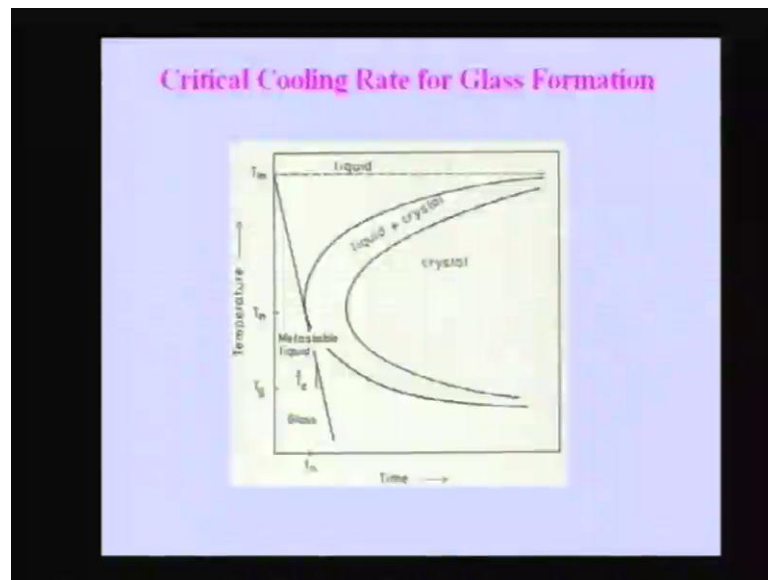


Advanced Materials and processes
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Lecture - 09
Amorphous Materials Part – III

Let us continue from what we have been talking in the last class, basically about the Amorphous Materials. Last class we talked about what are amorphous materials, what do they differ from glasses, how do they differ from glasses, how do we define a glass. And what are the various thermodynamic and kinetic conditions under which we get a glass.

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So, we were talking about the critical cooling rate, as you can see here. The critical cooling rate, which is the minimum cooling rate, that is necessary for the glass formation, which is you can see it from this curve. And here the T_n , the capital T_n is the temperature for the nose. And small t_n represents the time, for the nose. So, which are the two crucial parameters, which decide the slope of the critical cooling rate?

So, if the critical cooling rate is basically decided by these two. And $t \cdot c$ is the critical cooling rate, which is the lowest cooling rate; that you need to adopt, if you want to get a glass. This is similar to the martensite formation, which we talked yesterday. And they also depending on the type of glass, the c curve position is going to be different. For

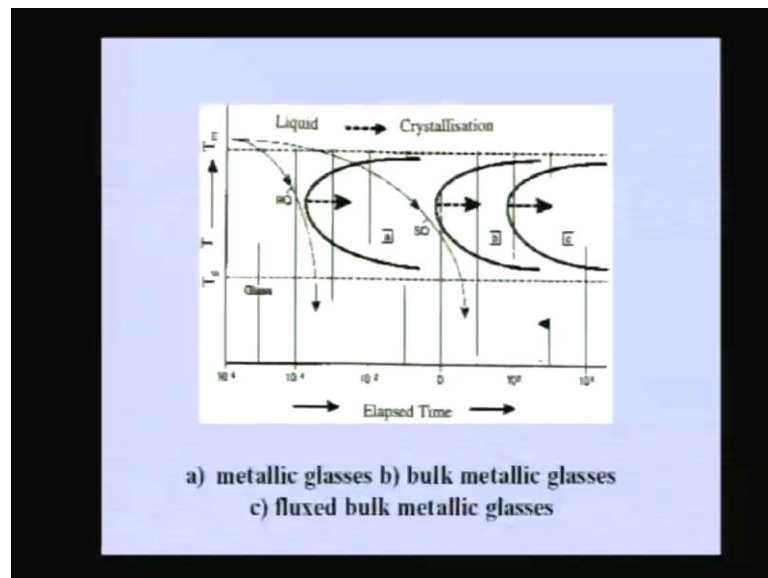
example, as I told you, for silicate glasses, the c curve is going to be shifted to a large extent to the right.

And because of which, you get a very easy glass forming ability, there is a term, which we usually define it as glass forming ability, which is similar to what is called harden ability. So, you should remember this glass forming ability, we will come to it again and again in future. So, this glass forming ability means, basically, how easy a glass can form or how easy a composition can be made into a glass.

So, that basically depends on, how difficult it is, for the crystal to form. Because, that is, what we have talked yesterday in the last class, that glass formation always happens, whenever a crystallization can be prevented. Similar to martensite, you will always get, when a paralite can be suppressed. So, if you cannot suppress the paralite formation, you cannot get martensite.

Because, once the austenite has transformed to a martensite, it would not, if the once the austenite has transformed to paralite. It would not transform to martensite. A paralite cannot transform to martensite, but an austenite can transformed to martensite.

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Similarly, once a liquid has already crystallized. Then, obviously, there is no question of forming glass, during cooling. You can always make a crystal into a glass. That is a different root all together, as we talked about solid state amorphization. So, you can take the crystal and make it into glass by definite roots. But, not by the rapid cooling root, which is, what we are talking about.

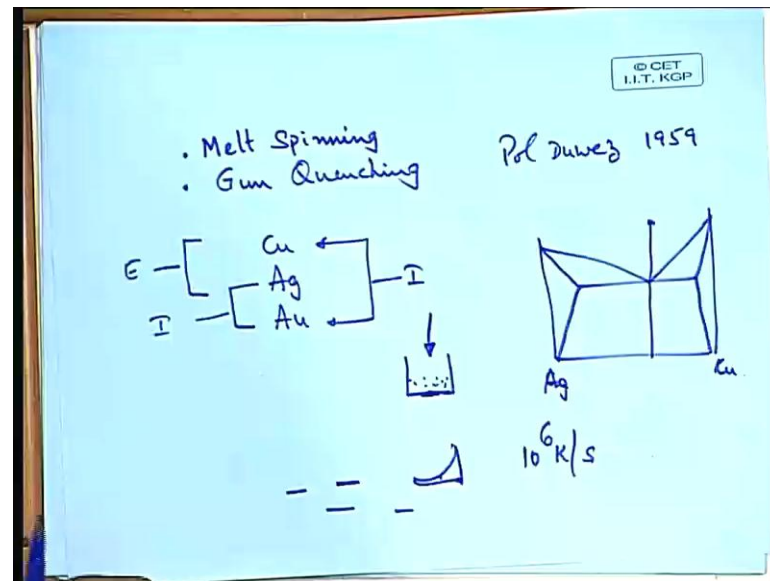
So, during cooling, once the crystal forms, a crystal cannot become a glass. So, as a result, a crystallization has to be prevented, for that you need the c curve to be shifted to the right as much as possible. So, that, you can have the slow cooling conditions, under which you can get a glass. So, that is what, a few examples are shown here. One is a conventional metallic glass, which is on the left, the A curve and which is also, actually exaggerated for you.

And the cooling rates, that you need, what is given RQ is the rapid quenching conditions. The cooling rates, that we regularly use, are the order of 10^6 Kelvin per second. So, this is the cooling rates, that are usually used for any typical metallic glass. Starting from the gold silicon glass, that we talked about it in the last class. But, there are a number of other glasses, that are available, which do not need that, high cooling rates.

One example, easy example from the conventional glasses is the silicate glasses itself. Where, if you cool at the rate of 10^2 Kelvin per second, you can get easily a glass. All the silicate glasses are very easy glass formers. But, in metallic systems itself, there are a number of new glasses people have found, by understanding the principles of the glass forming ability, which we will talk a little later.

That once you understand, under what conditions a glass will form, which kind of composition can easily form a glass. Then, you can really make glasses, which can form glasses very easily. These are called easy glass former. And such materials are now being called, as bulk metallic glasses. Why, we call them as bulk metallic glasses, is basically because, earlier the metallic glasses that were made so far, were only a thin films. Why they are thin films? Because they are prepared by fast cooling.

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The methods that are used are for example, one technique is called melt spinning. Second is called gun quenching. In fact, it is this gun quenching technique, which was the first technique of rapid solidification, which proposed by Pol Duwez in 1959. In fact, the discovery of these glasses is very interesting. If you go through the history, what you see is, that in 1959, Pol Duwez was thinking a lot about, solid solubility of a in b. Solid solubility of a solute into a solvent in metallic materials.

When, we look at these metallic materials, mostly in solid solutions, we see that, there are Hume Rothery rules, which decide, whether an element should dissolve into a solvent or not. And these Hume Rothery rules, we all know there are four rules. One is called the size factor, if the size factor is less than 15 percent. Then, you have solubility, if the size factor is less than 8 percent, then you can have a complete solid solubility.

And then, we talk about structure. If the structure of a and b is the same, then the chances of having a high solubility is more. And similarly, the electro negativity, if the electro negativity of a and b are close to each other. Then, you can have a good solubility and similarly, what is the next parameter? Valiancy, so if the valiancy of a and b are close to each other, then you can get a good solubility.

So, solid solutions are usually formed, when these four criteria are at least some of them are satisfied. So, then, when he was looking at various phase diagrams, he found interestingly one phase diagram, which is a copper silver phase diagram, which is a eutectic phase diagram. And if you carefully look at, copper, silver and gold, if you look

at these three elements, the three noble elements, the copper and gold form isomorphous. Silver and gold form again isomorphous, but copper and silver, this is isomorphous, this is isomorphous, whereas, this is eutectic.

If you look at these, the four Hume Rothery rules, you see that structures are the same. All are fcc copper, silver, gold, all are fcc and their atomic sizes are also very close. Though, there are small differences the electron negativities are also closer and the valiancy, they all have the same valiancy. So, looking at this in principle, copper and silver also should form an isomorphous, but it does not.

So, there are always exceptions for Hume Rothery rules, a number of exceptions are there, this is one such classic example. Then, Pol Duwez thought, maybe, if I take this liquid, because eutectic is what? Eutectic is that, where the two elements are soluble in the liquid state, but not soluble in the solid state or partially soluble in the solid state. In fact, the copper silver comes to that final type of a classification, that they are completely soluble in the liquid state and partially, soluble in the solid state. The maximum solubility of copper in silver is about 10 percent and silver in copper is about 10 percent in the solid state. So; that means, you get a phase diagram, which looks like this. This is the typical copper, silver phase diagram, I should put silver this side and copper this side, why is that?

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Melting points are different, copper has a higher melting point, 1083 silver has

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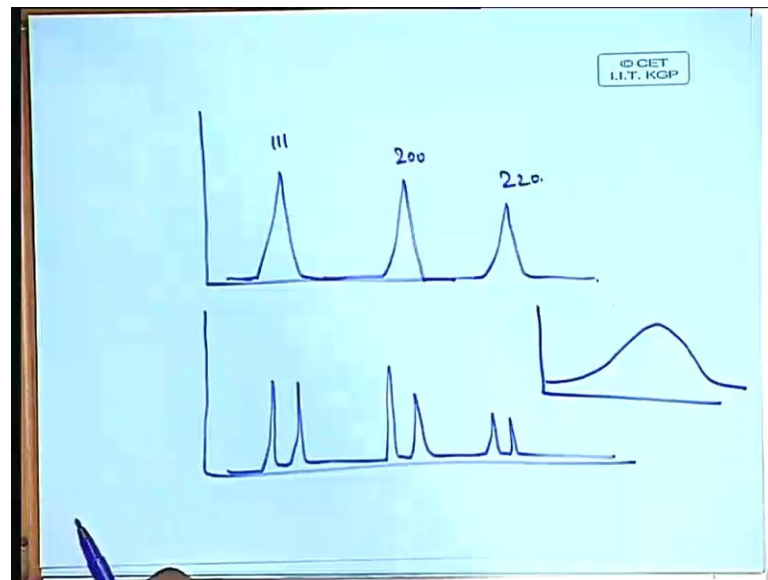
1064, 963 so anyway, so that is the copper, silver phase diagram. A typical eutectic phase diagram, whereas, the copper gold or silver gold or isomorphous. Then, what he did was, he took this alloy, eutectic alloy, heated to the melting, above the liquids, above the eutectic. So, that all the two elements a and b are completely soluble in each other. And then, try to quench it very fast.

How, did he do it, what he did was, he took the liquid in a small crucible, with a small hole in it. And close that hole, with a foil of a higher melting metal and then, melted the

copper and silver into that. And what he did was, once the liquid is molten. Then, through some organ gas, he pressurized the liquid. So, that it pierces through this hole and falls on to a copper block here.

So, once the liquid rapidly falls on this coppers block, what happens is, liquid gets atomized. And these liquid droplets will fall on to this and form as thin flakes. And these are what are called splats. And that is why; this is called splat quenching or gun quenching. Why, we call it gun quenching? Because, it is like a gun the liquid comes like a bullet, through that diaphragm, through that hole. And with this, he was able to achieve this 10^6 Kelvin per second. That was the first rapid solidification Technique.

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And what he observed, he observed that you have one phase, he has taken a eutectic, did an x-ray diffraction and he gets a peaks, which are just the normal peaks of this type of peaks. One corresponding to 111, another 200, another 220, this is, what you get, if you have a solid solution, silver, copper solid solution. Silver, copper solid solution, must be fcc. Because, silver is fcc, copper is fcc, so obviously, the solid solution should be fcc.

And that is what, you see here, but if this was conventionally solidified, under slow cooling conditions. What will you get? You get here, you get two peaks, for each peak, you will get two peaks, one corresponding to the silver, another corresponding to the copper. Because, you have silver solid solution and copper solid solution, that is, what is a eutectic mixture is, it is alpha plus beta, we say.

In this particular case, alpha beta both of them have same crystal structure. And obviously, there peaks will be the same, because both are fcc; you will have fcc peaks of both. So, but both of them, there lattice parameters being different. Though, the crystal structure is same, there lattice parameters are different. And it is the lattice parameter, which decides the d spacing and it is the d spacing, which decides the theta, in x-ray.

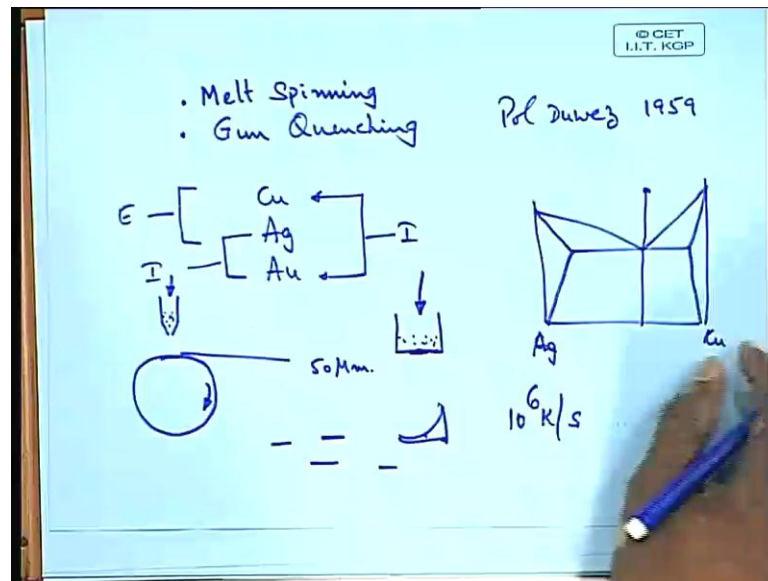
So, obviously, you will get two peaks, one corresponding to the silver and copper. We do not know, which has a higher lattice parameter depending on that. If the lattice parameter is high, then the d spacing is high, then the theta will be low. So, the element having the higher lattice parameter will be on the low angle side. The element having the lower lattice parameter will be on the high angle side. So, this is what you get, if it is conventionally made, but this is what you get, if it is rapidly solidified.

And that is what, he got in the silver copper and then, immediately, he started, taking a number of other eutectics. And thought, every eutectic should give you a solid solution like this and that is where, he stumbled upon the gold silicon system. He took the gold silicon, 8020 eutectic alloy and then, rapidly solidified and interestingly, what he got was an x-ray peak, like this.

Instead of getting a x-ray peaks, like this, which is, what he expected. That silicon should dissolve into gold completely and you should get a gold solid solution, which is an fcc solid solution. That you will get three peaks or four peaks, depending on the total theta range in which you have scanned. Instead of that, he gets a broad peak, like this and that has really been the birth of metallic glass, 1959.

Still, then, there was no metallic alloy, where people have observed a glass. And that is, when people have got into these metallic glass business. But, the problem there was, because of the fast cooling that you need to adopt by a technique, such as gun quenching, as you have seen here.

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Gun quenching, definitely gives you very thin films, thin ribbons, why it is thin, if it is not thin, if the cross section is not thin enough. Then, the cooling rate cannot be very high, the same thing we observe. When, you go to the other technique, which is very popularly used, which is called melt spinning. The reason, why it is called melt spinning, means, you are spinning the melt.

What you do here is, you take a liquid in a quartz tube, with a small hole in it, at the bottom and then, put the metal or the two elements, which you want to melt and make an alloy or you make the alloy prior, free alloyed metal, you bring it in put into that. So, that alloy is re melted. And once it is molten, it will not drop through that tube, why does it not drop, just because, you have melted a liquid; it cannot drop through a hole like that.

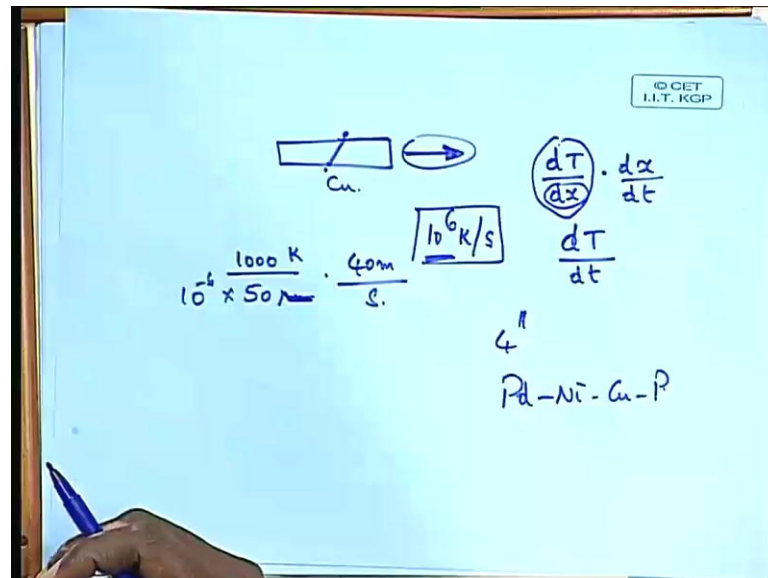
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Because, of the capillarity effect surface tension. So, what you do is, again as you have done in gun quenching, you take an argon and then, eject this liquid, through that hole. And then, allow it fall on to this copper wheel, which is rotating at around 4000 rpm or so, you can vary the rpm of course, to vary that cooling rate. And what happens, the moment liquid falls on to that is liquid is ejected out. And then you get a ribbon like this.

In fact, people have produced kilo meters of ribbons, like that continuous ribbons. In fact, there is a company in US, called Allied Signal Corporation and this Allied Signal Corporation their job is this to make ribbons of the order of around in a 4 inch width.

And the thickness of the order of course, you cannot produce thicknesses more than 50 microns here, melts spinning technique, the thicknesses are limited. In fact, it is that small thickness, which gives you that high cooling rate. In fact, one can calculate the cooling rate from this.

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If you have a sample like that, you have, let us take, this melt spinning and you assume that, you have exaggerated the thickness of it. Let us say, this is 1 melt spinning ribbon, the liquid is falling from that and the copper side is this, copper wheel side is this. So, how do you calculate the cooling rate here? One can easily calculate, if one notes, what the velocity with which, this is moving. That means, what is the velocity with which, the copper wheel is moving.

And second, if one knows, what is the temperature gradient here? Temperature gradient is always given as dT by dx and the velocity is nothing, but dx by dt . If we multiply these 2, what you get is this, dt by d , small t , which is nothing, but the cooling rate. So, what you need is, what is the velocity, linear velocity of this, the thin film, which is moving or the ribbon. That is moving. That means, once you know, the rpm, convert the rpm into linear velocity.

One can easily convert a rpm into linear velocity, because linear velocity can be given in terms of πd into rpm. Because, in one revolution, the wheel is moving by it is an amount equal into it is circumference. So, in one revolution, it moves by it is πd . So,

multiply the rpm by πd , what you get is, the velocity per minute and convert it into per second, you will get the linear velocity.

So, some distance per second, you will get and once you get that and calculate, what is the $\frac{dt}{dx}$, $\frac{dt}{dx}$ if you want to calculate, what you need, you need the temperature on top and temperature at the bottom. That is the difference in the temperature Δt . That means, if you know, what is the temperature at which the liquid is falling? That we know, because what is the melting point of the liquid we know, how much super heat, we are giving, that we know.

So, one can measure the temperature of the liquid metal in this quartz tube, there are parameters available. We can use optical parameters, measure that temperature. And what is the temperature at the bottom? Temperature at the bottom is the room temperature, which is that of copper. Copper wheel is always water cool to some extent. Sometimes, people cool do it by water cooling, but most of the time copper itself has such a high thermal conductivity, you do not need to cool it.

So, the copper is rotating at very high speed with a high thermal conductivity and because of which you can have a fast cooling. And so usually, if you use about 40,000, I mean 4000 rpm. And if you try to melt, let say, aluminum, you can easily reach 10 to the power 6, Kelvin per second very easy. So, that is, how you can one can calculate the cooling rates and these are the high cooling rates.

And this is feasible, basically because of the large $\frac{dt}{dx}$ and that is feasible, basically because of the small dx . Gradient will be higher, provided your thickness is smaller, for the same temperature difference. Of course, temperature differences, I cannot really increase, because melting points of the metals are fixed. So, I cannot really say, aluminum, I will start pouring from 10,000 degrees centigrade, nobody would do it.

So, as a result, the Δt is something, which you cannot really vary. The only thing that you can change is dx and that is why, what is here very small. And because, that is small, you are able to have high $\frac{dt}{dx}$ and which is what giving you this high cooling rate. For example, if you think of the temperature difference of the order of 1000, Kelvin let us assume and the dx is, for example, 50 microns, let us say.

If you think of 50 microns, so that would be something like, if you converted it into, put it as 50 microns and if this $\frac{dx}{dt}$ can be of the order of around very small number.

Because, you can see here, I mean rpm is almost 4000, 4000 means $d t$ by $d x$ by $d t$ is very large. Once, you put that number here, then you would see, that one can usually what we do is, about 40 meters per second. This is the type of linear velocities that we use.

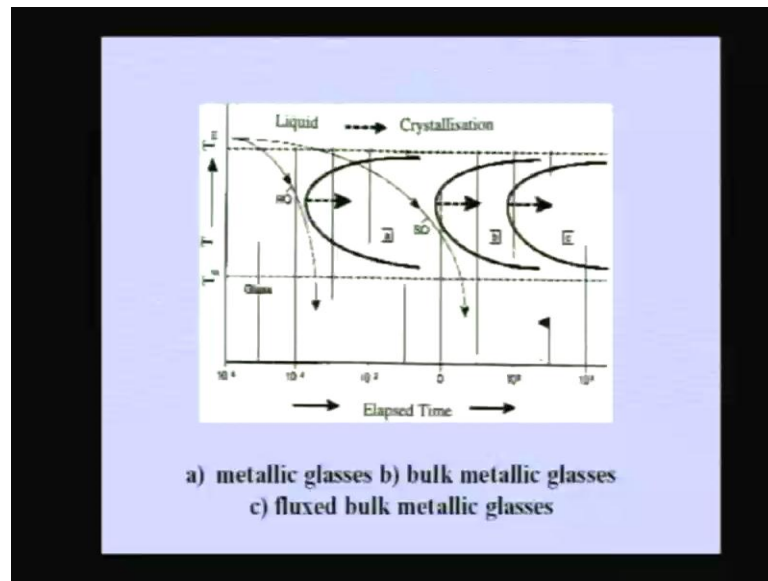
So, if you use in 40 meters per second and convert these microns into meters, you will see, you will get a very large number. Microns into meters means, if this is 50 into 10 to the power minus 6. So, you can see, how much you are getting, you will get a very large number. Though, this is a very crude method. So, because we have to consider, what is the velocity in the direction in which you have the gradient.

So, that means, what is called the contribution of this velocity or how much it is in that particular direction, where you have the gradient has to be considered. And if you consider that the velocity comes down a little bit. But, still you will definitely end up in 10 to the power 6 to 10 to the power 5, without any problem. So, that is the cooling rates that you get. And this was limited because, the glass forming ability of those alloys, which people have studied. Such as gold, silicon was very poor and that is why, you needed cooling rates of this order.

And nowadays, there are numbers of glasses available, which can be called as bulk glasses. Bulk glasses means; you can really produce thick alloys. In fact, people now have made 4 inch ingots, an ingot of a 4 inch, which is completely glass. The example is, palladium, nickel, copper, phosphorus alloy, which is the highest glass former. That is available as on today and when we go through these glass forming criteria, within a few minutes. We will come to know, why this alloy has a very high glass forming ability.

So, if you take such bulk metallic glasses, you can see the c curve there get shifted to the right, because there, the crystals are much more complicated and the liquid is very viscous. And because the liquid is very viscous, the diffusivity is very limited. And if the diffusivity is limited the incubation period for the crystal to form is going to be very large. And that is what exactly happens here.

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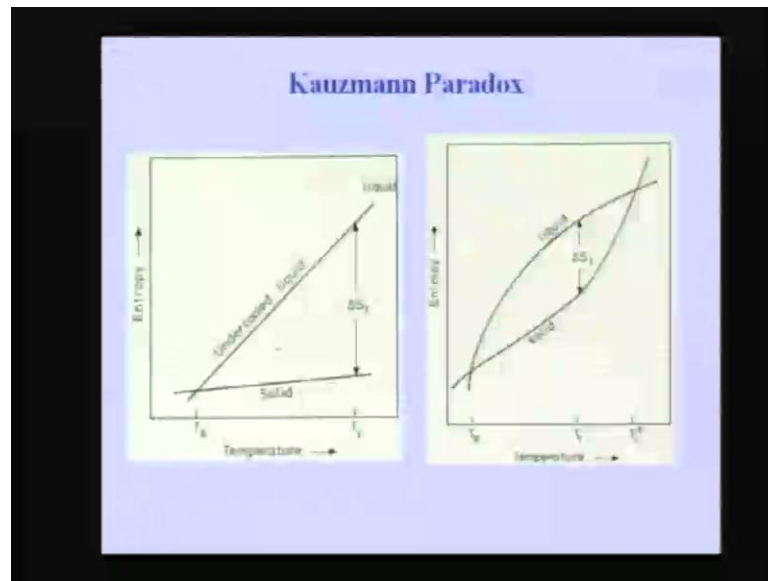


That you will see, that to the right and once the c curve is shifted to the right, then the cooling rate can be very low critical cooling rate. And that is what is, the b type of curve which you see here and then, the other one, which you see is, that if you can take this liquid and then, add some flux to it is. These are called fluxed glasses, when you add flux to it, then the viscosity further increases of the liquid. And when the viscosity further increases, then the diffusivity gets further reduced.

And hence the difficulty in the crystal formation increases more and because of which there are some glasses, particularly, palladium, nickel, copper, phosphorous glasses, which are called fluxed glasses. Where, people add some kind of a flux, which can enhance the glass forming ability and you, can get very easy glasses. Nowadays, getting about 5 millimeters type of rods is very easy, in many systems. You imagine, you think of 50 microns, from 50 microns now, we can very easily go to 5 millimeters.

And there are also cases were people have gone up to 50 millimeters without any problem. And I am talking of 4 inch, which is about 100 millimeters. So, that is the highest so far. But, this is in a special kind of a composition, which is palladium, nickel, copper, phosphorous.

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We were talking about thermodynamics in the last class. Thermodynamics of glass formation, we said when you take an entropy of a liquid, which is much higher than that of the solid. And at the same time, the entropy decreases more rapidly, with decreasing temperature, when compared to the solid. This is basically because; we said the C_p is much larger, in case of liquid when compared to solid.

And that is what, leads to, what is called the Kauzmann Paradox. Kauzmann was the first person to talk about this; I think it is about 1952 or so. So, that is was the time people have come across this and this is what is called Kauzmann Paradox. And the temperature at which this happens is called T_k . Kauzmann temperature or ideal glass transition temperature.

There is also, another interesting thing that happens, if you take a solid and start heating it above the melting point. In fact, this is an experiment, which lot of people, try to do. Can we really heat a solid, above the melting point, without it becoming a liquid, is a big question. We know that, we can take a liquid, cool it rapidly and when we cool it rapidly, we can make the liquid remain as liquid, without getting crystallized at temperatures below the melting point.

This is what we call under cooled liquid, whatever you see here, this is all under cooled liquid. At any temperature, below the melting point, it is all under cooled liquid, up to the glass transition temperature and at the glass transition temperature, it is no more under cooled liquid, it becomes a glass. Whereas, here if I take a crystal; that means a

solid crystalline solid, I should be very careful, now we are talking of glasses. So, a solid need not be always a crystal.

So, crystalline solid, we take a crystalline solid, and then start heating it above the melting point, what happens, as I keep on heating, the solid above the melting point, the vacancy concentration keeps on increasing very rapidly. And as the vacancy concentration, keeps on increasing, the entropy of the solid increases. Defects are increasing, so entropy is increasing, disorder is increasing. And the rate of increase of the vacancies in the solid is much higher than the rate of increase of vacancies in the liquid.

The reason is that, solid is a constrained material, where one can easily introduce the vacancies, because it is periodic arrangement of atoms. So, vacancies can get introduced very easily, because of thermal vibrations in a crystalline solid. So, one can either by you know bombarding a solid or just by heating it, above the melting point, one can introduce defects. How, we heat it, without making it into a liquid, we will talk about it a little later.

But, if you do that, you come across a situation, which is exactly opposite to what you have observed at the temperatures, below the melting point. That is the Kauzmann Paradox, where you have seen that liquid comes to a certain state, where the entropy of the liquid becomes below that of the solid. And here, you will come across a situation, where the entropy of the solid, becomes higher than that of the liquid. This is another Paradox again.

Because, we cannot imagine the solid to have higher entropy, then that of the liquid and that particular temperature is called entropy catastrophe. Tsi usually call, I is basically the instability, the letter I is used for instability, why we say instability, because at that temperature, the crystal is unstable. Because, it is entropy is going to be higher, if it crosses that temperature, it is entropy is higher than that of the liquid. And it avoids that, by just catastrophically becoming a liquid.

This would be a second order transition; normal melting is a first order transition. It is a nucleation and growth type of a process. In fact, you will easily observe this, when you take a ice cube from the fridge and try to observe, just put it on a table or just hold it and start seeing, how the ice melts. You will see it always starts at the corners first. The corners get a rounded off.

That means, the corners are the first to start melting, because that is the region, which is a high energy region. And that is where, the melting starts first. So, always melting is a nucleation growth phenomena like solidification. Solidification is also a nucleation growth; only difference is the melting does not need any super heat, whereas solidification needs a super heat under cooling.

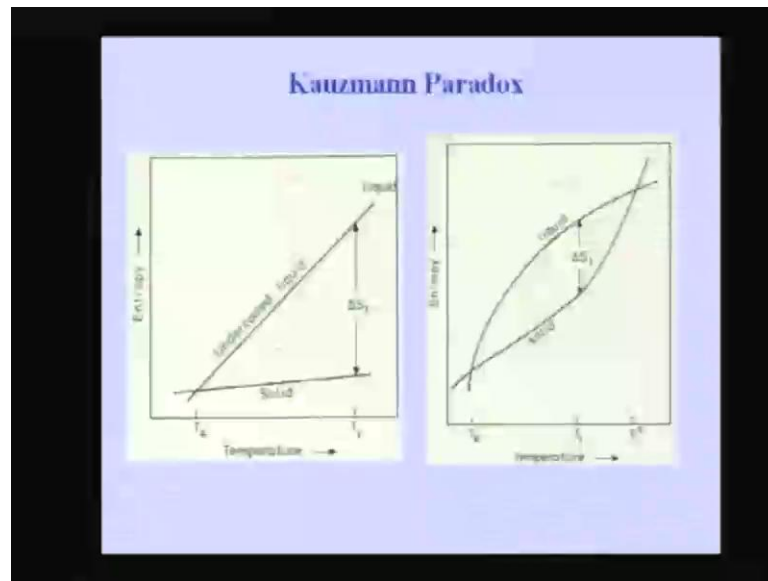
Basically, because during solid formation, you need to create a new surface, from the liquid, you need to create a new surface and to create a new surface, you need to spend energy. And you can spend energy, only if you have energy with you, you can spend money, only if you have money in your pocket, it is like that. So, how do you get energy, you get energy by under cooling.

If you under cool, there is a certain driving force available and that driving force is the energy in your hand. You can spend that energy on to the surface, which you are creating. So, that you can have the solidification taking place, this is typical solidification.

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Will come to the entropy, catastrophe, once again, so what you see here is that, if you are on the other side that, when a solid is melting, already the surface is there. So, then you need not have to create a surface. So, usually liquid does not need any super heat. So, what you see here, in the case of entropy catastrophe is that, as you keep on increasing the temperature, the entropy of the solid increases. So, rapidly that at a particular temperature, beyond the melting point, this happens definitely, beyond the melting point.

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Because, you can see T_f is here, the freezing temperature. T_{si} is beyond the freezing point. So, at that temperature, the entropy of the crystal becomes same as that of the liquid. And if you cross that temperature, its entropy becomes higher than that of the liquid. So, at that temperature, the solid suddenly transforms to a liquid. Uniformly, everywhere throughout the solid, it is like spinodal decomposition.

We talk in terms of spinodal decomposition in normal metals, that there nucleation occurs everywhere and then, suddenly it transforms. So, this is that kind of a thing. That it is a second order transition. That it occurs throughout the material. And we will come; talk about, what is the first order type, second order within a minute. So, and the crystal transforms to a liquid catastrophically, all of a sudden and that is why we call it an instability.

So, and because this is coming, because of the entropy it is called entropy instability. That is why, T_{si} term comes and this temperature is also people call it as isentropic temperature. What is the meaning of isentropic temperature, entropy is the same at that temperature. In fact, T_k is also another isentropic temperature. But, T_k because, it is Kauzmann, who has invented this, we give it in the name of him and people call it, as Kauzmann temperature.

Whereas, the temperature above the melting point is called isentropic temperature, but the question is how do we reach that, can anybody see it. It is almost next to impossible to see it, because that temperature is much above the melting point. This is

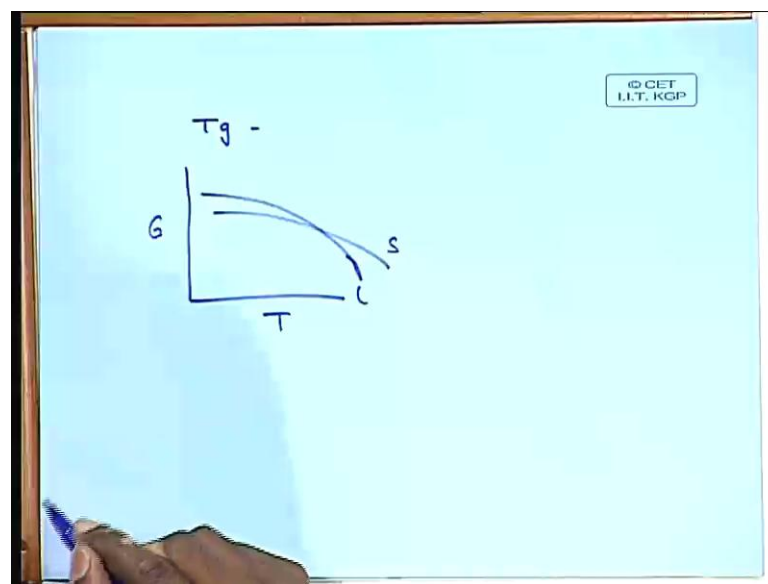
only theoretical. One can calculate this temperature for various metals. In fact, one chapter in my PHD, thesis was on that. So, I calculated those days on all these this, were 15 years back.

So, and one can do all that, but the point is this temperatures many times. For example, if you take aluminum, aluminum melting point is 660, if the T_{si} for aluminum would be of the order of 1400 or so. How do you reach 1400, it is almost next to impossible. People have, but reach at least 100 degrees super heat, above the melting point, by using special techniques.

What they do, they encapsulate this metal in a high melting metal and then, start heating. When, you encapsulate a low melting metal into a high melting metal; that means, it is embedded into a high melting metal. And once, you start heating it, the interfacial energies change. Usually, if you take a piece of metal and put it out and then, start heating it and this is expose to atmosphere. So, it melts at the melting point.

But, now if it is embedded, inside a high melting metal, it is melting point goes up, because melting is related to the interfacial energies. So, once you consider that kind of a situation, people have shown that for example, silver encapsulated in gold. People have observed about 50 degrees super heat. Such kind of things is possible and people have done it, but going to that high temperature is very difficult.

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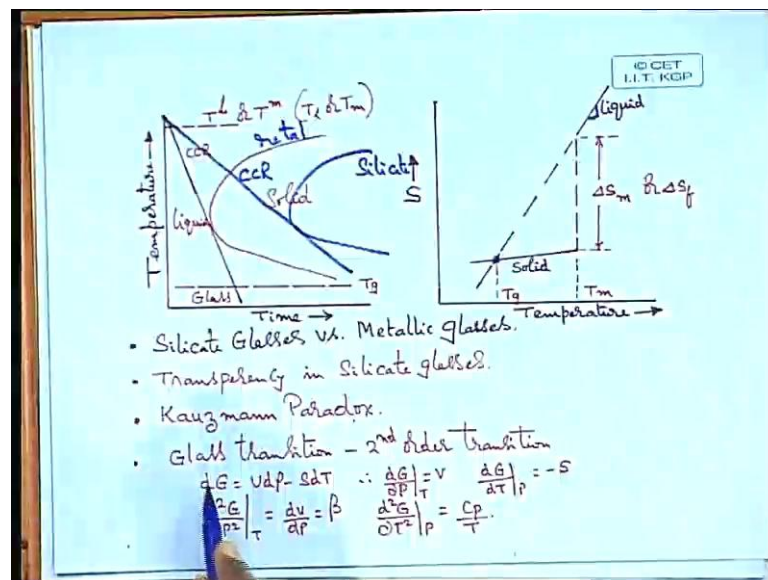


So, here, because we are talking of thermodynamics, we should talk a little bit about, what is this glass transition, T_g . T_g as I told you is second order transition, why it is

second order transition. What is a second order transition? A second order transition is what, were the second differential for free energy becomes discontinuous. For example, most of the phase transformation that, we know such as melting and solidification are all first order transformations.

If I plot the free energy versus temperature, I will see that, I have this kind of a curve, this is for the liquid and this is for the solid. That at the melting point, the free energy of the liquid and solid are equal, ΔG is 0. There is no discontinuity in the free energy at the melting point; it is continuous, at the melting point. But, if I choose the first differential of the free energy, what is the first differential of free energy.

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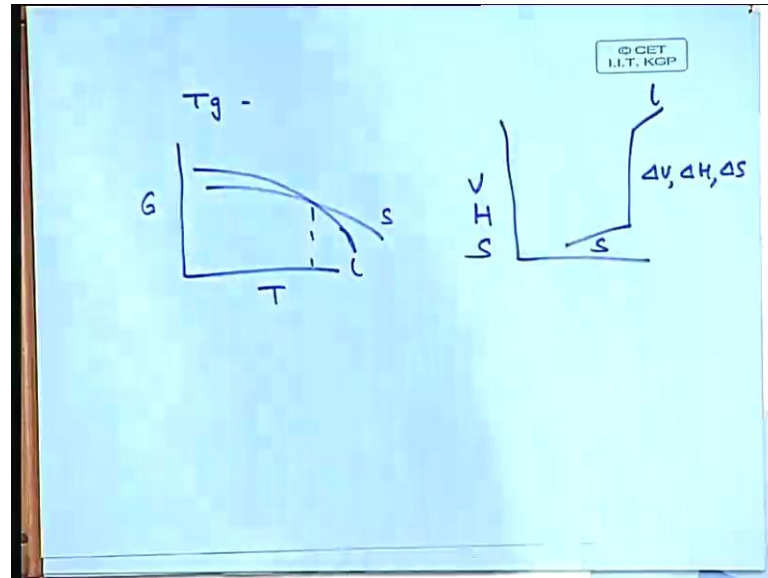


You can see here, yes, look at this, what is the typical expression for free energy, dG equal to $V dp$ minus $S dT$, all those people, who know the second law of the thermodynamics they know this. So, dG is $V dp$ minus $S dT$. So, if you look at the first differential of free energy with respect to pressure is nothing but V , dG by dp at constant temperature or dG by dp . It should be partial differential at constant temperature is nothing but V , volume.

And similarly the first differential of free energy with respect to temperature at constant pressure is nothing but, entropy. So, if I plot the entropy as a function of temperature. This is what I see here, what you have on the left, that at the melting point, there is a discontinuity. The entropy of the liquid is higher, the entropy of the solid is lower and there is a difference in the entropy.

If there is transformation between the liquid and solid at the freezing point, there is an entropy evolution entropy evolve. That means, there is decrease in the entropy, what is called Δs freezing or entropy of fusion. We call it or entropy of melting. So, this is typical first order transition.

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Similarly, if I plot volume also, I get the same situation. If I plot volume or enthalpy or entropy, all of these, I get a situation like this. This is the liquid, this is the solid and this is what is called ΔV or ΔH or ΔS of fusion. And this is a typical first order transformation. That means, the first differential of free energy is discontinuous at the transition temperature and the transition temperature for us is the melting point.

And what is the second differential? Second differential for the free energy, d^2G by dP^2 at constant temperature is nothing but, dV by dP , because first differential is V . So, second differential should dV by dP and what is dV by dP ? That is called compressibility. Rate of change of volume with pressure is nothing but, compressibility. When, I am pressurizing it, how the volume is changing that is what is called compressibility of a material.

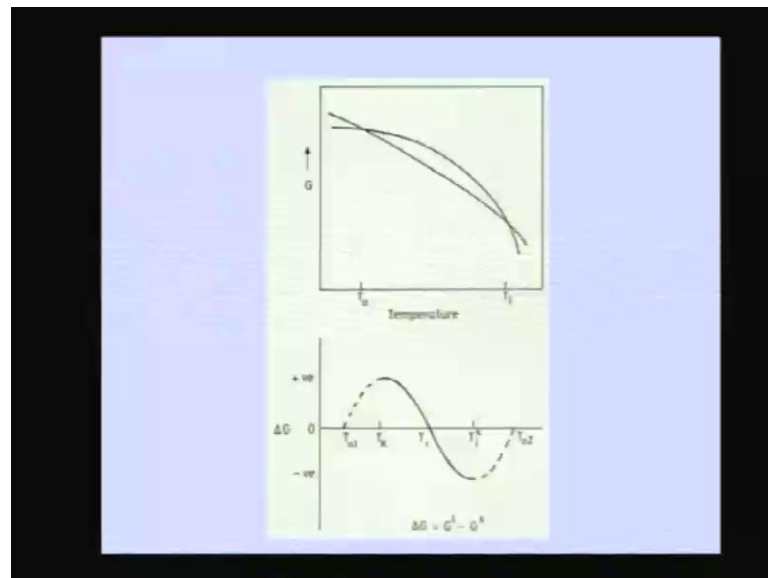
And what is the second differential of free energy with respect to temperature; it is nothing, but dS by dT . What is dS by dT is C_p by T . So, that is the second differential. So, if I am plotting a entropy versus temperature at the second order transition, the entropy does not change discontinuously. That is, what you see here at T_k , for example, entropy of the liquid is equal to entropy of the solid.

It is similar to what we have seen here, that in the case of the free energy, free energy of the liquid is equal to free energy of the solid. So, in a first order transition, ΔG is 0 at the transition temperature, but Δv or Δh or Δs is non zero entity. Because, they are discontinuous at the melting point, if I come to the second order transition, ΔG is 0 at the transition temperature Δv Δs and ΔH , this is ΔH here. They are all again 0, but the next differentials β and C_p are non 0.

So, if I plot the C_p as a function of temperature, for a glass transition. I will see, there is a discontinuity, the C_p of the liquid and the C_p of the glass will be slightly different at the melting point. Because, liquid is anyway more easily flow able or it is a fluid kind of a thing, whereas, glass is a solid. So, as a result C_p is slightly different. So, that is why C_p of the liquid and glass will be different at the melting point.

But the entropy of the glass and liquid, enthalpy of the glass and liquid, volume of the glass and liquid, they are all the same at the melting point. That is what, one of the parameter we are showing here, which is entropy. And one can show same thing for the enthalpy also and you can see that here.

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If I plot the free energy versus temperature, I know melting point, which is T_f . But, if I keep on decreasing the temperature at some other temperature much, below the melting point. We can come across another temperature, where free energy difference can be 0. That is the temperature, which is called iso free energy temperature. That means, were the free energy of the liquid is equal to free energy of the solid.

If I take it below the melting point, there will be a temperature, where again the free energy of liquid and solid will go to 0; one can prove all this thermodynamically. And if you look at the bottom figure, what you are seeing is all the temperature that we can think off, the crucial temperatures. One is the melting point, which is the T_f and above the melting point, if I am plotting of G_l minus G_s , ΔG , which is G_l minus G_s .

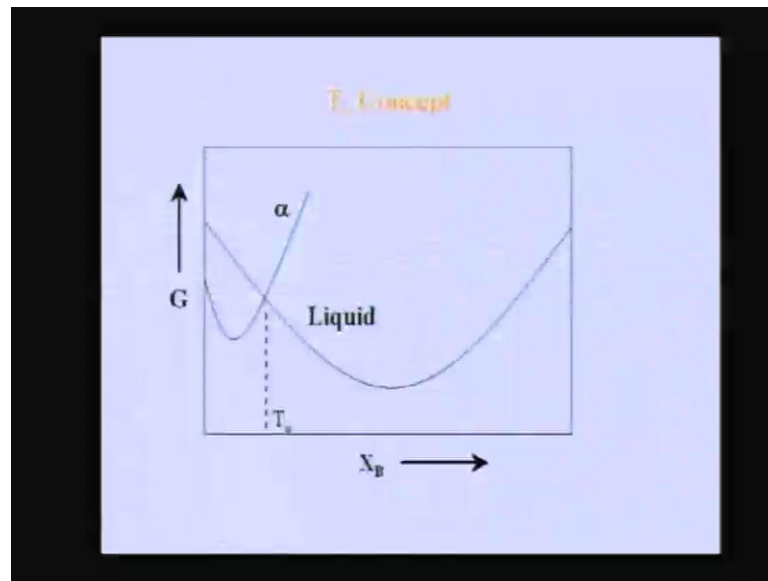
Above the melting point, which has a lower free energy liquid or the solid, above the melting point, liquid has lower free energy than solid. So, G_l minus G_s will be negative. That is, what you see here it is negative and the free energy becomes more and more negative up to the T_{si} . At the T_{si} , then you see, that there is an entropy catastrophe coming into picture.

That the entropy becomes equal for the parent phase and the product phase. And after that, there the free energy again if at all, somebody can reach those temperatures, one can show, that they decrease. And again, you reach a temperature, where the free energy again becomes 0. And similarly below the melting point, as you keep on decreasing the temperature. The ΔG is positive here, because the solid has a lower free energy than the liquid. So, G_l minus G_s is positive.

And that keeps on increasing up to a particular temperature, which is called T_k at that temperature the entropy of the liquid becomes again equal into that entropy of the solid. And that is the glass transition temperature, further it decreases. And finally, it goes to 0 and that is the T_{naught} temperature we talked about it. So, this is all the thermodynamics of glass formation, one can calculate all these temperatures, thermodynamically, provided.

You know, what is the entropy, what is the enthalpy of a particular phase and extra pull it to lower temperatures and one can calculate. Let us come to another important concept in the glass formation. In fact, most of the glasses, which we observe in various alloy systems are all based on this concept, which is called T_{naught} concept. What is a T_{naught} , we have talked it in the thermodynamic class. But, let us just brush it up here, because this is relevant at this particular point of time.

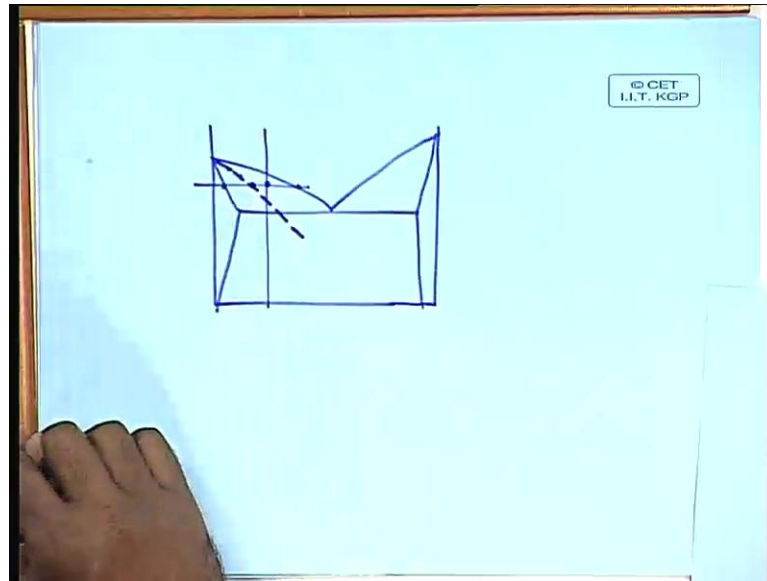
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If I draw the free energy of a liquid and the free energy of a solid, let us say a solid solution, which is alpha and the free energy of the liquid as a function of composition. I see that, at a particular composition, both these free energy curves intersect. What is the meaning of this particular composition, it means that at that particular composition, the free energy of the liquid is equal to free energy of the solid solution.

That means, ΔG for the phase transformation between liquid and solid is 0 at that particular composition. G of liquid is equal to G of alpha and that is, what is called iso free energy composition, where the free energy is equal. And if I am on the right side of this particular curve, what we see is that, if I am taking a liquid and cooling this liquid from high temperature.

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Let us take a typical situation of a eutectic, I take a eutectic like this and I am talking of at a temperature here, for an alloy, for that matter, let us say. This particular alloy, which is on the right side, I choose an alloy, which is like this. If I take an alloy and then, cool it to this temperature, because this free energy curve is always drawn at a fixed temperature.

If I cool it to that temperature and then look at, what is the free energy of the liquid, what is the free energy of the solid? I see that, the free energy of the solid is higher than the free energy of the liquid at any composition on the right of this particular intersection. And what does that mean, it means that, if the liquid has to transform to a solid, it is not possible for the liquid to transform to the solid.

Because, liquid has a lower free energy than that of the solid, for any phase transformation to occur, there should be a decrease in the free energy, we all know this. So, because of that, you see that on the right side of this T naught point, iso free energy point or X not point. In fact, it should not be basically T naught, it is X not. It is a composition at which the free energies are equal.

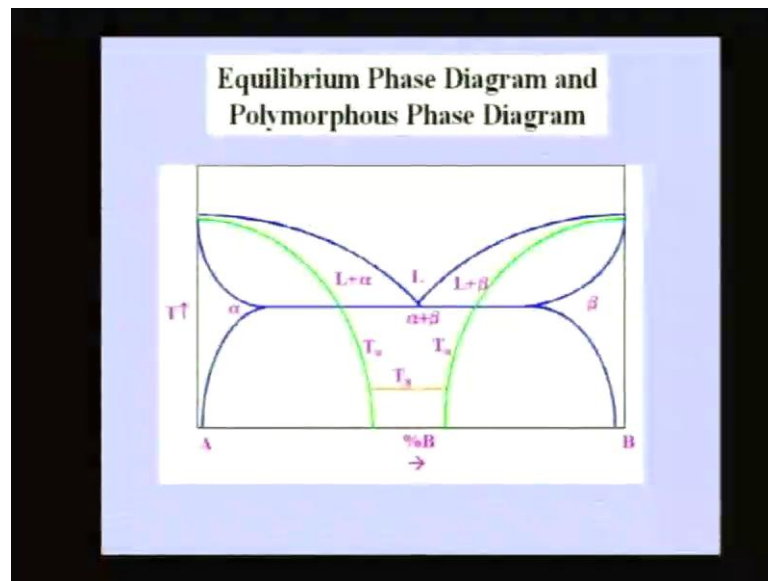
So, at that particular composition, if you consider at the compositions on the right side, there is no driving force, for the liquid to transform to the alpha. But, if I am on the left side, I see that liquid free energy is higher than the free energy of the solid solution. That means, if I choose a composition, which is some other lower solute contain. Then, I may see a situation, where the liquid free energy is higher than that of the solid.

So, solid can easily form with a same composition as that of the liquid. This is what is called partition less solidification; we talked about it in the thermodynamics class. And this particular intersection point, if I put it on the free energy curve on the phase diagram, it comes somewhere here. It is between the equilibrium solid composition and the equilibrium liquid composition. One can draw a common tangent and get the equilibrium solid composition and the equilibrium liquid composition.

And that particular T naught point will fall somewhere between the 2. This is the equilibrium solid composition, this is the equilibrium liquid composition and the T naught position is somewhere in the middle, because the intersection is always in the middle.

And now, if I do this at various temperatures at each temperature, I can get a different point. And if I join all of them, what I see is a curve like this and that is called the T naught curve and you will see this in the next slide.

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So, here what you are seeing is a T naught curve, where T naught for the alpha T naught for the beta is shown and if the any composition if you choose, if you cool it to such a temperature, that if the composition falls, below the T naught curve. If the temperature is below the T naught curve, for any alloy composition. You will see that particular alloy can transform to the solid having the same composition, which is, what we call the partition less solidification.

But, if the composition falls, such that, the temperature and composition coordinates are such that, we are above that curve than the liquid, cannot transform to the solid. Basically, because there is no driving force for the liquid to transform to the solid and it is all those liquids, which cannot transform to the solid. Those are the liquids, which will undergo a glass transition, if we can bring those liquid below the T_g .

So, the T_g is shown here and if we can come, below the T_g , if I choose any liquid, for example, the eutectic composition. If I choose and cool it, rapidly, such that, I bring the liquid, below the T_g . Because, I am at temperatures and compositions, such that, I am not intersecting the T naught curves. If I am not intersecting the T naught curves, then partition less solidification is not possible. Then, if I am just intersecting only the T_g , then I will see that liquid will undergo a glass transition, we will stop here and then start in the next class.