

# Thermodynamics And Kinetics Of Materials

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## Lecture 19

### Phase equilibria and phase transition in unary systems 3

So, as you can see that delta mu or the chemical potential difference is in the last lecture as we were discussing is a function of the chemical potential difference delta mu here is a function of the driving force d equals to minus delta mu. So, driving force is minus delta mu and delta mu is a function of T and P and as you can see when I simplify I take delta Cp which is the delta Cp is the heat capacity difference between alpha phase and beta phase.

$$\Delta\mu(T,P) = (\Delta C_p - \Delta S^\circ)(T - T_{tr}) - \Delta C_p T \ln \frac{T}{T_{tr}} + \Delta S_m^\circ (T - T_{tr})$$

$$\Delta T = T - T_{tr}$$

$$\Delta t = t - t_0$$

$$\Delta\mu = \left[ \Delta C_p - \Delta S^\circ \right] \Delta T - \Delta C_p T \ln \left( 1 + \frac{\Delta T}{T_{tr}} \right) + \Delta S_m^\circ \Delta P$$

$$\text{Let } \frac{T}{T_{tr}} = x$$

$$\frac{x}{T_{tr}} = \frac{T}{T_{tr}}$$

$$dx = \frac{1}{T_{tr}} dT$$

$$\Delta\mu = \left[ \Delta C_p - \Delta S^\circ \right] \Delta T - \Delta C_p T_{tr} \int_{T_{tr}}^T \frac{1}{x} dx + \Delta S_m^\circ \Delta T$$

$$= \left[ \Delta C_p - \Delta S^\circ \right] \Delta T - \Delta C_p T_{tr} \left[ \ln x \right]_{T_{tr}}^T + \Delta S_m^\circ \Delta T$$

$$= \left[ \Delta C_p - \Delta S^\circ \right] \Delta T - \Delta C_p T_{tr} \ln \left( \frac{T}{T_{tr}} \right) + \Delta S_m^\circ \Delta T$$

$$\Delta S^\circ = \frac{\Delta H^\circ}{T_{tr}}$$

$$\Delta G_m = \Delta H_m - T \Delta S_m$$

$$\Delta G_m = 0 \quad \text{at } T = T_{tr}$$

$$\therefore \Delta H_m = T_{tr} \Delta S_m$$

$$\Delta C_p \Delta T - \Delta C_p T \frac{\Delta T}{T_{tr}}$$

$$\Delta C_p \Delta T \left( 1 - \frac{T}{T_{tr}} \right) = - \frac{\Delta C_p (\Delta T)^2}{T_{tr}}$$

$$\Delta\mu = - \left[ \frac{\Delta H^\circ + \Delta C_p \Delta T}{T_{tr}} \right] \Delta T + \Delta S_m^\circ \Delta P$$

So, I am considering the alpha to beta transformation just giving a quick reprise and then also there is this delta S0 delta S0 is the difference entropy at the standard state standard state is defined by zero superscript is defined by a transformation temperature. Transformation temperature is the temperature at which alpha beta in equilibrium and also there is T minus TR, there is T minus TR this TTR basically is the transition temperature this is the transition temperature at which alpha and beta are in equilibrium alpha and beta are in equilibrium when we write alpha and beta in equilibrium we use this symbol reversible symbol right. And you have also if you when you did the algebra you could get delta CP TL and T by TR now if you see delta T is T minus T TTR or T minus T transmission temperature means there is a transmission temperature so this is TTR which is the transmission temperature and this is some temperature away from the transmission temperature but if delta T is small then this ln term can be approximated further. So for example I can write T minus TR by TR so T minus TR by TR if I do then basically I can write this ln 1 plus delta T by TR and then it is a logarithm and this is very small so basically I can expand on the expand this logarithmic series about this delta T by TR means

$T$  and the subscript is  $T_R$  right so  $T$  which is the transmission temperature so  $\Delta T$  is the means how far away is my temperature from the transmission temperature now if this  $\Delta T$  that is the deviation from the transmission temperature is small then I can use this  $\ln(1 + \Delta T / T_R)$  so basically  $T$  by  $T_R$  is written as  $1 + \Delta T / T_R$  and then basically I am taking only the first part of it right so basically the first part is  $\Delta T / T_R$  and right  $T$  transmission so  $\Delta T$  by  $T$  transmission and so that is what I have done so I can remove the  $\ln$  part right and you have the  $\Delta V_m^0$  that is again  $0$  basically denotes the standard that is the standard means the standard state here the standard state here is taken to be the transformation temperature  $T_R$  and say some  $P^0$   $P^0$  is the standard pressure  $P^0$  can be 1 bar 1 atmosphere whichever you want to so you can take some  $P^0$  and you can take the transformation temperature itself right to define the standard state or the  $0$  right it's the superscript if you look at the superscript  $0$  superscript  $0$  stands for transmission temperature and  $P^0$  pressure right now as you know  $\Delta$  is  $0$  that is the it's the difference in entropy of alpha and beta between alpha and beta difference entropy between alpha and beta in the standard state is related to the difference in enthalpy by the transmission temperature  $T_R$  right so and as we know that we can basically write this as I told you that we have only the we have taken only the first term so basically  $\ln(1 + X)$  is  $X$  plus  $X^2$  by  $2$  factorial plus so on but I am taking only  $\Delta T / T$  transmission because  $\Delta T / T$  transmission is very very small because the difference that the  $\Delta T$  that I am taking is  $\Delta T$  is really really small right so it's a very small deviation from the transmission temperature so as a result  $\Delta T / T$  transmission is very small right we can only take the first the we can take the first order term right first order term is the power 1 right so this is what I have done and if I take that I can simplify further that's what I was telling simplify further and then and if I simplify further I already have a  $\Delta T$  here and here again  $T_R - T$  is  $\Delta T$  but there is a minus sign because  $T - T_R$  is  $\Delta T$  so  $T_R - T$  is minus  $\Delta T$  so this becomes  $\Delta T^2$  whole square by the transmission temperature  $T$  remember this is  $T_R$  so this is something so this  $T_R$  is the transmission temperature or the temperature sometimes  $T_R$  can be replaced by  $T_b$  boiling  $T_b$  which is basically the boiling point which is basically the equilibrium between the liquid phase and the vapor phase or it can be melting point which is the equilibrium between the solid phase and the liquid phase so in this way I can basically write  $\Delta \mu$  as a function of  $\Delta H$  naught  $\Delta H$  naught is the enthalpy of transmission difference in the enthalpy of transmission right at the standard state calculated at the standard state and the difference in heat capacity right there is a difference in heat capacity and then there is this  $\Delta T$  and this is  $T$  transformation right so and then there is also  $\Delta V_m^0$   $\Delta P$  right so this is how we can calculate  $\Delta \mu$  and from  $\Delta \mu$  I can calculate the driving force because driving force is proportional to  $\Delta \mu$ .

ORDER OF A PHASE TRANSITION  $\alpha \rightleftharpoons \beta$

$$\left(\frac{\partial \mu^\beta}{\partial P}\right)_T - \left(\frac{\partial \mu^\alpha}{\partial P}\right)_T = V_m^\beta - V_m^\alpha = \Delta V_m^{tr}$$

$$\left(\frac{\partial \mu^\beta}{\partial T}\right)_P - \left(\frac{\partial \mu^\alpha}{\partial T}\right)_P = -S_m^\beta + S_m^\alpha = \Delta S_m^{tr} = \frac{\Delta H_m^{tr}}{T_{tr}}$$

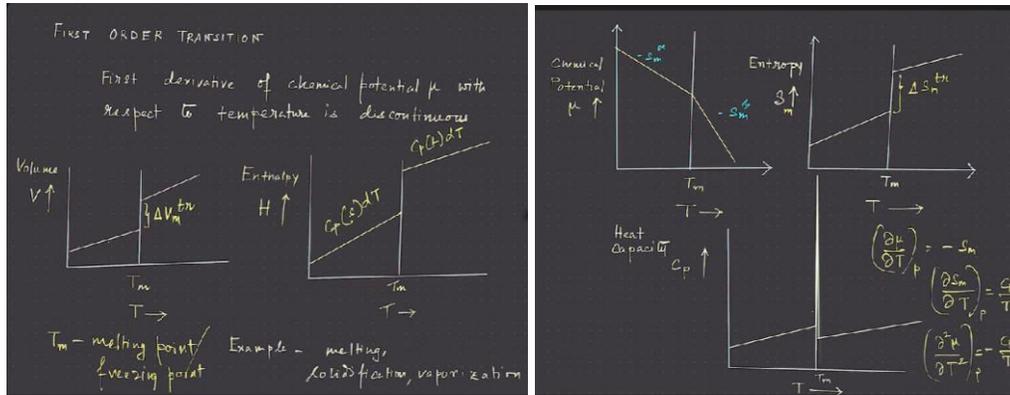
$\Delta V_m^{tr} \neq 0$   
 $\Delta H_m^{tr} \neq 0$

} melting,  
 vaporization,  
 solidification

Now I will come to a very interesting concept which is called order of a phase transition right order of a phase transition again I am considering a phase transition from alpha to beta or beta to alpha beta can be the liquid phase alpha can be solid phase right alpha is say for example alpha is solid beta is liquid then the phenomenon that we are talking about is melting again if it is alpha is the liquid phase and beta is vapor phase then the phenomenon that we are talking about is boiling or evaporation okay or alpha is solid and beta is say vapor then it is like we are talking about sublimation. So now as you can see here mu beta represents the molar free energy of the beta phase for a unary system right mu beta represents the molar free energy of the beta phase for a unary system and mu alpha denotes the molar free energy of the alpha phase for a unary system now if you see del mu beta del P minus del mu alpha del P is nothing but molar volume of beta the difference in molar volume of beta between molar volume of beta and molar volume of alpha molar volume of beta can be more or less than the molar volume of alpha and that we can think of delta Vm and this delta Vm at the transformation temperature right at the this is like a delta Vm due to transformation so this is delta Vm due to transfer the phase transition that has taken place so delta Vm with superscript here I am indicating that similarly I can look at the variation of this molar free energy with respect to temperature so for each phase so you have del mu beta by del T as a at a fixed pressure minus del mu alpha by del T at a fixed pressure which is nothing but minus Sm beta plus Sm alpha which is again delta Sm transformation or delta Sm transition now this delta Sm is again related to the the enthalpy of transformation that is delta Hm the molar enthalpy of transmission divided by the the transition temperature transition temperature so this is the transition temperature this is the enthalpy of transmission that is the heat that is means absorbed or given out during transmission from one phase to another now as you know that the delta Vm transmission is not equal to 0 whether you are considering melting vaporization or solidification similarly delta Hm transmission is not equal to 0 right all of these are not equal to 0 right so if you look at that you will see one very interesting one very interesting

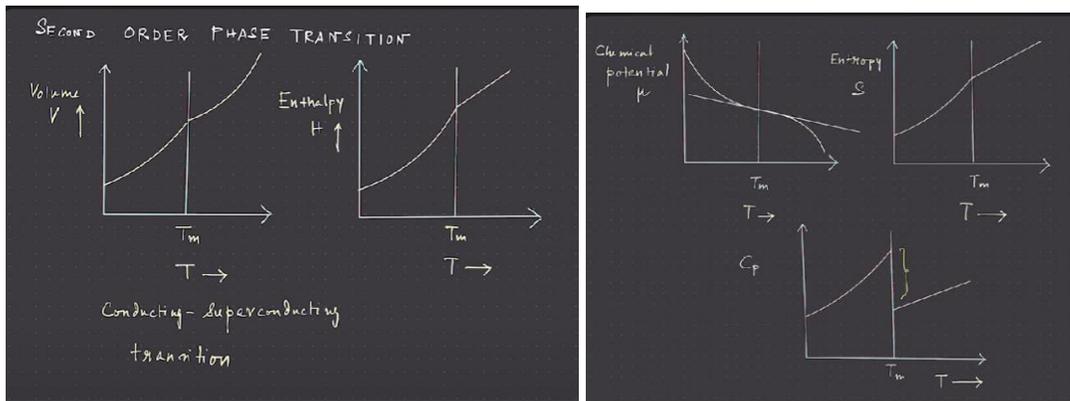
point means when you plot them for example volume if I plot volume versus temperature now you see this C is like the alpha phase say  $T_m$  is your melting point  $T_m$  so I am telling  $T_m$   $T_m$  is your melting point so I am talking about a melting transition or a solidification transition so  $T_m$  can be defined as a melting point or freezing point you can also call it freezing point now if you see this is your molar volume before transition right this is the alpha phase this is your alpha phase and this is your beta phase and see at this transition what has happened is that molar there is a  $\Delta V_m$  which is nonzero right this is  $\Delta V_m$   $T_r$  right this is the or  $\Delta V_m$  melting okay so basically this is the  $\Delta V_m$  transition or  $\Delta V_m$  melting it is better to write  $\Delta V_m$   $T_r$  so this is not 0 but you see a discontinuity here so you are seeing a discontinuity in the volume okay you are seeing a discontinuity of volume when you go from when there is this transformation so this is the alpha phase and this is the beta phase or you can think of this as the solid phase and this as the liquid phase and as you can see that there is a jump right there is a jump at the transition temperature or the melting point similarly for enthalpy so for enthalpy see for example here so from some temperature have start now in this case what I am talking about is like it is like a  $\Delta H = C_p dT$  so here we can think of this as  $C_p dT$  now once you have reached the melting temperature there is no sensible heat there is no  $C_p dT$  there is no rising temperature right so basically what has happened is you are at  $T_m$  but now you are changing the phase that is solid so this is say for example  $C_p$  s so if I think of this this is basically  $C_p$  s that is solid phase  $dT$  and this goes up to the transition temperature now at the transition temperature again there is a jump and you get say  $C_p$  l right so you see here the first derivative of chemical potential right the  $H$  is or  $V_m$   $V_m$  or  $\Delta H$  these are all first derivatives of the chemical potential or first derivatives of the molar free energy and those are discontinuous those show discontinuity right so basically if you think of this this is the solid phase then this is  $C_p$  s  $dT$  until the transition temperature then there is a jump and that jump is basically  $\Delta H_m$   $T_r$  which we also call as latent heat right latent heat of transition or heat of transition and then you have  $C_p$  l  $C_p$  l right so look at the enthalpy here so if you see here I am taking that it is  $C_p$  s and here it is so basically the enthalpy is increasing right so for example liquid has more heat content because liquid freezes to solid then it gives out heat right if liquid freezes to solid so we can easily understand that the liquid phase will have more enthalpy or heat content than the solid phase however if you look at the chemical potential of the free energy itself only thing that you see is that it varies a function of temperature this way but the slopes are basically corresponding to this corresponds to say  $S_m$  alpha this corresponds to the slope here corresponds to say  $S_m$  minus  $S_m$  alpha and this is minus  $S_m$  right so basically and again this is s by now if you look at the entropy now if you look at the molar entropy  $S_m$  let us call it  $S_m$  then again you have this discontinuity right this is the entropy of transformation right so where the first derivative shows this discontinuity the first derivative of the molar free energy of first derivative of chemical potential so jump then that those transformations are called first order transformations right those transitions

are called first order transitions now first order transitions example melting solidification vaporization right so these are so these are all examples of first order transition where you will see later there is a theory called Landau theory means which



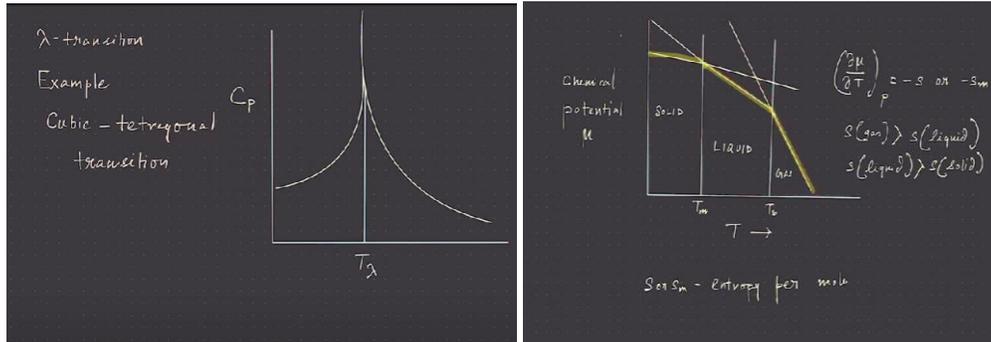
I'll talk about in the later means much later and there you also you can see a further discussion on this first order transition with a first order transition and second order transitions and higher order transitions now if you look at the first order transition what I told first derivative of the first derivative of the molar free energy or first derivative of chemical potential will be discontinuous right as you can see that  $S_m$  if you look at the change in  $S_m$  if you look at the change in  $H_m$  or if you look at the change in molar volume you will see that there is a first derivative these are first derivatives we molar volume is first derivative with respect to pressure enthalpy or entropy first derivative with respect to temperature so these show discontinuities now what about  $C_p$   $C_p$  as you know  $\Delta H = \int C_p dT$  so  $C_p$  will show so at the discontinuity there will be a very sharp rise in the heat capacity right it will basically go as very to very large value right there we are this because this is a discontinuity so it basically goes to as high as infinity right so there is a very large  $C_p$  at the transition temperature here the melting point so here if we look at melting points and  $C_p$  goes very very high as you can see here the  $C_p$  is varying like this and then suddenly it shoots up like this and then it comes back and it follows this so at the melting temperature you can see there is a  $C_p$  is the second derivative right this is the second derivative we have shown that right  $\Delta \mu = \int \left(\frac{\partial \mu}{\partial T}\right)_P dT$  for example  $\left(\frac{\partial \mu}{\partial T}\right)_P = -S$  and  $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$  so  $\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P = -\frac{C_p}{T}$  because this is something that we have discussed that  $\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P$  is basically going to be so if I look at  $\left(\frac{\partial \mu}{\partial T}\right)_P = -S$  and  $\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P = -\frac{C_p}{T}$  at constant pressure because  $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$  and I can think of this as  $-\frac{\partial S}{\partial T} = -\frac{C_p}{T}$  which is equal to  $-\frac{C_p}{T}$  but there is a minus so this is basically this is a minus sign  $\left(\frac{\partial \mu}{\partial T}\right)_P = -S$  so this is minus  $C_p$  by  $T$  right there will be a minus sign here this is something that we have shown earlier also so do not forget the minus sign because there is a minus sign here and as you know  $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$  the  $\left(\frac{\partial S}{\partial T}\right)_P$  temperature is here capital  $T$  temperature is no and at constant pressure this is equals to  $C_p$   $C_p$  is molar heat capacity by temperature right so basically  $\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P = -\frac{C_p}{T}$

square again at constant pressure is minus of  $C_p$  by  $T$  right so and at  $T$  equal to  $T_m$  as you can see it basically shoots up right it shoots up to a very large value now if you look at second order phase transition so second order phase transition means it is not like melting or melting is a first order transition then evaporation is a first order transition sublimation is a first order transition but second order is like conducting to superconducting transition so if you think of superconducting transition this is an example of second order a transition what is a second order transition the volume versus temperature if you look at volume versus temperature you will see that the phase derivative is continuous first derivative is continuous right it is continuous here right



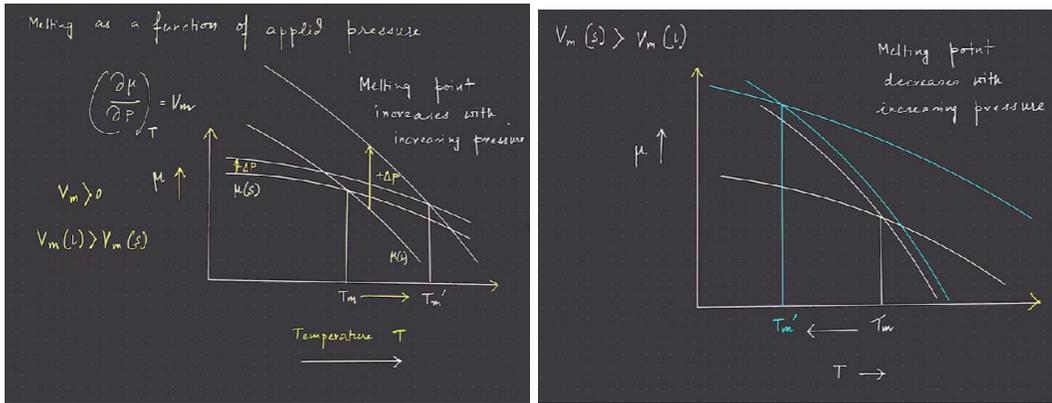
as you can see here it goes here and then goes up similarly there is a change but it is continuous right so enthalpy is continuous right molar enthalpy is continuous chemical potential as you can see here it varies this way very continuously so which tells you that the first derivative the slope the slope is this tangent this is also continuous right so entropy for example the change in entropy is continuous however if I look at the second derivative it shows discontinuity like  $C_p$  shows discontinuity so  $C_p$  there is a discontinuity so in second order phase transitions there is a discontinuity in the second derivative of chemical potential or molar free energy with respect to temperature right so if you can see here that the second derivative shows clear discontinuity and that corresponds to  $\Delta C_p$  right the  $C_p$  of the superconducting state and  $C_p$  corresponding to the normal conducting states right they are basically different there is an abrupt jump there but there is no abrupt jump for example in entropy of transmission or molar entropy of transmission or molar enthalpy of transmission or volume of transmission right there is no abrupt change there these are continuous but  $C_p$  shows a abrupt change right she's simply as you can see here by the nature of the slope that the slope changes right slope changes from one point to the other point so there is a change in slope but the but although there is a change in slope it is continuous but  $C_p$  becomes discontinuous because of this small kink here right if you see the kink here at the transition temperature and small change here this change itself is sharp so seems it is sharp this since this change is sharp that leads to discontinuity  $C_p$  and that is what characterizes a second order transition so some ferroelectrics also show this paraelectric to ferroelectric transition that are of second order right so there is yet

another transmission and first basically classified it so it's called a lambda transition is called a lambda transition lambda transition



for example it is like a cubic so basically you have a cubic crystal then you it cubic crystal means crystal with cubic symmetry it undergoes symmetry breaking and becomes a tetragonal means it becomes a tetragonal crystal that is there is a symmetry breaking in terms of the the crystalline symmetry has broken to tetragonal from cubic it has broken to tetragonal right one of the say cubic for example has three fourfold rotations but tetragonal will have only one fourfold rotation right so basically there is a symmetry breaking and this type of symmetry breaking transition often is called a lambda transition because although the first derivatives are continuous the CP shows the change in CP it mimics very much of the first order transformation so it goes very high it goes to infinity at the transition temperature it goes very high the CP abruptly changed to very high to very high value means basically CP approaches infinity at  $T$  equal to  $T_\lambda$  and then again it falls back right so and it shows this lambda like appearance right it lambda basically is represent this right this is how we write lambda so this exactly this CP follows this lambda type of a curve where there is a shoot-up at the transformation temperature so we can basically now use this information so basically for you need evenary systems using this in the system thermodynamics we could classify different types of phase transmissions or phase transitions right so for example first order transition which is like melting evaporation etc then there is this conducting superconducting transition which is a second order transition but the second derivative is discontinuous and then there is yet lambda transition where first and second derivatives need not be discontinuous however lambda transition is a very special type of transition where CP although the first derivative is not discontinuous ship CP shows behavior which is very much similar to that of the first order transition okay so how does a chemical potential change as you can see that for example below  $T_m$  solid so if you look at the solid curve here if you look at the solid curve here this is your solid and then this is your liquid so liquid has a higher energy gases even higher energy so solid has the lowest chemical potential or solid has a lowest molar flow energy and therefore solid is extend then beyond  $T_m$  liquid becomes the lowest energy state right liquid becomes the lowest energy state and you go further above boiling point gas gaseous state becomes more and more favorable right so basically as you know  $\Delta \mu$   $\Delta T$  equal

to minus s or minus s m right and s gas is greater than s liquid and s liquid is greater than s solid in general right so all this basically as you can see the slopes also from the slopes you can see that is gas is much steeper than s solid for example right so the if you characterize the slopes here is one slope this is another and this is the other one and it's very very steep right so this is changing chemical potential



so I have just for simplicity I have drawn with approximated them using straight lines now think of melting as a function of applied pressure so you can see now if you know this change in chemical potential or change in molar fluid energy as a function of pressure at constant temperature which is equal to molar volume now think of different cases say for example when you have this is your  $\mu$  solid now see I have drawn a parabola here and I am also approximating with it a slightly curved it's like a parabola right so this this guy and this guy basically represents so this  $\mu$  solid is this one so basically below  $T_m$  below  $T_m$  solid has a lower chemical potential or molar free energy than the liquid right now let us assume that  $V_m$  liquid is greater than  $V_m$  solid now  $V_m$  liquid is greater than  $V_m$  solid and you know  $\frac{\partial \mu}{\partial P}$  which is the slope is equal to  $V_m$  now  $V_m$  liquid is greater than  $V_m$  solid right so basically if you look at that if I change if I change the pressure if I change pressure for example so I am increasing so this is my  $T_m$  this is an original  $T_m$  at say one bar okay the yellow lines correspond to this yellow lines basically these lines these ones this one and this one or this temperature corresponds to some some pressure but now if you think of this if I if  $V_m$  liquid is greater than  $V_m$  solid and the  $\frac{\partial \mu}{\partial P}$  at a fixed temperature for example at a fixed temperature will be  $V_m$  and  $V_m$  liquid is greater than  $V_m$  solid now as you increase pressure the the the shift in the liquid free energy or molar free energy will be much greater than that of the solid right because  $V_m$  solid is smaller than that of  $V_m$  liquid so the with increasing pressure so this is like increasing plus delta P with increasing pressure right plus delta P you will see that the solid energy that is the solid guy the solid free energy will shift much less right because  $V_m$  solid is small compared to the liquid now if that is so if I again draw this so if I again try to intersect them because the intersection point is the point where they have equal chemical potential that is  $\mu$  solid equal to  $\mu$  liquid so that is the that marks the transformation and that is that gives me the transformation temperature now you see if I increase pressure then this

curve shift to the right the intersection point shifts to the right it is shifting to the right that means that means with applied pressure melting point will increase if  $V_m$  liquid that is the molar volume of liquid is greater than that of solid molar volume of liquid is greater than that of solid then the the the the the the change in energy or change in chemical potential will be much steeper for the liquid than that of the solid as a result the melting temperature or the transition temperature will shift to the right right to the right of the original melting temperature so you say as I increase pressure it will shift to the right right so it will melt at a higher means it will so basically thus the solid will melt at a higher temperature now if right the solid will basically this melting temperature increases means solid will basically melt at a higher temperature so solid retains means it retains its solidarity means it remains solid Tila law means it remains solid beyond  $T_m$  right so if there is an increase in pressure on the other hand if you think of so this is the point so if you look at this now this is molar volume of solid and this is molar volume of liquid now I am thinking of molar volume of solid to be greater than that of liquid now think of one common example where molar volume of solid can be greater than molar volume of liquid if molar volume of solid is greater than molar volume of liquid what does it mean to density okay and we have done this example so please try to map so this ice water transmission so have a carefully have a look at it and see this this this very interesting phenomenon see here this  $\mu$  this is again the the molar for energy or the chemical potential that is plotted along the y-axis against temperature now if you see here the volume of solid right here the volume of solid volume molar volume of solid or volume per mole of solid is greater than that of liquid as a result the solid shift that say for example this is my original curve this is my original curve okay original solid free energy or solid molar free energy but now because the molar volume of solid is much higher than that of the liquid now with an increase in pressure if I have some pressure then the solid free energy will shift to a much higher value right solid range you shift more and the liquid energy will shift only slightly that this is the original liquid so this is the this yellow line represents the original liquid free energy curve and this is the slight change in the liquid free energy curve as a function of pressure right if the pressure is increasing this way then the that for each temperature right  $\Delta \mu / \Delta P$  at each temperature basically it will give a much smaller rise than the solid so if that is so now if you look at the intersection the original intersection was here now the intersection has shifted here so original intersection was at this temperature now it has shifted to this temperature right this temperature so this at this temperature so it has shifted here when it was originally here right when there is an increase in pressure so if the molar volume the solid is greater than that of the liquid then the melting point is depressed or melting point decreases with increasing pressure if I apply it more pressure the melting point will decrease right so this is very interesting very simple thing but you just have to apply your logic and you can understand that and remember when I am talking about  $\mu$  the slope is what is changing right the  $\Delta \mu / \Delta P$  that means at a fixed temperature the derivative of the chemical potential as a function of pressure is the molar volume and that molar

volume basically that means if you have a  $\mu$  versus  $T$  curve in this at each  $T$  the the the the at each  $T$  if you have a  $\mu$  versus  $P$  curve then the slope basically if you have a  $\mu$  versus  $P$  curve then the slope basically gives you  $V_M$  but here at each  $T$  think of this that the solid has more molar volume than liquid so as a result the solid curve will shift more right because see this is where say although if I draw  $\mu$  versus  $P$  then volume molar volume is a slope however when I am drawing  $\mu$  versus  $T$  then at each temperature at at each fixed temperature there is a change in molar volume if molar volume of solid is more than that of liquid obviously the magnitude shift of the solid will be much more than that of the liquid and immediately you can follow that any temp at any temperature if that happens then basically the inter the original intersection point starts shifting to the left right this is a very interesting and very very interesting conclusion of the discussion and of the property right that change in molar volume with respect to pressure at any given temperature is equal to the molar volume and if the molar volume of solid is greater than that of the liquid think of what what is the relation between densities again density see if you have a single component system or a pure system then your molecular weight remains the same and molecular weight by molar volume basically gives you density so if density if molar volume of solid is greater than that of liquid is the solid lighter than liquid or not and if that is so then in such a case how will the melting point change as you increase pressure right and the pressure increase is given by this arrows right so you can see the pressure increase is indicated by how much the free energy or how much the molar free energy will shift right the molar energy will shift slightly here for liquid because  $V_{ML}$  is much much smaller than that of solid and as you can see here that's why in such a condition the  $T_m$  shifts to the left right so for example think of this example quickly  $\rho_{ice}$  is 0.917 and  $\rho_{water}$  is 0.999 so as a result if you look at this  $V_m$  is now  $m$  by  $\rho$  now if you so if you if you look at the  $\Delta \mu$  of ice then  $\Delta \mu$  of ice basically you have  $\Delta \mu / \Delta P$  equals to  $V_m$  and  $\Delta P$  here I am taking 2 bar and 1 bar temperature I have taken as 0 degree Celsius pressure is increased from 1 bar to 2 bar right pressure is increased from 1 bar to 2 bar so basically the  $\Delta P$  the change in pressure is 1 bar right which is basically  $10^5$  Pascal's and  $\Delta \mu / \Delta P$  at any fixed temperature is equal to  $V_m$  and  $V_m$  is calculated from  $m$  by  $\rho$  so now  $\Delta \mu$  right  $\Delta \mu$  by  $\Delta P$  at any given temperature is equal to so it is at 0 degree Celsius we are looking at so  $\Delta \mu$  by  $\Delta P$  is equal to  $V_m$  right so  $\Delta \mu$  ice is basically coming out to be 1.

$\rho(\text{ice}) = 0.917 \text{ g/cm}^3$       Temperature =  $0^\circ\text{C}$   
 $\rho(\text{water}) = 0.999 \text{ g/cm}^3$       pressure: 1 bar  $\rightarrow$  2 bar  
 $M = 18.02 \text{ g/mol}$        $\Delta P = 2 - 1 = 1 \text{ bar}$   
 $= 18.02 \times 10^{-3} \text{ kg/mol}$        $\left(\frac{\partial \mu}{\partial P}\right)_T = V_m = 10^{-5} \text{ Pa}$   
 $V_m = \frac{M}{\rho}$   
 $\Delta \mu(\text{ice}) = \frac{18.02 \times 10^{-3} \times 1 \times 10^5}{917} = 1.97 \text{ J/mol}$   
 $\Delta \mu(\text{water}) = \frac{18.02 \times 10^{-3} \times 1 \times 10^5}{999} = 1.8 \text{ J/mol}$

Applied pressure on vapour pressure of a liquid

Assumption

- Dissolution of pressurizing gas in liquid is ignored
- Gas solvation or attraction of liquid molecules by gas phase molecules is ignored

Vapour pressure in absence of pressurizing gas =  $P^i$



97 joules per mole and that of water comes out to be 1.8 joules per mole and if that is so you find out what happens to the melting temperature right  $\Delta \mu$  ice there is a change in ice is the the change in chemical potential of ice is 1.97 while that of water is 1.8 so water basically increases slightly while ice changes by a lot of amount so basically in this case the melting temperature will shift to the left with increasing pressure now you can think of apply the same thing like applied pressure on the vapor pressure of a liquid and in that case you can think of assumptions like dissolution of see for example you have a pressurizing gas here so this is your pressurizing gas and there is a liquid and on the liquid there is this vapor because there is a liquid vapor equilibrium so there is so basically this space in the container contains the inert pressurizing gas plus the vapor but see we are neglecting this the dissolution of pressurizing gas in the liquid is neglect is ignored because if we do not ignore it dissolution of pressurizing gas can change the property of the liquid completely or the nature of the liquid completely also there is something called gas solvation or attraction of liquid molecules by gas phase molecules which is again being noted here right now if the vapor pressure in the absence of pressurizing gas is  $P^i$  if it is  $P^i$  I want to see if there is a pressurizing gas what happens to the vapor pressure so you have my applied pressure is  $\Delta P$  my applied pressure is  $\Delta P$  my original vapor pressure is  $P^i$  right  $P^i$  is my original vapor pressure in the absence of the pressurizing gas and again note the assumptions right now if you in such case at the liquid vapor equilibrium as you know  $\mu$  liquid has to be equal to  $\mu$  basically is the molar free energy of liquid has to be equal to the molar free energy of the gas right again it's a very unary system so  $d\mu$  that means the change in molar free energy of liquid or the differential change in molar free energy of liquid has to be equal to  $d\mu$  that of gas right so basically  $\mu$  liquid equal to  $\mu$  gas from here it follows from here it follows this relation follows now  $d\mu_L$  is  $V_m \text{ liquid } DP$  right  $V_m \text{ liquid } DP$  and  $d\mu_G$  is  $V_m \text{ gas } DP$  right now assuming the vapor to be an ideal gas if you assume the vapor phase the vapor phase on liquid to be then ideal gas often that's a valid assumption you will see that  $V_m$  can be written as  $\frac{RT}{P}$  it can be written as  $\frac{RT}{P}$  so if it is an ideal gas then obviously  $V_m$  is  $\frac{RT}{P}$  right so now you have the change in  $\mu$  for the gas phase which is  $\frac{RT}{P} DP$  which is equal to change

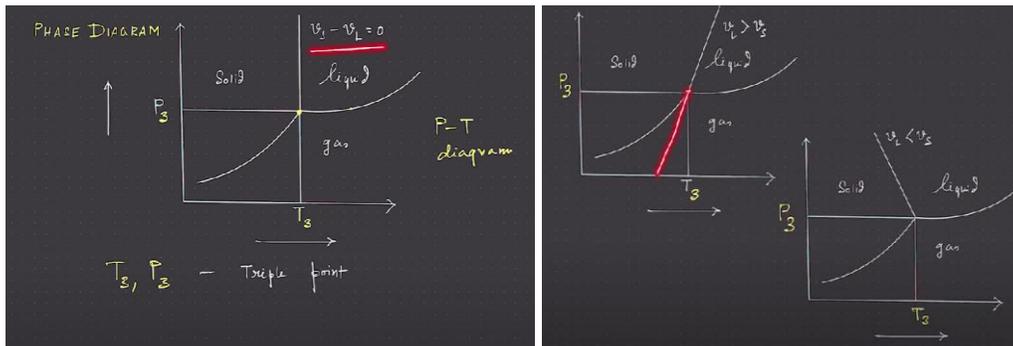
because at equilibrium it is equal to the change in molar free energy or chemical potential of the liquid phase which is equal to  $V_m \Delta P$  so basically you have  $V_m \Delta P$  let us assume that  $V_m$  does not change with pressure so  $P_1$  and this is  $P_1$  plus  $\Delta P$  right it starts with  $P_1$ ,  $P_1$  is original vapor pressure then there is the pressurized gas and that as a result the pressure above the liquid has changed to  $P_1$  plus  $\Delta P$  but here if you see  $P_1$  has gone to  $P$ ,  $P$  is basically so  $P_1$  has gone to some value  $P$  so if I look at this so basically  $\ln(P/P_1)$  is this equal to  $\Delta P / (RT V_m)$  right so you have an LN expression right here is a logarithm sign and here is this  $\Delta P$  and we know that  $\Delta P$  so as you can see the vapor pressure will increase by this amount  $P_1$  times  $e$  to the power  $V_m \Delta P / (RT)$  the molar volume of it is proportional to so it will exponentially vary

Applied pressure  $\Delta P$   
 At liquid-vapor equilibrium  
 $\mu(l) = \mu(g)$   
 or  $d\mu(l) = d\mu(g)$   
 $d\mu(l) = V_m(l) dP$   
 $d\mu(g) = V_m(g) dP$   
 Assume the vapor to be an ideal gas  
 $V_m(g) = \frac{RT}{P}$

$d\mu(l) = \frac{RT}{P} dP = d\mu(l) = V_m(l) dP$   
 $RT \int_{P_1}^P \frac{dP}{P} = V_m(l) \int_{P_1}^P dP$   
 $\ln\left(\frac{P}{P_1}\right) = \frac{V_m(l)}{RT} \Delta P$   
 $P = P_1 e^{\frac{V_m(l) \Delta P}{RT}}$

with the change in with  $\Delta P$  and it is balanced by  $RT$  right if we assume the vapor to be an ideal gas so as you can see here  $\ln(P/P_1)$  equals to  $V_m \Delta P / (RT)$  so this is  $P$  equals to  $P_1 e$  to the power right  $e$  to the power  $V_m \Delta P / (RT)$  right this is how the vapor pressure will change when there is an inert gas pressurizing the liquid now think of another thing so if you have a unary system you can have a you can basically map the stability like where solid means in which ranges of pressure and temperature solid will be stable at which ranges liquid will be stable at which ranges at what range gases will be stable so for example you have these white lines right these lines white or you can think of this so these these are the this is a phase boundary this is another phase boundary and this is another phase boundary and this marks the triple point where solid liquid and gas can coexist and these lines are basically phase boundaries which basically separate two phases right for example this line separates liquid phase from gas phase this line separates solid phase from liquid phase and this line separates solid phase from gas phase and as you can see the axis is a pressure temperature see we have used we can use different types of diagrams like  $\mu$  vs  $T$  diagrams and all but this is called a pressure temperature diagram or a phase stability diagram right it gives you the stable phases it maps the stable phases but as you can see here please note this is an interesting point if you have a single

solid like if this entire area this entire of area occupies a solid phase right solid phase is stable in this region now in this area only liquid phase is stable and in this area gas phase is stable however when three phases are so basically a two-dimensional area is representing either a solid phase or a gas phase or a liquid phase while a point represents an equilibrium between solid liquid and gas right all of this so this point is called triple point at which solid liquid and gas can coexist again this is a line and along this line solid and liquid are in equilibrium right two phases so basically the line represents two phases coin represents three phases so for a unary system a point represents three phases or coexistence of three phases a line represents coexistence of two phases and area represents existence of a single phase right so as you can see TTR PTR is the triple point or sometimes



I write it as say for example  $T_3$  and  $P_3$  so this is a triple point so this triple point for a unary system basically means that point or that so you can call this you can call this  $P_3$  and this you can call as  $P_3$  and this is the point this pressure and temperature corresponds to coexist so corresponds to a point where solid liquid and gas can exist but see that the coexistence of three phases gives you a point versus of two phases gives you a line you can see the dimensionality in the phase diagram and existence of a single phase is basically represented by an area why is that so for that to understand that another thing please know say when  $V_S$  minus  $V_L$  is equal to 0 so this is something that you find out why I have given enough hint so  $V_S$  minus  $V_L$  is equal to 0 you see it is basically parallel to the y-axis right this phase boundary that you have between solid and liquid is parallel to the y-axis however when solid is greater than means solid is greater than liquid that is this is the condition that means volume of liquid is less than that of the solid molar volume of liquid is less solid then you see the tilt towards the solid right you can see the phase boundary which is tilted this way right it represents some sort of a negative slope on the other hand when  $V_L$  is greater than  $V_S$  you have a positive slope as you can see here right the phase boundary has a positive slope with respect to axis right again this is the triple point so I can call it  $P_3$  and  $T_3$  right so  $P_3$  and again here it is this point is called  $P_3$  and let us call this  $T_3$  so that you don't get confused with the transition temperature so this is the so  $P_3$  and  $T_3$  represent this point and this point is the coexistence point but please have a note of the slope of the phase boundary between solid and liquid when  $V_L$  is less than  $V_S$  then it is inclined to it has a negative slope and if it is greater than  $V_L$  is greater than  $V_S$  it is a

positive slope right and when VL equal to Vs then basically which is very rare which is very hypothetical case you will have solid liquid boundary which is parallel to the axis now I will discuss why this area why single phases in a unary system in a unary system means is a single component system right component number of components equal to 1 number of components in a unary system

GIBBS PHASE RULE No. of Components = 1

$$\begin{cases} x - y + 2z = 4 \\ x + y + z = 3 \\ x - 5y + 8z = 4 \end{cases} \quad \left. \begin{array}{l} 3 \text{ eqs, } 3 \text{ unknowns} \\ \text{Unique solution: variables } x, y, z \end{array} \right\}$$

$DF = 0 \quad f = 3 - 3 = 0$

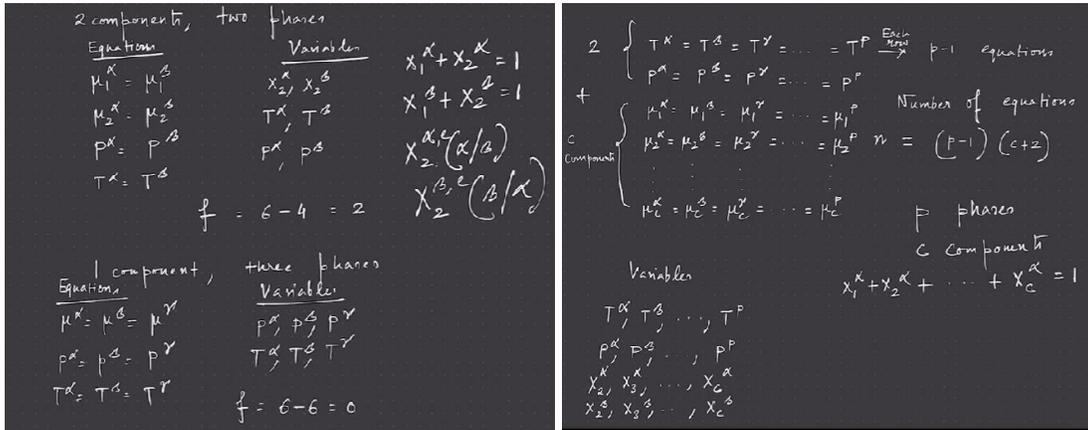
Degrees of freedom =  $f = \text{No. of Variables } (m) - \text{No. of Equations } (n)$

$$= m - n$$

$$\begin{cases} x - y + 2z = 7 \\ x + y - z = 2 \end{cases} \quad \left. \begin{array}{l} f = m - n \\ \text{Infinite solutions} = 3 - 2 = 1 \end{array} \right\}$$

so if I think of number of components in a unary system that is equal to 1 now in such a case you have a the single phase existence is present by an area two phase coexistence is present by line and three phase coexistence is present by point right you have seen that now why is it so so the answer lies in the in the the equilibrium that we consider right in a simple system the what are the equilibrium we have considered temperature thermal equilibrium the temperatures have to be equal across all phases and then pressures have to be equal that is mechanical equilibrium and the chemical potential of each species in each phase across all phases have to be equal like chemical potential of say if I have a component one then chemical potential of component one in phase alpha should be equal to that in phase beta should be equal to that in phase gamma if alpha beta gamma are in equilibrium right so now these basically give you the these means this rule this gives rise to this equilibrium gives rise to this rule called Gibbs phase rule and we can use this Gibbs phase rule to understand degrees of freedom and to understand the structure of a phase diagram like PT phase diagram for a unary system or structure of a phase diagram in a binary system or a multi component system right so how does it come it comes from this idea that if you have say for example let us look at a system of equations so it comes from the idea of if there are there are only cases if I have to solve this equilibrium conditions then I should have the number of variables which should be exactly equal to the number of equations then only I can exactly solve the equations other than that I will either have an over determined system or an under determined system where I can have infinite solutions or no solutions at all right for example if you have many equations but very few variables then your degrees of freedom so basically what I want to define here is the degrees of freedom in terms of unknowns or variables and equations and we will consider linear equations here right we will consider for simplicity only linear equation so you have for example let us look at this so you have three variables X Y and Z and you have three equations which are linearly independent and as a result you have three equations which

are linearly independent and three unknowns or three variables X Y Z and so basically this equation is exactly so you will have a unique solution to this right so unique solution means degree of freedom DF in short DF so or you can also call it F so this is equals to number of variables minus number of equations so in this case it is basically 3 minus 3 which is equal to 0 so here what you have is a unique solution to this problem however let us think of an equation like a set of equations like this X minus Y plus 2 Z equal to 7 and X plus Y minus Z equal to say 2 now in such a case you have three variables but you have only two



equations so you can have the freedom to choose either X or Y or Z so you can choose some value of X then you can solve it and the number of ways you can choose the value of X is infinity again I can choose Y and again the number of ways to choose the values is infinity again for Z the same so basically in this case the system will have the system will have infinite solutions so there is no unique solution or there is no unique equilibrium that you can ascertain in this case so basically here F which is equals to M minus N M is the number of variables and N is the number of equations is basically 3 because you have X Y Z three variables and two equations which is equal to so degrees of freedom is positive one it is not equal to 0 right now we can think of another system for example I give you a system like X plus Y equal to 3 3 X plus 2 Y equal to 4 X minus Y equal to minus 1 and then X plus 7 Y equal to 11 so I have four equations I have two variables now think of this you have two variables so F equals to M minus N M is the number of variables and N is the number of equations which is basically 2 minus 4 which is equal to minus 2 now as you can see here I can take any two equations and solve but it does not it may not satisfy the solution may not satisfy the third equation or the fourth equation so in such a case you have basically in an ordinary approach if you do not use a least squares approach there is no solution to it right there is no solution so you have no solution so and degrees of freedom is minus 2 right as you can see here so when degrees of freedom are 0 then only you have a unique solution otherwise you do not have a unique solution either you have infinite solutions or you have no solutions so just apply the same concept supply the same concept to a multi component multi-phase system now multi component systems remember we are talking about unary systems but we will generally define a multi component system obtain

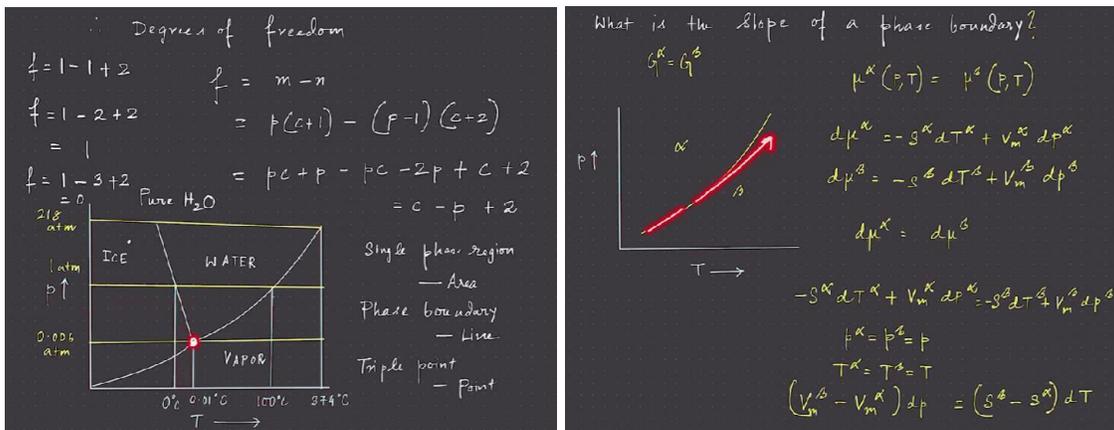
the Gibbs phase rule then we'll apply to two one component systems but as an example I can take one component in a multi component system one component is one of the systems and two phases now if you have one component and two phases then you have three equations  $T^\alpha = T^\beta$ ,  $P^\alpha = P^\beta$  and  $\mu^\alpha = \mu^\beta$  at equilibrium right these are the equilibrium conditions and this gives you three equations but what are the unknowns  $T^\alpha$  is unknown  $T^\beta$  is unknown  $P^\alpha$ ,  $P^\beta$ ,  $\mu^\alpha$  and  $\mu^\beta$  these are basically not these are the energies themselves right this because it's a single component system you cannot think of chemical potential of component one keeping other components constant so basically you have only four variables but you have three equations so degrees of freedom basically so one component two phases degrees of freedom is one right if you have one component two phases degrees of freedom is one right now think of two components and two phases so you have two components right like one and two are the two components then you have this equation right the chemical potential of component one in alpha equal to complete potential of component one in beta when alpha and beta are in equilibrium similarly for component two and then you have  $P^\alpha = P^\beta$  and  $T^\alpha = T^\beta$  now if you see if I solve these two equations what I basically get are the compositions right compositions of the alpha phase and beta phase now to see the compositions can be expressed in terms of mole fraction of component two and if it is so mole fraction of component one in each phase can be obtained from the mole fraction of component two because  $x_1^\alpha + x_2^\alpha = 1$  similarly  $x_1^\beta + x_2^\beta = 1$  but we do not know  $x_2^\alpha$  which is in equilibrium with the beta phase right  $x_2^\alpha$  equilibrium we do not know similarly we do not know what will be the composition of B in the beta phase which is in equilibrium with alpha phase right so we do not know that so basically we do not so there are two unknowns here so we can see two unknowns here not four because  $x_1 + x_2$  is

Phase  $\alpha$ :  $T^\alpha, P^\alpha, x_2^\alpha, x_3^\alpha, \dots, x_c^\alpha$   
Phase  $\beta$ :  $T^\beta, P^\beta, x_2^\beta, x_3^\beta, \dots, x_c^\beta$   
Phase  $p$ :  $T^p, P^p, x_2^p, x_3^p, \dots, x_c^p$

For each phase, no of variables  
 $= 2 + c - 1 = c + 1$   
Variables  $m = p(c + 1)$

equal to one right in each phase the component one and component two if it's a two component system then the mole fractions of component one and component two in each phase will add up to one so if I know one then I know the other right so basically the independent variables so what are the independent variables we have two variables here we have  $T^\alpha$ ,  $T^\beta$  and  $P^\alpha$ ,  $P^\beta$  so total six variables and if you see I have one equation two three four so four equations so if you have two components two phases you

have two components and two phases you have degrees of freedom which is equal to two right now think of one component three phases like the triple point if you have one component three phases then you have  $\mu_\alpha = \mu_\beta = \mu_\gamma$  this gives you two equations  $P_\alpha = P_\beta = P_\gamma$  two equations  $T_\alpha = T_\beta = T_\gamma$  equations are calculated by counting the equal to signs right so you have one two three four five six equations so six equations and what are the variables again it's a single component system so  $\mu_\alpha = \mu_\beta = \mu_\gamma$  does not really give you any mole fraction right it's for us one component so what are the variables  $P_\alpha P_\beta P_\gamma$  and  $T_\alpha T_\beta T_\gamma$  so basically you have six variables and your six equations you have degree of freedom is equal to zero as you can see a triple point is unique and it's a unique point so immediately



you can see the the the the it is a unique point similarly when I tell one component two phases I have a degree of freedom one one means basically a one-dimensional line which is basically a one-dimensional curve which is basically a line right which is basically the phase boundary which has two phase coexistence right now look at a more generalized description that we have like P phases you have P phases and you have C components so you have P phases and you have C components what are your equilibrium we have four subsystems or phases the same equilibrium applies if you are considering symbols a simple system so you have  $T_\alpha = T_\beta = T_\gamma$  and see you have P phases so you have P minus 1 equations right similarly for  $P_\alpha P_\beta P_\gamma$  up to P with superscript P right because superscript P is the nodes and number of phases so basically the total number of phases so this is phase P right this corresponds this is phase P this is phase gamma this is phase beta this is phase alpha the pressures have to be equal right across all phases right when there is mechanical equilibrium right so then here also you have P minus 1 equations similarly for each species say if you have C up to C species like 1 2 3 up to C then you have  $\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma$

mu 1 beta up to mu 1 P again P minus 1 equations so for all components if you have that you have C components so you have C times P minus 1 equations and then these two equations are there so sorry these two rows these two rows are also there which will also have P minus 1 equations so you have this 2 here so you have this 2 and you have this so 2 plus C so total C plus 2 rows are there and each row contains P minus 1 equations so total number of equations n equals to P minus 1 into C plus 2 right P minus 1 into C plus 2 now C you have component 1 up to C right again if you see any phase x 1 x 1 alpha plus x 2 alpha plus x 2 C sorry x C x C alpha x C alpha x C alpha so C components are there is equal to 1 that means one of the components you can choose any one of the components

$$p = p^{\circ} + \frac{\Delta H^{\alpha \rightarrow \beta}}{\Delta V_m^{\alpha \rightarrow \beta}} \ln \left( \frac{T_m}{T_m^{\circ}} \right)$$

if  $T_m - T_m^{\circ}$  is small,

$$\ln \left( \frac{T_m}{T_m^{\circ}} \right) = \ln \left( 1 + \frac{T_m - T_m^{\circ}}{T_m^{\circ}} \right) \approx \frac{T_m - T_m^{\circ}}{T_m^{\circ}}$$

$$p = p^{\circ} + \frac{\Delta H^{\alpha \rightarrow \beta}}{T_m^{\circ} \Delta V_m^{\alpha \rightarrow \beta}} \Delta T_m$$

to be dependent and all others are independent so if you have that you have T alpha to T P right T alpha to T P these many variables then P alpha to P P and then x 2 alpha x 3 alpha x C alpha similarly x 2 beta x 3 beta x C beta similarly x 2 P x 3 P x C P so basically if I write it for phase alpha the number of components are T alpha the number of variables are basically T alpha P alpha x 2 alpha x 3 alpha up to x C alpha for phase beta T beta P beta x 2 beta x 3 beta x C beta right so 2 3 C I haven't included one because I have taken one as the dependent component right now for phase P also you have T P P P x 2 P x 3 P up to x C so for each phase for each phase the number of variables are two variables are here and here this will be if x 1 is included becomes C variable say 2 and C but x 1 is a dependent variable so I am taking only the independent variable so 1 2 and all this C minus 1 variable so you have 2 plus C minus 1 which is C plus 1 variables for each phase but that means the number of variables for each phase if you have C plus 1 variables for P phases will have P into C plus 1 variables now it becomes very easy I can find degrees of freedom as number of variables minus number of equations number of variables minus number of equations which comes out to be if you just simplify this C minus B plus 2 if temperature and pressure both are taken then it becomes C minus B plus 2 however for condensed phases that is solid and liquid often we ignore pressure and if we ignore pressure then the degrees of freedom will become F equals to C for condensed phase systems that means there is no gaseous phase the pressure the pressure term the pressure volume work is neglected in such a case the F can be written as C minus B plus 1 we are not considering pressure as a variable at all we are always assuming the pressure to be equal everywhere

right if it's a purely condensed phase system that is it contains only solid phases and liquid phases no gaseous phase right as soon as there is as soon as you have a gaseous phase we cannot really use  $C - B + 1$  but we should use  $C - B + 2$  because in gases  $PV$  work is not negligible right so again this is a diagram for single phase this is a single component system are so it's a single component system and the single component systems pure water and  $H_2O$  can basically exist as ice it can exist as water it can exist as vapor so please look at the negative slope between the ice water line and also look at the phase boundary free the degrees of freedom in the phase boundary ice and water in equilibrium that is there are two phases right ice and water in equilibrium there are two phases so  $F$  equals to  $C$   $C$  is basically one component  $1 - 2 + 2$  so  $1 - 2 + 2$  so basically you have one component one component and you have two phases and plus 2 so  $F$  equals 2 so at the phase boundary which is  $2 - 1$  which is equal to 1 right so basically it presents a line therefore it is always a line similarly if you have a triple point at the triple point  $F$  equals to you have three phases so minus 3 and you have one component and plus 2 this is what a unary system so this comes out to be 0 so triple point is uniquely different on the other hand if you look at any single phase then you have one component and only one phase and two degrees of freedom right you can basically specify in this area you can specify one point where you have a at that point you can define a pressure you can define a temperature right so so basically at any point so basically if you have a single phase system you can define it independently pressure and temperature right you once you fix pressure and temperature then degree of freedom will go to 0 unless you fix pressure and temperature in a single phase region it will not go to 0 so degrees of freedom will be 2 which represents a two-dimensional area right you have this area right single phase is always so in a unary system or a single component system a single a single phase like ice or water or vapor means where I am not talking about in coexistence they will be represented by two-dimensional areas because I can independently specify if I can independently specify pressure and temperature but once I have specified these two degrees then my degrees of freedom becomes 0 now I can uniquely solve the problem in the on the other hand on the other hand along a line let us look at a line so you have this line where your two phases are coexisting now I can either choose a temperature once I have chosen the temperature the pressure is automatically fixed once I have chosen the temperature the pressure is automatically fixed now at the triple point both pressure and temperature are fixed right you cannot have multiple triple points in a unary phase diagram in a  $PT$  unary phase diagram now one very important question we have these slopes but how do you determine what is an equation that determines the slopes what is the equation that determines the slopes so we move on to something called low shear scalar equation again the derivation is very simple I'll quickly go through it so if you look at the  $\mu$  if you look at two phases alpha and beta which are coexisting and this is the phase boundary this is your phase boundary then along the phase boundary  $\mu$  alpha along the phase boundary so this is your phase boundary along the phase boundary  $\mu$  alpha equals to  $\mu$  beta and

$\mu_\alpha$  and  $\mu_\beta$  are functions of pressure and temperature right mole number because it's a single component so it does not depend on the mole number so  $d\mu_\alpha$  is as you know or  $d\mu_\alpha$  is nothing but  $G_\alpha$  equals to  $G_\beta$  and  $\mu_\alpha$  is basically molar free energy so or  $G_\alpha$  equals to  $G_\beta$  or  $\mu_\alpha$  equals to  $\mu_\beta$  so  $d\mu_\alpha$  equals to  $S_\alpha dT_\alpha - P_\alpha dV_\alpha$  right  $dG$  goes minus  $SdT$  plus  $VdP$  right so this is molar volume this is molar entropy right this is also molar entropy of beta phase this is molar volume of beta phase right this is for alpha phase and you have  $dT_\alpha$   $dT$  corresponding to alpha phase you have  $dT_\alpha$  and you have  $dP_\alpha$   $dP_\alpha$  and  $dT_\alpha$  similarly for beta phase you have  $dT_\beta$  and  $dP_\beta$  now at equilibrium that is at the two phase coexistence you should have  $d\mu_\alpha$  equals to  $d\mu_\beta$  so you have minus  $S_\alpha dT_\alpha$  plus  $V_m^\alpha dP_\alpha$  equals to minus  $S_\beta dT_\beta$  plus  $V_m^\beta dP_\beta$  but as you know from the mechanical and thermal equilibrium that  $P_\alpha$  has to be equal to  $P_\beta$  equals to  $P$  say some  $P$  okay so  $P$  is say some some value right  $P_\alpha$  equals to  $P_\beta$  equals to  $P$  and  $T_\alpha$  equals to  $T_\beta$  equals to  $T$  now if that is so I can rearrange so basically what I have done is  $P_\alpha$  and  $P_\beta$  I put as  $P$  and  $T_\alpha$  and  $T_\beta$  I put as  $T$  so then I can write this as so I have  $V_m^\alpha$  here I have  $V_m^\beta$  here so I can take  $V_m$  this way right so this becomes  $V_m^\beta$  minus  $V_m^\alpha$   $dP$  and I can take the  $S_\beta$  term this way which was positive so  $S_\beta$  minus  $S_\alpha$   $dT$  right so basically what is  $S_\beta$  minus  $S_\alpha$  it is  $\Delta S_{\alpha \rightarrow \beta}$  right  $\Delta S$   $\Delta S_{\alpha \rightarrow \beta}$  is  $S_\beta$  minus  $S_\alpha$  this is  $\Delta V_{\alpha \rightarrow \beta}$  right

$$\begin{aligned}
 (V_m^\beta - V_m^\alpha) dP &= (S_\beta - S_\alpha) dT \\
 \Delta V_m^{\alpha \rightarrow \beta} dP &= \Delta S^{\alpha \rightarrow \beta} dT \\
 \frac{dP}{dT} &= \frac{\Delta S^{\alpha \rightarrow \beta}}{\Delta V_m^{\alpha \rightarrow \beta}} \\
 &\text{Clausius Clapeyron Equation}
 \end{aligned}$$

so that's what I am writing so  $V_m^\beta$  minus  $V_m^\alpha$  is  $\Delta V_{\alpha \rightarrow \beta}$   $dP$  because  $\Delta S_{\alpha \rightarrow \beta}$  so this is a transformation  $dT$  so now you can see now you have this pressure so you have the pressure and temperature axis like pressure and temperature as the axis pressure temperature axis so  $\Delta P$   $\Delta T$  right  $\Delta P$  so this curve if you look at the slope of this curve right is  $P$  as a function of  $T$  right how  $P$  changes is a function of temperature is what is plotted now as you can see the slope of this curve is given by at any point is given by  $\Delta P / \Delta T$  and  $\Delta P / \Delta T$  or  $dP / dT$  is nothing but  $\Delta S_{\alpha \rightarrow \beta}$  so this is the entropy of transmission and this is the molar volume of transmission that is the change in molar volume during transmission from alpha to beta and this is the entropy of transmission remember again  $\Delta S_{\alpha \rightarrow \beta}$  is the same as  $\Delta S_{\beta \rightarrow \alpha}$  only there is a negative sign similarly for  $\Delta V$  so this basically these equations are called as Clausius-Clapeyron equation now this equation can be used for all these boundaries like solid liquid boundary for liquid vapor boundary and solid

vapor boundary say for example if you use it for the solid liquid boundary then you are considering  $T_m$  or melting or freezing point  $T_m$  again is a function of pressure right  $T_m$

Solid-Liquid boundary

$T_m \rightarrow$  Melting or freezing point

$\alpha$  (Solid)  $\xrightarrow{\text{melting}}$   $\beta$  (Liquid)  
 $\xleftarrow{\text{freezing}}$

$\mu^\alpha = \mu^\beta \quad (G^\alpha = G^\beta)$

$H^\alpha - TS^\alpha = H^\beta - TS^\beta$

or,  $H^\alpha - H^\beta = T(S^\alpha - S^\beta)$

or,  $\Delta H^{\alpha \rightarrow \beta} = T \Delta S^{\alpha \rightarrow \beta}$

$T = T_{tr} = T_m$

Clausius Clapeyron Equation

$$\frac{dP}{dT} = \frac{\Delta S^{\alpha \rightarrow \beta}}{\Delta V_m^{\alpha \rightarrow \beta}} = \frac{\Delta H^{\alpha \rightarrow \beta}}{T \Delta V_m^{\alpha \rightarrow \beta}}$$

Let  $T_m^0$  be melting temperature at pressure  $P^0$

$T_m$  " " " " "  $P$

If  $\Delta H^{\alpha \rightarrow \beta}$  and  $\Delta V_m^{\alpha \rightarrow \beta}$  do not vary with  $T$ ,

$$\int_{P^0}^P dP = \frac{\Delta H^{\alpha \rightarrow \beta}}{\Delta V_m^{\alpha \rightarrow \beta}} \int_{T_m^0}^{T_m} \frac{dT}{T}$$

can change the function of pressure we already know and we are looking at solid to liquid which is basically melting where heat is absorbed right melting means it is absorbed and freezing means heat is evolving right and you have  $\mu^\alpha = \mu^\beta$  and you have also  $G^\alpha = G^\beta$  which means  $H^\alpha - TS^\alpha = H^\beta - TS^\beta$  again you arrange so  $\Delta H^{\alpha \rightarrow \beta} = T \Delta S^{\alpha \rightarrow \beta}$  and the  $T$  the transmission temperature  $T_m$  that is the transmission temperature is nothing but  $T_m$  right the melting point so if you have that  $dP/dT$  becomes this equation right  $\Delta S^{\alpha \rightarrow \beta} = \Delta H^{\alpha \rightarrow \beta} / T_m$  which can be presented means basically since  $\Delta H^{\alpha \rightarrow \beta} = T_m \Delta S^{\alpha \rightarrow \beta}$  I can write  $\Delta S^{\alpha \rightarrow \beta} = \Delta H^{\alpha \rightarrow \beta} / T_m$  right so basically this becomes  $\Delta H^{\alpha \rightarrow \beta} = T_m \Delta V_m^{\alpha \rightarrow \beta} dP/dT$  now this  $T$  is nothing but  $T_m$  right now let us think of this this is a general  $T_m$  right this is a  $T_m$  which again is a function of this melting point of this transition temperature this transition temperature is a function of  $P$  and  $T$  right it can change as a function of pressure it can change the function of the means basically if I change the pressure basically if I'm looking think of this if I am changing pressure automatically I am fixing temperature right if you look at Gibbs phase rule so basically  $T_m$  can change as a function of pressure right and so how does that change so let  $T_m^0$  let us look at this at  $T_m^0$  with the melting temperature at pressure  $P^0$  now  $T_m$  let  $T_m$  be the melting temperature at pressure  $P$  now if  $\Delta H^{\alpha \rightarrow \beta}$  and  $\Delta V_m^{\alpha \rightarrow \beta}$  do not vary much right we assume them to be nearly constant but we can actually assume we can basically think of temperature dependence but if we ignore the temperature dependence for a while if you do not ignore then all this  $\Delta C_p$  and all this stuff will

Liquid - Vapor boundary

$$K(\text{Liquid}) \xrightleftharpoons[\text{Condensation}]{\text{Evaporation}} \beta(\text{Vapor})$$

$$\frac{dP}{dT} = \frac{\Delta H^{vap}}{T \Delta V_m^{vap}} \quad V_m^g(gm) \gg V_m^l(liquid) \quad \therefore \Delta V_m^{vap} = V_m^g$$

Let the vapor phase be an ideal gas

$$V_m^g = \frac{RT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta H^{vap}}{T \left( \frac{RT}{P} \right)}$$

$$\frac{dP}{P} = \frac{\Delta H^{vap}}{RT^2} dT$$

$$d \ln P = \frac{\Delta H^{vap}}{R} \frac{dT}{T^2}$$

$T = T^*$     $P = P^*$  (Vapor pressure)

$T = T$     $P = P$

$$\int_{P^*}^P d \ln P = \frac{\Delta H^{vap}}{R} \int_{T^*}^T \frac{dT}{T^2}$$

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

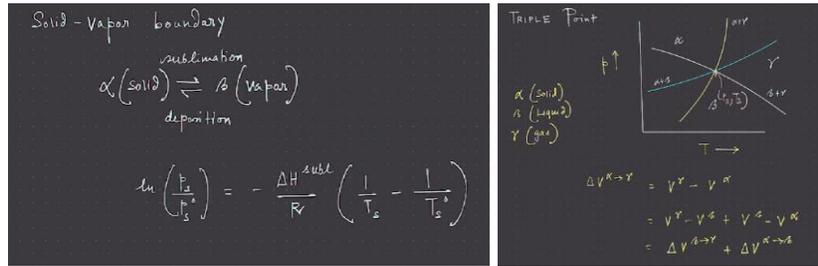
$$P = P_0 e^{-\chi} = P_0 \exp \left( -\chi \right)$$

$$\frac{P}{P_0} = \exp \left[ - \frac{\Delta H^{vap}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right]$$

$$\chi = \frac{\Delta H^{vap}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

come in but if I don't if I want to ignore for the time mean this delta H alpha to beta and delta Vm alpha to beta as a function of temperature that temperature dependence is ignored and we are assuming to be constant independent of temperature then we can basically easily integrate this equation so you have P naught to P dP right so deep so basically this guy this guy will come here with dP and this guy there and there is a T term that is there so dT by T will be there and you have this right so this T will be there dT by T and this and this will be separated and there is a dP right so there is dP there is no pressure that has to so you have delta H alpha to beta and this one so these guys remain as it is here and you have dP here and dT comes dP goes here and this is dT by T so this is dT by T and dT by T is nothing but dLn T it is nothing but dLn T right so you have dLn T and you have this Tm0 as the melting temperature right Tm0 is the melting temperature pressure P naught and at so Tm naught is the melting temperature pressure P naught and at temperature and at pressure P it is Tm then basically we can write P equal to P naught plus see this is we are assuming that delta H alpha beta and delta Vm alpha beta do not change with temperature right we can use their temperature dependence or functional dependence of temperature can be used then we will have to use delta Cp and how it varies with temperature but if we ignore that for time being these guys constant right this guy basically I know if once I know this so I know this term then I have P equals to P naught plus this term into Ln right because dLn T right dT by T is nothing but dLn T so which is basically if I integrate it is Ln Tm by Tm naught because Tm naught and Tm are the integration limits right this is the lower limit is the upper limit so this is Ln Tm by Tm naught right Ln by Tm naught and this term and so if Tm by Tm naught is small then Ln Tm by Tm naught again I am using the same trick so Ln 1 plus Tm minus Tm naught by Tm naught which is approximately equals to so this is approximately equal to only the linear term right the other terms will be anyway smaller right because it is whole squared whole cubed and so so basically I can think of this Tm minus Tm naught as delta Tm by Tm naught and so we can just write this as P equals to P naught plus delta H alpha to beta delta Tm and there is a Tm naught delta Vm alpha to beta right so basically this is for a solid liquid boundary so we can easily find out how find out how to determine the solid liquid boundary equation similarly we can do it for a liquid vapor boundary where you have alpha to beta transformation evaporation and condensation and so basically alpha is liquid

and beta is vapor evaporation will give alpha to beta and condensation will give beta to alpha and we can assume that for gas the molar volume of gas is much much larger than



that of the liquid so then we have this equation  $dP/dT$  equals  $\Delta H_{\text{vaporization}} / T \Delta V_m$  vaporization so if you and if you assume the vapor phase to be an ideal gas then you can write  $V_m \beta$  equals to  $RT/P$  which we have done so basically if we follow this equation you get something like  $d \ln P$  equals to  $\Delta H_{\text{vaporization}} / RT^2$  so I will basically continue in the next class in the next week I will finish this I will finish this Clausius Clapeyron equations but you can quickly go through it and you can understand it so this is for the liquid vapor boundary similarly we can do it for a solid vapor boundary and for triple points how to determine you basically if you know thus so for example if you are looking at a transformation from alpha to gamma you can divide subdivide it into gamma to beta and beta to alpha so I will continue all this discussion in the next week's lecture okay so thank you.