

# Thermodynamics And Kinetics Of Materials

Prof. Saswata Bhattacharya  
Dept of Materials Science and Metallurgical Engineering,  
IIT Hyderabad

## Lecture 18

### Phase equilibria and phase transition in unary systems 2

So, we are considering phase equilibrium in a unary system. Unary means it is a single component system. It is a single component system. It has only one component. Now, if it has only one component, then something interesting can be done because we know chemical potential. So,  $\mu$  is the chemical potential.

Unary system - Single Component system

$$\mu_i = \left( \frac{\partial G}{\partial N_i} \right)_{T, P, N_j \neq i} = \left( \frac{\partial U}{\partial N_i} \right)_{S, V, N_j \neq i}$$

Chemical potential of species  $i$

$N$  moles of one component (pure system)  
pure Fe, Si, Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>O

$$\frac{G}{N} = G_m \text{ or } \bar{G} = \frac{\Delta G}{\Delta N} = \left( \frac{\partial G}{\partial N} \right)_{T, P} = \mu$$

Free energy per mole

Chemical potential in a unary system is the same as molar free energy of the system

So,  $\mu$  is the chemical potential which can be defined in terms of, we have defined chemical potential various times. So, we have defined with respect to say for example, this is the change in energy with respect to change in mole number of species  $i$  keeping  $n_j$  that is not equal to species  $i$  that is all other species concentrations or mole numbers constant, entropy constant, volume constant. After we define the Gibbs free energy, we told  $\mu$  is nothing but change in Gibbs free energy as a change in mole number of again  $\mu_i$ . So, if I tell  $\mu_i$ ,  $\mu_i$  is the change in  $\mu_i$  is the chemical potential.

So, it is the chemical potential  $\mu_i$  is the chemical potential of species  $i$ . Now, chemical potential of species  $i$  is nothing but partial derivative of Gibbs free energy with respect to mole number of species  $i$  that means how the Gibbs free energy will change as a function of mole number of species  $i$  means if there is a small change in the mole number of species  $i$  keeping  $n_j$  that is all other species mole numbers constant, temperature constant, temperature constant, pressure constant and all other species mole numbers constant. So,

this is how define the chemical potential of species i. However, or component i you can call it species i or component i, but when we have a single species or a single component, you have a single component or single species or a single compound. So, it is like a pure species, it is like a pure silicon or pure iron or pure water.

So, it is like a so there is no nothing else in the mixture only n moles of one component, n moles of one component and one component only. So, this is basically like we are looking at phase change or phase transition in a single component system which is a pure system. So, in that way it is a pure system. So, pure means it can be like pure iron there is no mixture with carbon or anything else right. So, it is pure iron or you can think of pure silicon or you can think of pure alumina right or water.

So, whatever you are talking about here we are thinking of whether it is a compound or an element we are looking at pure system there is no mixture. So, note that now if that is so then the molar free energy. So, molar free energy is g by n right the n moles of one component right only one component. So, in a unary system in a unary system g by n is free energy it is free energy per mole which can also be written as g m or g bar. Now g m or g bar is now basically I can write this as g by n right it is an intensive property.

So, I can write it as delta g by delta n I can write it is also as a derivative of g with respect to n at constant temperature and pressure right del g del n which gives me mu. So, g by n which is an intensive quantity it is a molar free energy that is free energy per mole is identical with the chemical potential of the component that is present the system. Since there is one component then therefore we are not using any subscript here. So, we are not using any subscript here right because there is only one component mu. So, mu or g m now have become one or identical.

$dG = VdP - SdT + \mu dn$

$d\mu = d\left(\frac{G}{n}\right) = v_m dP - s_m dT + \mu d\left(\frac{1}{n}\right)$

$d\mu = v_m dP - s_m dT$  — UNARY  
 chemically homogeneous system

$\left(\frac{\partial \mu}{\partial T}\right)_P = -s_m$

$\left(\frac{\partial s_m}{\partial T}\right)_P = \frac{C_p}{T}$

$C_p = \text{molar heat capacity}$

$S_m > 0$

So, chemical potential in a unary system is the same as molar free energy of the system ok. Now as we know that d g is equal to V d p minus S d t plus mu d n right d g right it is

a total differential and it is an exact differential equal to  $V dp - S dt + \mu dn$  right in week 4 lectures if you look at the Lagender transform how we derived the thermodynamic potentials and then how we express those exact differentials right where we have mechanical reservoir and thermal reservoir then it becomes  $V dp - S dt + \mu dn$  right. Now if I since I have a single component I can write  $dG$  by  $n$  ok which is nothing but  $dG_m$  right. So, it is nothing but  $dG_m$  equal to  $dG$  by  $n$  which is again now if I do  $dG$  by  $n$ . So, everything volume becomes divided by  $n$  right volume by  $n$ .

So, if it is  $V/n$  it is equal to  $V_m$ . Similarly  $S/n$  right all of these are intensive properties because the ratios of total entropy by total mole number. So, this becomes  $S_m$ . So, you have  $V_m dp - S_m dt$ , but now you have  $\mu$  you have  $\mu$  which is already an intensive property, but now you have  $dn$  and you are doing. So, but it is a single component system.

So,  $n/n$  becomes 1. So, it is  $d$  of 1. So, this term goes to 0. So, this term does not exist right and  $dG_m$  is nothing but  $d\mu$  right this is equal to  $d\mu$ . So, and because this guy goes to 0.

Now you have for a single component system what I mean by this system you have  $d\mu$  basically you have  $d\mu$  which is equal to  $V_m dp - S_m dt$  right. This is not differential form right change in  $\mu$  in a differential form can be expressed. So, it is a it is again an exact differential and  $d\mu$  because  $V_m dp - S_m dt$  and again it is a chemically homogeneous right because it is a unary single single component system it is a chemically homogeneous system right. Everywhere chemically it is identical right. If it is iron it is always iron right wherever.

So, iron in BCC form, but the composition is iron right. If the atoms of iron only we are considering in a BCC form right in the BCC crystal structure. If it is FCC iron BCC iron is called ferrite or FCC iron is called say austenite. So, austenite or ferrite all of these are for the pure element iron right there is no other component in the mix right. So, that is why I am again and again repeating so that you understand the nuances here.

This is why we can use chemical potential or molar free energy in an interchangeable way. So, basically there is no distinction here between chemical potential and molar free energy right. So, now as you have already seen before the if I look at the from this equation. So, if this is the equation that you are talking about. So, this is called say unary say let us call this equation unary.

Now, from this unary equation you can write the partial derivative right. This is a total derivative right. It is an exact differential it is a total derivative  $d\mu$  equals to  $V_m dp$

minus  $S_m$  d t. Now, if I fix pressure right if I fix pressure then d p goes to 0 and you have  $\frac{d\mu}{dt}$  equals to minus of  $S_m$ . Now,  $S_m$  is molar entropy which is always positive right which is always positive.

So, change in chemical potential or molar free energy with temperature at fixed pressure is given by minus  $S_m$ . As you can see if  $\mu$  is plotted as a function of t. So, you look at this curve if  $\mu$  is plotted as a function of t then  $\frac{d\mu}{dt}$  at constant pressure is minus  $S_m$  which is basically the slope of this curve. So, if I have this curve I go to any point and I go to any point and draw. So, I basically get the slope and the slope as you can see since  $S_m$  is always greater than 0  $S_m$  greater than 0.

So, minus  $S_m$  means it is always negative right the slope is negative as you can see here the slope is negative right the slope has to be negative here as you can see here right. So, because this is minus  $S_m$  and  $S_m$  is greater than 0. Similarly, again from Maxwell relations or from the different the partial derivative properties we know that  $\frac{dS_m}{dt}$  is nothing but  $C_p$  by T where  $C_p$  is the molar  $C_p$  here is stands for molar heat capacity right it is molar heat capacity means heat capacity per mole of the substance under consideration or phase under consideration. So,  $\frac{dS_m}{dt}$  is  $C_p$  by T right  $\frac{dS_m}{dt}$  is  $C_p$  by T and you have  $\frac{d\mu}{dt}$  which is minus  $S_m$  and as you can again I just want to tell you that this is negative slope and this is negative because this is minus there is minus and  $S_m$  is always greater than 0. Do not forget this part right the entropy the molar entropy for this phase will always be greater than 0 right.

So, if molar entropy is greater than 0 minus  $S_m$  is basically going to be negative right the slope is negative. So, you can check that, but now you have this condition also right  $\frac{dS_m}{dt}$  p again constant pressure you have  $C_p$  by T. Now, you can combine these two equations right combine these two. So, if I combine these two what do I get I get instead of  $S_m$  I am putting.

The image shows handwritten mathematical derivations and a graph. The derivations are as follows:

$$\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P = -\left(\frac{\partial S_m}{\partial T}\right)_P = -\frac{C_p}{T}$$

Curvature of  $\mu$ -T curve

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

$$\left(\frac{\partial^2 \mu}{\partial T^2}\right)_P = \frac{\partial}{\partial T} \left(\frac{\partial \mu}{\partial T}\right)_P = -\left(\frac{\partial S_m}{\partial T}\right)_P = -\frac{C_p}{T}$$

$$\left(\frac{\partial^2 \mu}{\partial P^2}\right)_T = \left(\frac{\partial V_m}{\partial P}\right)_T = -V_m \beta_T$$

$$\beta_T = -\frac{1}{V_m} \left(\frac{\partial V_m}{\partial P}\right)_T$$

The graph shows chemical potential ( $\mu$ ) on the vertical axis and pressure ( $P$ ) on the horizontal axis. A curve is plotted that starts at a low pressure and low chemical potential, rises steeply, and then curves downwards as pressure increases, illustrating a negative slope at higher pressures.

So, I know  $S_m$ . So, I just do  $\frac{\partial \mu}{\partial T}$  again I do  $\frac{\partial}{\partial T}$  of  $\frac{\partial \mu}{\partial T}$  at a constant pressure. So, this becomes equal to minus  $S_m$  right. So, basically I have  $\frac{\partial \mu}{\partial T}$  which is equal to minus  $S_m$ . So, what I am now doing it is constant pressure that I am doing  $\frac{\partial}{\partial T}$  of  $\frac{\partial \mu}{\partial T}$  again at constant pressure this becomes  $\frac{\partial^2 \mu}{\partial T^2}$  which is nothing, but minus  $S_m$  right it is  $\frac{\partial^2 \mu}{\partial T^2}$  right  $\frac{\partial}{\partial T}$  of  $\frac{\partial \mu}{\partial T}$  is nothing, but  $\frac{\partial^2 \mu}{\partial T^2}$  square.

I have just erase this. So, that there is no space constraint. So, basically again to tell you  $\frac{\partial^2 \mu}{\partial T^2}$  with pressure constant is nothing, but  $\frac{\partial}{\partial T}$  of  $\frac{\partial \mu}{\partial T}$  pressure constant which is nothing, but minus  $S_m$  right  $\frac{\partial}{\partial T} p$  which is nothing, but  $C_p$  by  $T$  the minus sign. So,  $\frac{\partial^2 \mu}{\partial T^2}$  is minus  $C_p$  by  $T$  right this is minus  $C_p$  by  $T$ . So,  $\frac{\partial^2 \mu}{\partial T^2}$  basically gives what it gives me the curvature. So, this gives me the curvature of  $\mu$  vs  $T$  curve right gives me the curvature and this gives me the slope of  $\mu$  vs  $T$  which is always negative because  $S_m$  is greater than  $C_p$ .

Now and this gives me the curvature right curvature means basically we are looking at how the curvature how the shape will look like right. So, because we have a is it a positive it is a negative curvature right in general  $C_p$  is positive temperature is positive. So, minus  $C_p$  by  $T$  means it has a negative curvature see it has a negative curvature. Now, let us go to constant temperature.

So, if I fix temperature. So, I will just remove this part because it will clutter the stuff I have to share the slides later. So, if you see  $\frac{\partial \mu}{\partial p}$  is equal to  $V_m$  right because if you look at this equation unary right labeled as unary you see  $\frac{\partial \mu}{\partial p}$  at constant temperature. So, if you look at that this  $dT$  is 0 and  $\frac{\partial \mu}{\partial p}$  is nothing, but  $V_m$ . Now if I plot  $\mu$  as a function of  $p$  then you get say some curve like this again for solid liquid and gas it will be different right the molar volume change in the solid or in the liquid will be much much smaller compared to gas right. So,  $\frac{\partial \mu}{\partial p}$  will give you it is a schematic curve it gives you key curve like this if that is again what is  $\frac{\partial^2 \mu}{\partial p^2}$  which is nothing, but  $\frac{\partial V_m}{\partial p}$  right because  $\frac{\partial \mu}{\partial p}$  is already  $V_m$ .

The image shows a handwritten derivation on a dark background. It starts with the partial derivative of chemical potential with respect to pressure at constant temperature,  $\left(\frac{\partial \mu}{\partial p}\right)_T$ , which is equal to the molar volume  $V_m$ . This is then equated to  $\frac{RT}{p}$  for an ideal gas or perfect gas. Finally, the integral of  $d\mu$  from  $p_i$  to  $p_f$  is shown to be equal to  $RT \int_{p_i}^{p_f} \frac{dp}{p}$ , which results in  $RT \ln\left(\frac{p_f}{p_i}\right)$ .

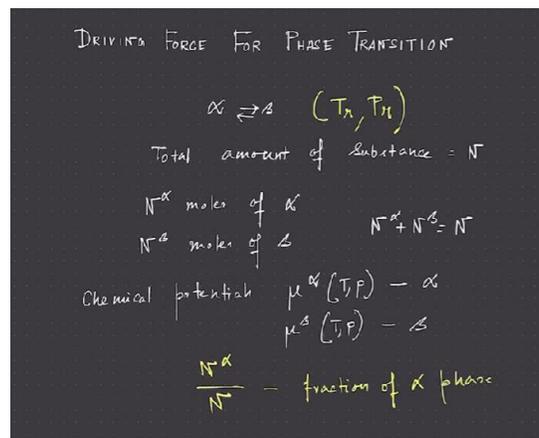
$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_m$$

$$= \frac{RT}{p} \quad \text{for ideal gas or perfect gas}$$

$$\int_{p_i}^{p_f} d\mu = RT \int_{p_i}^{p_f} \frac{dp}{p} = RT \ln\left(\frac{p_f}{p_i}\right)$$

So,  $\frac{d^2 \mu}{dp^2}$  is nothing, but  $\frac{dV_m}{dp}$  which is  $-V_m \beta_T$  where  $\beta_T$  is the isothermal compressibility it is the isothermal compressibility. So, remember  $\beta_T$  has a negative sign here  $\beta_T$  has a negative sign here and there is also another negative sign here. So, you please tell me whether the slope will be increasing or decreasing if you look at this curve this is the slope right is the slope increasing or decreasing. So, this is something to think about right you think about it. Now for an ideal gas this  $V_m$  can be written as  $\frac{RT}{p}$  right because  $pV_m$  equals to  $RT$  right  $pV_m$  equals to  $RT$   $R$  is universal gas constant which is 8.

314 joules per mole kilogram right and  $V_m$  is  $\frac{RT}{p}$  and now if you have that you have this equation where is the equation here  $d\mu = V_m dp - S_m dt$ . Now if you have this equation. So, you are integrating with from initial state to final state again I want to tell you initial state to final state depends only on the states it does not depend what path has been followed whether it is an irreversible path or a reversible path does not matter. So, in the case of ideal gas or perfect gas sometimes in books it is called or perfect gas. Now you have  $d\mu$  which is  $\frac{RT}{p} dp$  by  $p$  again integrating from initial to final state which is  $RT \ln \frac{p_f}{p_i}$ .



So, basically if I know the final pressure if I know the initial pressure. So, basically I know the change in  $\mu$  right from the initial state the final state or change in molar free energy from the initial state and the change in molar free energy when between the final state and the initial state right change in molar free energy between the final state and the initial state. Now I will look at the driving force for phase transition for example, this phase transition which is  $\alpha$  transpose to  $\beta$  or  $\beta$  transpose to  $\alpha$  again depends on the temperature. Now if I tell that the temperature of transition is  $T_c$  or  $T_r$  then at  $T_r$   $\alpha$  and  $\beta$  are in equilibrium at  $T_r$   $\alpha$  and  $\beta$  are in equilibrium. Now think of this that a solid is converted into liquid solid instantly does not 100 solid does not convert

to 100 liquid there will be during the process of solidification you will see that there is a zone between alpha and beta which is basically having a combination of alpha and beta.

So, basically it is not like so alpha and beta coexist right. So, at the at the transition temperature at the transition pressure again I have to define a transition pressure. Now at the transition temperature at the transition pressure what will happen the total amount of systems cannot be destroyed total amount systems remains as it is. However, at the transition temperature and pressure you will have a combination of alpha and beta right it is a mixture of two phases right. However, both phases are unary that means both phases contain only one component, but both phases are possible right at the transition temperature and pressure.

Now if I tell the total number of substance in the system is  $n$  or  $n$  moles of total substance is what we are considering. So, I can tell we have out of this  $n$  moles  $n_\alpha$  moles of alpha and  $n_\beta$  moles of beta. So, and we also know that  $\mu_\alpha(T, p)$  and  $\mu_\beta(T, p)$  are basically the molar free energies of alpha and beta as a function of temperature and pressure right.  $\mu_\alpha(T, p)$  is the molar free energy of alpha as a function of temperature and pressure and this is  $\mu_\beta$  which is same right. So,  $n_\alpha$  is a mole fraction of alpha phase remember this is not  $n_\alpha$  is the amount of alpha phase.

So, basically if I tell I know the total amount which is  $n$  so  $n_\alpha$  by  $n$  this quantity signifies what. So,  $n_\alpha$  by  $n$  basically tells you a fractional quantity that is a quantity that is which is basically the amount of alpha in terms of mole fraction. Again if I know the density or molar volume I can also convert to volume fraction right. So, basically  $n_\alpha$  by  $n$  quantifies the amount of alpha phase in the system or the fraction of alpha phase in the system or phase fraction right  $n_\alpha$  by  $n$ . So, this is fraction of alpha phase is a fraction of alpha phase.

Similarly  $n_\beta$  by  $n$  is a fraction of beta phase right. Now if I know  $\mu_\alpha$   $\mu_\alpha$  is the molar free energy of alpha phase. Now if I multiply the amount of moles of alpha phase that is  $n_\alpha$  so I get  $G_\alpha$  which is  $n_\alpha \mu_\alpha$  at a given temperature and pressure. Similarly I can write  $G_\beta$  equals to  $n_\beta \mu_\beta$ . Now total  $G$  is  $G_\alpha$  plus  $G_\beta$  which is  $n_\alpha \mu_\alpha$  plus  $n_\beta \mu_\beta$ .

Now if I have this I can basically write a differential so this is  $dG_\alpha$  plus  $dG_\beta$ . So, now I can first calculate  $dG_\alpha$  what if this is  $G_\alpha$  and this is  $G_\beta$ . So, basically what we want to see is  $dG_\alpha$  is minus  $S_\alpha$  again this is  $SM$  right molar entropy. So, molar entropy of alpha phase times the amount of alpha phase times  $dT$  again  $V_m \alpha$   $dP$  and  $\mu_\alpha dn_\alpha$  right. This  $n_\alpha$  please note that this  $n_\alpha$  does not denote a component for the amount of phase alpha present in the system.

$$\begin{aligned}
 G^{\alpha} &= N^{\alpha} \mu^{\alpha} \\
 G^{\beta} &= N^{\beta} \mu^{\beta}
 \end{aligned}
 \left. \vphantom{\begin{aligned} G^{\alpha} &= N^{\alpha} \mu^{\alpha} \\ G^{\beta} &= N^{\beta} \mu^{\beta} \end{aligned}} \right\} \Delta \text{ a given } T \text{ \& } P$$

$$G = G^{\alpha} + G^{\beta} = N^{\alpha} \mu^{\alpha} + N^{\beta} \mu^{\beta}$$

$$dG^{\alpha} = -S^{\alpha} N^{\alpha} dT + v_m^{\alpha} N^{\alpha} dP + \mu^{\alpha} dN^{\alpha}$$

$$dG^{\beta} = -S^{\beta} N^{\beta} dT + v_m^{\beta} N^{\beta} dP + \mu^{\beta} dN^{\beta}$$

Degree or Extent of transition

$$f = \frac{N^{\beta}}{N} \text{ from } \alpha \text{ to } \beta$$

$$1 - f = \frac{N^{\alpha}}{N}$$

At constant T and P

$$dG = \mu^{\alpha} dN^{\alpha} + \mu^{\beta} dN^{\beta}$$

f = mole fraction (or volume fraction of  $\beta$ )

$$\begin{aligned}
 G(N, T, P, f) \\
 &= N(1-f) \mu^{\alpha}(T, P) + Nf \mu^{\beta}(T, P) \\
 &= N \mu^{\alpha}(T, P) + Nf \left[ \mu^{\beta}(T, P) - \mu^{\alpha}(T, P) \right]
 \end{aligned}$$

Similarly I can write for dG beta which is minus S beta n beta dT plus Vm beta n beta dP plus mu beta dn beta. Now the degree or extent of transition right the extent of transition again is given by the internal process variable or this extent of transition now I can define as zeta which is an order parameter which is n beta by n right. So, this is the extent of transition from alpha to beta. We are writing zeta which is n beta by n.

Now if you and 1 minus zeta is n alpha by right. Now see zeta is an order parameter which basically tells you the amount of beta phase and the amount of alpha phase in fraction right phase fraction of alpha phase phase fraction of beta phase in terms of moles right. If we give the molar volume information then you can also give it in terms of volume fraction of the phase right in terms of volume fraction of the phase. Now at constant temperature and pressure as you know dG is mu alpha dn alpha plus mu beta dn beta. All this S dT and V dP that dP dT all go to 0 right. So, dG just becomes mu alpha dn alpha plus mu beta dn beta.

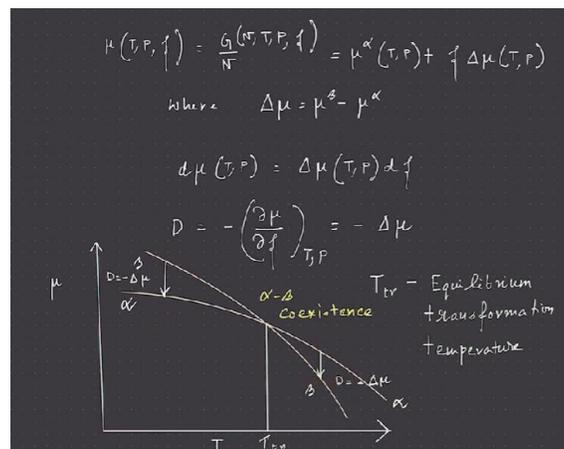
Now zeta is mole fraction or volume fraction of beta right that's what we are telling right. So, zeta is the extent of transition but zeta can also be defined as the mole fraction or volume fraction of beta. Now if I express G of the mixture in terms of n, P, T and zeta then I can write this is n alpha so you have G right. So, it is G is n alpha mu alpha right. So, basically I am writing n 1 minus n into 1 minus zeta right.

1 minus zeta is basically the mole fraction right which is n beta by n right. So, 1 minus zeta is n alpha by n right. So, into mu alpha right into mu alpha right and this is the G and this will be n zeta mu beta as a function of temperature and pressure. Now if I write this basically I can write this like alpha is my parent phase so I can take alpha phase out so this becomes n mu alpha T P right n mu alpha T P plus n times zeta where zeta is a internal process variable which represents the volume fraction of beta n zeta times mu beta minus 1 right. So, if I take n zeta common so n zeta common then I have mu beta minus mu alpha

right                      mu                      beta                      minus                      mu.

Now if I do this then I can write  $\mu$  as a function of  $T$ ,  $P$  and  $\zeta$ .  $\zeta$  is the order parameter which is which is equal to  $G$  by  $n$   $n$   $T$ ,  $P$  and  $\zeta$  which is basically  $\mu$   $T$ ,  $P$  basically gives you  $\mu$   $\alpha$   $T$ ,  $P$  and  $\zeta$  times  $\Delta \mu$   $T$ ,  $P$  right.  $\Delta \mu$  is nothing but a chemical potential difference which is basically  $\mu$   $\beta$  minus  $\mu$   $\alpha$  right. So,  $d\mu$  we can also write the  $d\mu$   $d\zeta$  is basically  $\Delta \mu$  right. So, we can write  $d\mu$  as a function of temperature and pressure is nothing but  $\Delta \mu$  times  $d\zeta$  right and the driving force right driving force for this  $\alpha$   $\beta$  transformation is given by minus of  $d\mu$   $d\zeta$  or  $dG$   $d\zeta$  which is basically nothing but at constant temperature and pressure which is nothing but  $\Delta \mu$  right  $\Delta \mu$  is the driving force minus of  $\Delta \mu$  right minus of  $\Delta \mu$  and this we can clearly understand right minus of  $\mu$  is the driving force right.

So, because if there is a chemical potential difference or if there is a potential difference then something flows right and the driving force is the negative of this potential difference right. So,  $d$  is equal to minus of  $d\mu$   $d\zeta$ . Now if I think of this I have this  $\beta$  phase if you see this clearly this is my  $\beta$  phase and this is my  $\alpha$  phase now you see you have this transition temperature  $T_{tr}$  right and this is my  $\beta$  phase and this is my  $\alpha$  phase. So, this is my  $\alpha$  phase this is my  $\beta$  phase and  $\beta$  phase is transformed to  $\alpha$  phase. So,  $\beta$  phase is transformed to  $\alpha$  phase or  $\alpha$  phase can transform to  $\beta$  phase.



Now think of this  $d$  is minus  $\Delta \mu$  right then  $\Delta \mu$  is  $\mu$   $\beta$  minus  $\mu$   $\alpha$ . Now if just look at this picture now if you see there is a transition temperature at which this is the  $\alpha$   $\beta$  coexistence right this is the  $\alpha$   $\beta$  coexistence point. Now if you are below  $T_{tr}$  you are seeing  $\beta$  is having more energy per mole than  $\alpha$ . So,  $\beta$  will

transform to alpha right beta will transform to alpha. Now so here beta will transform to alpha and  $d$  is equals to minus delta mu right.

So, which is basically minus delta mu which is mu beta minus mu alpha mu beta is greater than mu alpha so beta will transform to alpha. Now if I go above  $t_r$  so basically  $d$  is minus delta mu but now you see that the alpha phase has higher energy than beta phase. Alpha phase has higher energy or higher mu than beta phase. So, this is mu beta minus mu alpha so as you can see this is minus of delta mu where delta mu is mu beta minus mu alpha which is nothing but mu alpha minus mu beta and mu alpha minus mu beta is positive so as a result alpha will try to transform to beta along this line right. Alpha will try to means along some line along some path alpha will try to transform to beta.

$$\begin{aligned} \text{If } T > T_{tr}, \quad \mu^\beta < \mu^\alpha, \quad \Delta\mu = \mu^\beta - \mu^\alpha < 0, \\ D = -\Delta\mu > 0 \\ \alpha \text{ phase is thermodynamically unstable} \\ \text{and transforms to } \beta \text{ phase} \\ \text{If } T < T_{tr}, \quad \mu^\beta > \mu^\alpha, \quad \Delta\mu = \mu^\beta - \mu^\alpha > 0 \\ D = -\Delta\mu < 0 \\ \alpha \text{ phase is thermodynamically stable} \\ \text{and does not transition to } \beta \\ \text{If } T = T_{tr}, \quad \mu^\beta = \mu^\alpha, \quad \Delta\mu = 0, \quad D = 0 \\ \alpha \rightleftharpoons \beta, \quad \alpha \text{ and } \beta \text{ are in equilibrium} \end{aligned}$$

So, as you can see below  $t_m$  it is beta which is having higher chemical potential or beta which is having higher molar free energy. On the other hand when you are above well above transition temperature you see that the alpha phase right this is the alpha phase is the alpha point and this is the beta point. So, basically definitely the beta phase has lower free energy than alpha and the driving force is such that alpha phase spontaneously transforms to beta right. Here alpha phase spontaneously transforms to beta here beta phase spontaneously transforms to alpha here. So, beta transforms to alpha here and alpha transform into beta is here right.

Now if  $t$  is greater than transition temperature as you can see this is what I have written here mu beta is less than mu alpha delta mu which is mu beta minus mu alpha is less than 0. So,  $d$  is minus delta u which is greater than 0 right which is basically greater than 0. So, alpha phase that means what so basically what I am telling is if  $t$  is greater than  $t_r$  then alpha phase is basically  $d$  is positive right  $d$  is positive that means alpha phase is thermodynamically unstable as you can see here thermodynamically unstable and transforms to beta phase. So, if  $t$  is greater than  $t_m$  mu beta is less than mu alpha right it

has the lower free energy or lower free energy per mole now  $\Delta\mu$  is a driving force which is  $\mu_\beta - \mu_\alpha$  which is like basically less than 0. So, minus of  $\Delta\mu$  will be greater than 0 minus of  $\Delta\mu$  is the driving force and that is greater than 0.

So, as a result what happens if the driving force is greater than 0 alpha phase is thermodynamically unstable and spontaneously transforms to beta phase. Now, think of if  $T < T_r$  then  $\mu_\beta$  is greater than  $\mu_\alpha$ . So,  $\Delta\mu$  which is again  $\mu_\beta - \mu_\alpha$  is now greater than 0. So,  $d$  which is minus of  $\Delta\mu$  is less than 0. Now, if that means what we are telling is if  $T$  is less than  $T_r$  so see this is where  $T$  is greater than  $T_r$  this is the case  $T$  is greater than  $T_r$ .

Now, I am going to  $T < T_r$ . So, this is the case. Now, think of alpha changing to beta which is thermodynamically not possible because alpha is a more stable phase beta is the unstable phase right. So, alpha is the thermodynamically stable phase. So, alpha does not transition to beta if alpha transitions to beta it will require means if beta if alpha is transformed to beta then it will require some sort of a push from outside. So, that alpha can transform to beta right it has to be it cannot be a spontaneous process alpha to beta transformation when  $T < T_c$  alpha to beta transformation when  $T < T_c$   $r$  is definitely not a spontaneous process why because  $d$  is negative and alpha itself is a thermodynamically stable phase. So, if I want to convert a thermodynamically stable phase to a thermodynamically unstable phase then basically I require to supply some enormous amount means I do not know means we have not quantified yet we will quantify but  $d$  is less than 0.

So, this it is impossible for alpha to spontaneously transform to beta however it is some it is possible to do some work on the system so such right do some chemical work or some such work or mechanical work on the system. So, that the alpha phase which is a thermodynamically stable phase transforms to a beta phase right in general without any external force without any external stress this type of transition will never occur spontaneously without external stress as transition does not occur that means it is not a spontaneous order natural transition or natural transition is the one which does not require any external push right it does not require any external push. Remember the sign if  $d$  is positive then alpha phase or the right if  $d$  is positive which is basically  $\mu_\beta - \mu_\alpha$  which is negative of  $\mu_\beta - \mu_\alpha$  you can immediately understand that alpha phase is a thermodynamically unstable right. So, basically if I telling  $\mu_\beta - \mu_\alpha$  and  $d$  is greater than  $T_r$  if  $d$  is greater than  $T_r$  alpha is a thermodynamically unstable phase right alpha is a thermodynamically unstable phase and it transforms to beta phase correct. But here alpha to beta transformation alpha itself is a thermodynamically stable phase and it has to transform to beta which is not possible spontaneously however in a non spontaneous way if it is possible then you have to make some work done you have to make

some work and means provide some work from or external external force from outside for this reaction to happen and that force can be very large and because alpha is the minimum energy state here right.

So, alpha is the more stable phase than beta phase. So, alpha cannot does not transform to beta spontaneously. So, we will just add this term spontaneously ok. So, if T equals to transition temperature as you know that mu beta there is a molar free energy of or chemical potential of beta or molar free energy of beta because it is a unary system equal to molar free energy of alpha and therefore delta mu is basically 0 if delta mu is 0 driving force is 0 if driving force is 0 alpha and beta are in equilibrium and the transformation from alpha to beta or beta to alpha are equally likely. On the other hand if T is greater than TTR then mu beta basically mu beta is less than mu alpha right if mu beta is less than mu alpha and delta mu is less than 0 and T is positive and as a result alpha phase which is thermodynamically unstable at this temperature right T is alpha phase which is thermodynamically unstable at this temperature will transform to beta phase. So, in this case in this case so we can write what is delta S IR which is basically nothing but d by T which is basically mu alpha minus mu beta by T which is d minus delta mu by T or delta S IR will be equal to 0 at T equal to T right.

$$\Delta S^{ir} = \frac{D}{T} = \frac{\mu^\beta - \mu^\alpha}{T} = -\frac{\Delta\mu}{T}$$

$$\Delta S^{ir} = 0 \quad \text{at } T = T^*$$

$$\frac{d\dot{f}}{dt} \propto \frac{D}{RT} \quad (\text{in a linear kinetic theory})$$

$$\frac{dS^{ir}}{v_m dt} = \frac{D}{T} \frac{d\dot{f}}{v_m dt} \left( \frac{d\mu}{v_m dt} = -D \frac{d\dot{f}}{v_m dt} \right)$$

rate of molar entropy production
rate of phase transition

Now note that how will this transmission at what rate will this transmission takes place we can now use a kinetic theory and tell del zeta del T is proportional to d by RT right where d is the driving force right d is the driving force del zeta by del T we can write is proportional to not R is not equal d by T. So and d is the driving force remember so it is basically now telling the rate at which this transmission will take place or rate at which the liquid will starting liquid will completely convert to a starting solid say for example or starting alpha will completely when alpha is thermodynamically unstable so alpha is

thermodynamically unstable where when the alpha is thermodynamically unstable when T is greater than T R right. So it will spontaneously transform to beta but at what rate it will transform is basically you can if you want that then you can insert this time right on this internal process variable or order parameter so this is basically evolution of order parameter this is evolution of order parameter as a function of time which is proportional to d by T again you don't have to care about the kinetic theory at all but what I am telling is that the how zeta will transform is a part of kinetic theory it is not a part of thermodynamics but in thermodynamics means or equilibrium thermodynamics but in equilibrium thermodynamics one thing you have to always appreciate that when we are talking about thermodynamics we are talking about driving forces we are defining driving forces right and this driving force basically if it is positive then you do have so if the driving force is positive then basically then basically there will be a spontaneous transformation from one phase to the other right because the first phase the initial so when when d is greater than 0 we can immediately see means we can immediately understand that the phase that has high energy is the is the unstable phase and we are looking at that unstable phase as starting point and we are trying to transform it to beta phase however this will proceed as a function of time how fast or how slow is not in the ambit of thermodynamics right so you have to use the kinetic theory and so as a result we can write this type of equations right so this is now if I write this equation del zeta del T where delta SIR is already defined as minus delta mu by T now if you can see d SIR by VM right what is d delta S is d by T right delta S is d by T right so what I am trying to say and zeta d d zeta is what we write right so basically what I am trying to say is that this I can replace with d SIR so d SIR by VM dT equal to d by T del zeta so d by T del zeta or d zeta VM dT right so this is basically rate of so this equation is called rate of molar entropy production which I will describe later right rate of molar entropy production now if we think of driving force of function of temperature and pressure then you can see the driving force if you look at d mu alpha so you have again you are looking at the transmission from alpha to beta or beta to alpha or beta to alpha

Driving force as a function of temperature T and pressure P

$$d\mu^\alpha = -s^\alpha dT + v_m^\alpha dP \quad \text{--- (1)}$$

$$d\mu^\beta = -s^\beta dT + v_m^\beta dP \quad \text{--- (2)}$$

$$\text{(2) - (1)} \quad d(\mu^\beta - \mu^\alpha) = -(s^\beta - s^\alpha) dT + (v_m^\beta - v_m^\alpha) dP$$

$$d\Delta\mu = -\Delta s dT + \Delta v_m dP$$

$$\Delta\mu(T,P) = -\int_{T_{eq}, P_0}^{T, P} \Delta s(T,P) dT + \int_{T_{eq}, P_0}^{T, P} \Delta v_m(T,P) dP$$

At equilibrium  $\Delta\mu(T,P) = 0$

Assume that for a phase transition,  $\Delta Q_p$  is constant

$s^T$  and  $v^T$  are zero

$$\Delta s(T,P) = \Delta s^\circ(T_{tr}, P_0) + \Delta C_p \ln \frac{T}{T_{tr}}$$

$$\left(\frac{\partial \Delta\mu}{\partial T}\right)_P = -\frac{C_p}{T}$$

now if you look at  $d\mu_\alpha$  which is  $-S_\alpha dT + V_{m,\alpha} dP$  and  $d\mu_\beta$  which is  $-S_\beta dT + V_{m,\beta} dP$  then you can write  $d\mu_\beta - d\mu_\alpha$  so basically this is your equation set 2 and this is 1 this is equation number 1 and then what you are doing is 2 minus 1 so you get  $d\mu_\beta - d\mu_\alpha = -S_\beta dT + S_\alpha dT + V_{m,\beta} dP - V_{m,\alpha} dP$  which is basically  $d\mu_\beta - d\mu_\alpha$  is nothing but  $d(\mu_\beta - \mu_\alpha)$  so  $d(\mu_\beta - \mu_\alpha)$  is nothing but  $d\mu$  right it is nothing but  $d\mu$  which is basically  $-S_\beta dT + S_\alpha dT + V_{m,\beta} dP - V_{m,\alpha} dP$  right now you can integrate you can integrate so you know the  $d$  of  $d\mu$  so you can integrate  $d\mu$  as a function of say for example the temperature so you can take limits as say you can think of  $P_0$  as the pressure right it's like  $P_0$  can be 1 bar like  $P_0$  is the reference pressure and  $T_{tr}$  is the transition temperature and you are integrating up to some temperature now if you have that you because minus  $dS$   $dP$   $dT$  plus  $V_{m,\beta}$  right again here  $P_0$  is the  $P_0$  is the standard pressure and now you are going to  $P$  bar and here  $T$  is constant as you can see so  $P_0$  to  $P$  so here we are looking at  $dV_{m,\beta} dP$  and here it is  $dS dT$  now at equilibrium

The image contains two panels of handwritten mathematical derivations. The left panel defines  $\Delta v_m(T, P) = \Delta v_m(T, P_0) = \Delta v_m^0(T_{tr}, P_0)$  and explains the terms  $\Delta S^0$  (change in molar entropy at  $T_{tr}$  and  $P_0$ ) and  $\Delta v_m^0$  (change in molar volume at  $T_{tr}$  and  $P_0$ ). It then shows the equation  $\Delta \mu = - \int_{T_{tr}, P_0}^{T, P} \left[ \Delta S^0 + \Delta C_p \ln \frac{T}{T_{tr}} \right] dT + \Delta v_m^0 (P - P_0)$ . The right panel shows the derivation of  $\Delta \mu(T, P) = (\Delta C_p - \Delta S^0)(T - T_{tr}) - \Delta C_p T \ln \frac{T}{T_{tr}} + \Delta v_m^0 (P - P_0)$ . It includes the substitutions  $\Delta T = T - T_{tr}$  and  $\Delta P = P - P_0$ , and the integral  $\Delta \mu = \left[ \Delta C_p - \Delta S^0 \right] \Delta T - \Delta C_p T \ln \left( 1 + \frac{\Delta T}{T_{tr}} \right) + \Delta v_m^0 \Delta P$ . A substitution  $z = \frac{T}{T_{tr}}$  is used to evaluate the integral, leading to  $\Delta \mu = T_{tr} \left[ \frac{\Delta C_p}{T_{tr}} \Delta T - \Delta C_p \ln z \right] + \Delta v_m^0 \Delta P$ .

$\Delta \mu$  has to be equal to 0 now assume that for a phase transition  $\Delta C_p$  is constant right there is no difference in  $\Delta C_p$  so basically what I am trying to say that  $\Delta C_p$  and  $\Delta S^0$  and  $\Delta v_m^0$  are also 0 so I am simplifying the problem as much as possible so I have taken isothermal compressibility to be 0  $\alpha$  to be 0 or insignificant and we are telling that for a phase transition  $\Delta C_p$  there is a change in heat capacity for or the difference in heat capacity between the  $\alpha$  phase and the  $\beta$  phase are basically we are assuming it to be

constant right now in that case I can write  $\Delta S$  so from here I can write  $\Delta S$   $dP$  because  $\Delta S_0$  at  $T$  transition right at the transition temperature and at  $P_0$  plus we can write  $\Delta C_P \ln T$  by  $T$  right so that is your  $\Delta S$   $dP$  now you can also so right you require the  $\Delta S$   $dP$  information right you require the  $\Delta S$   $dP$  now this is how I am defining it right that because  $\Delta S$   $dP$  is nothing but the  $\Delta S_0$  which is basically the change in entropy at standard state that is which is a function of transition temperature  $P_0$  right and then there is this  $\Delta C_P \ln T$  by  $T_0$  right why this  $\ln T$  by  $T_0$  why because we are looking at integration integration here and we are telling that there is a so where from  $C_P dT$  is coming this term is coming is from  $\Delta S$   $dT$  which is basically  $C_P$  by  $T$  right  $\Delta S$   $dT$  equal to  $C_P$  by  $T$  so you are using this and you are using this and then if you integrate and now you have the molar volume again the molar volume change at  $T$  and  $P$  we are telling that it is the same as that at  $P_0$  and that is basically the same as  $\Delta V_m$  now  $\Delta S_0$  is a change in molar entropy at the transition temperature and  $P_0$  means  $P_0$  is the standard pressure and  $V$  and  $\Delta V_m$  is a change in molar volume at transition temperature and again the  $P_0$  bar which is the reference pressure right reference pressure is  $P_0$   $P_0$  can be 1 bar then  $\Delta \mu$  I can integrate and again if you remember that this is very simple because we have taken  $\alpha$  and  $\beta$   $T$  to be 0 okay as for simplicity now you can integrate this and basically you get  $\Delta S_0$  here  $\Delta C_P$  here and  $\Delta V_m$  here right and there is a because  $V_m dP$  right  $V_m dP$  so  $\Delta V_m dP$  so  $dP$  is basically  $P$  minus  $P_0$   $P_0$  is your reference pressure  $P_0$  is your reference pressure in bar or it can be in atmosphere but remember  $P_0$  can be 1 bar it can be 1 atmosphere it can be anything and  $T_{tr}$  is your transition temperature where both phases are in equilibrium right and now you are looking at  $\Delta \mu$  now  $\Delta \mu$  basically gives you the driving force right which is  $\mu_\beta$  minus  $\mu_\alpha$  right so it is giving you the driving force because  $d$  is minus what is  $d$  we have defined it  $d$  is minus of  $\Delta \mu$  right  $d$  is minus of so you have  $d$  minus of  $\Delta \mu$  and  $\mu$  is nothing but here although we are talking about this  $\Delta \mu$  is nothing but  $\Delta G$  bar you can call it also  $\Delta G$  bar or  $\Delta G_m$  which is  $G_m \beta$  minus  $G_m \alpha$  right so this is  $\Delta \mu$  is basically the difference in chemical potential between  $\beta$  phase and  $\alpha$  phase or difference in molar free energy between  $\beta$  phase and  $\alpha$  phase which is related to difference in entropy at the temperature of interest and pressure of interest and only thing when we do the integration please note that you have to take not only the transition temperature is something sometimes you miss that you have to take the transition temperature as well as the pressure right you also have to take the so in the case of  $dt$  your pressure is fixed at  $P_0$  in the case of  $dP$  your pressure change is also accounted for  $P_0$  it goes to  $P$  right and then you do this integration and you take into account this equation so this is the equation so that it comes to  $\Delta C_P$  and  $T$  by  $T$ . Now once you have done all of these and you have defined or you know these quantities then you can basically calculate it right  $\Delta \mu$ . Only thing remember in this formula you can make it more complex you can take  $C_P$  as a function of temperature you can take  $\alpha$  you can take  $\beta$   $T$  that is the isothermal incompressibility and then you will get basically so then

you will get a slightly more complicated equation for delta mu right slightly more complex equation for delta mu.

The image shows two panels of handwritten mathematical derivations. The left panel starts with  $\Delta S^0 = \frac{\Delta h^0}{T_{tr}}$  and  $\Delta G_m = \Delta H_m - T \Delta S_m$ . It then shows  $\Delta G_m = 0$  at  $T = T_{tr}$ , leading to  $\Delta H_m = T_{tr} \Delta S_m$ . The next step is  $\Delta C_p \Delta T - \Delta C_p T \frac{\Delta T}{T_{tr}}$ , which simplifies to  $\Delta C_p \Delta T \left(1 - \frac{T}{T_{tr}}\right) = -\frac{\Delta C_p (\Delta T)^2}{T_{tr}}$ . The final result is  $\Delta \mu = - \left[ \frac{\Delta h^0 + \Delta C_p \Delta T}{T_{tr}} \right] \Delta T + \Delta v_m^0 \Delta P$ . The right panel starts with  $\Delta \mu(T, P) = (\Delta C_p - \Delta S^0) (T - T_{tr}) - \Delta C_p T \ln \frac{T}{T_{tr}} + \Delta v_m^0 (P - P_0)$ . It defines  $\Delta T = T - T_{tr}$  and  $\Delta P = P - P_0$ . The main derivation is  $\Delta \mu = \left[ \Delta C_p - \Delta S^0 \right] \Delta T - \Delta C_p T \ln \left(1 + \frac{\Delta T}{T_{tr}}\right) + \Delta v_m^0 \Delta P$ . A substitution  $z = \frac{T}{T_{tr}}$  is used, leading to  $dz = \frac{1}{T_{tr}} dT$ . The integral  $\int \frac{\ln z}{z} dz$  is evaluated from  $\frac{T_{tr}}{T_{tr}}$  to  $\frac{T}{T_{tr}}$ , resulting in  $\ln \left(\frac{T}{T_{tr}}\right) - T + T_{tr}$ .

Now if I look at this you do a little bit of algebraic manipulation which I have done here say for example I have taken  $T$  by  $T_r$  to be  $Z$  so  $Z$  is at so  $dZ$  is  $1$  by  $T_r dt$  and all this stuff then basically what you get is delta so delta mu that is the change in the potential between alpha phase and beta phase is basically related to the difference in specific the heat capacities of the two phases delta is 0 so delta is 0 is the difference in entropy of the two phases at the reference temperature and reference pressure and then there is a  $T$  minus  $T_r$  right  $T_r$  is the  $T_r$  is the transmission temperature plus minus you have this term okay so it is like  $\Delta C_p T \ln T$  by  $T_r$  if you go through this if you go through this derivations you will easily understand this part and then this is nothing but  $\Delta v_m^0 V$  minus  $P$  right so now remember delta is 0 and we have seen that just for the ice water problem and also other problems we have seen that so at so delta is so at constant pressure delta is 0 is nothing but delta is 0 by  $T_r$  right so basically if that is so because  $\Delta H_m$  as you can see here is equal to  $T_r \Delta S_m$  so  $\Delta S_m$  is  $\Delta H_m$  by  $T_r$  so basically now you can write this equation  $\Delta C_p \Delta T$  minus  $\Delta C_p T \frac{\Delta T}{T_r}$  which is delta so take the  $\Delta C_p$  common  $\Delta T$  common so this becomes  $1 - \frac{T}{T_r}$  which if I integrate which I get minus  $\Delta C_p \Delta T$  square by  $T_r$  right because I get minus delta so you have  $\Delta C_p$  where is that huh so when I am integrating so remember what I am trying to do here is this I am telling so here you have  $\Delta C_p \Delta T$  minus  $\Delta C_p T \frac{\Delta T}{T_r}$  by  $T_r$  so when it become  $\Delta T$  by  $T_r$  it has so I have taken a small difference so basically you have this  $T$  and  $T$  by  $T_r \ln T$  by  $T_r$  is gone so you have this so you just required to take  $\Delta C_p \Delta T$  is common so this becomes  $1 - \frac{T}{T_r}$  which is basically going to be  $\Delta T$  by  $T_r$  so if I integrate I get so delta mu equals to minus of  $\Delta H_0$  plus  $\Delta C_p \Delta T$  by  $T_r$  into  $\Delta T$  right and  $\Delta v_m^0 \Delta T$  now remember this is one thing there is an  $\ln$  and you have done this so how did you do this  $\ln \Delta C_p$  is here  $T$  minus  $T_r$  aha and then there is a  $\Delta C_p T \ln T$  by  $T_r$  so now we have taken this term yeah so if you integrate you get this term so delta mu basically has a  $\Delta H_0$  term there is a change

in enthalpy at the tangential temperature and then it has this  $\Delta C_p \Delta T$  term and so basically this is nothing but a little bit of algebraic manipulation where we are talking about  $C_p$  and that the difference in specific heat capacities but we are not considering that this part as you can see it is simply  $\Delta V_m$  into  $\Delta p$  we are not considering any effect due to thermal expansion or isothermal compressibility right so that's the so next in the next lecture I will talk about order of phase transition and also I will introduce this phase diagram and the Clausius-Clapeyron equation.