Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 17
Phase equilibrium – Part 2

All right, let us now, discuss about the thermodynamics of phase transition.

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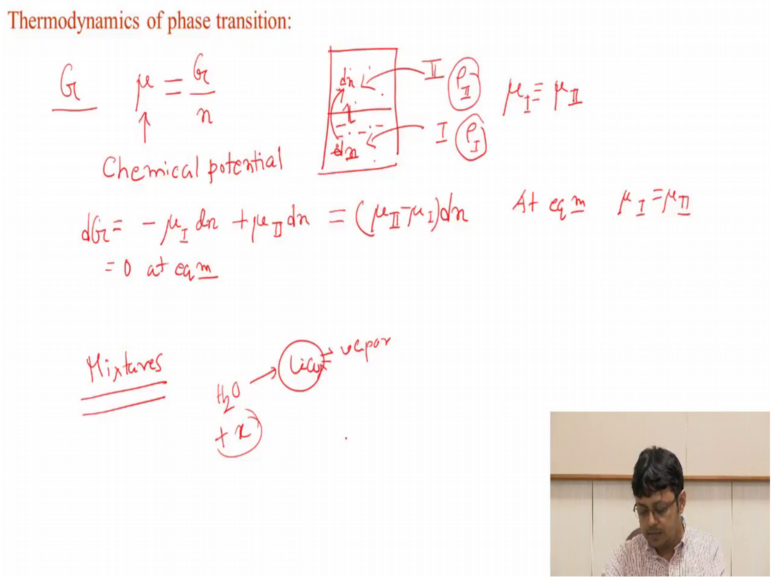

Thermodynamics of phase transition:

G $\quad \mu = \frac{G}{n}$

Chemical potential

$\mu_I = \mu_{II}$

$dG = -\mu_I dn + \mu_{II} dn = (\mu_{II} - \mu_I) dn$ $\quad$ At eq^{m} $\mu_I = \mu_{II}$

$= 0$ at eq^{m}

Mixtures

$H_2O \rightarrow$ liquid $\rightleftharpoons$ vapor

$+ x$

Now, as we said that the natural choice is to take the Gibbs free energy and we are going to ask this question how the Gibbs free energy changes, but instead of taking the Gibbs free energy we will use the Gibbs free energy per mole which we denote as mu and where this mu is known as the chemical potential.

So, chemical potential is nothing, but the Gibbs free energy per unit mole. Now, what this chemical potential means? Again, suppose, we have separated the system into two phases where this is phase 1 and this is phase 2. Now, if the system is in equilibrium. So, then we know that the densities will be different in this phase suppose this will be rho 1 and this will be rho 2, suppose this is a liquid and this is the corresponding vapor. So, the liquid is in equilibrium with the vapor. In that case, although the densities are different that characterizes the phases are different the chemical potential in those two phases must be the same.

Now, if there is a difference in the chemical potential for example, suppose we just put the liquid and then just wait and watch then what will happen then slowly the liquid will evaporate and some molecules of the liquid from will actually vaporize and go into the vapor phase which means there will be a initially there will be a chemical potential of the liquid. So, we are calling it as a mu one and then the change in the Gibbs free energy chemical potential is nothing, but Gibbs free energy per unit mole. So, suppose dn amount of moles actually went from the liquid phase to the gas phase. So, this amount is dn.

So, the change in Gibbs free energy will be minus mu 1 dn. similarly, for phase 2 the change in Gibbs free energy will be mu 2 into dn. In this case, it will be plus dn because it has gained some molecules. So, the total change in the Gibbs free energy which we denote here as a differential change will be nothing, but mu 2 minus mu 1 into dn and at equilibrium when the equilibrium will eventually attain then we said that mu 2 and mu 1 will be equal which means the Gibbs free energy will be 0 at equilibrium. So, there is no net exchange of molecules between the two phases. However, always keep in mind that any equilibrium beta chemical equilibrium between two phases or a physical equilibrium between two phases or a chemical equilibrium involving some reaction always it is a dynamic equilibrium, meaning some molecules are going into the liquid from the liquid phase to the vapor phase and similarly some molecules from the vapor phase are going into the liquid phase. But, it is doing it in such a way that then there is no net change.

So, we can write when the net change is 0 the chemical potentials have been equal or in other sense the there is no change in the Gibbs free energy. Now, we will use this simple concept and build up all the other concept subsequently. Now, this chemical potential is an important quantity and we just the example which we just said is that the chemical potential of say one substance is decreasing and the chemical potential of the other substance is increasing, what does it mean? It means remember that some molecules are actually going from the liquid phase to the other phase, which means that initially mu 1 and mu 2 were different and as time progresses the mu 1 in this case, it will decrease because it has a higher chemical potential. That is why, the molecules are going from the origin of higher chemical potential to the region, or from lower chemical potential which is the vapor phase and slowly the mu 1 decreases and the mu 2 also increases and at some point the mu 1 and mu 2 will be equal so that there will be no net exchange between these are two phases.

We will draw a particular diagram when you talk about the mixtures in the next class, where I will talk about the; what happens if you have a two component system something like we have drawn here this is right. Now, and one component system and they are will talk about say two component in the sense here the example was supposed to take water in it is own liquid and vapor form where the liquid and vapor are in equilibrium, but suppose if we add something else also in the sense that if we add some salt or something which we denote as x, then the salt can be actually inside the liquid and then we can talk about the mixtures. So, it is not a pure liquid it is now a solution, where we have a solute and the solvent, we will discuss it eventually. But, let us not consider only the one component system and how the phase transition happens for a one component system.

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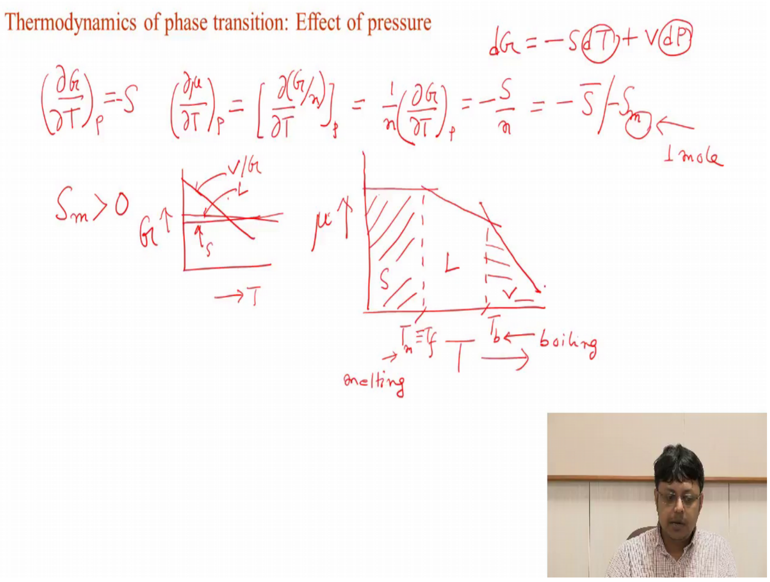

Thermodynamics of phase transition: Effect of pressure

$$dG = -S\,\boxed{dT} + V\,\boxed{dP}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial \mu}{\partial T}\right)_P = \left[\frac{\partial (G/n)}{\partial T}\right]_P = \frac{1}{n}\left(\frac{\partial G}{\partial T}\right)_P = -\frac{S}{n} = -\bar{S} / -S_{\boxed{m}} \leftarrow 1\text{ mole}$$

$$S_m > 0$$

Now, we already discussed what how the variation of the Gibbs free energy looks like if we vary the temperature or pressure, because remember that dG was nothing, but minus SdT plus VdP. So, if we vary the pressure and temperature, the Gibbs free energy will also change and we showed that you can show it just directly from that equation that del G del T variation of the Gibbs free energy keeping the pressure constant is nothing, but minus S. Now, what will be the value of del mu del T P? Remember that, mu is nothing, but the Gibbs free energy per unit mole. So, we can write it as G by n keeping the pressure constant, since n is constant n is just the number of moles we can just write it as del G del T at constant pressure which is nothing, but minus S divided by n. So, this is change the entropy per unit mole.

So, we call it as a molar entropy we can either write it as S bar something like the notation who are using for molar heat capacity cp bar and cv bar or sometimes we just write it as minus m with a suffix m, but the m stands for it a denotes that it is for quantity of one mole only.

So, similarly, we can also get a relationship for pressure variation, but before that let us first try to consider what will be the nature of the curve. Now, this molar heat capacity is always greater than 0, for any substance for any phase. Now, think about it we already discussed that the gas phase the S m or the more entropy sorry, it is not a heat capacity this entropy it is S and then this entropy will be always positive and so we can write that since S is positive minus S is negative, but the slope of the curve will be always negative for any substance. Now, what does it mean, we already drew a curve like this that for gas actually it will be very steep decrease we can draw it even slightly more steeper way like this for liquids it will also change, but not much something like this and for solid it will not change almost at all. So, this is for vapor or gas this is for liquid and this is for solid.

Now, suppose we are increasing the temperature and the phases are also changing in the sense that it is going from a solid phase to liquid phase and from liquid phase to the gas phase. Now, how it will look like, then you can always argue that suppose initially at low temperature the solid was the more stable form and the variation of the pressure with temperature which is the del what the variation of the Gibbs free energy with pressure. In this case, actually we are not plotting the pressure remember it will be the Gibbs free energy and in this case, we are just plotting the mu which is the chemical potential.

So, for solid because at low temperature in this region will have the existence of solid only, it will change a little and then when it starts forming the liquid then there will be a sudden change in the slope of del G del T P and that temperature is nothing, but the melting temperature which we can call as T melting and then when the liquid starts forming the vapor at the boiling temperature, you will have even a steeper curve where this temperature is nothing, but the boiling temperature we can write it as suffix b similarly, we could write it as suffix m do not get confused with the suffix m here which stands for one mole and here it stands for the melting it is a melting temperature and b for it is a boiling temperature. Now, the melting temperature is also the freezing temperature.

So, if you think the reverse process that we are going from liquid to the solid. So, the liquid freezes into the solid just like the solid melts into the liquid. So, this region is nothing, but the region where actually the solid is present, but the solid is the most stable form similarly this region is the liquid region and this region is the vapor region. So, we can see how the chemical potential changes as we make a transformation from say low temperature to high temperature, but the system undergoes from a solid phase to a vapor phase through a liquid phase.

Now, we can think of the effect of pressure under this condition and in a similar way we can say that how the this pressure effect will be manifested.

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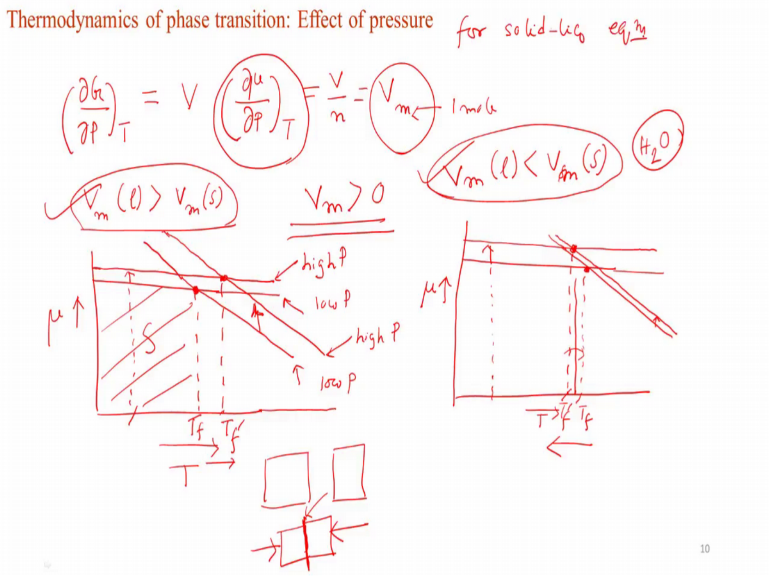
Thermodynamics of phase transition: Effect of pressure

We already know that del G del P T if you remember from previous lecture that is nothing, but V. So, we are considering here del mu and in the similar way del mu will be nothing, but we have to divide basically by the number of moles. So, I am just doing it directly. So, it will be V by n or we will just denote it as V suffix m or this m is for 1 mole or this is basically and 1 molar substance. Now, suppose we are applying pressure. Now, usually when we have change the substance going from say liquid to or solid to liquid usually the molar volume increases from going from solid to liquid. So, try to think about it we are showing the same curve which is nothing, but mu versus T how the chemical potential changes for a for a substance if we keep on increasing the temperature and involving the phase transition.

So, for solid it was almost no change, you can just draw it like this and then at some temperature it started melting. So, you can draw it like this. Now, suppose let us also stretch it a little bit and also stretch this line a little bit. So, at this point we had the T f which is the freezing point which is of course, equivalent to the melting point. Now, suppose we are increasing the pressure. So, if we increase the pressure what will happen and as we see here that this del mu del P T is nothing, but equivalent to V m.

So, in the solid phase if we keep on increasing the pressure since molar volume is in any phase is always positive increasing pressure means the Gibbs free energy will increase for a particular temperature. So, the increase in pressure for the solid the new line will be here and remember that this is basically that increase keeping the temperature set at a particular temperature where the solid exists we are increasing the temperature sorry increasing the pressure and we see that the Gibbs free energy or the chemical potential increases by some amount which will be proportional to the molar volume of the solid.

Similarly, if we apply the same pressure for the liquid the molar increase in the molar volume will be much more the reason is molar volume of liquid is more than the solid. So, we see a very interesting situation here this curved for the solid. So, this is a high pressure and this is low pressure and similarly this was high pressure then this is low pressure. So, what we see here earlier the curves at the low pressure were crossing here and now, at high pressure the curves are crossing here which means the freezing point will now, be shifted towards right. So, by applying pressure we see that there it causes at an n and enhancement in the freezing point or melting point well those are all equivalent.

So, for example, if the substance was melting at say 50 degree centigrade and now, it is melting at say with the increased in pressure it is melting at 60 degree centigrade something like that. It happened because we chose a particular condition that the molar volume of the liquid is greater than the molar volume of the solid. Now, think about a situation where the molar volume of the liquid is less than the molar volume of the solid and we already know that this happens in the case of water. Now, for water the curve definitely will look like something like that as before suppose we had solid and liquid variations like this I will have an interesting situation here. So, if we apply pressure this is mu versus T curve and this was suppose the freezing point and if we now apply pressure, the molar volume of the solid will increase because remember in either case whether this condition is valid or that the molar volume of liquid is less than the solid or molar volume of liquid is greater than the solid this condition is always true the molar volumes are always positive which means if I apply pressure it will increase. Now, the question is how much it is increasing in the solid phase compared to the liquid phase that changes in the earlier case the solid phase was increase in the solid phase or change in the molar volume in the solid phase was little compared to the liquid phase.

In this case, we will have just the opposite scenario suppose this is the increase of the molar volume at some constant pressure. Now, for the liquid let us suppose that the change in the molar volume is very little. So, this is the change in the molar volume. Now, you can see the curves are crossing earlier here now they are crossing here. So, not here sorry they are crossing this is the upper curve they are now crossing here at this one.

So, we have very interesting situation that the new freezing point has now shifted towards left, earlier case it was basically shifting towards right we could call it as tear prime and now tear prime is here. So, we see that the freezing point of some substance for example, water is lowered if we as we apply the pressure. Now, you have experienced it if you suppose take 2 cubes of ice you bring them together and then just press them very hard.

So, what will happen at the interface here the pressure will be very high and if you can maintain the pressure in such an extent that suppose the temperature which you are sitting is somewhere here. So, meaning that you had a temperature initially where the freezing point was higher which means ice was stable from. Now, you are increasing this you are basically taking these 2 blocks of ice together and giving huge pressure and at the interface what happens due to the increase in the pressure because the pressure will be felt at the interface of these 2 cubes and then as a result what will happen the freezing point will shift towards left and suppose you were you initial temperature which you started with is say minus say 1 degree and suppose, the freezing point is minus 2 degree. So, the freezing point or melting point has lowered which means at that temperature minus 1 degree ice should melt.

So, as a result what it will do is that at this region ice will melt into water and then this water actually form a uniform phase basically ice is ice is melting from one cube ice is also getting a melting the other cube and then you form water in the inter facial region and then all of a sudden you realize the pressure again. So, what will happen since this is an equilibrium process then the freezing point will again be elevated. Now, you are sitting at minus 2 degree centigrade, but your freezing point is again say 0 degree centigrade. So, you are at lower temperature. So, again that water will immediately freeze and what will happen that freezing of that water which are generated at the interface will make 2 pieces of the ice stuck together. So, you cannot remove it.

So, that is an interesting demonstration where you bring 2 solids let them melt by applying pressure so that they form a liquid and then all of a sudden aim again release the pressure. So, that the liquid again forms the solid and then you have a uniform solid phase. So, similarly you can think of our transformation just like here we are discussing the transformation between a solid and a liquid you could also think of it transformation between a liquid and its vapor. Now, for that we will discuss an interesting situation, but a liquid and is in equilibrium with it is vapor. Now, we are still considering the effect of pressure. So, here we are considering in the earlier case we are considering the effect of pressure for solid liquid equilibrium.

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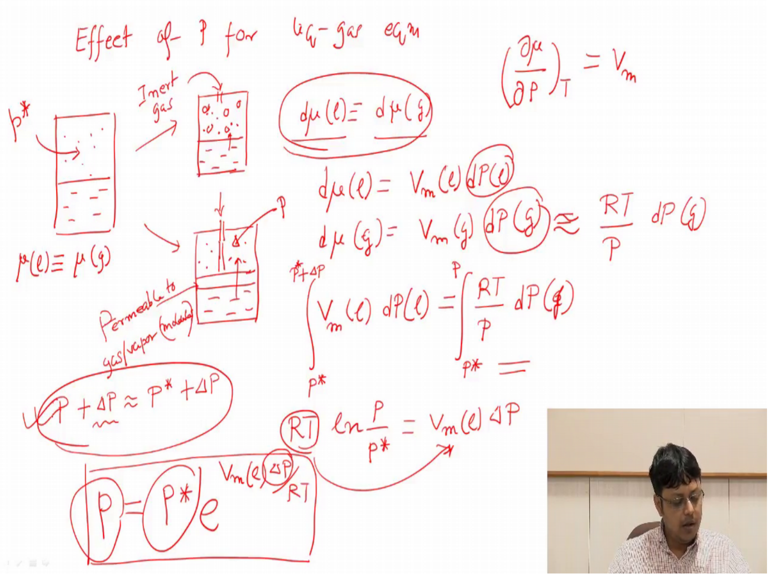

And, now, we are considering the effect of pressure for liquid gas equilibrium. Now, the question is how do you create or increase of pressure on a liquid. Now, you can think of a very interesting experiment suppose again that I have our sealed container and that liquid initially was in equilibrium with its vapor. So, the chemical potential must be equal in the two phases otherwise there will be a mass exchange which is not happening at equilibrium, so, the chemical potential is same.

Now, suppose we make some arrangement or in one case you can make an arrangement like this, you can very simply make a hole here and you insert some say inert gas say you insert argon and suppose this is water. So, what will happen, initially you had some water molecules. Now, on top of it you will have some argon molecules. So, the pressure will exert it on the liquid will be more and as a result more and more vapor water molecules is coming to the vapor phase you could also device it in some other way that you could actually insert a piston something like this and suppose this is the water and the piston touches the surface of the water and this is a very special piston where if I keep on pressurizing the liquid of course, the you know that more and more vapor will form and if the vapor forms then what will happen the vapor should come out.

So, the piston should be permeable to gas molecule solid gas or vapor molecules only, but it is not permeable to the liquid molecules, but to the liquid. So, this permeable only to the gas, but not to the liquid if we make an arrangement and keep on pushing this piston then also it will create a pressure on the liquid and the pressure of the liquid will increase which means more and more molecules will come into the vapor of course, the pressure of the paper will also increase. Now, that is a demonstration of how we can increase the pressure for a system consisting of a liquid in equilibrium with its vapor.

Now, let us consider here actually there is no inert gas only paper. Now, we would like to formulate the situation. So, what we are saying is that initial I had the chemical potential of the liquid is identical to the chemical potential of the gas or the vapor. Now, suppose in this change we make something where we write that the change in the chemical potential for the liquid as d mu also should be identical to the change in the chemical potential of the gas if after application of the pressure the system comes to a new equilibrium.

So, always we are thinking about from one equilibrium to another equilibrium, so, initially there was no pressure the only pressure was basically the vapor pressure of the liquid and then we applied pressure by inserting an inert gas. By the way the condition for this case the inert gas should be that the inert gas is only in the vapor phase. So, that it is applying a pressure on the liquid, but it does not get dissolved if it gets dissolved into the liquid then it cannot pressurize the liquid, that is one of the necessary condition for the experiment.

Or, other way was that we insert a piston and where by inserting piston or by inserting the inert gas the effect will be more and more vaporization of the liquid because pressure is applied on the liquid. So, the vapor phase pressure also increases and if we apply a constant pressure then we will we can think that there will be a situation where again the vapor has increased from the initial phase, but then there is no more exchange between the liquid and the vapor no more net exchange, then again we have the same chemical potential which we could write as the which we have denoted as the change in chemical potential of the liquid is equivalent to the change in chemical potential of the gas.

Now, we are just going to equate these two things and try to understand how the pressure will vary under this condition now. So, if the changes are equal of course, the changes should be equal because it has gained an equilibrium. Now, let us think that the liquid when we keep a pressure what is d mu liquid. So, by definition remember that del mu del P at constant temperature is nothing, but the molar volume. So, the del mu of liquid will be nothing, but not the d mu of the finite differential will be V m we denote it as V m liquid into some change in pressure which we call as dP for the liquid similarly for the gas phase we can write it that that will be the more volume of the gas times some change in pressure for the gas remember this change in pressure initially the pressure exerted by the for the gas and the liquid were same why because the only pressure was the vapor pressure which was created by the vapor or the gas.

Now, we have an interesting situation. We have some increased vapor pressure, but there is also an additional pressure this additional pressure is coming either from the piston or this additional pressure is coming from the inert gas. So, the vapor pressure or the vapor pressure of the vapor has increased, but that pressure is not identical to the pressure exerted on the liquid. The pressure exerted on the liquid is the pressure of the vapor pressure plus the additional pressure because we are still keeping that piston and keeping a constant force on the liquid.

So, this dP and this dP are different. So, that is the key point here and the trick is of course, for gas we can approximate it to be an ideal gas and we can write away right it is RT by v sorry RT by P and because it would not be inert which is a molar volume and for the gas and then it is a pressure of the gas and then we can write just dP of the gas. Now, since these two are equal in the new equilibrium the changes have been equal. So, you can equate these two equations and we could write that the molar volume of the liquid into the change in pressure for the liquid is nothing, but equal to the corresponding change in the gas phase which we wrote as RT by P into the change in pressure in the gas phase.

So, you can right away integrate this equation by writing, please follow here. So, I am just integrating it like this. So, let us integrate here. Now, suppose initially the gas or the vapor pressure was p star. So, this pressure is p star. So, the pressure on the liquid initially was also p star. Now, what is the final pressure of the gas suppose the final vapor pressure is P which is basically this thing which is P. Now, here the final pressure will be P plus delta P, where this delta P is nothing, but the extra pressure that is coming from the piston or from the inert gas.

Now, this P plus delta P we will approximate it to be equal to P star plus delta P, the logic goes as follows because suppose there was a vapor pressure P star initially and that got enhanced to P and in the new situation the pressure exerted on the liquid is the new vapor pressure plus the additional external pressure which is done either by mechanically or by inserting a inert gas. However, this pressure which we are keeping on the liquid by the inert gas or say through the piston will be this delta P will be much higher than the change in the vapor pressure itself meaning the P star to P that change will be very little compared to the external pressure.

So, we can always write this or approximate this under that condition. So, the upper limit will set it as P star plus delta P and then we can easily integrate this equation you can see that we will have if I just bring this RT part here. So, we could write that in this case it will be from this integration we are writing the right hand side first it will be ln P by P star because there will be an RT, but the temperature was constant we are only considering the effect of pressure and then that will be equal to V m. If we consider that the molar volume did not change during that process and of course, the molar it is a molar volume of liquid and which does not change too much over pressure that is why you are considering it to be constant although it is not a exactly constant and then since we made it P star plus delta P and P star. So, the integration is simply just delta P.

So, we can just rewrite you can just put this RT here and right instead of the logarithmic form as an exponential form. So, that we can get the pressure of the gas or the vapor which means actually the final vapor pressure is the initial vapor pressure times e to the power V m of the liquid phase into delta P divided by RT. So, this is a variation of the pressure, but the initial pressure was P star with respect to or this is basically how the pressure of the vapor pressure will change if we apply an external pressure which is delta P. So, as you can see that if we keep on applying the pressure which is delta P the which is coming through the P star or through the inert gas we see that the pressure of the vapor pressure actually increases exponentially. So, it is a huge increase we can create in the vapor pressure.

So, here always keep in mind that we got this equation by making this assumption which is a fair enough assumption because the external pressure which we were exerting is much more than the little change in the vapor pressure which was caused by vaporizing the liquid more by applying the external pressure. Now, let us consider another interesting application where we will talk about.

Now, the variation of the Gibbs free energy for, say two phases where the phases we denote as say alpha and beta. Now, as before we already discussed the phase boundaries and other things we showed you the diagrams for phase transition. So, we will now try to again give a explanation from the Gibbs free energy point of view what about phase boundaries, how they will look like? Will they look like a they will for various are linearly or there will be a some non-linear variation or the how will be the explicit nature of these curves.

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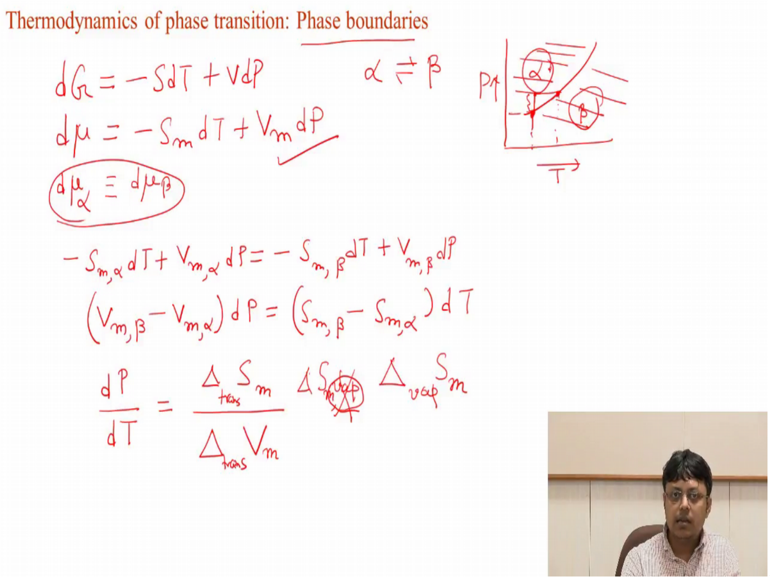

Thermodynamics of phase transition: Phase boundaries

$dG = -SdT + VdP$

$\alpha \rightleftharpoons \beta$

$d\mu = -S_m dT + V_m dP$

$\boxed{d\mu_\alpha \equiv d\mu_\beta}$

$-S_{m,\alpha} dT + V_{m,\alpha} dP = -S_{m,\beta} dT + V_{m,\beta} dP$

$(V_{m,\beta} - V_{m,\alpha}) dP = (S_{m,\beta} - S_{m,\alpha}) dT$

$\frac{dP}{dT} = \frac{\Delta_{trans} S_m}{\Delta_{trans} V_m}$ $\Delta S_{m\,\cancel{vap}}$ $\Delta_{vap} S_m$

So, to understand that let us first start with our original equation as you know that it is minus SdT plus VdP and similarly, we could write because we are right now using the language of a chemical potential. So, instead of chemical Gibbs free energy we can write actually chemical potential per unit Gibbs free energy per unit mole which is nothing, but the chemical potential. So, the corresponding equation for chemical potential will be nothing, but by dividing both side here by the number of moles. So, it will be minus S m which is the molar entropy plus it will be V m which is the molar volume.

Now, at equilibrium suppose there are two phases one phase I call as alpha and the other phase I call as beta this alpha and beta are in equilibrium and so at equilibrium the change in alpha phase must be compensated by an equal change in the beta phase. So, that is the condition for equilibrium. So, this is the condition when we are sitting on those lines those lines which separate the phases, that is very important meaning suppose I have an arbitrary line suppose this is the phase boundary in the pressure temperature plot and where one phase exists as alpha one phase exist as beta and the question is if I increase the pressure suppose initially I had at some pressure say this pressure and this temperature where the point was lying on the phase boundary.

Now, if I increase the pressure I have to also increase the temperature to again go to the same condition where basically the chemical potential of alpha and beta are equal. So, the chemical potential of alpha and beta are equal only along this line in this region the chemical potential of alpha is lower than beta in this region or in these special temperature combinations the chemical potential of the beta is lower that is why beta is the more stable phase here and alpha is the more stable phase here and on the line the chemical potentials are just equal. So, we are talking about phase boundaries of the lines. So, that underlines the chemical potentials are equal and let us just use the equation which we just wrote for chemical potential. So, we can just write say I am writing the first alpha phase. So, minus S molar volume for alpha dT plus the molar volume of alpha dP should be equal to minus S molar entropy of the beta phase into dT plus molar volume of the beta phase into dP.

So, you can just recollect all the S m's and S alphas sorry V m's together and we can easily get I am writing the equation for the first. So, say V m beta minus V all I was writing m first V m alpha. So, the difference in the molar volume in the beta and alpha phase times dP will be equal to S m beta molar entropy in the beta phase minus molar entropy in the alpha phase into dT or we could write that dP dT, because dP dT is nothing, but the slope of this curve when the equilibrium is attained is nothing, but the change in the entropy or the molar entropy in that particular transformation divided by change in the molar volume in that particular transformation.

Now, usually suppose you are talking about say vaporization process, but the liquid is going into the vapor. So, then we can actually use or subscript as vapor, but we cannot write it as S vapor because it is meaningless. It is a vaporization is a process which means the it is it happens during the transformation. So, what we write instead will write this transformation as with a small suffix that it is delta vaporization of S will not like delta s vaporization and we will use the molar sign. So, in general, we are just writing it as a crumbs meaning it is some transformation for vaporization it will be we will just use it as vap from denote or it can be sublimation it can be any other process.

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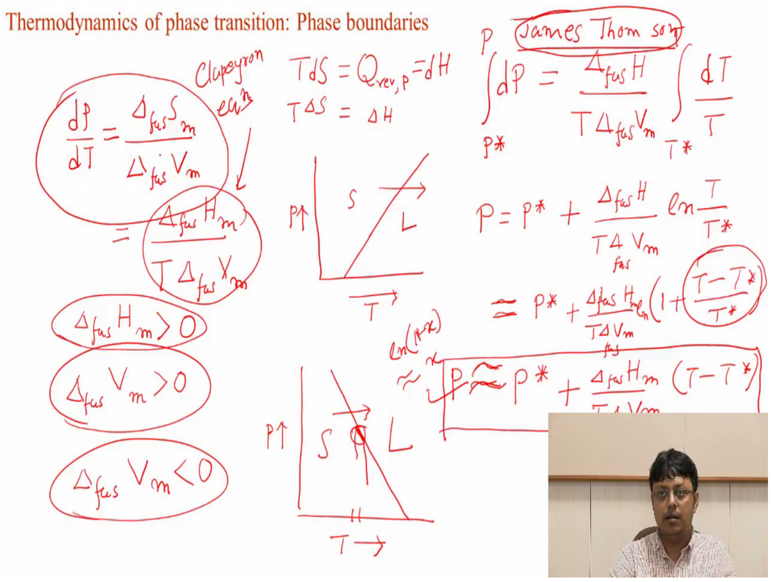

Thermodynamics of phase transition: Phase boundaries

Now, what we ultimately get from this for example, suppose we are talking about solid to liquid transformation which is nothing, but known as fusion. Now, when we talk about fusion then this quantity dP dT is nothing, but delta fusion S divided by delta fusion of V and these are all molar quantities, but remember that if the if we do a phase transformation at constant pressure then TdS is nothing, but the Q reversible and which in this case since it is a constant pressure process it is nothing, but the enthalpy associated with that.

So, instead of writing the S we could actually write it as delta S, T delta S will be nothing, but delta H. So, we can use this relation and write instead of delta S will be writing as delta H by T. So, it is delta fusion of the change in enthalpy due to fusion divided by the corresponding change in the molar volume and in this case it is molar entropy a molar enthalpy. So, as you can see that usually this delta fusion of this quantity has to be greater than 0, because whenever you are doing say solid to liquid which is a fusion process it will melt and then actually the heat content of the associated enthalpy change will be more because you are supplying heat to the system.

Similarly, the molar volume are any change in the fusion that is now, interesting quantity when you go from solid to liquid whether the molar volume is increasing or decreasing something like we discussed just before that if I apply pressure how it will look like and we showed that in the new versus t curve that for water were actually the opposite trend has happened the freezing point actually drops from the actual freezing point if we apply more pressure. In this case, we are now, trying to plot it in the pressure temperature plot where usually we show all the phase transformations instead of showing it on the mu versus T plot we are showing it on the P versus T plot which and remember that all the phase diagrams are drawn in pressure versus temperature plot where we get all the critical points a triple points and many other interesting thing. So, now, it depends on whether this thing is positive or not if this is positive then the slope of the curve which is dP dT will be a positive. So, I have solid here I have liquid here and this is a pressure versus temperature curve.

So, this is observed when for example, for carbon dioxide which we just discussed that solid liquid phase boundary was a had a positive slope which means dP dT was 0, which means actually the change in the molar volume going from solid to liquid was actually positive. However, for water we had just the opposite situation and remember that delta H fusion is always positive for if it is for carbon dioxide or for water because you are doing a melting process when you are supplying it. So, that has to be positive, but for water this will be just opposite. So, what we will have is something like this, but the solid exists here liquid exists here and going from solid to a liquid you see a negative slope. So, we see a very interesting behavior when you talk about solid to liquid transition for any system.

Now, think about an interesting situation for this transformation which we are right now talking about the fusion process we could also integrate the equation which is dP dT is delta H fusion divided by T into delta V fusion you should not call it as a delta V fusion it means actually delta fusion of V m. So, if we want to write it or integrate it we can easily do it. So, suppose we had an initial pressure which is P star going to a final pressure which is P, and then we have the say for example, vaporization or fusion whichever process we are considering divided by here we will have T into delta fusion into molar volume and usually or during the change of the transformation we are assuming this is more or less constant meaning this change is not the slope of the curve it is positive or negative.

But, it is a very steep slope, in the sense it is not changing too much and then we can integrate it this is nothing, but dT over T say the temperature is going from T to T star to T and then what we have here is P is nothing, but equal to P star plus we have actually taken P minus P star and move to P star in the other side and we have that the fusion change in enthalpy due to diffusion and change in the molar volume due to fusion and we have ln T by T star, but since we are considering only as say for is small change in temperature suppose we are considering only this much change and asking what is the change of the curve dP dT here. So, then we can or what is the slope of the curve dP dT here. So, we can say that we can make an approximation we can write ln x if x is small or if the x is small. In fact, we can write ln 1 plus x as almost equal to x. So, that condition will just apply.

So, we will we are just writing it very cleverly as delta fusion H divided by T into delta fusion V m and within the ln where just writing it as 1 plus T minus T star divided by T star. So, basically we added 1 and subtracted 1 and then we can easily write it. So, this is my x right now. So, we could write it as basically P is nothing, but P star plus delta fusion H which is a molar quantity and T into delta V fusion or sorry it will be delta fusion fee molar quantity and which is multiplied by T minus T star. So, this is a very interesting equation which was actually put forward by Thomson, but it is not William Thomson or Lord Kelvin it is basically John Thomson which is the brother of William Thomson was the brother of William Thomson.

So, we see that this is a very interesting equation where we can actually talk about how the pressure changes during the process of fusion when the solid is going into the liquid. Now, as I have drawn here you can see already we have drawn it as a linear, but the linearity is only an approximation. So, the curve actually is non-linear, but over a small range of temperature you can approximate it is linear. So, we showed that this change in the volume or the molar volume is can be positive or negative depending on the substance for ice it is negative for carbon dioxide it is positive. So, the solid liquid phase boundary at the solid liquid phase boundary the slope of the curve is positive for carbon dioxide, but negative for water.

Now, just like we discussed the vapor sublimation process or fusion process not the sublimation process it is a fusion processes is going from solid to liquid sublimation is going from solid to vapor. So, we can also talk about sublimation in the similar way. So, let us. Now, talk about the vaporization process where basically the liquid is going into the vapor. Now, all we are going to do is the same treatment, but for we. Now, have one phase which is vapor phase and we can just use the ideal gas equation and that is the purpose of doing this thing.

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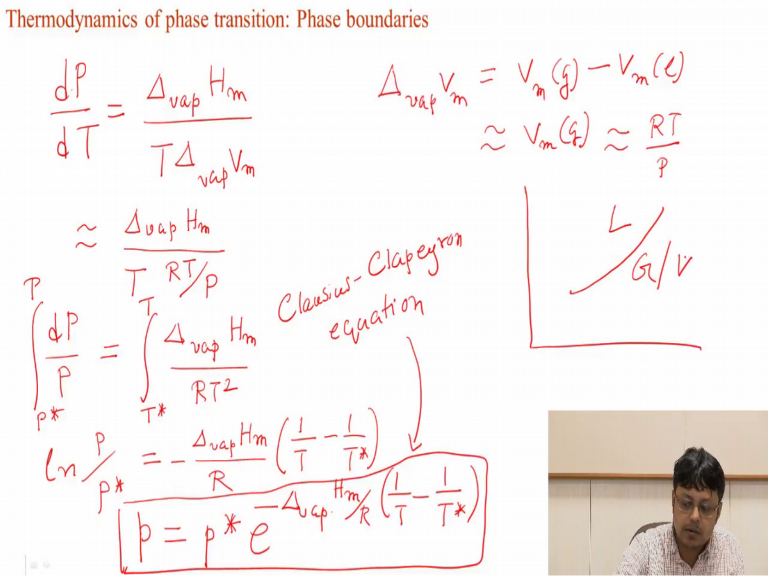

Thermodynamics of phase transition: Phase boundaries

$$\frac{dP}{dT} = \frac{\Delta_{vap} H_m}{T\Delta_{vap} V_m}$$

$$\approx \frac{\Delta_{vap} H_m}{T \; RT/P}$$

$$\Delta_{vap} V_m = V_m(g) - V_m(l) \approx V_m(g) \approx \frac{RT}{P}$$

$$\int_{P^*}^{P} \frac{dP}{P} = \int_{T^*}^{T} \frac{\Delta_{vap} H_m}{RT^2}$$

$$\ln \frac{P}{P^*} = -\frac{\Delta_{vap} H_m}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

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

Clausius-Clapeyron equation

So, what we are going to do is dP dT which is delta vaporization as before we are using the similar notation divided by T into delta vaporization V m and now, this delta vaporization think about it. What is that change in the molar volume due to vaporization this is nothing, but the molar volume of the gas or vapor minus the molar volume of the liquid and since the more volume of the gas is much larger than the molar volume of the liquid we can just approximate it to be the molar volume of the gas itself.

So, we can write it further assuming that it is behaving as an ideal gas we can write it as delta of molar enthalpy change for vaporization divided by T and then this quantity we can further approximate as RT by P it is a molar quantity that is why I am writing RT by P not NRT by P you could write it as RT by p. So, this P will go into the denominator in the numerator here, so, denominator on the left hand side. So, we can easily figure out. So, it will be dP by P is delta vaporization H m divided by RT square.

So, as before we can integrate from some initial pressure which is P star corresponding to a temperature T star going to a pressure P and temperature T and the left hand side will be ln P by P star right away and the right hand side is now, delta vaporization H m divided by R and then there will be a integration of one over T square is a minus 1 over

T. So, I will have a minus sign here and I will have 1 over T minus 1 over T star or you could include the minus sign inside and write 1 over T star minus 1 over t.

So, then we found a very interesting equation that how the pressure varies with respect to change in temperature and it is nothing, but e to the power of minus delta vaporization molar volume divided by R times 1 by T minus 1 by T star. Now, this equation is known as Clausius Clapeyron equation. In the earlier case, when we talked about the fusion process remember we also got a similar equation here dP dT and this equation was named as Clapeyron equation.

The Clapeyron equation talks about the melting process or the fusion process and it talks about the slope and we saw that it goes as P is equal to P star into delta H divided by T into delta V into T minus T star. So, it is a linear live adding with your temperature. But, when a moment to introduce the gas since we are using an ideal gas equation where actually the pressure is inversely proportional to the volume and that leads to a very interesting situation and we can actually plot the Clausius Clapeyron following the Clausius Clapeyron equation how it looks like. So, the liquid vapor boundary look like something like this. So, it will be liquid and it will be the gas or the vapor.

So, together you can think of that if we want to write it the all the different transformations which is melting or fusion then vaporization and also there is sublimation, but for sublimation it will be similar like the melting because it is between two condensed phases as we it is not between two conferences which is from one condense phase going to the gas phase. So, just like our treatment of Clausius Clapeyron equation which is going from liquid to the vapor. If we consider the solid to the vapor then you will also see that for the vapor phase we can again write the write it in terms of the ideal gas equation and then we will get a logarithmic relation which means actually we will get an exponential function for change in pressure as a function of temperature.

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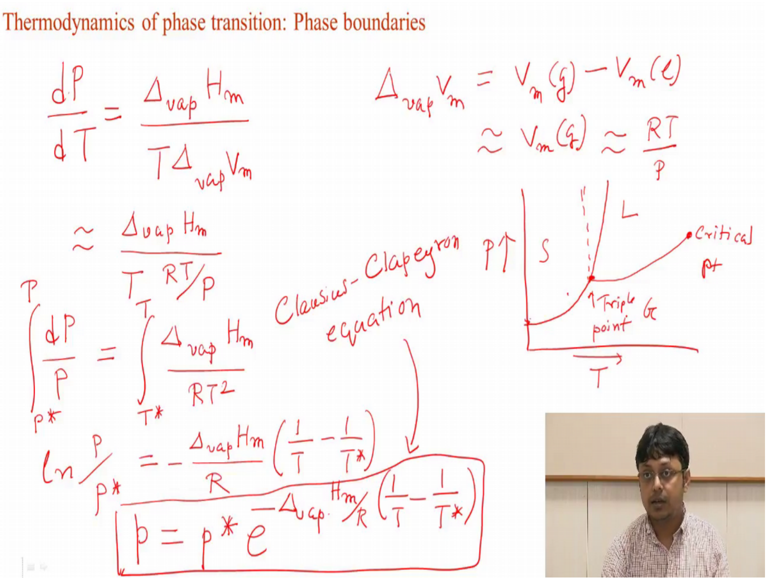

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Clausius-Clapeyron equation

$$\ln \frac{P}{P^*} = -\frac{\Delta_{vap} H_m}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

$$\boxed{p = p^* e^{-\Delta_{vap} H_m / R \left(\frac{1}{T} - \frac{1}{T^*}\right)}}$$

So, if following the Clausius Clapeyron as well as the Clapeyron equation, if we want to plot the pressure and the temperature at very low temperature of course, in this case the usually the solid form will be the more stable and this will be the solid form and this will be the gas situation because that have it is very high temperature and in between you will have the liquid phase and initially from solid to gas it should be something like an exponential thing. We have not discussed it is the sublimation process.

But, it follows the same logic just like between gas and liquid it will be similar and then the triple point will reach and then there will be a solid to gas equilibrium and we are also the we will we will get a similar exponential like behavior, but it will be slightly more flatter in the sense this curve will be slightly more steep this solid to gas because the reason is there is a huge change in the from going from solid to gas and then between the solid and liquid the slope will be almost linear and it will be positive if the change in the more volume going from solid to liquid is positive or it could be slightly negative something like we discussed for water. So, then this will be the critical point and this will be the triple point.

So, we see that using a very interesting or very lucid thermodynamic argument starting from the Gibbs free energy change at constant pressure and temperature we get the conditions for equilibrium and then we ask this question how basically if we vary the pressure or temperature how the Gibbs free energy per unit voltage is the chemical potential changes.

And, based on that argument we try to calculate the quantity how the pressure changes with temperature as we make the phase transformation which means how the phase boundaries or the how what are the equations for the phase boundary. So, all these equations are the Clapeyron equation or the Clausius Clapeyron equation describe the equation of these curves which curves those curves which separate the phases or separate as our acts as a boundary between the different phases.