somewhere you get the peak. Usually this kind of S curve, people usually call it. We always observe, when we talk of about fraction transformed versus time. You must have heard about, what is called Avrami exponent, John Sarbanes Avrami equation. That is where we talk about, this is what is called sigmoid type of a transformation. So, this is as for as the transformation is concerned. And what you get is a T x.

So, and this is the classic example of a glass. If it is an any other amorphous material, it will not show this class transition. And straight away show a T x, because as I told you amorphous material can be obtained, not only from the liquid. But, also from either the vapor or also from the solid, by solid sate amorphization. But, usually those which are made from the solids state or from the vapor state, do not show a glass transition. There can be one or two exception, but usually not.

That is why the term glass is usually referred to as that amorphous material, which is made from the liquid. And that is why we usually define it as, as a configurationally frozen liquid, what is this, what does this mean? That mean, when I am freezing the liquid, this is what happens when the liquid is cooled, what you see on right side. As I keep on decreasing the temperature, the viscosity of liquid keeps on increasing.

The eta which is shown there, is viscosity in terms of points. And once the viscosity reaches a critical value of about 10 to the power of 14 poise, which is the usual definition for a solid. We define solid the mechanical definition of a solid is that, which is rigid. And you get rigidity when the viscosity reaches above 10 to the power 13 or 10 to the power 14 poise. So, that is a definition of a solid.

So, when you keep on cooling the liquid, without any crystallization happening. What happens is that liquid will remain as liquid, the only thing that will happen, is it is viscosity keeps on increasing. And there is a particular equation, people call it as Vogel-Fulture equation, which defines the viscosity. And the viscosity once it reaches about 10 to power 13 or 14, we call it as a glass, because at that temperature this liquid wants to become a solid, because already the viscosity has reached that of a solid. So, it wants to become a solid, but this solid is different from normal solid. Because, it is structure is the same as that of the liquid. It has not become a crystal it is a solid, but having the structure of a liquid. And that is why, at that particular temperature, the atoms which are in the

liquid cannot move anymore, because it is a rigid solid. And because of that kind of a situation, we say that the atoms get configurationally frozen. That means, the atomic configuration which is there in the liquid gets frozen. The atoms remain where they are. And that is what gives you a solid, which is nothing but a glass. And it is structure will be same as that of the liquid. But, it is for all practical purposes, it is a solid. Because, it behaves like a solid with a rigid structure, and that is a glass.

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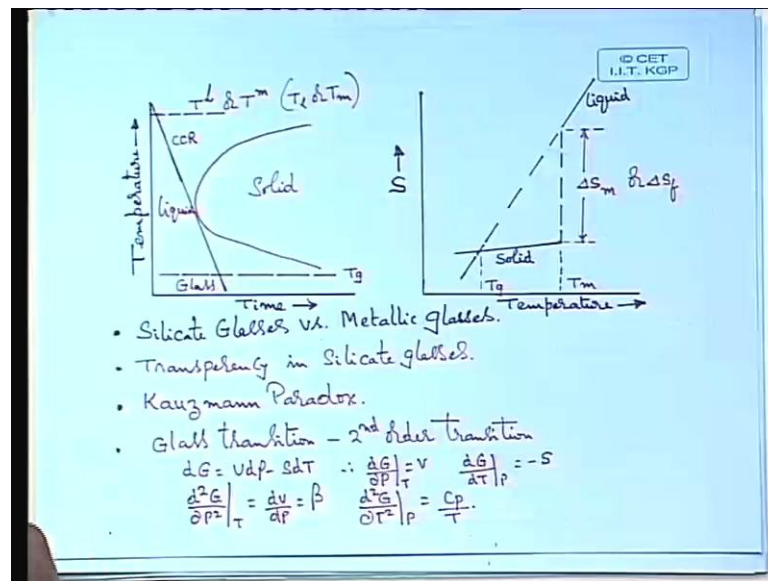
And this glass you obtain, by basically cooling a liquid, as I told you. And when you take a liquid, you cool the liquid, every liquid wants to became a crystal, is it not. As we know that usually, whenever I cool aluminum, it becomes FCC aluminum. I cool iron it becomes BCC iron, but it does not become a glass, is it not. But, whenever there is a liquid to crystal transition, if we plot a TTT diagram such a transformation.

We are all aware of TTT diagrams, in our heat treatment of a steels, where austenite transforms to paralite. We draw exactly a similar diagram. And then show that what is the time required for the paralite to form at each temperature. Exactly similar to this kind of a plot; where the fraction transformed as a function of time. If you try to plot for the paralite to form let us say.

You will see a time at which the transformation starts, we say start of transformation. And finally, end of transformation. And this start of transformation will give you, what is called incubation period, yes is called incubation period. That means, that is the

minimum time that is required, at any given temperature for the product phase to come out, from the parent phase. Why do you need that minimum time? Because the atoms have to come together to form a unit cell. And then that unit cell has to grow.

So, the time require for the unit cell to form. That means, the time required for the nucleus to form, because this particular time, defines the times for nucleation. And the rest of the time is the time of growth. And finally, the finish time we get. ((Refer Time: 19:07)) So, the time required for the nucleation, is what is the incubation period? In case of austenite to paralite. It is a time required for the paralite to nucleate, which is the two phase mixture, and in case of here, an amorphous in case of a crystalline solid. At any given temperature the time required, we can talk about it. And that is the incubation period for the solid to form. And the only difference between a paralite formation, and a solid formation from liquid, what could be the difference? The paralite formation from austenite and solid formation from the liquid. If you compare the TTT diagrams of these two, will you find some differences.

And if so what are those differences?

Student: ((Refer Time: 20:01))

Quite large, definitely one thing is that, paralite is not a single phase, it is a two phase mixture. A two phase mixture has to nucleate from a solid state. First of all, it is also nucleating from a solid state, one has to remember that. In a solid state the diffusion is much lower than in a liquid state. So, here a solid is coming out of the liquid, where in the liquid the atoms can move very easily.

So, the incubation period is very small. So, that means the TTT diagram is push to the left. So, it is almost touching the vertical axis. I have drawn it this way, just to exaggerate the situation. And show you what is called the critical cooling rate. But, otherwise the this curve is almost touching the left side. And again this also depends on, what this particular position of this c curve.

So, called c curve also for the same liquid to solid transformation also. It depends on something else, what else it depends on…

Student: ((Refer Time: 21:21))

No, the composition anything else

Student: Crystal structure

Crystal structure, yes the more complicated the crystal structure is, the more right it is shifted. It is like, in steels we talk about harden ability. You add certain alloying elements to increase the harden ability. That means, you shift your TTT diagram to the right. Exactly, similarly if you choose a crystal structure, if the liquid is giving a particular crystal structure, which is much more complicated. For the atoms to come together to form a nucleus is more difficult.

That is why, the time required at any given temperature is going to be longer. That is why the TTT diagram is shifted to the right. And this is what exactly you see, in case of silicate glasses. In case of silicate glasses, the crystal structure of silicate is nothing but the network of silicate chains ((Refer Time: 22:23)) 2 chains, each silicon atoms having a bond with 4 oxygen atoms, around it. And that is a covalent bond.

And such kind of clusters of silicate clusters are arranged, in a three dimensional network kind of structure. That is the type of silicate structure. And such a silicate structure is so complicated. That from the liquid, if a silicate crystal has to nucleate it is very difficult. And that is why, every silicate liquid can easily become a glass. Just melt the silicate liquid, pour it into a small even, a small thing like as a small cooling rate, such as a sand casting you can get a glass.

Whereas, in a normal metal or an alloy is very difficult. Because, most of the metals are alloys have a such simple crystal structures. Like FCC, BCC and all that the formation of a crystal is very easy. And so you can get a glass, only when you can suppress the crystal to form. Similar to the, we have a clear cut analogy to our martensite formation. You can get a martensite, from an austenite only when you can suppress paralite formation, is it not.

So, if you can suppress the paralite formation, then you can get a martensite. Exactly similarly here, if you can suppress the crystal formation, then you can get a glass. And that is what Turnbull has said long back, in 1950's itself. That every liquid would like to become a glass, unless crystallization intervenes, this is what a famous statement made

by Turnbull. Turnbull is called a father of undercold metals, because he was the first fellow to study undercold liquid metals.

And he said that, it is because the reason for this statement is that, liquid and glass structure is the same, is it not, there is a same structure. So, every liquid would like to become a glass very easily, because there is no activation barrier for the liquid to become a glass. There is a same structure, where is the activation barrier, whereas for a liquid to become a crystal there is an activation barrier. But, because the glass can form only below a certain temperature called glass transition temperature, ((Refer Time: 25:06)) which is what you see here.

You have to keep the liquid, as liquid until you reach the glass transition temperature. And during this process usually liquid is a metastable. Because, above the melting point, you can see here above the melting point, it is a stable liquid. Once you are below the melting point, liquid is a metastable liquid. And this metastable liquid, can transform to a solid, crystalline solid. If the activation barrier is small, that is what happens in normal metals and alloys.

If it is a silicate, then it is much more difficult for the silicate crystal to come out. So, the liquid will keep on getting undercold, until it reaches a glass transition temperature T g. And then that liquid will transform to a glass. So, you need a minimum cooling rate, which is called critical cooling rate CCR, for getting a glass. What is this minimum cooling rate? It is nothing but the tangent for the C curve. If you draw a tangent for the C curve, that will tell you the minimum cooling rate, which is required to avoid any crystal to form.

This is true, whether it is a silicate crystal or a metallic crystal. The only difference is, the CCR may be different for different situations. The CCR for a silicate will be very low. If I want to put a silicate here, it would be somewhere like this. And the critical cooling rate would be something like this this is for a metal, I would say this is for a silicate. So, the critical cooling rate, you can see is much smaller for a silicate glass. The critical cooling rate for a metal or an alloy is much larger.
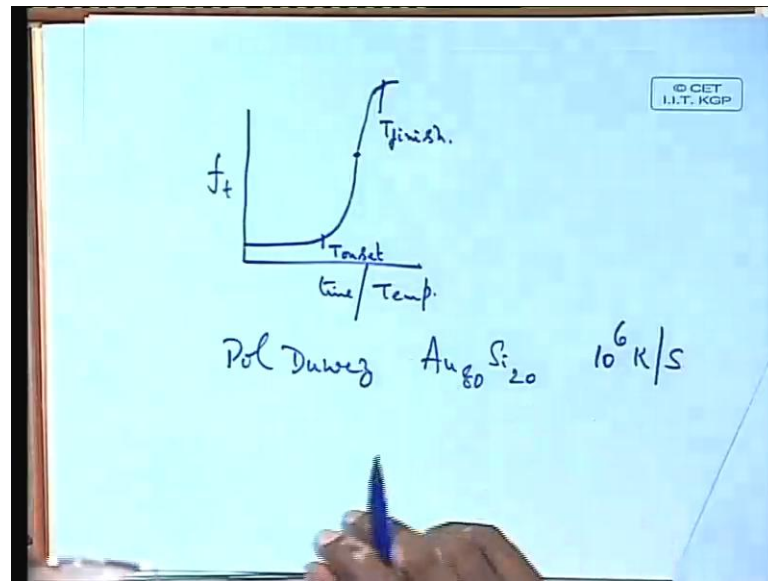
And in fact till 1959, when a person by name Pol Duwez, took a gold silicon alloy. 80 percent gold and 20 percent silicon alloy. And cooled this liquid very rapidly, at a cooling rate of the order of 10 to the power 6 Kelvin per second. You can see, what is the cooling rate. If you want to get just an idea, what is the typical cooling rate that we are talking about, take a sand casting. Sand casting, cooling rate is usually of the order of 1 to 10 Kelvin per hour.

And if it is very slow, one can increase by putting some or something like that to about 10 Kelvin per second, metallic molds for example. We can get about 10 to 100 Kelvin per second. So, about two orders of magnitude of to the power of 10 as per second is what you can achieve by normal metallic molds. And here we are talking of 10 to the power 6, which is almost 4 orders higher.

So, this is by a special technique, we will talk about it later, when we talk about rapid solidification processing as a technique, for producing advance materials. So, there we will see how to achieve this kind of a high cooling rate. And here shown that which such high cooling rates, one can achieve a glass very easily. Whereas, a silicate glass one can achieve just with 10 degrees Kelvin per second or 100 degree. Maximum you need is only 100 degree Kelvin per second. So, that is what you need for a silicate glass.

So, one needs to go beyond the critical cooling rate, which is a system dependent. As I just now told you even in metals and alloys also, depending on the type of system. The

critical cooling rate will be different. So, obviously one has to consider, what is the critical cooling rate. And one can make in principle, even a pure metal one can make a glass. Provided he uses such a cooling rate higher than the critical cooling rate for a pure metal.

And in fact, people have shown, that pure nickel can be made into a glass by cooling at a rate of the order of around 10 to the power 14 Kelvin per second. Using a technique which is laser, by laser, using picoseconds lasers, people have used picosecond lasers and they have been able to obtain glasses even in pure metals.

In picosecond laser, theoretically one can achieve around 10 to a 14 to 15. Though practically there can be difficulties to achieve that. So, that is the kind of things one can achieve. And what is also important for you to note that, the terminologies that we use a different in different text books. So, just I wanted to show you for example, T m people show some cases like this, some cases like this. But, whatever it is as long as we stick to one terminology.

So, this is as far as glass formation is concerned. But, these are all kinetics of the glass formation. Let us try to look at the thermodynamics of the glass formation. What is the thermodynamics of glass transition. What is a glass, basically when you talk in terms of thermodynamics. Glass is a random arrangement of atoms. And we are saying it is the liquid which is nothing but a configurationally frozen liquid is a glass.

So, if you take a liquid. And keep on cooling it, you have to under cool the liquid up to the glass transition temperature. That is when you get a glass, is it not, you have to under cool the liquid, without any crystallization coming into picture. You have to prevent crystallization, suppress crystallization. And still keep on under cooling the liquid up to the glass transition temperature, that is when you get a glass.

So, if you keep on cooling the liquid. And look at the entropy, you see that the entropy of the liquid and the entropy of the solid are different always. Why, because the liquid is more random. So, it is entropy has to be different. And we know that, it has a higher entropy, is it not. Any random material has a higher entropy, we know this from the second law of thermodynamics.

So, and if you now compare the liquid and the solid. The entropy of the liquid, decreases rapidly with temperature. When compared to that of the solid. Why does it decrease rapidly, because entropy is nothing but integral CPDT by T, is it not. Enthalpy is integral CPDT, so entropy is CPDT by T integral. So, as a result, so it is the CP, which decides the rate at which the entropy drops. That means, if I find out d s by d t, which is the slope of the entropy as a function of temperature. That means, slope of this ((Refer Time: 32:42)) curve.

That slope of this curve is nothing but CP by T, is it not. And that CP for a liquid is always higher than the CP for the solid. Heat capacity of a liquid is higher than heat capacity of the solid, this we all know. And because the heat capacity is higher the liquid free the entropy, decreases more rapidly than the solid. So, when you reach the melting point, at the melting point liquid can transform to a solid with a release of the entropy, which is called entropy of fusion.

Delta S f or delta S m entropy of melting, that is at the melting point. But, if we somehow suppress the solid to form at that melting point, by cooling the liquid rapidly let us say. If I keep on cooling the liquid rapidly, then at the melting point, there you are not providing sufficient time, which is higher than the incubation period. That is required for the crystal to form. Then crystal will not form, if the time that you are allowing is smaller than the incubation period. At that temperature melting point obviously, crystal cannot form.

So, then you can really undercool the liquid. And if you keep on under cooling the liquid, and look at how the entropy changes. The entropy basically one can extrapolate, assuming the CP to be constant. Though that is a very crude assumption, for all easy explanation one can assume that. If I assume CP to be constant, the slope of it of the entropy is fixed. So, you will have a straight line. And that straight line, if you keep on extra polling to, letting to the lower and lower temperature.

You reach a crucial stage, where the entropy of the liquid, the entropy curve, intersects that of the solid. And once it intersects, if you look at the temperature below that intersection. You have a situation, where the entropy of the liquid is less than that of the solid. I think in thermodynamics class, we talked about it. This particular temperature is what is called carbon temperature the Kauzmann paradox.

Because it is that temperature at which the liquid does not know what to do. Because, it comes to a situation, where the liquid if it goes below that temperature. It is entropy is lower than that of the solid, which is something, which is unimaginable for us. Because, we know that a solid is more ordered, then a liquid. And as a result it always has lower entropy, then that of the liquid. So, as a result it is not possible for a liquid to have a lower entropy than that of the solid. So, at that temperature liquid transforms to a glass, having the same entropy as that of the liquid at that temperature

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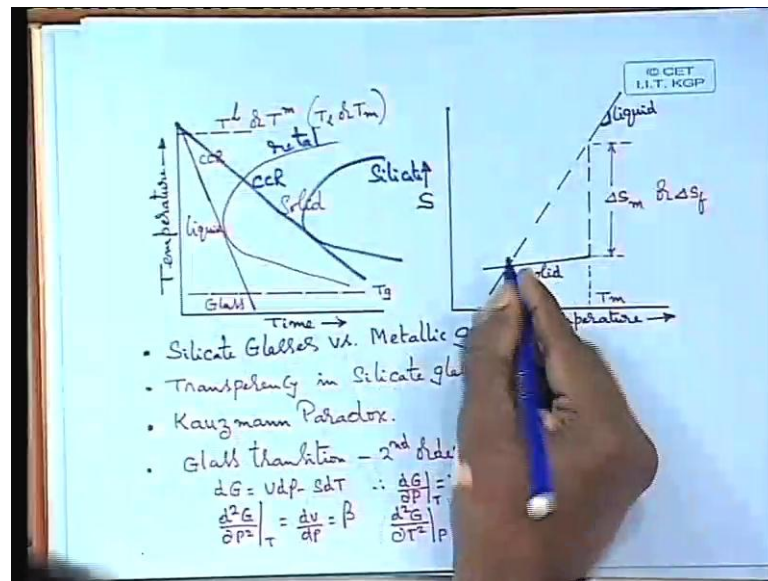
So, what is the entropy of the glass, entropy of the glass, is same as that of the liquid at the T k or T g. And that particular temperature is actually called the Kauzmann temperature. Or the ideal glass transition temperature. It is a thermodynamic glass transition temperature. I should tell this very specifically to you, because the actual glass transition temperature, which we usually observe is a function of the cooling rate that one uses, when a liquid is cooled, the higher the cooling rate that we are using. Usually the lower the T g, one can get to some extent. Though it is not a very significantly changes, but changes over a small range.

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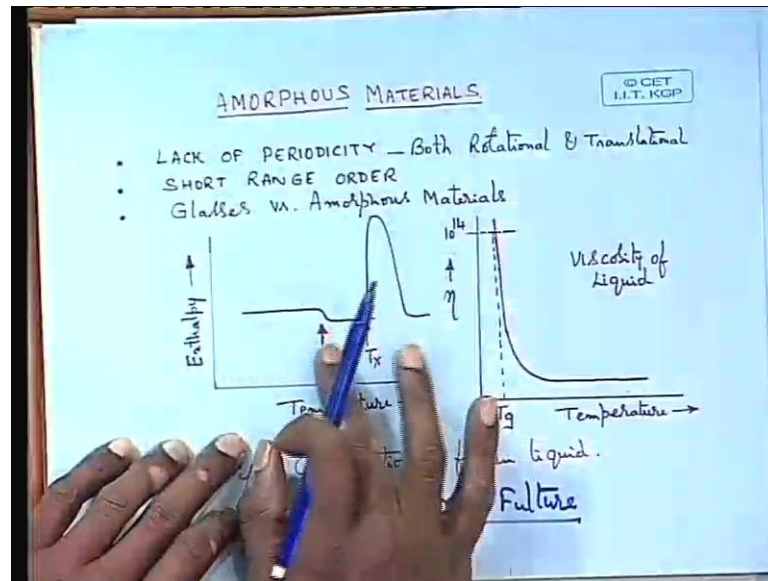
As a result the glass transition temperature, that we observe usually when a glass is heated. That T g which you see in the DSC, is not the real ideal glass transition temperature, which is the kinetic glass transition temperature, which people usually refer to. But, the difference is not too much, may be of the order of 10 to 20 Kelvin are so.

Student: ((Refer Time: 37:11))

Can that is what I am telling you, to a very small extent, because there is an inertia in the liquid. Whenever you are cooling a liquid very rapidly, there is an inertia in the liquid for it to even transform to a glass. So, as a result the T g to some extent goes down. That is usually happens at very high cooling rates. So, otherwise for all practical purposes, one can take this as T. So, we will stop here, and then take up the next class later.