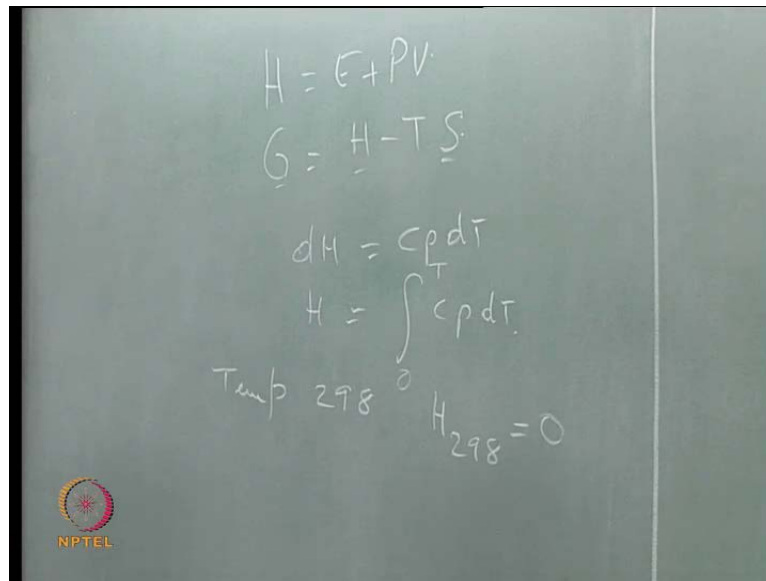


**Advanced Metallurgical Thermodynamics**  
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**Lecture No. # 02**  
**Free Energy, Stability, Equilibrium in a Unary System**

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$$H = E + PV$$
$$G = H - TS$$
$$dH = C_p dT$$
$$H = \int_0^T C_p dT$$

Temp 298,  $H_{298} = 0$

Last class we have started the basic equation in thermo dynamics. We started with this, all of you are aware of it, then we introduced the second law, which is basically we said it is this. And that is what introduces two new parameters, which are one is entropy, and another is the free energy. And we said the stability of all the phases is actually related to the free energy, and let us go a little details into this, and see how to represent free energy as a function of temperature, and how does that give us information about the stability of phases. To understand that, first let us look at how to evaluate the H, and S. If you look at it, we all know that  $dH$  is  $C_p dT$ , this every one of you know. So, as a result I can write it as  $H$  is integral  $C_p dT$ , where  $T$  goes from let say 0 to  $T$ .

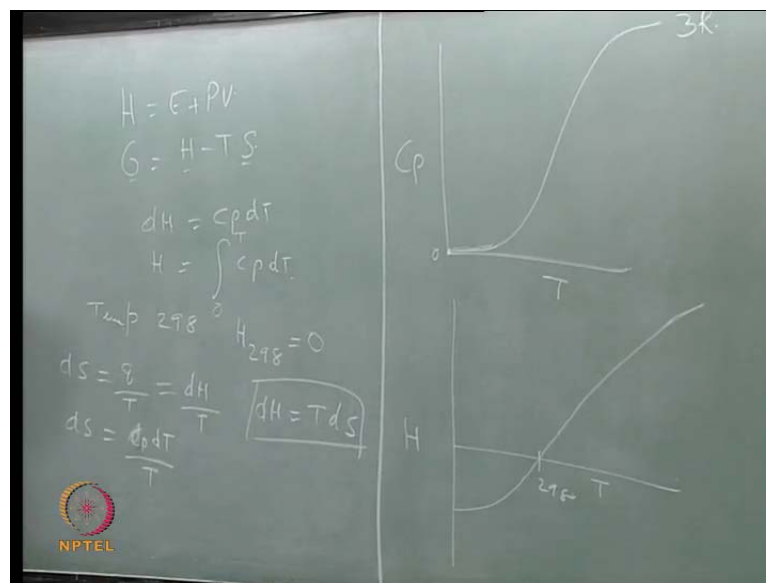
Usually enthalpy in thermo dynamics we have what are called standard states. So, when I want to all these are actually relative numbers. We have so, unit to set up some particular condition, which we call it as standard state, and that condition that we set up is at a temperature called 298, which is room temperature. So, we define  $H$  at 298 as 0. For

most of the materials, you can even change that depending on that particular condition, you can change this number depending on the particular circumstance, but usually we assume H at 298 as 0, and if you assume that, and then try to plot.

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So, that is why this become negatives so, that is what we are going to see it right now.

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So, if you plot  $C_p$  as a function of temperature, we know that  $C_p$  goes something like this a typical  $s$  curve, all of you are aware and  $C_p$  goes to 0 at absolutely 0, this is 0. And we also know that the maximum value we reach is approximately around  $3R$  and now, if I try to plot  $H$  as a function of temperature, you would see the  $H$  as a function of temperature would go something like this, where here at 298 it is 0 and below 298 actually it is negative. So, in the principle if I define  $H_0$  as 0 then; obviously, this everything will be in the positive quadrant. So, this is the typical way of representation of the  $H$  and once I know  $H$  is represented that way.

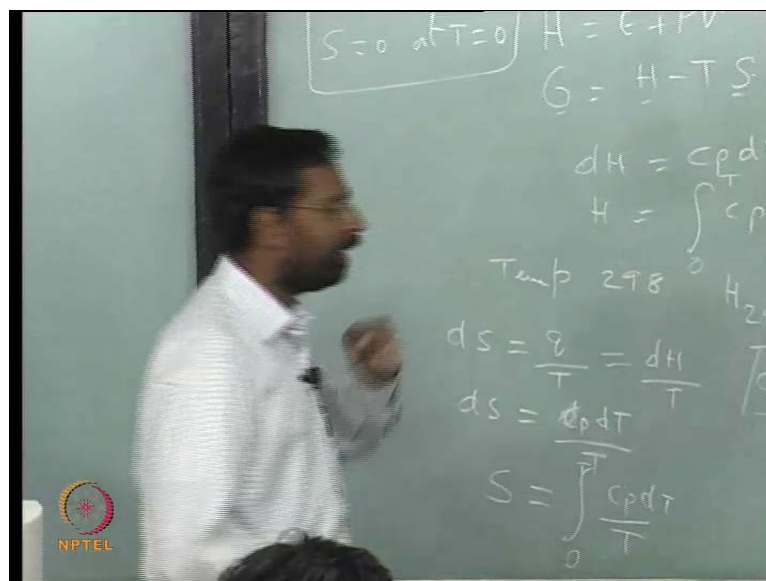
I can also start defining  $s$ , because  $s$  the way we define the second law the entropy term is  $ds = q/T$  actually and  $q$  at constant pressure is known to be as  $dH$ . So, actually  $ds$  is  $dH/T$  and that also leads you to the other (no audio from 03:47 to 03:52) equation, which is a very useful as we go along, we see this because this becomes useful when we are defining the free energy more easily. So, you can see that,  $ds$  is  $dH$

by T. If  $ds$  equal to  $dH$  by  $T$  then I can simply write  $ds$  equal to  $C_p dT$  by  $T$ , because  $dH$  I have already define it as  $C_p dT$  is not it.

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You can always, because **because** 0 is a term which is an ideal term, which you rarely reach and if somebody as to experimentally measure anything mirror accepting a few physicists. Most of us who deal with a chemical engineers or metallurgical engineers or material scientist, most of us deal with room temperature. So, as result, we start at room temperature. So, most of the applications demand temperature beyond room temperature not really sub 0 to large extent. So, as a result, we understanding this and in principle even if you take it as that it is only a scaling factor things get changed. So, as long as one sees, you know then you can start calculating what it is at error temperature, it is not a big problem it is only changing some cut in number some reference is required. So, this is a more easier reference for us to deal with room temperature is easier reference.

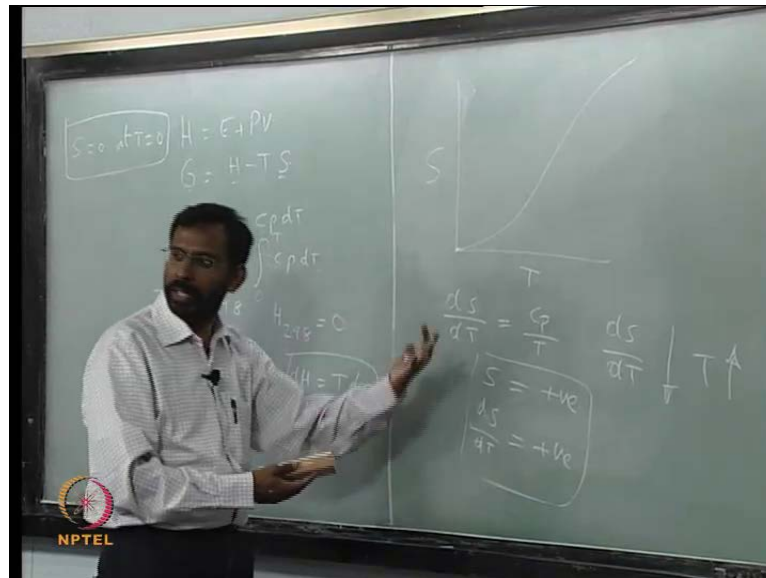
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Once I understand this, I can even write now as  $S$  as integral  $C_p dT$  by  $T$ . Again, going from 0 to  $T$  let say and this is, where we define a third law of thermo dynamics, where  $S$  equal to 0 at  $T$  equal to 0. So, that integral we assume it to be 0 and because we also known that the  $C_p$  itself goes to 0 there are no vibrations, when there are no vibrations there is no thermal entropy **there is no thermal entropy** please remember. We will come to the configurational entropy little later and this configurationally entropy need not have

to go to 0 or absolute 0. Thermal entropy is 0, because there are no atomic vibration. If there are no atomic vibration there is no randomness created by atomic vibration. So, the crystal is perfect atoms remain where they are and they do not move. And as a result they do not cause any randomness inside the material.

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So, this is how we basically define this and in principle I can also plot, if I plot S versus temperature **S versus temperature** would S versus T if you plot S versus T also would have a curve like this basically it comes from the C p type of curve. It would be something similar to C p curve and it goes to 0 at absolute 0. And then keeps on increasing and not only keeps on increasing, if you carefully observe a d s by dT. If I take d s by dT is what C p by T. So, because it is C p by T in principle at very high temperatures this slope should come down as you increase the temperature, but there is a small h here that C p is also increasing with increasing temperature. If C p verse constant then I can say the slope keeps on decreasing as the temperature increases. An entropy increases with increasing temperature, but what we are talking is the slope of this entropy; that means, the rate at which this entropy increases with increasing temperature is going to decrease as the temperature increases.

So, initially it will be a steeper curve and later it becomes a kind of shallower curve. And in principle this curve will never become let say 0; that means, the slope of this curve will never become 0, it will become 0 only, when either this I mean C p become 0 and C

P never becomes 0 at higher temperature, we know pretty well. So, it will still have a low slope, but it will maintain certain positive slope. So, not only  $s$  is positive  $ds$  by  $dT$  is also positive this is a very important thing that you need to understand. The rate of change of entropy with temperature is always positive, because  $C_p$  is positive. The lowest value that it can go is 0 and that is only at absolute 0 and at absolute 0 we do not really talk about rate of change, because it is one single temperature.

So, as result you can see that, but what is important is  $ds$  by  $dT$  decreases as  $T$  increases, because  $C_p$  does not increase at the same rate as  $T$ . If you remember some of you might have gone through a how we express  $C_p$  a plus  $b$   $T$  plus  $c$   $T$  power minus two. So, there is an expression, which is used for  $C_p$  to fit that particular curve, which we have drawn before how does the  $C_p$  change with temperature. So, it fits to almost a at a in a very small range when I look at it can be fitted as a plus  $b$   $T$ , but if you take the whole range then you see particularly at low temperatures the  $C_p$  change with temperature is very small.

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The image shows a chalkboard with the following handwritten equations:

$$G = H - TS$$

$$= E + PV - TS$$

$$dG = dE + PdV + VdP - Tds - sdT$$

$$dH + VdP - dH - sdT$$

$$dG = VdP - sdT$$

$$\left. \frac{dG}{dT} \right|_P = -S$$

In the bottom left corner of the chalkboard, there is a small circular logo with a star and the text "NPTEL" below it.

So, this is one important point that you need to remember and will keep bringing this concepts as we go to the free energy. Now, let us look at the free energy and that is the most important thing for us, because as we said the whole stability is dependent on free energy. Now, let us try to expand this I said just now  $G$  is  $H$  minus  $T S$  and if I write it more elaborate this  $H$  we know already is  $E$  plus  $P V$ . So, I can write it as using these

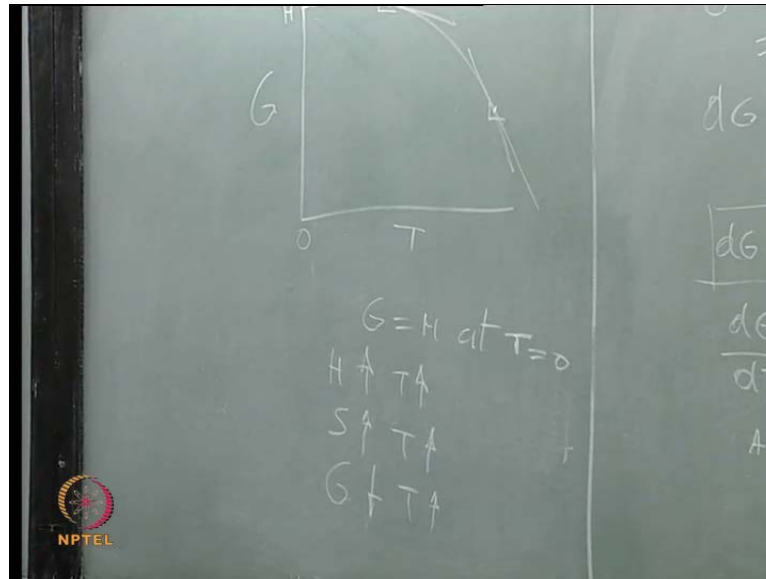
two equations. For example, I can write it as  $E + PV - TS$ . Now, let us differentiate this, if you try to differentiate it I can write it as  $dG = dE + PdV + VdP - Tds - SdT$  because it is a partial differentiation and minus  $Tds$

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minus  $SdT$  perfect. Now, if you look at it  $dE + PdV$  is  $dH$ . We all know that  $dH$  is define in terms of that and  $Tds$  is  $dH$ , where did we define somewhere here  $Tds$  is  $dH$ . So, in principle this is  $dH + VdP - dH - SdT$ . So, as a result these two get cancelled and you end up in an expression that  $dG = VdP - SdT$  this is a very very profound Maxwell's equation. And that leads you to a lot of interesting things such as what is called anyone knows, we talk about Clausius Clapeyron equation **Clausius Clapeyron equation** comes from there we will see as how does it come.

So, this tells us that a constant pressure, if I take  $dG$  by  $dT$  at constant pressure is what is minus  $S$ . And  $S$  is never negative, we already define  $S$  is what the degree of randomness and a degree of randomness can never be 0 it can maximum, it can be minimum, it can be 0. The lowest value of  $S$  can be only 0 and then you it will be more than 0 at all other temperature. As a result, because  $S$  is positive  $dG$  by  $dT$  has to be  **$dG$  by  $dT$  has to be** negative, because there is a negative sign before the  $S$ . And if the  $S$  would have been negative then the  $dG$  by  $dT$  would have become positive. So,  $dG$  by  $dT$  is always as I can write as  $S$  is positive  $dG$  by  $dT$  is always **is always** negative, what does that tell me, it tells me that, if I plot  $G$  versus  $T$ . Let say any material like this, I try to calculate, what is the free energy of this material and how does it change as a function of temperature. And if I plot that let us **let us** delete this, because this way we have gone through are you sure you are aware of this.

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So let us, if we now plot G versus T (No audio from 13:31 to 13:40) how should the free energy curve look like?

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So, it decreases is this fine I would say it is not fine?

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Yes when will be is fine

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Yes when S remains constant this plot is perfect, what is this tell you it tells you that it is a linear relation. A linear relation means what? Slope is constant what is the slope of free energy versus temperature slope is minus of entropy and this is decreasing fine. So, the minus is taken care, but the slope is constant there, if the slope is constant it tells you that entropy is not changing as the function of temperature, but we know pretty well that the entropy changes with temperature.

So now, can you tell me how should it change? So, this is wrong. So, what is the best way?

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Yes it should decrease like this to an extent that as I come closer and closer to absolute 0. The slope should tend towards 0, because at absolute 0 entropy 0. So, the slope of free energy versus temperature should go to 0 at absolute 0. This slope is 0 at any other temperature, the slope is higher and the slope keeps on increasing for example, if I look at slope here, I draw a tangent let say here, and I draw another tangent here. This tells me the slope at this point **this tells me the slope at this point** you can see the slope here is higher, the slope here is lower. So, at a higher temperature at any higher temperature the slope of G versus T is going to be higher and that is what higher in a negative sense keep that in mind definitely we are the whole curve is the slope is negative at all temperature slope is negative, at only once temperature the slope goes to 0, at no other temperature slope is either 0 or negative.

This is the temperature, where the slope goes to 0 at any other temperature slope is negative. So, that is what you see this is negative and that absolute value of the slope is the entropy. And that absolute value of the slope, because it is higher at higher temperatures, we will see this is the typically nature. And now, if I find out what is this value can you tell me? What is G at absolute 0 depending on what is there on the right side you...

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H very easy G equal to H at T equal to 0 is not it. So, this value is nothing but, H whatever it is and at any temperature if I draw a tangent and extrapolate this tangent to the absolute 0. For example, if I extrapolate this tangent to this value, this intercept is what

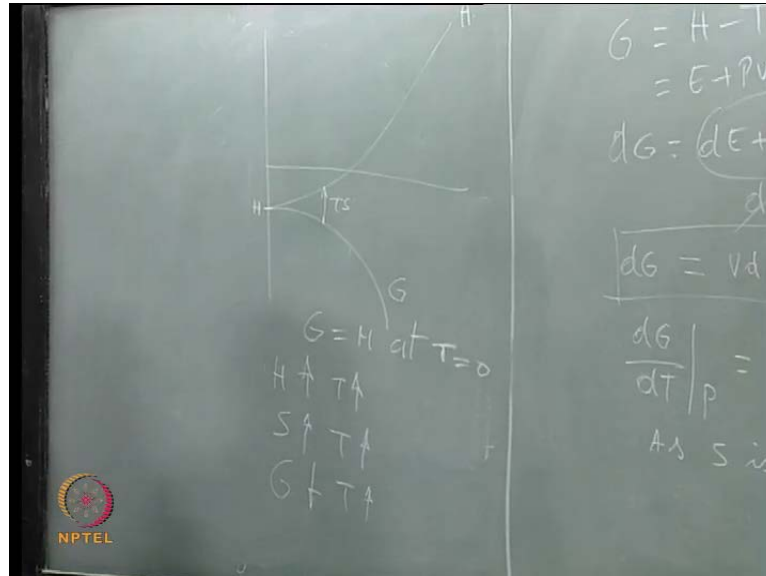
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H, because is this G is H minus T S and slope is the S. We are talking of d G and this **this** value is the intercept. So, you will always get the intercept as the H at so, at different different temperatures and in principle you can see as I increase the temperature the slope is increasing. As a result the intercept also will increase, which also gives you an idea that the H increases with increasing temperature. So, where this particular tangent is going to intersect the vertical axis is going to keep on increasing. And that gives you an idea that the H of any material, H of any phase that we are talking is going to **chang** increase with increasing temperature and at the same time. So, not only H increases with



temperature, we also see S increases with increasing temperature and G decreases with increasing temperature (No audio from 18:07 to 18:12) **fine**.

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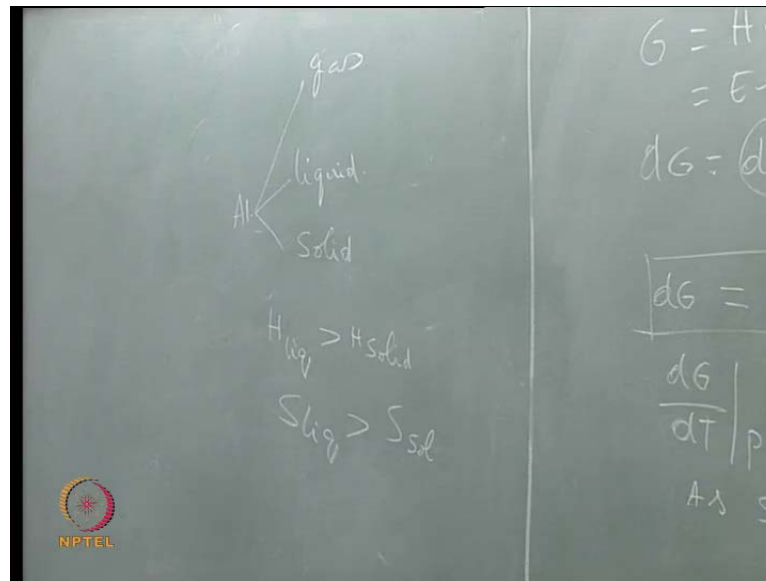


And in principle, if I write both G and H in the same thing you would see we have just now seen H is H goes something like this and you see G would go something like this. And at absolute 0 this is the H value and this is increasing, whereas this is decreasing and this difference between these two is what?

**(( ))**

T S very easy. And this difference keeps on increasing as we go to higher and higher temperature that tells you that both T is increasing and S is increasing as a result you would see the difference keeps on increasing. So, in principle we can plot like this. Now, let us try to understand if this is all clear. So, we should know how to do so, from now onwards, whenever you draw free energy be **very** very very clear that G cannot be a straight line as a function of temperature, which you would have possibly drawn a number of times before. So, this has to go into your mind that G the slope of it being nothing but, entropy it can never be constant and entropy is never constant.

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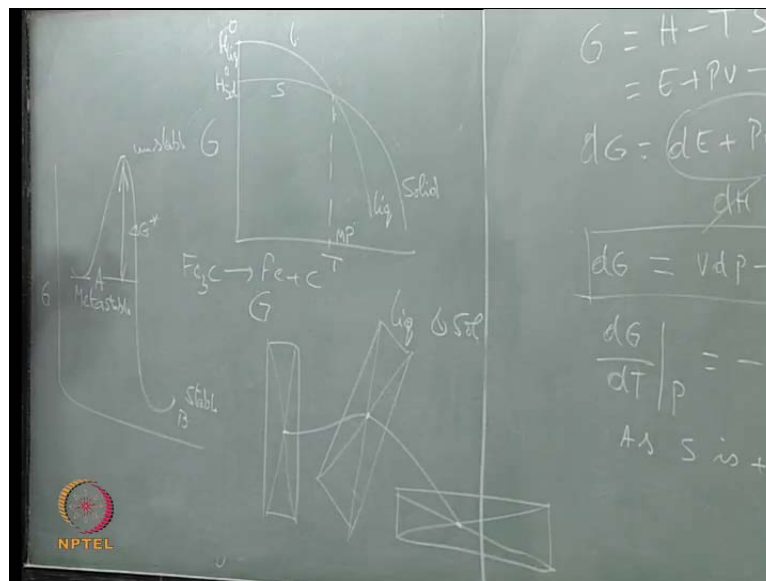
So, once this is clear let us try to understand what is the necessity of  $G$ ? Why should people introduce this concept called  $G$ ? Earlier people thought the stability of phases, when do I say something is more stable, I compare let say two things, when I compare two things. Let say simple case, let say I am talking about aluminum **aluminum** it can be a liquid, it can be a solid, it can be a gas. Let say I am comparing a liquid and solid, if I consider the enthalpy of liquid and enthalpy of solid. What is higher? Liquid is higher Why is it higher? Because the  $C_p$  of the liquid is always higher than the  $C_p$  of the solid, heat capacity of liquid is always higher than the heat capacity of the solid why? The vibrations are more in a liquid, when compare to a solid. As a result,  $C_p$  is higher and if  $C_p$  is higher, because  $H$  is nothing but integral  $C_p dT$ .

You can say  $H$  of liquid is always higher than  $H$  of solid. So, as a result, if I say that at melting point solid is changing to liquid, it is going from a lower enthalpy state to a higher enthalpy state. Now, a reverse transformation, where the liquid is transforming to a solid, it is going from a higher enthalpy state to a lower enthalpy state is not it. So, as a result, I am seeing that below the melting point a phase with a lower enthalpy is stable that is the solid, above the melting point a phase with a higher enthalpy is stable. So, if I use enthalpy as a stability criterion. I have difficulty in the sense that I cannot say a phase with a lower enthalpy is always stable. I cannot say this, because I myself I am

able to see that the liquid is stable above the melting point and liquid always as higher enthalpy. So, how can I say that this phase having a lower enthalpy is always stable.

Same problem comes, if I take entropy, if you see entropy of a solid and entropy of a liquid. Entropy of a liquid is again higher than that of the solid. So, I can say liquid entropy is higher than solid entropy. Again, I am in the same situation that I can never say the phase with a lower entropy is always the stable or a phase with a higher entropy is always stable. I can see this reverse phenomena happening above the melting point the phase with a higher entropy is more stable and below the melting point a phase with a lower enthalpy is more stable. And if I take this lower enthalp entropy or a lower enthalpy phase, which is solid and take it above the melting point I cannot retain as the solid, it immediately start transforming into a liquid though it as a lower entropy and low enthalpy, it does not want to remain. So, that is where people thought what is that that will help us to be able to understand the stability in terms of one parameter and that turns out to be free energy and how to understand that.

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If I try to now, plot G versus T for this liquid and solid. Let us try to super impose the free energy of the liquid and free energy of the solid. On this curve and see what happens for example, I can draw a curve something like this and then say this is the free energy of the solid. It is satisfying whatever I have said before, that it slope goes to 0 that absolute 0 and it is slope keeps on increasing in a negative sense as the temperature is increasing

is it **fine**. Now if I super impose a liquid free energy curve on this, how that should beat, what should be the characteristics of that with respect to this curve?

**(( ))**

At 0

**(( ))**

Higher free energy

**(( ))**

And why a higher free energy

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Because, it has higher enthalpy at absolute 0 free energy is equal to enthalpy. And the liquid enthalpy is always higher than the solid enthalpy. Next, second thing is that, its slope should be higher. So, if the slope is higher than I will see that the curve will be something like this, whenever you have two curves one with a higher slope than the other; obviously, they both have to intersect. It is not possible to have two curves with a different slope not intersecting. So, as a result you would see that this is nothing but H of the liquid at absolutely 0 this is H of solid at absolutely 0, which is higher.

And now this is the curve for the liquid and then I look at this curve, it gives me very interesting phenomena, what is that interesting phenomena? There is an intersection here is not it. And, if I look at what is there above the intersection, what is the nature of the curves above the intersection and what is the nature of the curves before below the intersection, what you see is that, above the intersection the liquid curve is always below that of the solid curve; that means, liquid has a lower free energy than the solid above that intersection.

And below the intersection, if I look at it the solid is always below that of the liquid is not it. This is the solid curve, this is the solid; this is liquid. So, the solid curve is below that of the liquid so; that means, the solid has a lower free energy than the liquid below the melting point and above the melting point I mean I am **sorry** I have already used the term. This particular point is what we call it as the melting point that particular

intersection of the two free energy curve is we called it as a melting point, why we call it as melting point because below beyond the temperature. I see that the liquid free energy at all temperatures is lower than the solid free energy and because it is lower I can now say the liquid is more stable above the melting point, because it has lower free energy and similarly, when I come to the temperatures below the melting point. I can see that the solid free energy is lower than the liquid free energy at all temperatures. So, at all temperatures below melting point, I can always say the solid is more stable because it has lower free energy.

Now, we have one parameter which tells you that if that is lower the phase is stable and that parameter is this free energy gives free energy. So, if the free energy is lower than it is stable is the free energy is higher than it is what we called it as, what we called it? It could be **it could be** meta stable or unstable this is what that is where we end up into the regime of kinetics. Always we say thermo dynamics tells you what is feasible it does not mean that it would happen is like this. For example, if I look at this is, this is some state called A, this is another state called B let say, and if I am plotting this in terms of the free energy. The free energy of the A is higher than the free energy of the B, but it does not mean that this A will immediately going to be B.

For example, a simple example could be even this, if you look at this duster, if I leave it this dusters on this table and I keep this buster in this form, what is having a more lower free energy this **this** is form; obviously, because the C G is lower, if the C G of it is lower I can say yes this has lower **lower** energy state. And if I am keeping it here, it has higher energy state, but I can keep this like this for ever, until I push it, I can keep it forever; that means, this higher energy state is able to remain in a higher energy state forever almost until somebody gives you.

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Activation we called it as activation that is what this is called activation barrier. This is what we call it as delta G star, we will talk about it more later, but just this gives you and how to understand this, if you look at it, if you take this state, this is the duster and if I say that I draw a join all this both the diagonal. And I say this represents the free energy that is the C G of that, if I say that represent the energy of the system and from there it comes to this level, where I join again and say this represent that energy and between

these two states, when this is going from this state to that state. You come to a state like this, which is inclined and that state if you carefully observe and that state if you join you see that the C G of that is higher.

So, it is going from a lower energy to a higher energy and then further coming down that is what we call it like an activation hill and so, it goes to and this particular state is what we call it as unstable state, because if you keep this in this state, it will not remain suddenly it falls of either this direction or that direction. So, that is the interesting about unstable state either it come to a meta stable state this is the meta stable state, this is the stable state. So, it can either shift this direction or this direction depending on in which direction you are force is. So, you can see that this is the different between a thermodynamics and kinetics. So, thermodynamically, we say this is more stable. In principle this should become this, but it is not happening many of you might of heard of, all of you know about steels a suppose, if I look at the microstructure of steel, what would I see in microstructure of steel.

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Parlite what is parlite?

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Ferrite and cementite, do you know that this cementite is not a stable state?

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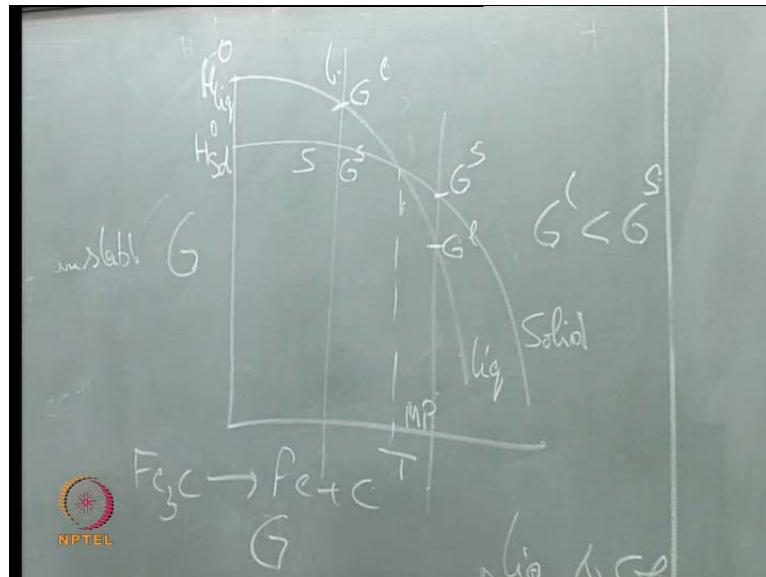
So, meta stable. In principle, if I take this cementite to higher temperature and heat it, it becomes ferrite or alpha or (( )) plus carbon graphite. In principles cementite is not stable, but we see the steel at room temperature cementite exists forever for ages nothing happens to it, cementite remains as cementite. You make a mild steel and then just leave it and it remains why because it as a large activation barrier for that  $Fe_3C$  to split into iron plus carbon and unless you provide that activation barrier, it would not change. And, as a result that activation barrier you are providing by heating the sample to a higher temperature. In fact, that is what we do, when we convert one of the cast irons into another cast iron have you heard of that. There is a treatment, what is the treatment called?

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Maliblization, where you take a white cast iron, which has semantide network, semantide phase and you heat it to above nine hundred thousand degrees centigrade, where that semantide splits and gives you graphite. So, in principle one can even people when they do faradizations of steels, if they do faradizations of steels for a very long time. You would see the semantide faradize that are forming can even split and you get ferrite plus graphite people have done this and see. So, in principle, if you can provide that particular activation any meta stable state would like to go to a stable state otherwise it would remain in a meta stable state forever. So, this is the difference between thermo dynamic, thermo dynamics tells you that this is the stable state.

In principle the system would like to be here, but it can still remain here, because it is you are not provider. So, it is like local minima. People talk about local minima this is kind of a global minima. So, it remains in small trust there and if you push it, it will go up and then come down. So, it is like that. So, you can see that this is the basic concept of the free energy.

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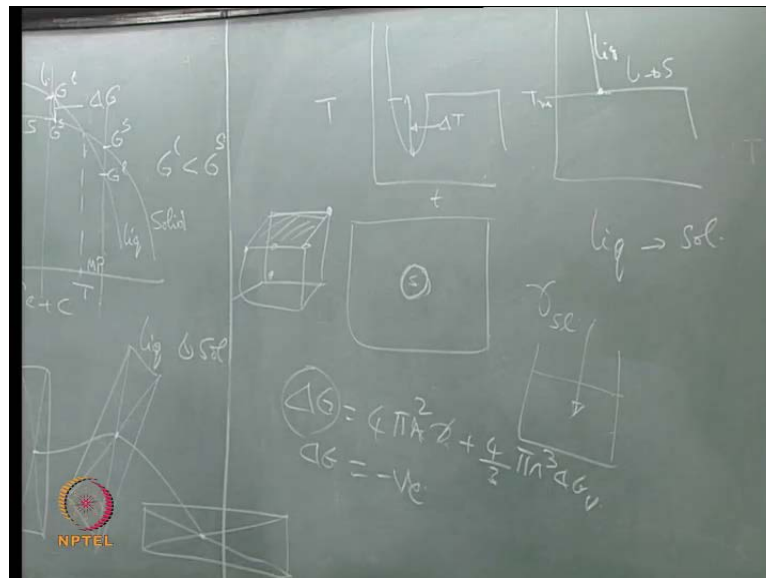


So, we have now define that this free energy is a concept, which we can use for understanding what is stable and what is met stable. I can only say it is meta I can say for example, I have to tell you this again clearly that if I am at this temperature; that means, I have a taken a solid heated to this temperature, what should happen when I heat the solid

to this temperature. It should become a liquid why? It should become a liquid because solid has this free energy at that temperature; liquid has this free energy at this temperature. So, liquid has a lower free energy than that is of the solid this I can call it as  $G_s$ , this I can call it as  $G_l$ .  $G_l$  is lower than  $G_s$ .

In principle solid should become a liquid it is possible that solid can still remain as solid which we call it as meta stable solid. If the conditions are not ripe enough for the solid to become liquid in case of solid to liquid it does not happen, because solid to liquid transformation is much faster than liquid to solid transformation. You see the reverse happening more easily, if I take a liquid cool it to the temperature like this you can see that liquid has a higher free energy  $G_l$  is higher,  $G_s$  is lower. In principle liquid should become a solid, but there are many **many** cases, where liquid does not become a solid and remains as what is called an under cooled liquid and in fact, that is the principle behind getting a glass we will slowly see a little later. For example, may be you know the time has come so, let us see right now (No audio from 35:20 to 35:25) or **no** let us leave it unnecessary we are deviating, we will talk about liquid to glass transition little later we will see.

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So, you can see that this liquid can remain as liquid the reason is from a liquid if you imagine for a solid to nucleate, if you have a whole liquid bunch of liquid and you have a solid coming out of the liquid. You have a problem what is the problem?



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It has to create a new surface. This surface did not exist before is not it that surface has to be created though the liquid has a higher free energy than the solid and liquid wants to transform into a solid. You would see that because this solid the new surface which we call it as interface interfacial area between the liquid and solid and that is represented by one what is called interfacial energy called  $\gamma_{S-L}$ . And every surface, every interface is associated with certain energy that energy has to be spend that energy.

You have to **you have to** create that particular surface and to create that surface you need to have certain energy with you and if that creation of the surface is difficult the liquid does not become a solid. And if you have seen what are called cooling curves at some stage are have you seen how does a pure metal liquid become a solid. If I take ferrous melt a solid put a thermo couple there inside and then switch off the furnace and then watch how the temperature of this liquid is changing as a function of the time and I plot that  $T$  versus small  $t$ . And I usually see this kind of thing for a pure metal many of you might be aware of this and why does this happen.

In principle I expect that it should be like this liquid, this is the liquid and once I bring it to melting point, this is the melting. This liquid should transform into a solid at that temperature, but the liquid does not transform to solid. This liquid to solid transformation does not occur suddenly here at the melting point, but the liquid have to be cooled to below the melting point to some temperature before this liquid actually starts transforming why is that, that is because when you cool this liquid from this melting point to an certain lower temperature this what we call it as under cooling, this is what we call it as  $\Delta T$  under cooling, when you provide that under cooling, what is happening to the free energy let say from the melting point I have brought to this temperature

Once I bring it to this temperature there is certain, what is called driving force. At the melting point, what is the driving force 0 and that is what we define it as equilibrium. So, in a **in a** single component system equilibrium as is define as that, where the free energy of both the phases is equal that is what it is **at the** at the intersection. At the intersection  $G$  of  $s$  is equal to  $G$  of  $l$  this is the definition of equilibrium and so, we say this is the melting point, where the free energy of the both the phases is equal and if the free energy

of both the phases is equal for any of the transformation either from liquid to solid or solid to liquid there is no driving force.

If I take a liquid keep it at the melting point in principle. It will not become a solid similarly, if I take a solid heat it up to the melting point and just hold it there. In principle, it should not become a liquid excepting if you heat it by very **very** small amount. It could be let say third decimal in terms of the temperature. You need some small driving force for this solid to become liquid similarly, for the liquid to become solid you need a driving force the only difference between a solid and a liquid can be easily understood. If you take an ice cube from a fridge let say somehow you have taken a ice cube without holding it and you have just leaving it in the air let say and the **the** atmosphere is above the 0 degrees. So, this ice cube has to melt how does it start melting, where does the melting start surface anything **(( ))** corners first is it starts that is why, you will see that the ice cube the corner start becoming rounded first why is that so, because than the next stage is actually the adjusts after that actually is come to surface.

The reason is the

**(( ))**

Surface energy the surface energy is highest at the corner why is that so, surface energy comes from what is called broken bounds? If you take an material for example, a solid if I take, inside the solid ice for example, if I am taking ice **ice** has the structure do you know what is the structure, what is the crystal structure of ice, little louder.

**(( ))**

h c p hexagonal, it is a hexagonal structure. So, this hexagonal structure if I think of the atoms which are on the surface in a hexagonal structure you remember what is the coordination number, twelve; that means every atom should have twelve nearest neighbors. So, you will have six in the plane three above the plane; three below the plane **am I right**. Now, if you imagine that there is an atoms sitting here that atom has six atoms in that plane three atoms below that plane, but there are no three atoms above that plane so; that means, that particular atom there have certain number of broken bounds in principle, it is three by twelve **three by twelve** out of the twelve bounds that it should have three bounds are not there.

As a result that particular atom is at high energy state, because it is not having all the atoms which suppose to have been as if you think of an atom which is at the centre somewhere here. It has all the required number of atoms around it as per the coordination number. So, the atom here is in a much better state when compare to atom here. So, this is at a higher energy state so similarly, if I take this corner. This corner would have more number of broken bounds and if I now think of a solid. (No audio from 42:45 to 42:51) Think of solid and now consider this corner and this edges and this surface. You can easily see the corner would have more number of broken bounds the edge would have next level than the surface than the atoms inside.

So, energy level go by that hierarchy the any atoms sitting at the corner of a cube would have the highest energy and that atom that particular region, because it is a highest at highest energy it was transform first to something, which is lower energy state why because I am at temperature above the melting point, am at room temperature I said at room temperature the liquid is more stable than the solid. So, ice cannot remain as ice it wants to transform to liquid. So, that particular region which is highest energy immediately transforms then comes the edges **edges** start become rounded and then the surface and so, the actual melting start from the surface and goes into interior why because the surface area is available for it.

Now, if I take a liquid and try to make it a solid, where is the surface available for the liquid until you think of I pore this liquid into a mold, sir the mold is there has the surface for the solid to nucleate and that is the reason why. In most of the casting process the solidification starts at the **at the** mold interface mold liquid interface and there are interesting people who do what is called container less solidification. In our department there is a professor I do not know how many of you heard of Fanny Kumar he as set up what is called levitation facility is very interesting to see please go and see. This is the first levitation facility in the country, where you take a piece of metal like this. You levitated it, it is standing in the air now and then you heat it using a let say an induction heating or any heating let say electron beam heating any heating you can heat it and melt it. Once it is molten, it becomes liquid and this liquid droplet is floating in the air now and you switch off the heating source.

Now, it starts cooling and you can actually observe how does it solidify, where does the nucleation starts very **very** interesting phenomena lot of people have struggle to

understand this whole concept of nucleation, where does the nucleation start and in fact, long back there is a great man by name (( )) who has done, what is called droplet immersion technique, what he has done is he has taken liquid metal allowed it, to go through a nozzle and made it into a stream of droplets and emersion of droplets by kind of atomization kind of thing, when you do this droplets of different different sizes form and different different sizes. You look at it the smaller droplets will have lesser number of heterogeneous nucleating sites, because people knew for quiet sometime that this kind of solidification is happening only because of heterogeneous nucleation.

Otherwise in principle, it should be this why because, when I under cool I am providing sufficient energy. And when this energy is equivalent to this surface energy that is when solidification will start, until the energy that I have in my pocket like you want to spend something you should have something in your pocket is not it. Unless you can say I can use my credit cards are always so, otherwise you should have something. So, here also is situation so, unless you have a driving force some energy available with the liquid excess energy that is available with liquid. It cannot spend that it should have sufficient excess energy that is sufficient for creating a new surface that is when solidification will start. So, the liquid will keep on under cooling, until you get sufficient energy that is available.

We are going to slowly may be next class relate this to this. There is the relation between delta G and delta T will see that also, what is the relation? And you will see that when I provide sufficient under cooling and at least graphical. You can see as I increase the delta T because as I go more and more away from the melting point. This is increasing, I can see that, but in principle one can calculate that also. So, I say that at a given delta T there is a certain value of delta G and if that delta G is equivalent to that of the surface that is why if you remember anybody, who has done some nucleation.

You would write this expression for a spherical nucleus that is coming out like this we say there are two terms  $4\pi r^2\gamma$  plus  $\frac{4}{3}\pi r^3\Delta G_v$ , when I am creating a spherical nucleus inside liquid this is the energy that is given out, this is the excess energy of the liquid were as this is the energy that you need to create for a spherical particle. This is  $4\pi r^2$  the surface area multiplied by this, this is per unit area always, this is the energy that you need to create, this is the energy that you are providing. So, you would see that unless this is equal to this. You would never see the free the transformation taking place in such way that this overall delta G has to become

negative, when this is negative than solidification will occur. If that is 0 or positive solidification will not occur.

So, that is the reason, why we need certain under cooling that is the reason why people saw that usually you do not see this is, what we call it as homogenous nucleation. This is what we call it as heterogeneous nucleation. Heterogeneous nucleation occurs, when there are already certain particles available in the liquid. In fact, that is one of the concepts of what is called grain refinement inoculation people regularly use this term. So, if I add certain practical in to my liquid. And pore it in to the mold. Now, this particle if they have a similar crystal structure as that of the solid that is coming out then this surface energy is very low, whenever the structure is similar. You must have heard of what is called epitaxy anything can grow every easily if the structure is similar. So, you would see that if I had practical, which have the same (( )) same or similar crystal structure has the solid that is coming out. You would see that would easily nucleate. So, that is why there is specific nucleating sides for specific type of solids.

You do not add everything for everything for example, in aluminum alloys. We know for example, there are something as t i b two titanium boride titanium carbide t i b two is hexagonal. If you carefully observe there is a similarity between hexagonal and aluminum, what is the crystal structure aluminum f c c. So, what is the similarity between f c c and f c p.

(( ))

Close pack structure yes anything in terms of any planes is there any similarity atomic planes.

(( ))

Any plane of h c p does it have any similarity with the any plane of f c c, because why I have to say this is nucleation always occurs on a plane. It cannot occur anywhere, it happens on a surface that is why planes are important. There is a certain plan in f c p, which is exactly similar to another plane in f c c, how much of crystallography you know, 1 0 0 sorry, what is the closest pack plane in f c p? What is the indices of it, 0 0 0 1 - the 0 0 0 1 plane is similar to another plane in f c c, can you think of it 1 1 1 prefect. So, the aluminum can nucleate on on that particular 0 0 0 1 of titanium boride very easily

with it is 1 1 1 plane parallel to that the basal plane of that t i b two, and then the nucleation (( )) I think will stop with this, thank you very much.