

Course on Phase Equilibrium Thermodynamics
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Lecture 12
Gibbs free energy as a function of Temperature and Pressure

Hello everybody, so if you recollect in the last class what we have done we are trying to relate the non-measurable properties with the measurable ones the importance of the non-measurable properties being that they were important to find out the heats of different type of reactions to find out whether the reactions can be spontaneous or not to relate the path functions with the state functions and so on and so forth.

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$$dh = c_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP = c_p dT + v(1 - \beta T) dP$$

$$T ds = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_P dP = c_p dT - v \beta T dP$$

$$g(T, P) \quad dg = -s dT + v dP$$

At constant pressure - $\left(\frac{\partial g}{\partial T} \right)_P = -s$

More useful form - $\left(\frac{\partial \Delta g / T}{\partial T} \right)_P = -\frac{\Delta h}{T^2}$ **Gibbs Helmholtz Equation**

Important to derive temperature dependence of equilibrium constant in chemical reaction equilibrium

Now doing that during the course of the discussion I had mentioned that the 2 most frequently used measurable properties are those of temperature and pressure because they are easily measurable and they can be easily controlled and regulated, accordingly if you remember what we have done in the last class, we have tried to express enthalpy change and entropy change in terms of changes in pressures and changes in temperature.

And of course we have done a lot of other things also and in each of the cases we are trying to relate different types of properties different properties in terms of the PVT behavior of the gases and where we came to realize the importance of the PVT behavior of the gases, now before we

proceed I would like to spend some more time in order to understand the variation of Gibbs free energy with temperature and pressure.

Now if you look at this particular equation the variation we find is quite straightforward, okay. Since Gibbs free energy it is related with changes in temperature and pressure, we are having straightforward manner, so immediately we understand that the variation of Gibbs free energy with temperature is given by means of the entropy of the process and the variation of Gibbs free energy with pressure is given by the volume of the process.

Now just as I have mentioned earlier for Gibbs free energy also we will be primarily dealing with the molar Gibbs free energy variation with temperature and pressure. So let us see first at constant pressure what do we get? At constant pressure we will find $\Delta G / \Delta T$ at constant P that is nothing but equal to minus of the molar entropy of change but we need to remember that molar entropy itself it is a non-measurable property. So therefore we find that the more convenient equation or more convenient relationship will be to express Gibbs free energy in terms of some measurable parameters for that what do we do?

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$$g = h - Ts$$

$$\frac{g}{T} = \frac{h}{T} - s$$

$$\left[\frac{\partial (g/T)}{\partial T} \right]_P = \frac{\partial}{\partial T} \left(\frac{h}{T} \right)_P - \left(\frac{\partial s}{\partial T} \right)_P$$

$$= \frac{1}{T} \left(\frac{\partial h}{\partial T} \right)_P - \frac{h}{T^2} - \left(\frac{\partial s}{\partial T} \right)_P$$

$$= \frac{C_p}{T} - \frac{h}{T^2} - \left(-\frac{C_p}{T} \right) = -\frac{h}{T^2}$$

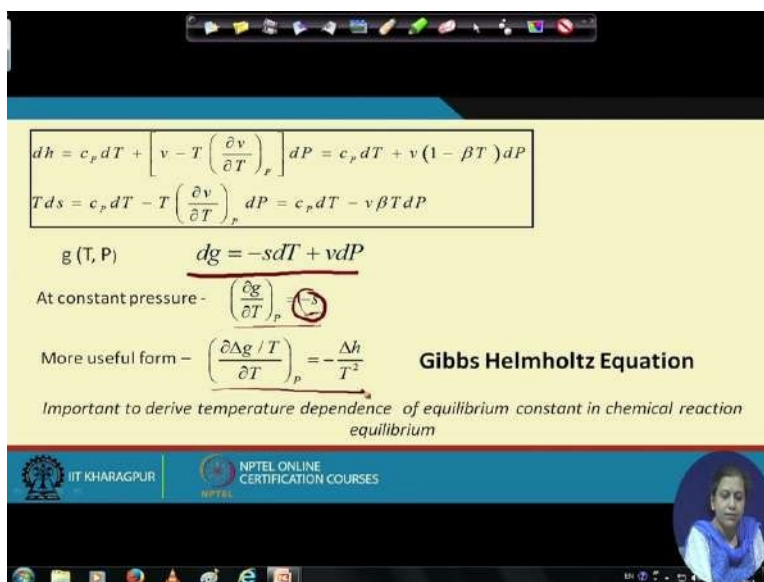
$$\left[\frac{\partial (\Delta g/T)}{\partial T} \right]_P = -\frac{\Delta h}{T^2}$$

We write down or rather we use the energy, g equals to h minus Ts which can otherwise be written down as g by T equals to h by T minus s . Now suppose we differentiate $\partial g / \partial T$ with P at constant pressure, what do we get? We get $\partial / \partial T$ of h by T at constant pressure minus $\partial s / \partial T$ at constant P which is nothing but equals to 1 by T $\partial h / \partial T$ at constant P minus h by T square minus $\partial s / \partial T$ at constant P , now what is $\partial h / \partial T$ at constant P ?

If you recollect this is nothing but equal to C_p , so this becomes C_p by T minus h by T square. If you recollect we had already derived what is $\partial s / \partial T$ at constant P that too is equal to minus C_p by T which gives you or rather which relates the variation of Gibbs free energy as a function of temperature this is related in terms of the enthalpy of the process.

Or in other words if we try to relate $\partial \Delta g / \partial T$ with ΔT at constant pressure this is nothing but this can be related to the enthalpy change of the process

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$$dh = c_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right] dP = c_p dT + v(1 - \beta T) dP$$

$$T ds = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_P dP = c_p dT - v \beta T dP$$

$$g(T, P) \quad dg = -s dT + v dP$$

At constant pressure - $\left(\frac{\partial g}{\partial T} \right)_P = -s$

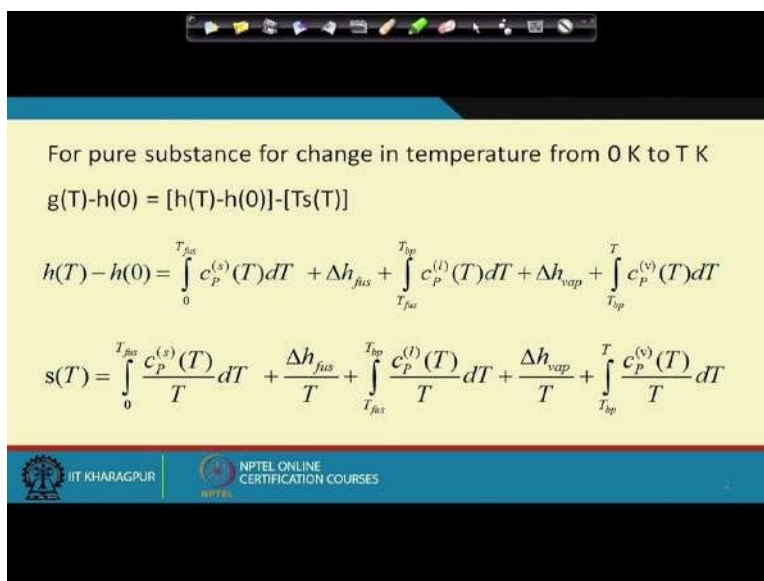
More useful form - $\left(\frac{\partial \Delta g / T}{\partial T} \right)_P = -\frac{\Delta h}{T^2}$ **Gibbs Helmholtz Equation**

Important to derive temperature dependence of equilibrium constant in chemical reaction equilibrium

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And this particular equation I would like to mention this Particular equation it is very important it is known as the Gibbs Helmholtz equation and it is very important to derive the temperature dependence of equilibrium constants in chemical reactions.

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For pure substance for change in temperature from 0 K to T K

$$g(T) - h(0) = [h(T) - h(0)] - [Ts(T)]$$

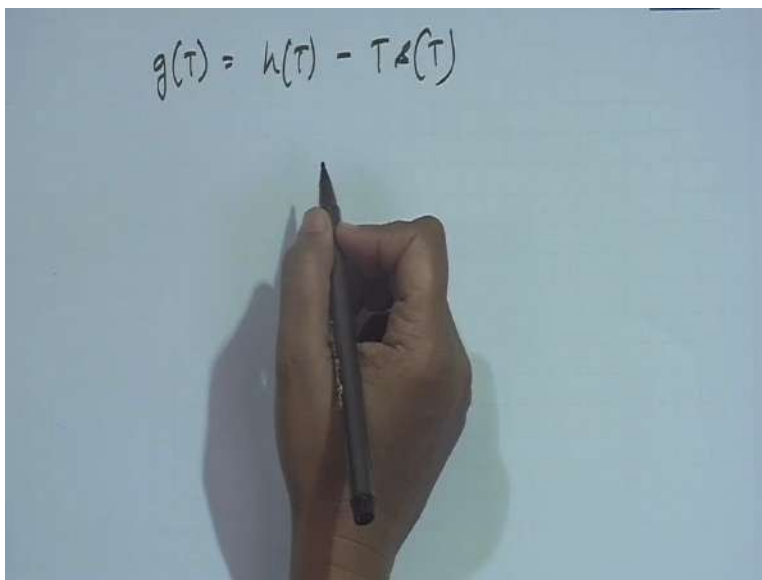
$$h(T) - h(0) = \int_0^{T_{fus}} c_p^{(s)}(T) dT + \Delta h_{fus} + \int_{T_{fus}}^{T_{bp}} c_p^{(l)}(T) dT + \Delta h_{vap} + \int_{T_{bp}}^T c_p^{(v)}(T) dT$$

$$s(T) = \int_0^{T_{fus}} \frac{c_p^{(s)}(T)}{T} dT + \frac{\Delta h_{fus}}{T} + \int_{T_{fus}}^{T_{bp}} \frac{c_p^{(l)}(T)}{T} dT + \frac{\Delta h_{vap}}{T} + \int_{T_{bp}}^T \frac{c_p^{(v)}(T)}{T} dT$$

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Now suppose and we would like to find the, for a pure substance how does Gibbs free energy change? As a pure substance it is heated from say 0 degree Kelvin to some particular temperature very high temperature T degree Kelvin.

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Here also we use the same equation in order to find it out we find that g as a function of T , it is h as a function of T minus Ts . Now suppose we start from a very low temperature say 0 degree Kelvin, now the substances they remain solid under that particular condition, right?

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For pure substance for change in temperature from 0 K to T K

$$g(T) - h(0) = [h(T) - h(0)] - [Ts(T)]$$

$$h(T) - h(0) = \int_0^{T_{fus}} c_p^{(s)}(T) dT + \Delta h_{fus} + \int_{T_{fus}}^{T_{bp}} c_p^{(l)}(T) dT + \Delta h_{vap} + \int_{T_{bp}}^T c_p^{(g)}(T) dT$$

$$s(T) = \int_0^{T_{fus}} \frac{c_p^{(s)}(T)}{T} dT + \frac{\Delta h_{fus}}{T} + \int_{T_{fus}}^{T_{bp}} \frac{c_p^{(l)}(T)}{T} dT + \frac{\Delta h_{vap}}{T} + \int_{T_{bp}}^T \frac{c_p^{(g)}(T)}{T} dT$$

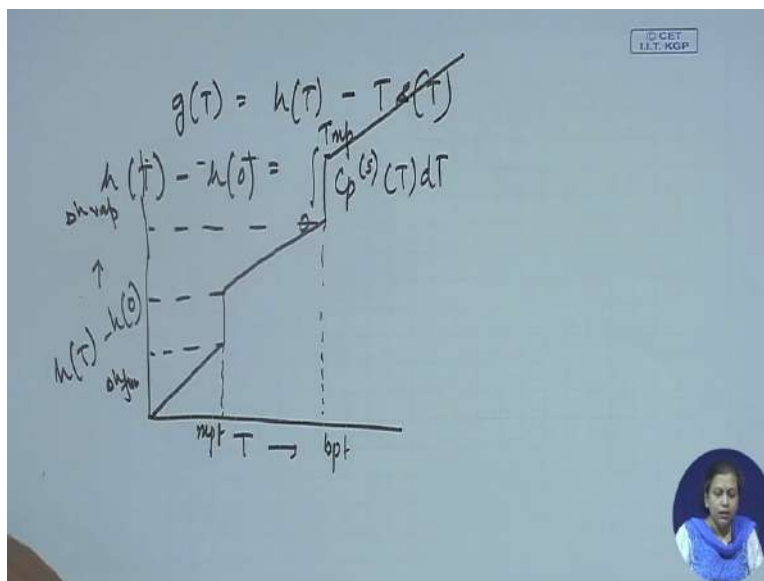
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So therefore if we try to evaluate $h(T) - h(0)$, what do we find? We find that initially it is a solid and the solid it is heated from 0 to some particular melting point of this solid, so it is given by this particular expression as I have already written down here, so therefore sorry this is the

expression in heating when the solid is being heated from 0 Kelvin to the melting point I continue the heat further what happens the solid starts melting, when the solid starts melting then we have to get the latent heat of fusion.

Once the entire solid has melted away then the liquid starts heating and this is the expression or this is the enthalpy change for the liquid heating from its melting point to its boiling point then the vaporization process starts and the substance it starts absorbing the latent heat of vaporization, finally the entire substance has vaporized it is in a vapor state and then the heat the vapor to the high-temperature some high-temperature say T, right?

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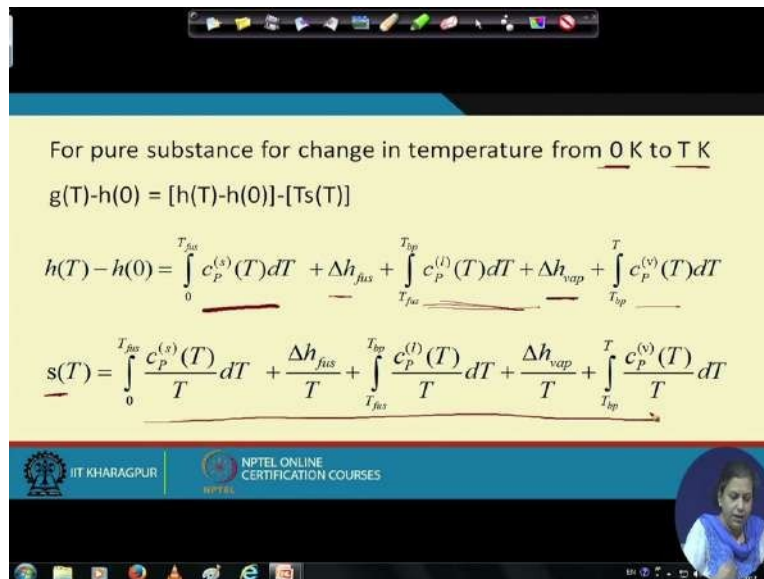
So therefore this whole expression gives the enthalpy change of the pure substance when it is heated from a temperature of 0 degrees centigrade to a higher temperature T Kelvin such that at T Kelvin the substance remains in the gaseous state. Now for this particular substance if we try to plot $h(T) - h(0)$ as a function of temperature, what do we find?

We find that for this particular case initially what happens? Initially the solid gets heated since I plotted $h(T) - h(0)$ it starts from the origin $h(0)$ is nothing but it is this molar standard enthalpy of the substance at 0 Kelvin at an 1 bar pressure. So therefore usually it is the ideal gas enthalpy at 1 bar pressure that the gas behaves or it remains or behaves as an ideal gas. So therefore this continues till the melting point of the solid.

After that what happens it absorbs Δh fusion but does not change in temperature, next again there is a liquid heating which continues till the boiling point and after that again there is a latent it absorbs the latent heat of vaporization in this particular case this is the latent heat of vaporization Δh vaporization and in this particular case this is the Δh fusion and then finally after that it's going inside the vapor phase it is being heated.

So therefore if we plot $h(T) - h(0)$ the enthalpy change of a pure substance when it is being heated from 0 Kelvin to some particular higher temperature the curve it has something of this sort.

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For pure substance for change in temperature from 0 K to T K

$$g(T) - h(0) = [h(T) - h(0)] - [Ts(T)]$$

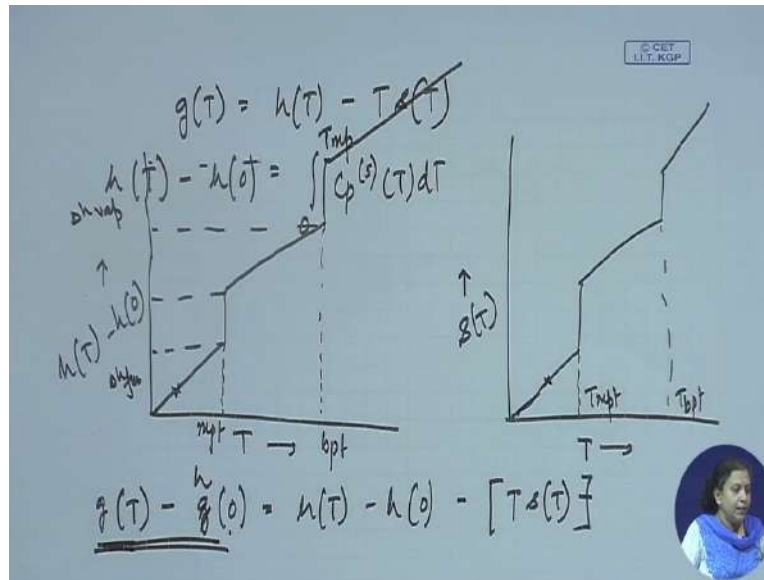
$$h(T) - h(0) = \int_0^{T_{fus}} c_p^{(s)}(T) dT + \Delta h_{fus} + \int_{T_{fus}}^{T_{bp}} c_p^{(l)}(T) dT + \Delta h_{vap} + \int_{T_{bp}}^T c_p^{(v)}(T) dT$$

$$s(T) = \int_0^{T_{fus}} \frac{c_p^{(s)}(T)}{T} dT + \frac{\Delta h_{fus}}{T} + \int_{T_{fus}}^{T_{bp}} \frac{c_p^{(l)}(T)}{T} dT + \frac{\Delta h_{vap}}{T} + \int_{T_{bp}}^T \frac{c_p^{(v)}(T)}{T} dT$$

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Now if you plot the entropy change for the same substance when it is being heated? It is given by this particular expression.

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Now for this case also if I plot s as a function of T or s as a function of temperature, now here I would like to mention actually this particular expression it should have been $g(T)$, suppose I express $g(T)$ as a function of $h(0)$ since I would like to keep the same standard state for enthalpy as well as the Gibbs free energy, the actual expression is $h(T) - h(0) - T[s(T) - s(0)]$ which is nothing but 0.

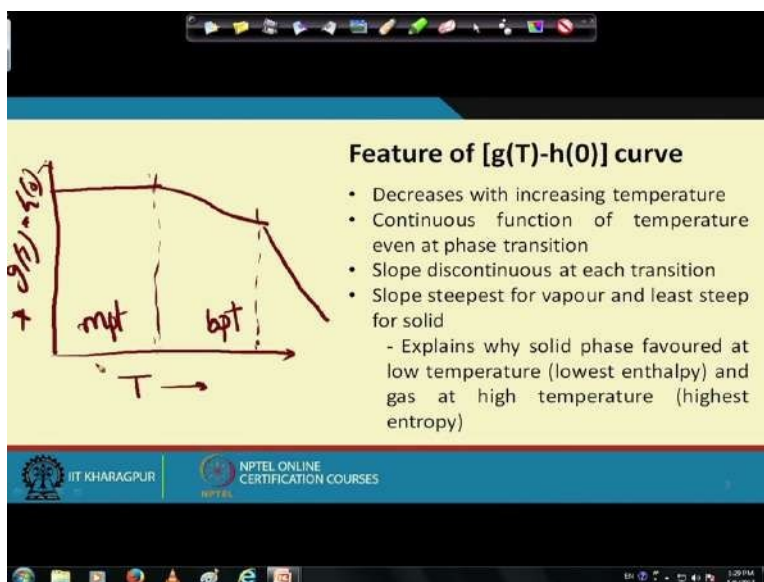
So therefore I plot $s(T)$ as a function of temperature and this is the exact expression that we are going to give see and with this case also we will find that the nature of graph is the same. Initially it's heated and the solid increases in temperature its entropy also increases then we have for one particular, during the melting process it absorbs Δh_{fusion} at T_{fusion} in this particular case it is absorbing Δh_{fusion} at T_{fusion} and after that again the liquid gets heated then it absorbs $\Delta h_{\text{vaporization}}$ at the boiling point and then the heating it continues.

So therefore in this case also we will find the nature of the curve is just the same while it is in the single phase the entropy rises the temperature rises and when the change of phase occurs that entropy rises at a constant temperature and so on and so forth. So this is nothing but the melting point of the solid and this is nothing but the boiling point of the solid.

Now in order to obtain $g(T) - h(0)$, so what do we need to? For each particular point we need locate the point here and we need to subtract $T s(T)$ from here from this particular expression to

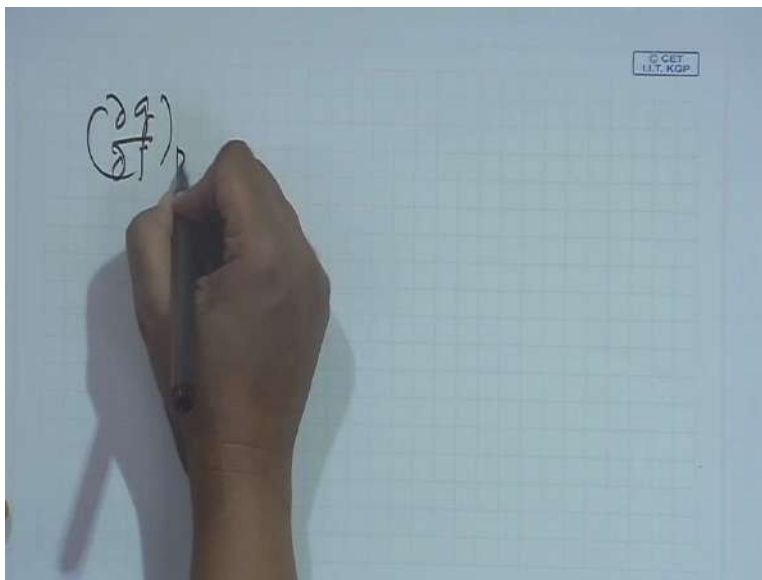
get the resultant g_T minus g_0 . Now let us see that while the enthalpy curve and the entropy curve they were more or less similar in nature with just differences in the magnitude of the different quantitative measures.

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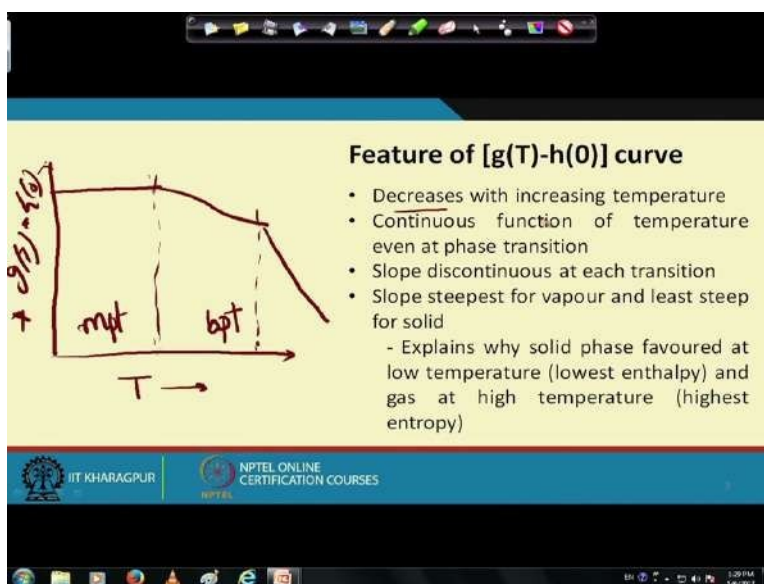


Let us see the nature of the g_T versus h_{h0} curve, in this particular case what should be the nature of the curve let us see? The nature of the curve in this case, Suppose we plot this, the x the y axis is g_T minus h_0 and the x axis is T degree Kelvin, right? So what is the nature of the curve that you would expect when we subtract T of sT from h_T minus h_0 , we find that the nature of the curve is completely different, it is something of this sort where we find that this corresponds to the melting point of the substance this corresponds to the boiling point of the substance.

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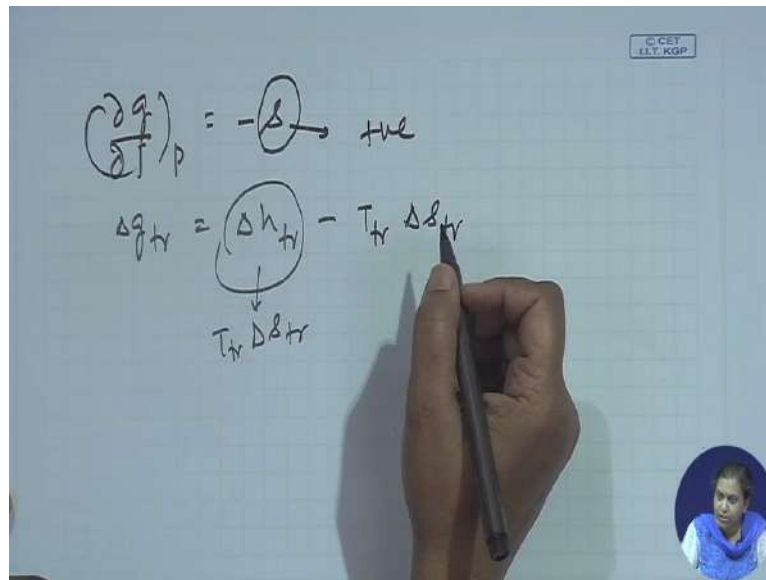


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So in this particular case what do we find? We find that there are some unique features of the Gibbs free energy variation with temperature curve as compared to the enthalpy variation and the entropy variation. The first thing we find that if we see $\left(\frac{\partial g}{\partial T}\right)_P$ is nothing but equal to minus s . So therefore we find that since s is an infinitesimally positive quantity. So therefore the slope is always going to be negative which is shown here it decreases with increasing temperature number 1.

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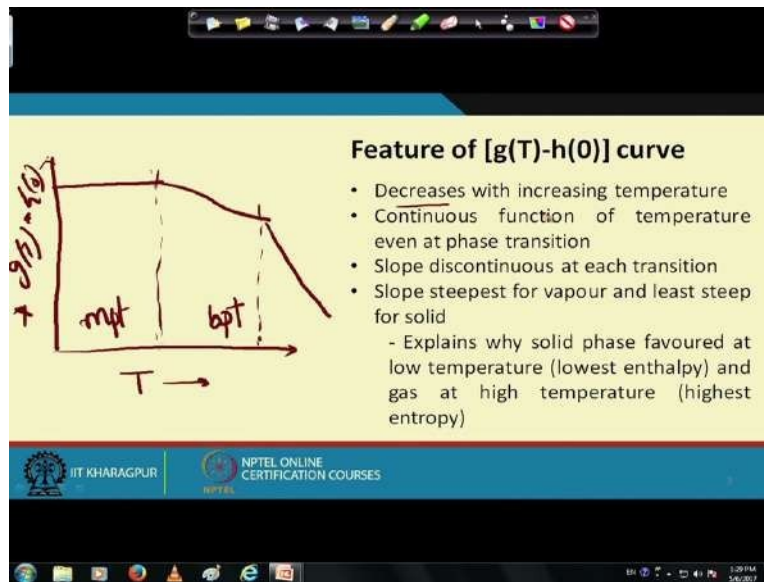


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$$\left(\frac{\partial g}{\partial T}\right)_P = -S \rightarrow +ve$$
$$\Delta g_{tr} = \underbrace{\Delta h_{tr}}_{T_{tr} \Delta s_{tr}} - T_{tr} \Delta s_{tr}$$

Number 2 is we find that it is a continuous function of temperature even at phase transition, why does this happen? In a nut phase transition, what is Δg transition equals to? This is equal to Δh transition minus T transition into Δs transition, right? And what is this Δh transition equals to? It is nothing but T transition into Δs transition because at a transition temperature the entropy increases by absorbing the heat and the heat is only used up as the latent heat for that particular transition.

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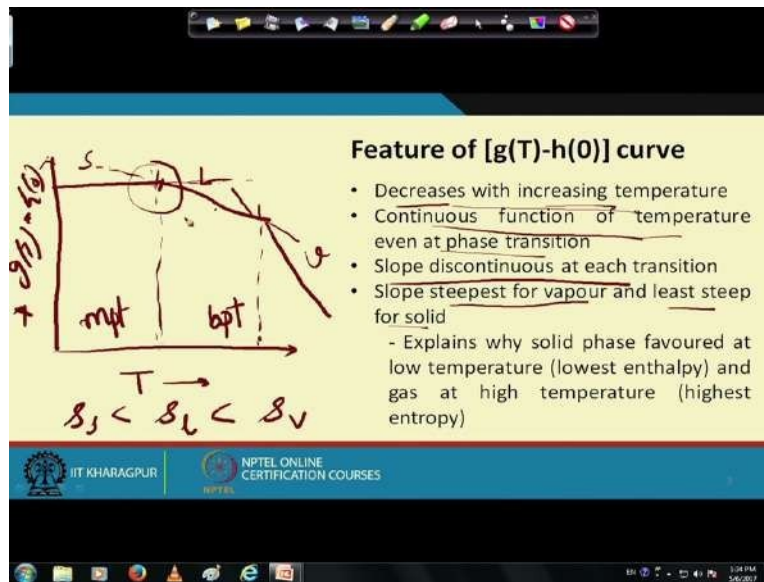


So therefore we find that at the generation temperature this term and this term are equal as a result of which Δg transition equals to 0 and this explains why even if it increases with increasing temperature and we find that even at phase transition we find that the Gibbs free energy it is a continuous function for function of temperature and this signifies that at phase transition when the 2 phases are in equilibrium under that condition Δg transition equals to 0.

But even if it is a continuous function of temperature we need to remember that the slope becomes discontinuous at each transition, why? But what is the slope the slope is nothing but minus s . So therefore if we are we are concerned with this particular portion then in that particular portion we will find $\Delta g / \Delta T$ at constant P this is going to be minus s entropy of the solid.

On the other hand if we are concentrating on this particular portion we will find that for sorry this is Δg . If $\Delta g / \Delta T$ at constant P this will correspond to the entropy of the liquid. We very well-know that entropy of the liquid is greater than entropy of the solid. So this explains why even if Gibbs free energy is a continuous function of temperature even at phase transition the slope becomes discontinuous at each transition the slope corresponding to the changes in the entropy before and after the transition.

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And we very well-known that s of solid it is less than s of liquid which is less than s of the vapor phase, so naturally what does it suggest? It suggest that the negative slope it is steepest for the vapor phase which I have shown here this particular case corresponds to the solid this corresponds to the liquid state and this corresponds to the vapor phase. So we find that the slope is steepest for the vapor phase and it is least steep for the solid phase.

Now there is another interesting thing that we can observe, if we observe the points near the phase transition very closely we find suppose at the phase transitions we try to extend the 2 curves say we try to extend the solid curve beyond the melting point, we try to extend the liquid curve again below the melting point.

Now what do we find? We find that even if the liquid were to exist below the melting point its Gibbs free energy would have been higher as compared to the solid phase and we find that even in the solid would have existed beyond the melting point its Gibbs free energy would have been higher as compared to the liquid phase. So therefore since a system or a or any particular substance is stable only for a minimum Gibbs free energy condition at conditions of constant temperature and pressure it automatically suggests why a solid is favored at low-temperature below the melting point? Why the liquid is favored at high-temperature beyond the melting point?

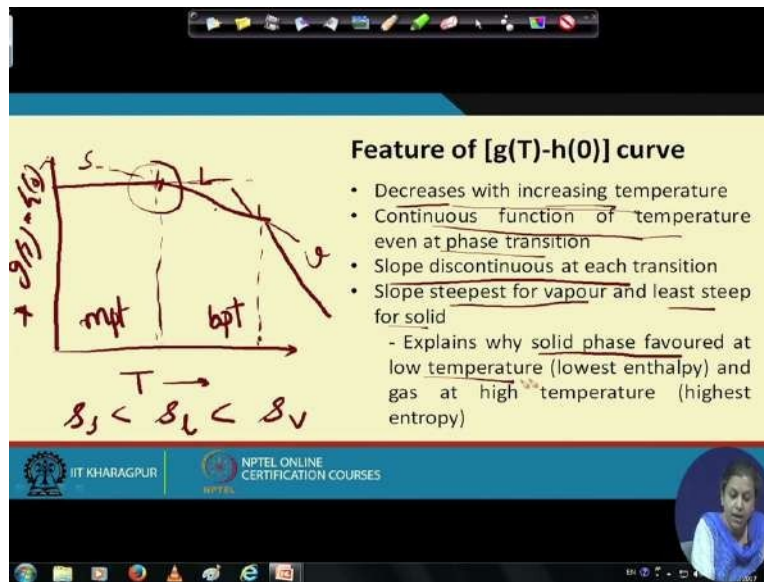
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Handwritten notes on a whiteboard showing thermodynamic derivations:

- Top left: $\left(\frac{\partial g}{\partial T}\right)_P = -S$ (with a circled minus sign and "true" written next to it)
- Top middle: $\Delta g_{tr} = \Delta h_{tr} - T \Delta s_{tr} = 0$ (with Δh_{tr} circled and $T \Delta s_{tr}$ written below it)
- Top right: $g = h - Ts$ (with h circled and "Imp at high temp" written next to it)
- Middle left: $\left(\frac{\partial g}{\partial T}\right)_P = -S$ (with "Imp at low temp" written next to it)
- Middle right: $S_L > S_g$ (boxed)
- Bottom left: $\left(\frac{\partial g}{\partial T}\right)_P = -S_L$

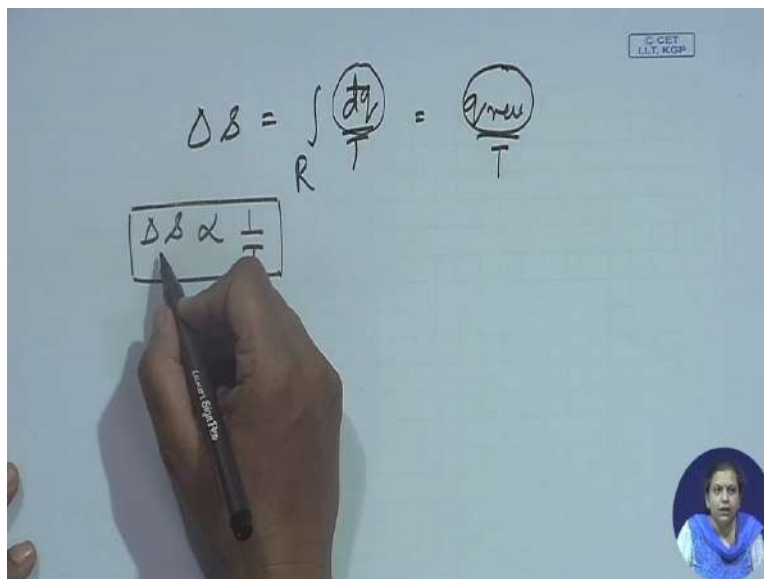
And from the same logic we can also understand why the vapor phase exists beyond the boiling point? And why the liquid phase exists below the boiling point? And if we recall once more, again I would like to say that g is nothing but equals to h minus Ts as I had already discussed earlier since s is associated with T , so therefore this particular term this becomes important at high-temperature this we had already discussed earlier and naturally this particular term this is important at low-temperature.

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So therefore what do we conclude? We conclude that a solid is solid phase is favored at low-temperature, why? Because it has the lowest enthalpy and the vapor is favored at high-temperature, why? Because it has the highest entropy, so the existence of the gas at high-temperature is due to the entropic contribution to Gibbs free energy while the existence of solid at low-temperature is due to the enthalpic contribution at the low-temperature phase.

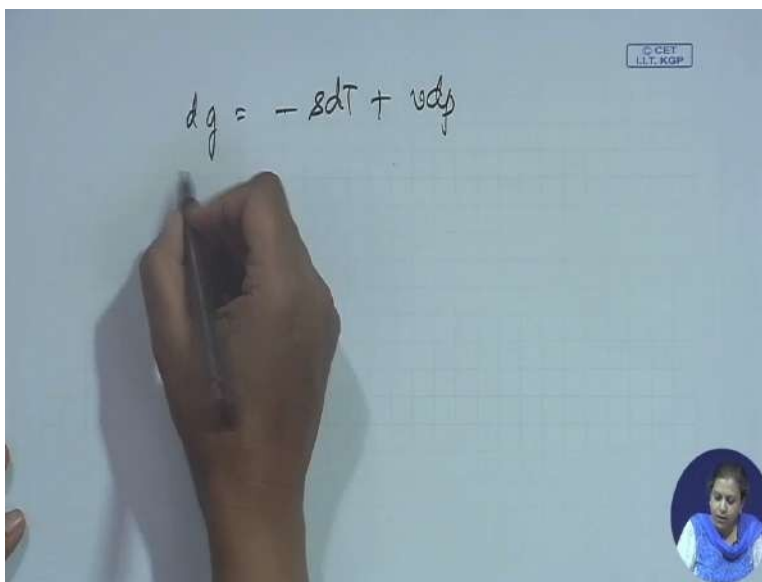
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$$\Delta S = \int_R \frac{dq}{T} = \frac{q_{rev}}{T}$$
$$\Delta S \propto \frac{1}{T}$$

Now here it will not be out of the place to just mention something which I have forgotten to mention while I was discussing entropy. How did we find out or what is the expression to find entropy? It is nothing but integral dq by T , right? Or in other words we will find that if we give the same amount of heat suppose this is q this is a reversible, so this is q reversible by T .

Suppose I give the same amount of q reversible to a substance at different temperatures, we find that the change in entropy it will be proportional to the or rather inversely proportional to the absolute temperature which signifies that if the same amount of heat is applied reversibly to a substance at different temperatures then the entropic change will be much more for lower temperature as compared to the entropic change at higher temperature this is almost similar to understanding that if you sneeze in a very quiet library the disturbance of the people around will be much more as compared to if you sneeze in a very busy shopping mall. So therefore this is something which I had forgotten to mention, so I thought it will not be out of the place if I mention it here.

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Now let us discuss the variation of Gibbs free energy with pressure. Now what do we know again if I recollect the equation dg equals to minus sdt plus vdp , right? So therefore $\frac{dg}{dp}$ at constant T it is nothing but equal to the molar volume of that particular solid.

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The slide contains the following text and equations:

At constant temperature - $\left(\frac{\partial g}{\partial P}\right)_T = v$ $\Delta g = \int_{P_1}^{P_2} v dP$

For liquids and solids g almost independent of pressure, $g \approx g(T)$

For ideal gas - $\Delta g = \int_{P_1}^{P_2} \frac{dP}{P} = RT \ln \frac{P_2}{P_1}$

- Logarithmic Increase with pressure (entropic effect)
- Important in chemical reaction equilibrium involving gas phase reaction

For real gases - Concept of fugacity ...

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So therefore we find that at constant temperature if we are talking then this should be $\frac{dg}{dP}$, so there it gives us $\frac{dg}{dP}$ at constant T equals to volume from where we can find out the and

the Gibbs free energy change for any process when a system goes from P_1 to P_2 is nothing but equal to $v dP$, right?

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At constant temperature - $\left(\frac{\partial g}{\partial P}\right)_T = v$ $\Delta g = \int_{P_1}^{P_2} v dP$

For liquids and solids g almost independent of pressure, $g \approx g(T)$

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For real gases - Concept of fugacity ...

So therefore from here for solids and liquids what can we say? For solids and liquids we can say that your Δg in this particular case, this is equal to say suppose g at say P_2 this is equal to g at P_1 plus v into P_2 minus P_1 , right? And since this or it can also be written as $v \Delta P$ which is almost equal to 0 for liquids and solids which tells us that g at P_2 is almost equal to g at P_1 for liquids and solids or in other words Gibbs free energy it is more or less insensitive to pressure for liquids and solids.

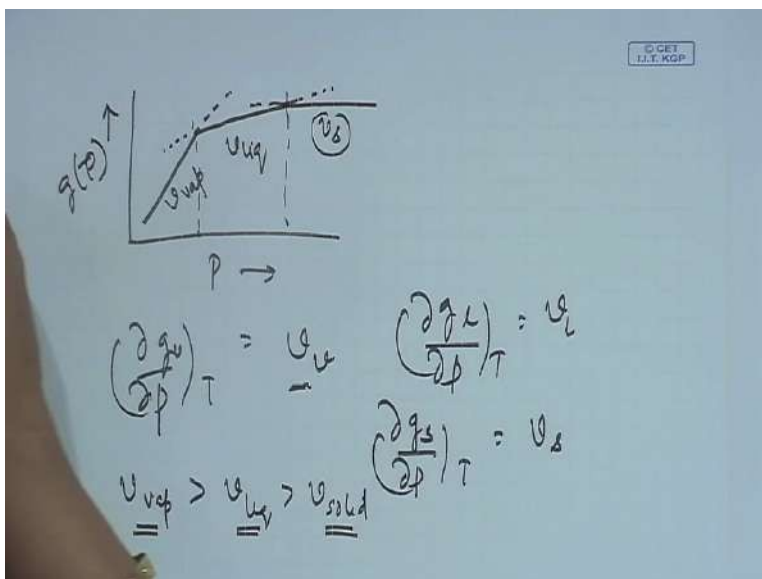
Now what happens for an ideal gas suppose we say, say we take up one mole of an ideal gas, right? For one mole of an ideal gas this is going to be integral $v dp$ integral and we know this is nothing but $RT \ln P$ which gives us the expression as $RT \ln$ integral P_1 to P_2 this is also P_1 to P_2 , this is nothing but $RT \ln P_2$ by P_1 , so therefore what type of expression is this? We find that for an ideal gas the variation of Gibbs free energy with pressure exhibits a logarithmic effect which is nothing but due to the entropic effect because if you remember the enthalpic change of an ideal gas with pressure equal to 0 which we have already derived.

This particular equation it is particularly very important in chemical reaction equilibrium involving gas phase reactions, right? So therefore we had discussed how Gibbs free energy varies

with pressure for liquids and solids, we found out how Gibbs free energy varies for ideal gas and it is very evident that if you are dealing with real gases then naturally we have to know how the molar volume of the real gas varies with pressure or which again we have to refer to the PvT behavior of the gases.

And we will be discussing after one or 2 classes that while trying to find out the variation of Gibbs free energy with pressure for a real gas. We come across a concept of fugacity and we define another important property which is the fugacity we will be discussing it and we will be discussing in details the variation of Gibbs free energy with pressure for real gases shortly.

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Well but before that, before I end the class what I would like to do in this particular case is that I would like to discuss just like the way I have found out how Gibbs free energy varies with temperature in the same way I would like to find out how Gibbs free energy it is a function of pressure, right? So what type of graph would you expect in this particular case?

We know again let me write down the equation $\Delta g / \Delta P$ at constant T this is equals to v , now we take up the same substance that we had done we start heating it or rather we start compressing it from a very low pressure where the substance naturally at that low-pressure it usually exists in the gaseous phase as we start compressing it, so therefore in the gaseous phase what do we find as we start compressing it?

The $\Delta G / \Delta P$ at constant T that will be corresponding to the molar volume in the vapor phase, so this is $\Delta G_v / \Delta P$ at constant T that will correspond to the molar volume. Now this will continue till the vapor does not condensed to the liquid phase, once it has condensed to the liquid phase we will find that $\Delta G_L / \Delta P$ at constant T this is going to correspond to the molar volume of the liquid phase and then again beyond the melting point we find that $\Delta G_s / \Delta P$ at constant T this will be corresponding to the molar volume of the solid phase.

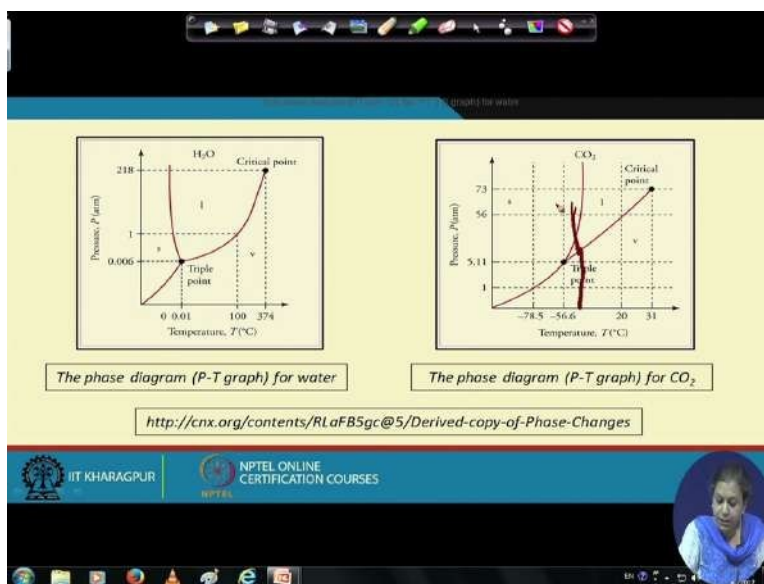
Now what do we know? We know that volume it is also a positive quantity, so from there what do you understand? We find that the variation or the slope of Gibbs free energy versus pressure is always positive or in other words Gibbs free energy keeps on increasing as pressure increases this is the first thing, the other thing what do we find? That at low pressure we always encountered a vapor phase, right?

So therefore at low pressure what will you expect? We are going to expect something of this sort where the slope corresponds to the vapor phase, fine. Then beyond the pressure corresponding to the or the pressure under which condensation occurs we find that the liquid phase exists and the slope will be corresponding to the molar volume of the liquid phase and beyond the condition where the liquid is going to form the solid phase we find that it is going to correspond to the molar volume of the solid phase.

There is one more thing that we know, we know that v of the vapor phase this is greater than the v of the liquid phase which is greater than v of the solid phase, so what does that explain? It explains two things, the first thing is Gibbs free energy always increases with pressure it always has a positive slope, the slope is the steepest in the vapor phase which is less steep in the liquid phase and it has the minimum steepness in the solid phase.

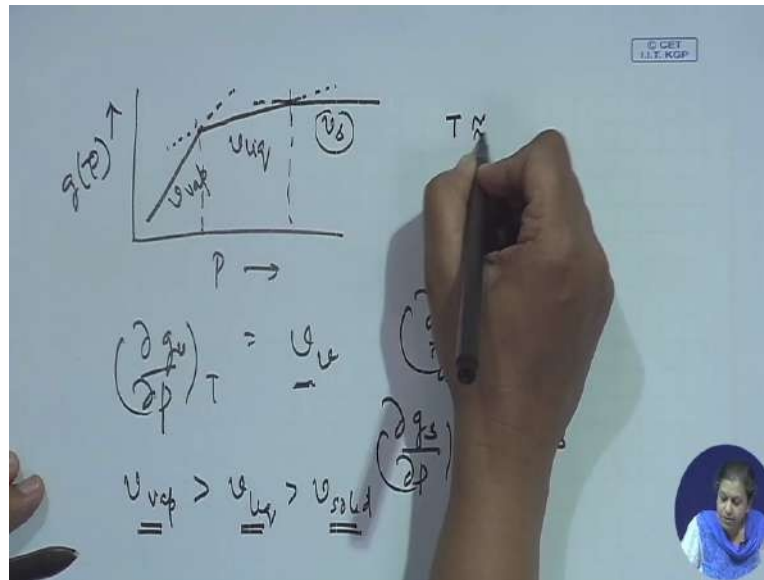
Again the way I have described or I have discussed while discussing the variation of Gibbs free energy with temperature in this case also if we extrapolate the curves on either side of the transition points it automatically becomes clear why we encounter the vapor phase below a particular pressure below the transition pressure while we encounter a liquid phase above the transition pressure and again in the same way if you are working with the liquid and the solid phase it automatically becomes clear why the solid is favored at the highest pressures and the liquid is favored at intermediate pressures right?

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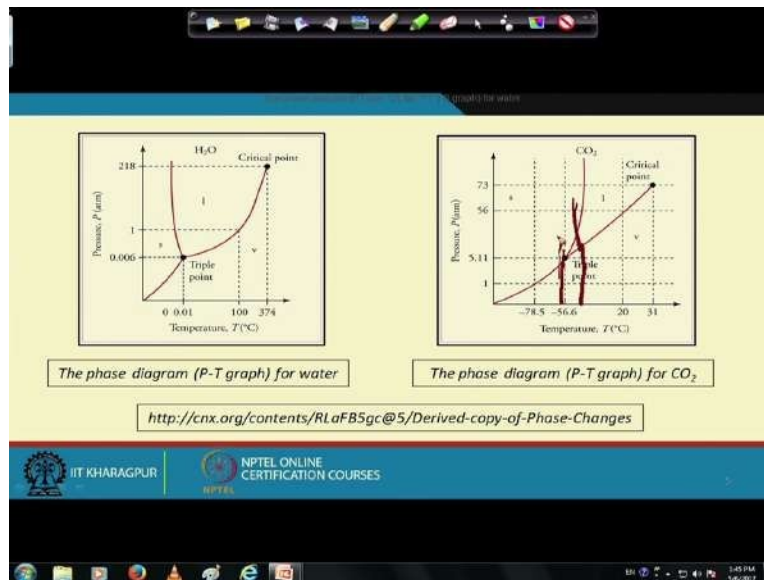
Now just one thing I would like to mention that this particular nature of the curve that I have drawn this particular nature it is for a normal substance say for carbon dioxide and this particular curve has been drawn for some particular position near the triple point say for instance it has been drawn under this particular point and the things which I have drawn is I have taken a vertical line from very low pressure I keep on following the vertical line and then we find that initially there is the vapor phase then we have a liquid phase and then we have a solid phase at a higher pressure.

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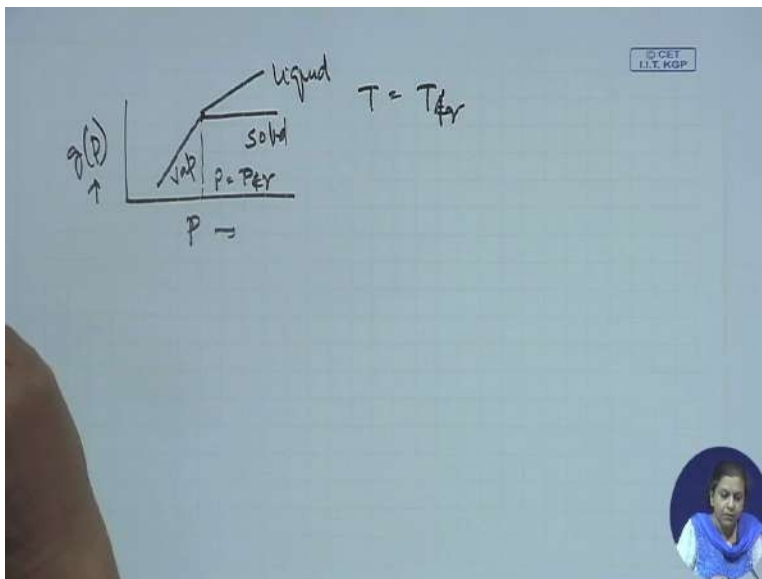
So therefore this particular the graph has been drawn for a condition where T it is close to the triple point but it is greater than it is greater than the triple point but it is close to it, it is far removed from the critical point, do you think that the Gibbs free energy variation with pressure it will have the same characteristics at constant temperature no matter which temperature I select,

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For example suppose instead of drawing it for a condition near the triple point suppose I try to draw it at the triple point exactly at the triple point suppose I try to draw. In this particular case do you expect the same nature of the graph to hold?

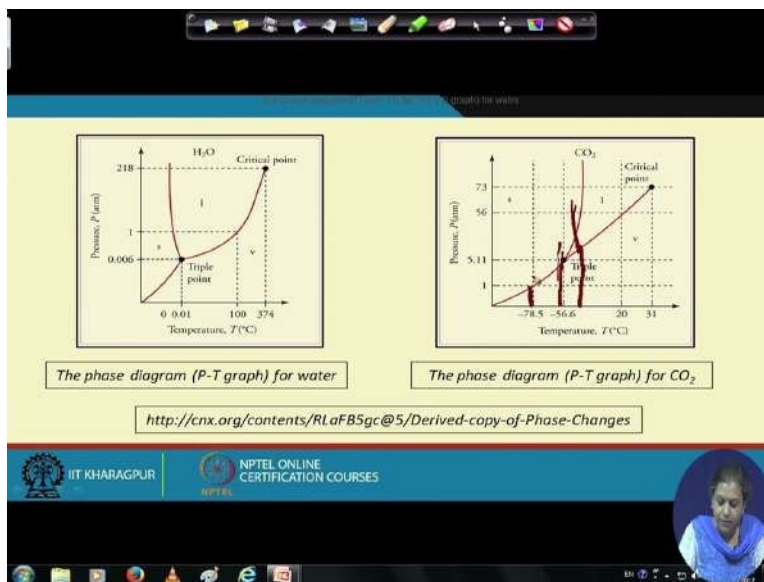
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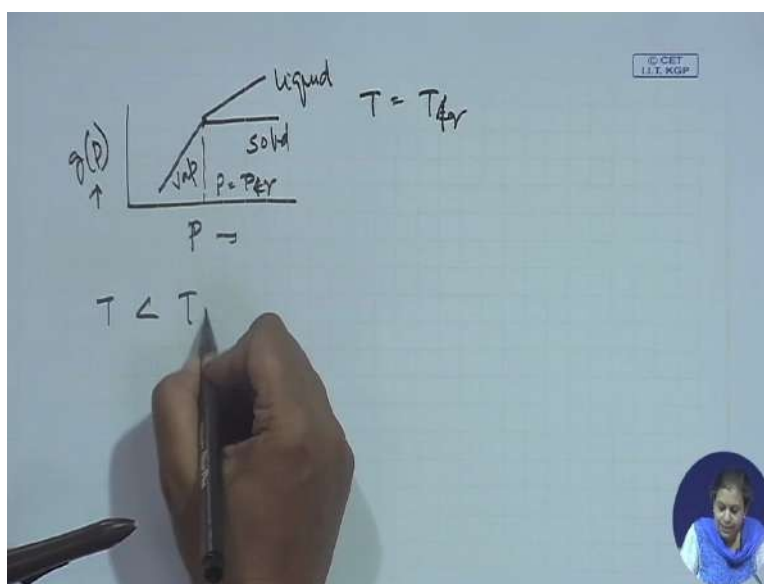
In this particular case, what is the nature of the curve that you are going to get? g_p as a function of P , in this particular case you will find that at the triple point this is the vapor phase and here we find that this is going to be the solid phase, this is the vapor phase, this is the solid phase and the liquid phase is going to exhibit the nature of the curve something of this sort and this particular situation is for P equals to P_c and for any other pressure other and this particular curve has been drawn for T equals triple point, this is also the triple point.

We find that at P equals to P triple point all the 3 phases have got the same Gibbs free energy, so they are all of them are equally probable of existence but once we start increasing the pressure from the triple point pressure at the triple point temperature we find that there is greater likelihood of the solid to exist over the liquid phase.

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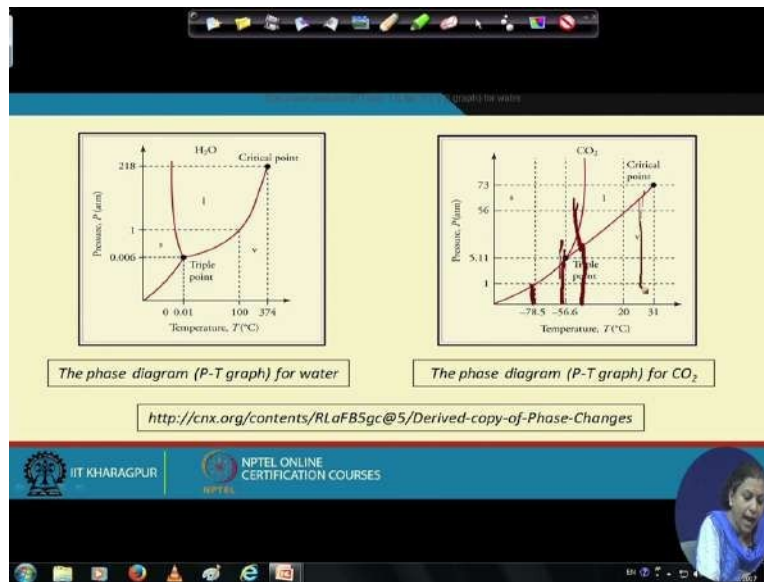


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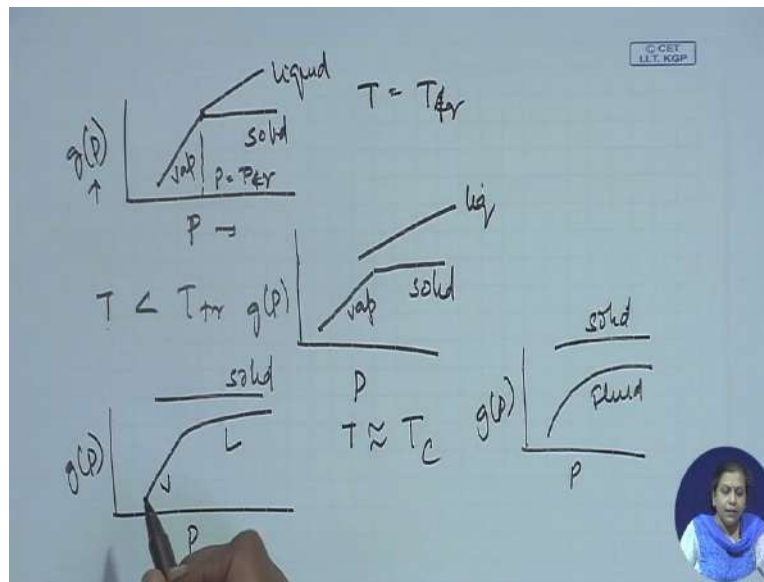
In a similar way suppose we would like to plot it at some other temperature where T is less than the triple point temperature, in this particular case what type of curve did you think you are going to expect? We have the vapor phase at low pressure we have the solid phase here this is the vapor phase, this is the solid phase and the liquid phase will be existing we never have a liquid phase for the temperature conditions less than the triple point.

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Now suppose instead of this we try to plot it near the critical point at the critical point as all of you know more or less the vapor and the liquid phases they become indistinguishable and the molar volume of the vapor is almost equal to the molar volume of the liquid.

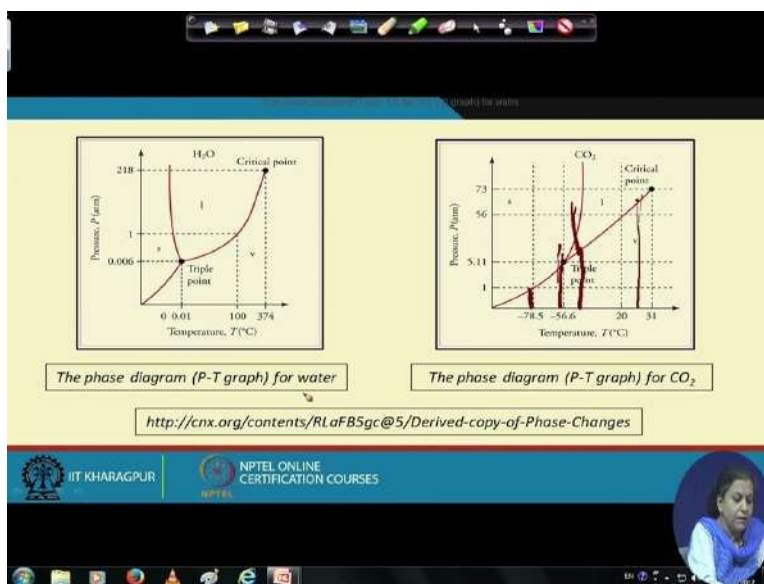
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So if we plot $g(p)$ versus p at P for a condition say P almost close to T equals to T_c , what do you expect? You expect that more or less since the slope of the curves are going to be almost equal at the transition places and you find that the solid exists above the vapor and liquid coexistence curves for all particular conditions.

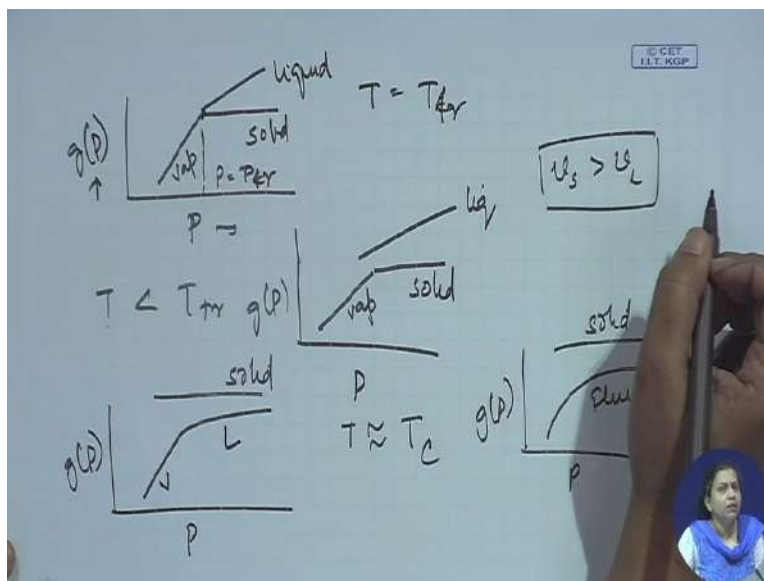
And at P equals to T_c you have just a continuous curve throughout that is no discontinuity in the curve and the solid phase this is just a fluid portion and the solid phase curve it remains above the fluid curve under all particular conditions.

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Now before I end I would just like to mention that all these curves that I have drawn here they are for a pure substance and for example carbon dioxide or benzene or anything, do you expect the same types of curves to hold when we are going to deal with water?

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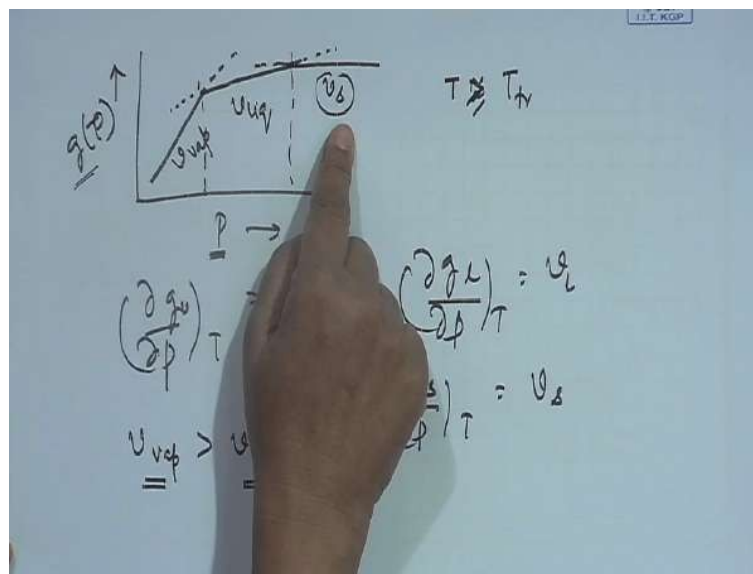


If you note the PT curve for water it is very evident that the solid liquid coexistence curve has got a slight negative slope as compared to the light positive slope for carbon dioxide, benzene or any other normal substance this is because as we all know that the molar volume of the solid is

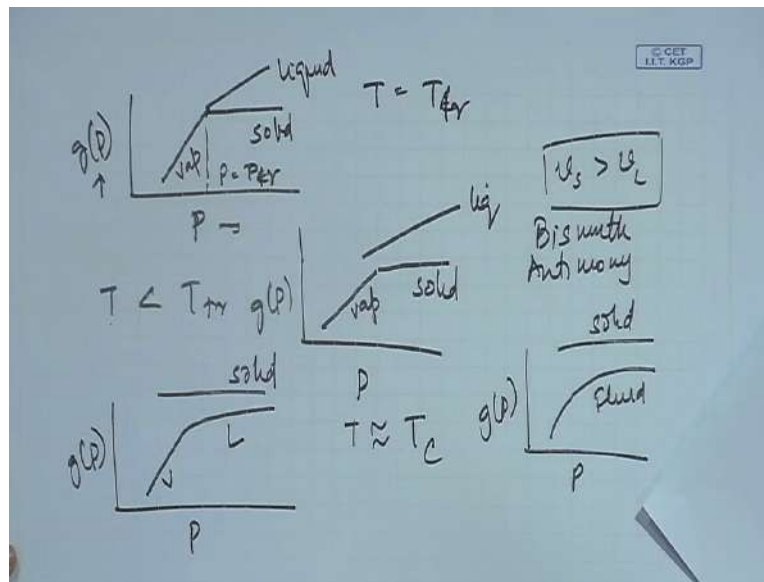
greater than the molar volume of the liquid in case of water, there are 2 other substances which also exhibit this particular characteristic the 2 substances being Bismuth and Antimony, for these thing we have some particular differences when we try to plot the g versus P curves at the triple point and for conditions less than the triple point.

I leave this as a home assignment for you, try it out and try to find out the g versus P curves for different conditions or rather for water at the triple point and less than triple point and in case you have doubts you can get back to us and we can clarify the doubts.

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But as I hint it is very evident more or less the curves get inverted, the situations which you had got for g equal this particular situation is going to exist for T less than triple point and we find that this particular situation is going to exist for T equal to triple point or slightly higher than the triple point.

So with this more or less we have come to an end to our discussions on property estimations and the properties of homogeneous systems which primarily comprise of one phase I would just like to mention that these components which we have dealt with they are homogeneous systems they can be single component they can be a mixture of components but due to the processes which are undergoing there is no change in composition there is just change in volume.

Or in other words to be more specific so long our discussions were confined to closed systems, in the next class we are going to deal what happens when the changes that we have discussed are also accompanied with changes in composition as well, we are first going to deal for single component systems and then we will be dealing with multi-component systems, have a good day.