Advanced Chemical Thermodynamics & Kinetics
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Lecture – 03
Review of Classical Thermodynamics 03

So, in the last part of this lecture we emphasized that the correct quantity of the thermodynamic quantity to look at under constant pressure and temperature is the Gibbs free energy or the change in Gibbs free energy.

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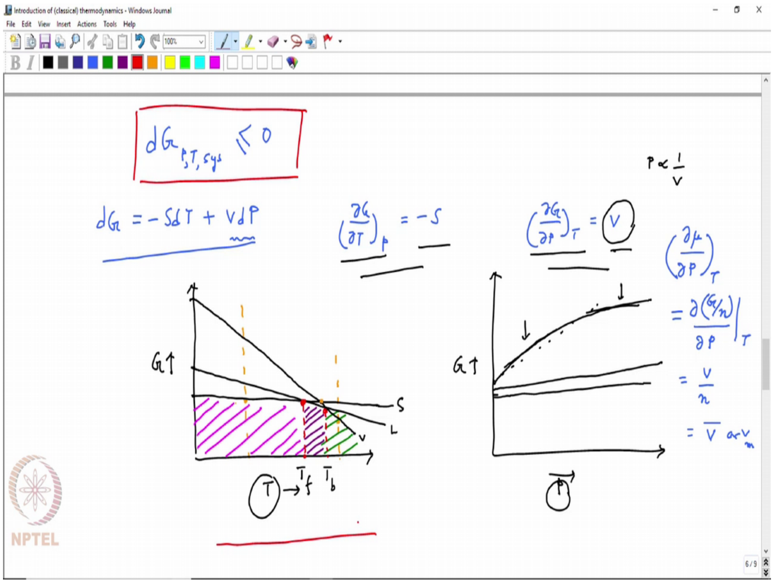

$\boxed{dG_{P,T,sys} \leq 0}$

$P \propto \frac{1}{V}$

$dG = -SdT + VdP$

$\left(\frac{\partial G}{\partial T}\right)_P = -S$

$\left(\frac{\partial G}{\partial P}\right)_T = V$

$\left(\frac{\partial \mu}{\partial P}\right)_T = \frac{\partial (G/n)}{\partial P}\Big|_T = \frac{V}{n} = \overline{V} \text{ or } V_m$

Because, if that change in Gibbs free energy is negative then the process is spontaneous and if we are considering some equilibrium process so, that will be 0 and this is the Gibbs free energy change of the system.

So, now we are going to actually consider how this Gibbs free energy changes with respect to parameters like pressure and temperature and how we can actually use it for discussing chemical or physical chemical transformations. Now, one of the very interesting things as you, if you remember that equation for dG we did not write it in the last part. So, dG will be SdT minus VdP and minus SdT plus VdP and then we can actually very easily see that this del G del T P so, that will be if I keep the pressure constant. So, this term goes to 0 and that will be nothing, but minus s and similarly del G del P T is V.

Now, what are the implications of this equation? So, let us draw a diagram just to give you a feeling how the Gibbs free energy changes with respect to temperature and pressure. So, if I increase the temperature and if I plot how the Gibbs free energy changes now that is equivalent to the change in entropy, but with a negative sign.

Now, the absolute entropy according to the third law of thermodynamics which you have not discussed so far so, there could be a residual entropy in the system, but entropy is always positive, it is 0 or positive. Now in a very ideal close to 0 temperature, the entropy is 0, but always you will have a residual entropy. So, we can say that entropy is always positive in the sense that the slope of this curve del G G versus T at constant pressure will be negative.

Now, if we take a gaseous substance or a vapor substance in a vapor phase, the slope the usually the molar entropy of or the entropy of the gas will be very very high. So, we will start from a very high point compared to liquid and solids and the decrease will also be much steeper compared to liquids we will start somewhere at a below the gaseous entropy value. So, it will be a it will have some slope, but of course, it will be less and for solids it will be even less, it will be something like this.

Now, it is not increasing so, let me just redraw the liquid and solid curves once again. So, let us say the liquid is something like this and the solid is something like this. So, everybody is decreasing, but the liquid and the vapor solid and the vapor, the decrease is such a much much lower rate than the solid. So, if we plot it the variation of the Gibbs free energy with respect to temperature at constant pressure, so, we will get a curve and the slope of this curve will be equal to the change in entropy and or the absolute entropy.

Now, as you see here. So, the slope is given by that del G del T P and that is minus S. Now, S is always positive and then minus S will be always negative, but for gaseous substance the slope will be much higher and also see that we are starting from a very high value. For liquids it will be slope will be less because the entropy of liquid is less than the gas so, it will be something like this and for solids it will be even less and then the change will also be much at a much smaller rate.

So, we will have a typical curve like this, where this is for the vapor phase, this is for the liquid phase and this is for the gas phase. And, similarly if we want to study the variation of the Gibbs free energy versus pressure at constant temperature so, the slope is equal to the volume. Now, of course, for it is a volume is a positive quantity to increase, but for solids for example, there will not be much change. So, it will be almost flat to the a x-axis something like this, for liquids it will slightly increase not decrease. So, we can actually say it will be slightly increasing. For liquid it will be a little bit increasing, a little bit more than solid, but again liquids are less compressible. So, the volume will not change much. For gas it will keep on increasing.

Now, the question is how it will increase, will it increase linearly? But, we know that if the form ideal gas equation that if I increase the pressure the volume will actually drop. So, this is actually a positive number, but the slope as we can see will change as I am increasing the pressure. So, the curve will look like something like this because as you can see here the slope here and the slope here are actually different; the slope here is much more than the slope here. So, the gas will have a curved will be plot for G versus T G versus P.

Now, the question is if we actually vary the pressure and temperature simultaneously the question is how will you generate surface or generate a Gibbs free energy change how do you plot that thing. Now, the interesting thing is that this condition that we have already written that del G has to be equal to 0, if there is an equilibrium.

Now, you can see from this curve that this solid and the liquid are basically crossing at some temperature and similarly, the liquid and the gas are also crossing at some temperature, which means at this temperature at that particular pressure who I mean for this curve actually kept the pressure constant. For that pressure at this temperature these defines actually condition where the Gibbs free energy because the y-axis was Gibbs free energy for the gas as well as the liquid at the same, which means actually the liquid and the gas are is in equilibrium. And in this case actually this is the, this point which I have I am drawing right now is basically an intersection of the liquid and the solid line.

So, this should be S and then if the liquid and the solid are in equilibrium that temperature we call as the melting point or the freezing point and similarly, at this temperature as you can see here the vapor and the liquid lines cross and then we call it as a boiling temperature. So, we write it as a T b. So, come back to it we I will draw it more clearly and see what are the effects of that and of course, we see that there is a cross point for solid and liquid also, but that point is lying much higher.

So, as you can see that what is the implications of these lines is that say for example, if I take a arbitrary temperature at a fixed pressure this is all drawn for a fixed pressure. So, at this temperature we see the solid curve is lying much lower. So, which means the Gibbs free energy of the solid is the much less compared to the Gibbs free energy of liquid or gas or vapour. So, we see that the solid is the most stable phase at this temperature and pressure.

Similarly, if I draw a line here, I see that the vapour is the most stable phase here. So, similarly this solid to liquid transition will not happen at this pressure the way we have drawn it because I see that up to their T f temperature this entire region the solid is the let me actually use some other color. So, the solid is the most stable form so, this region because this curve for the solid actually lies lower and then there is a region where actually the liquid is the more stable region.

So, this region as you can see and then above that the gas is the most stable region. So, we see this particular region the vapor has the least Gibbs free energy. So, we see actually a transition from solid to liquid and liquid to vapor in this diagram and how we can increase the temperature keeping the pressure constant.

Now, the question is if we actually vary the pressure and temperature simultaneously how it will look like. Definitely, so, there will be some we can actually draw some lines where the Gibbs free energy change is 0, or meaning that the two phases are in equilibrium and that particular diagram which we call as a phase diagram which is actually a variation of the pressure versus temperature. And, we are drawing some lines and those lines represent basically the conditions for equilibrium between two phases is known as a phase diagram.

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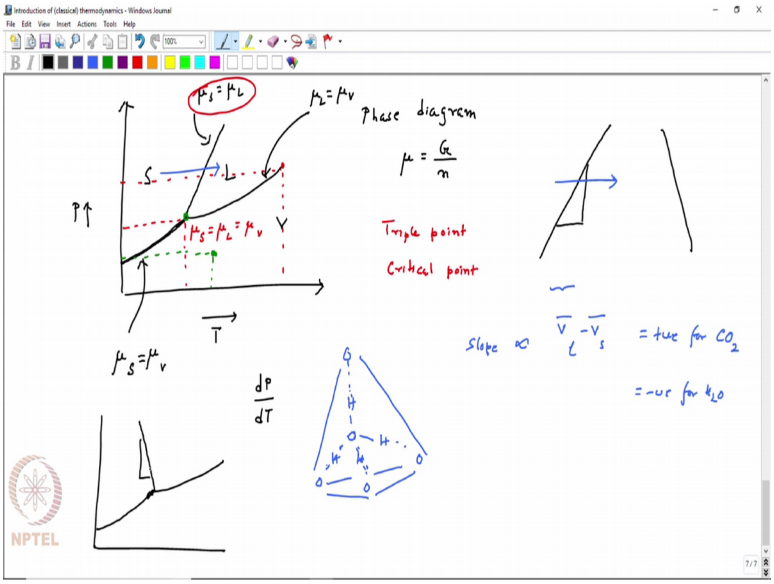

So, I will draw typical phase diagram and it looks like something like this and we are plotting it say a pressure versus temperature. So, what we see here that here this region we call it as a vapor region. So, at a, say very high temperature and low pressure region so, this will be the region of the vapour and this will be the region of the solid which is at a very high pressure or low temperature and similarly this will be the region for the liquid.

And, these lines represent the line or the which represent basically phase transitions and on these lines the Gibbs free energy of the two phases are equal. So, basically if I want to write down an equation for this line. So, it will be something like Gibbs free energy per unit mole of which you also call as chemical potential we have not discussed about chemical potential until now. So, chemical potential is defined nothing, but that gives for energy per unit mole.

So, this chemical potential of the Gibbs free energy is per unit mole must be equal for the solid and the liquid, solid and the vapor because it is the line which is joining the solid and the vapor. And similarly, this line will represent a region where the liquid is in equilibrium with the vapor and similarly, for this line the solid is in equilibrium with the liquid.

So, we see that under a particular combination of pressure and temperature one phase will basically dominate. Suppose, if I choose a particular point in the phase diagram suppose this point. So, this point represents a particular combination of pressure and temperature and that pressure temperature we see the Gibbs free energies minimum for the vapor phase. So, the substance will actually exist as a vapor. So, what we do is that for various substance, we actually draw a phase diagram, because phase diagram is very fundamental to our understanding and it will give you every information how one phase actually gets transformed to the other phase and under what conditions or a particular phase is stable.

Now, we see that these three lines are actually meeting at a point, which means at this point all these three phases are in equilibrium; meaning, we have a very interesting condition here that the chemical potential of the solid is identical to the chemical potential of the liquid which is also identical to the chemical potential of the vapor. So, this pressure temperature combination where actually the three phases coexist we call it as a triple point. Similarly, the point up to which the liquid vapor phase exists; now whenever we talk about phase we talk about basically an existence of a phase boundary between two macroscopic phases, just something like you have a glass of water say and say for example, I have a water and we can see and the water has a surface.

So, and then we say that this is basically a phase boundary this is a liquid water and then the water is in equilibrium with water vapor, because this is a closed system. So, some water will vaporize, but then quickly it will reach the vapor pressure. So, then no further evaporation net evaporation will happen a I mean molecules are of course, leaving the surface and the molecules which are also coming back to the liquid from the vapor phase.

So, this will be under equilibrium and then will have a vapor in equilibrium with it is liquid which is right now the situation and the two phases the vapor phase and the liquid phase are separated by a well defined boundary, that I can see here. But, if we actually keep on hitting any substance something like say water liquid water then we will actually see at a particular combination of temperature and pressure the phase boundary vanishes and this thing we usually discuss when we talk about the properties of real gases where we show that, ok.

So, after certain point you do not see any I mean like you do not see any particular appearance of the boundaries. So, the boundary all of a sudden vanishes and that point you call as a critical point. So, above the critical point you have actually a state which is known as a supercritical state, it is it behaves as a vapor like, but it is not a true vapor it is neither a vapor non liquid. So, it is called as a supercritical liquid.

Now, the phase diagram as I have drawn here represents a typical phase diagram again, but of course, the slope of this solid liquid curve I mean needs some attention, because the way I have drawn it solid liquid curve slope is something like this it is very much exaggerated because it will be at the slope will be much less compared to the solid vapor or the liquid vapor slope. And it will be something like a steep slope, but the question is whether it is a positive or negative slope. Now, it will be a positive slope now, what is this slope let us try to first understand.

Now, this slope means actually it is a slope of this curve which is dP dT so, that slope. Now, you can show that again from the very fundamental equation that we have the alpha phase or basically at chemical potential of a particular phase and chemical potential of the other phase and you can show that this ultimately if I want to write an equation that will be basically dictated by how much change you have in the chemical in the molar volume.

So, as you can see here so, if I want to actually will come to that full equation, but before that let us say if I just change the pressure with respect to or change the temperature keeping the pressure constant that we already discussed, but here if you see if I change the pressure with keeping the temperature same that is nothing, but equal to volume.

So, if I were talking about say the change in chemical potential with respect to pressure keeping the temperature constant. So, chemical potential is nothing, but the Gibbs free energy per unit mole. So, we can right away write this like this and so, ultimately will have nothing, but V divided by n and V divided by n is nothing, but molar volume which we wrote as write as V bar or we write it as V suffix m.

So, what we see here is that if I apply pressure keeping the temperature more or less constant which is somewhere here. So, like I am assuming this change in temperature is small. So, then you can say that it will depend on the difference in the molar volume.

Now, for a substance like say carbon dioxide going from say solid to liquid because we are traversing, if I go from here to here so, it is basically we are going from solid to liquid region and if I go from solid to liquid you will see that the liquid volume is large then the solids volume.

So, basically a slope more or less equal to the change in the molar volume, solid to liquid transition which is basically molar volume of the liquid minus molar volume of the solid or let us actually use the V bar notation and subscript as liquid minus solid and that will be basically the slope will be proportional to that and then what we argue is that that is positive for a substance let us say for carbon dioxide.

But, for water we know when ice melts into water up to 4 degree centigrade, 0 degree to 4 degree centigrade, the ice structure actually collapses because I such a very much open structure which you have studied. It has a like one water molecule is tetrahedrally surrounded by 4 water molecules like this, which you have already studied and this is through hydrogen bonding you know about this and that hydrogen bonding is basically causing the ice to have a more open like structure. So, we can just clearly show this thing.

So, these are the covalent bonds and plus every water molecule will also have hydrogen bond. So, this is kind of the structure of ice which we, I mean kind of except it is not a fully I mean correct structure, but it has an open structure like this and then when it melts so, the volume actually collapses. So, for that the slope is negative for water.

So, this particular slope the way I have drawn it will be something like this and the slope will be negative. So, the way we should draw the phase diagram for ice or a phase diagram for water is something like this, but again this is an exaggerated drawing. It would not be exactly like this it would be the slope will be very less because the change in the molar volume again will be much smaller, but change in the per degree rise in the temperature.

Now, so, the phase diagram so, will basically will tell you how what temperature and pressure combination one particular phase is most stable and secondly, where you the phase boundaries exist how and at what temperature and pressure you can actually switch from one phase to the other phase.

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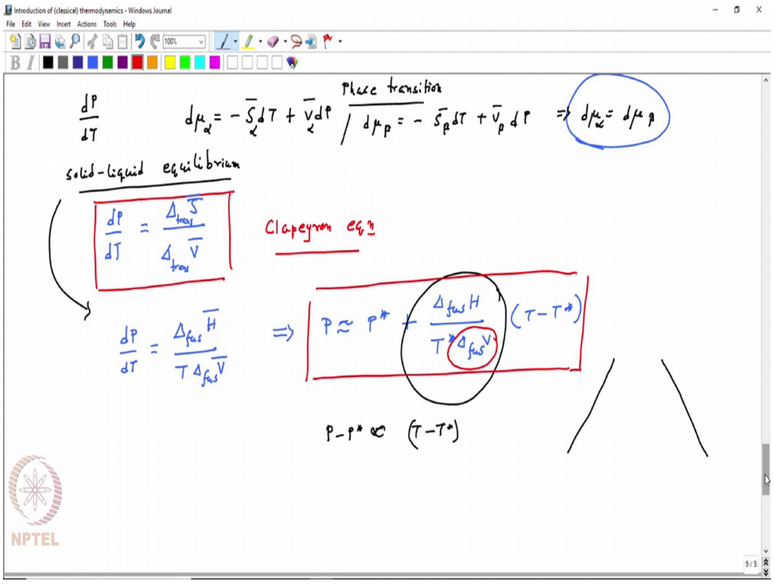

$\frac{dP}{dT}$

$d\mu_\alpha = -\bar{S}_\alpha dT + \bar{V}_\alpha dP$ / $d\mu_\beta = -\bar{S}_\beta dT + \bar{V}_\beta dP \Rightarrow d\mu_\alpha = d\mu_\beta$

Phase transition

solid-liquid equilibrium

$$\boxed{\frac{dP}{dT} = \frac{\Delta_{trans}\bar{S}}{\Delta_{trans}\bar{V}}}$$

Clapeyron eqn

$$\frac{dP}{dT} = \frac{\Delta_{fus}\bar{H}}{T\Delta_{fus}\bar{V}} \Rightarrow \boxed{P \simeq P^* + \frac{\Delta_{fus}H}{T^*\Delta_{fus}V}(T - T^*)}$$

$$P - P^* \propto (T - T^*)$$

Now, when we talk about these phase diagrams so, we actually talked about these slope of this curve dP dT and that is the most important for phase transitions. Now, the question is, if we consider say solid liquid equilibrium. So, for solid liquid equilibrium, now you can think what will be the dP dT? Now, dP dT, now you can show that from again starting from the very fundamental equation which we had written for dG let us go back. So, we know that dG is minus SdT plus VdP.

So, what we have to do here is we are talking about the dG per unit mole. So, we can write it as d mu is a minus SdT plus VdP, but this is for particular phase let us say a phase alpha. So, I can write it as S alpha and V alpha and since I am writing mu I have to use a V bar and S bar notation, because it is a molar entropy and molar volume. And, similarly we can write it for another phase which is beta like d mu beta is something like minus S beta dT plus V beta dP and at the equilibrium we know that d mu alpha is nothing, but equal to d mu beta. And from that you can actually equate a ha all these two equations and you just call it that dP terms and the dT terms and then what you will see here this will be nothing, but dP dT is nothing, but the change in the molar entropy or S bar and divided by the change in the molar volume.

Now, this is the change due, during a phase transition because only for the phase transition we have this condition that d mu alpha equal to the d mu beta because the two phases are in equilibrium which means the Gibbs free energies are equal or the chemical potentials are equal. So, we actually write it as transition. So, delta suffix transition means actually for a particular transition. For example if we are talking about solid liquid equilibrium for solid liquid equilibrium this equation which is a dP dT is. So, this equation is known as Clapeyron equation. So, there is a S bar do not forget it is a molar quantity.

So, this is known as Clapeyron equation and the Clapeyron equation takes a different different form if we talk about different different equilibrium. For solid liquid equilibrium this dP dT will be nothing, but so, delta S fusion. So, if we, during the phase transition, so the associated heat change or the reversible heat change is nothing, but equal to the enthalpy. Because, we know that when the phase transition is happening it is happening at constant pressure and temperature.

So, delta S we can actually replace by delta q reversible by T which is actually delta h by T and that process we call it as a fusion it is a solid to liquid equilibrium and vice versa. So, we write the transformation as fusion. So, that is why I am writing a fus subscript, it will be delta h divided by sorry it is a dq reversible by T if you remember the change formula for entropy and will have T delta fusion into molar volume and this is also more orient helping and then we can actually integrate this equation and after a few approximations you can show that the pressure will be approximately equal to some initial pressure which I am calling as P star plus delta fusion H divided by T star. So, T star is the temperature corresponding to pressure P star and delta fusion V into T minus T star. So, that is how the pressure actually goes with integrated form how the pressure actually varies with temperature.

So, if I know that thing that basically tells me the equation of that line which line which is the solid liquid phase boundary. So, the equation of this line is something like this and as we can see it is a linear equation. So, it depends of course, on the change in the molar volume so, this quantity. So, and as we can see that it is nothing, but P minus P star is something like if we can write it in a simpler way, so, P minus P star is basically proportional to T minus T star, but it depends on the proportionality constant if this constant is positive. So, then I will have a linear increase and if this is negative like for water it will have a negative slope.

So, that is what we are trying to tell when we are discussing the slope of this solid liquid equilibrium phase boundary. Now, similarly we can actually about a liquid vapor equilibrium on the or the solid vapor equilibrium. The solid vapor will not discuss because it will be just like the liquid vapor equilibrium.

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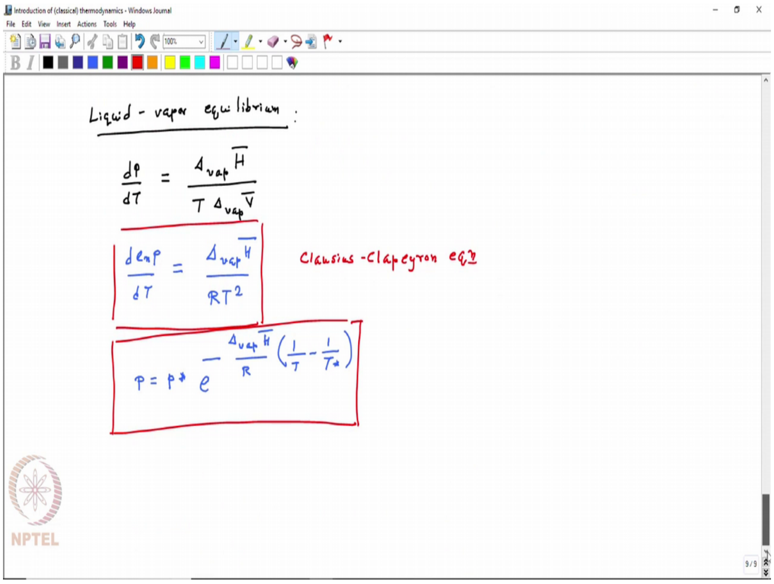

Liquid - vapor equilibrium :

$$\frac{dP}{dT} = \frac{\Delta_{vap}\overline{H}}{T\,\Delta_{vap}\overline{V}}$$

$$\boxed{\frac{d\ln P}{dT} = \frac{\Delta_{vap}\overline{H}}{RT^2}}$$

Clausius - Clapeyron eqn

$$\boxed{P = P^{*}\, e^{-\frac{\Delta_{vap}\overline{H}}{R}\left(\frac{1}{T}-\frac{1}{T^{*}}\right)}}$$

For liquid vapor equilibrium this slope dP dT. Now, which is actually which as a thing like we can always write it as a, the transformation as a vaporization in this case. So, and again we can actually say that the change in entropy at constant pressure is nothing, but dq reversible by d and at constant pressure dq is nothing, but dH. So, we can write it for a of course, for a reversible process and we are considered in an equilibrium and you are assuming reversibility so, divided by T into delta vaporization into molar volume. So, that eventually you can actually now use pV equal to energy of the ideal gas equation for one phase which is the vapor phase and if you use that then you can actually get simpler form for this equation and that is now as you can see this T actually we can write it as a RT by P and then you can I mean do all the manipulation not the T sorry that delta vaporization of P.

So, there will be two volumes and one of the volumes you can actually write it as RT by P and then finally, it will be dP by P and which you can I write d ln P dT is delta vaporization H divided by RT square. Now, this equation either in it is differential form or in the integrated form is known as remember that the original equation was known as

Clapeyron equation for the general equation of phase transition and then we approximated it for solid liquid equilibrium.

So, for solid vapor equilibrium. So, this modified form of the Clapeyron equation is known as Clausius Clapeyron equation. Now, you can further integrate the Clausius Clapeyron equation and then get a relationship how the pressure varies with temperature in an integrated form and then that you will see that it will be something like e to the power minus delta vaporization of H. So, I should write it as a delta vaporization of H. So, it is a enthalpy change for vaporization divided by R into 1 minus T minus 1 minus T star, where actually the pressure the, if the pressure is P, the temperature is T and if the initial pressure we took as a P star and the initial temperature was T star.

So, this is the integrated form of this Clausius Clapeyron equation and thus we see that starting from a very basic fundamental understanding that how one should look at the spontaneity and or the equilibrium of the process from the systems perspective. We said that most of the chemical transformations are undergoing under constant temperature and pressure. So, the Gibbs free energy is the correct quantity to look at and if we actually see the or analyze the Gibbs free energy then we find that this change in the Gibbs free energy can happen with respect to pressure and temperature because these are the natural choices. And if we vary those conditions how the Gibbs free energy is changing and then we figured out that it will be very important for phase transition where actually one phase is basically transforming into the other phase and there is a equilibrium between the two phases at a particular pressure temperature.

So, that equilibrium we denote actually the existence of a phase boundary and we basically derived the equations for those lines which actually separates the two phases in a phase diagram and that is basically the Clausius Clapeyron equation. And, then the next thing what we do is that depending on the nature of this phase transition we also talked little bit about the classification of this phase transition and which is known as R n fus classification. We talk about first order phase transition. So, you could talk of second order phase transition we also talked about like some other phase transitions which you cannot categorize as first order or second order phase transitions.

Now, before I conclude this part let us actually have a discuss about the what will be the effect of say if I apply pressure how what will be the effect on the freezing point and the melting point. So, we are actually trying to go back to this curve which we draw very early here. So, we want to actually want to study or see, if I actually apply pressure how basically the melting point and the freezing points are going to change.

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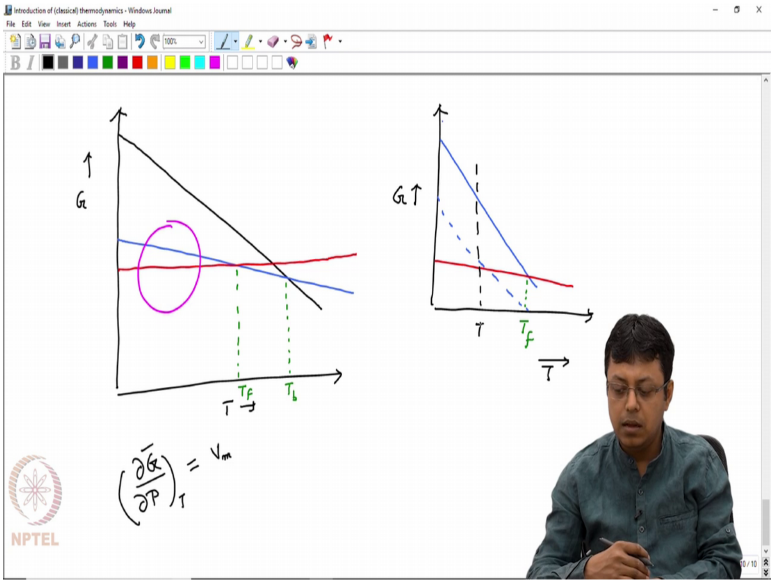

$$\left(\frac{\partial \bar{G}}{\partial P}\right)_T = V_m$$

So, let us just draw this figure once again more clearly and so, what I am saying here I have a G versus or mu verses T curve for the solid which I wrote as the black curve and then let us draw another curve let us say in blue for the liquid. Suppose, this is something like this and then we also have a curve for the solid and let us actually draw a curve like this. So, the solid and liquid the difference will be less so, the that is why the drawing has to be very perfect and then we have something like this, alright.

So, now, see the freezing point is basically the intersection of the curves which are the intersection of the solid and the liquid. So, we just write it as T f and similarly, the melting point or sorry the boiling point is basically the intersection of the liquid which is the blue curve and the black curve which is the vapour curve so, that is the boiling point.

Now, suppose I am applying pressure and I am I want to understand how these curves are changing, particularly the freezing point like we will just talked about the freezing important thing for the time being. So, let me actually draw it once again so freezing point is nothing, but the intersection of the solid and the liquid. Now, suppose I am actually exaggerating at that curve. So, for liquid I was using blue line and suppose that the in the normal case as you know that we just draw it once again, suppose I am zooming this these two curves these two curves means just the blue and the red curve. And, if I zoom that so, suppose this is the original blue curve which is at a low pressure and then there is a red curve which is also at a low pressure. And now we will see the effect of increase of the pressure on this and this is basically we will call that as a normal freezing point or T f. So, this is again T versus mu curve or T versus G curve, if it is per mole than it is mu.

Now, so, this is the normal freezing point at that temperature the Gibbs free energy for the red curve and the blue curve are the same which means the two phases are in equilibrium, which happens during freezing basically melting. Now, if I apply the pressure, if the change in the molar volume because you know that if keeping the temperature same if I apply pressure, so, what will happen? So, the equation is del G del P keeping the temperature same is nothing, but equal to the volume.

Now, if I use a Gibbs free energy per unit mole which is nothing, but mu this will be more volume, but it is not necessary to use the molar volume concept. It is just supposed to volume for some fixed amount of mole and if we just think about that the change in the molar volume at a very high pressure, the molar volume you know what it is going to happen. So, basically at low pressure, the molar volume for a less thing for a liquid there will be some change in the molar volume usually at a higher pressure the change in the molar volume will be basically much less and in that solid also the change in the molar volume will be much more less.

So, in the sense that if I actually apply pressure of course, the molar volume is going to decrease because I am actually applying the pressure and now the question is if this is at a low pressure curve, but the high pressure curve will lie. So, for liquid also what I am saying it will drop say it is dropping like this, but it will be a kind of parallel line with respect to the original line. Why it is parallel line because if you remember that we are suppose we are keeping temperature constants, suppose some temperature. At this temperature I am asking if I apply pressure what will happen, so, just the volume it is since it is proportional to the volume del G del P at constant temperature the molar volume is decreasing. So, I will just have a decrease in the in this curve and then or basically I will have a increase in the curve.