Phase Transformation in Materials
Prof. Krishanu Biswas
Department of Material Science & Engineering
Indian Institute of Technology, Kanpur

Lecture – 03
Free Energy, Stability of Phases

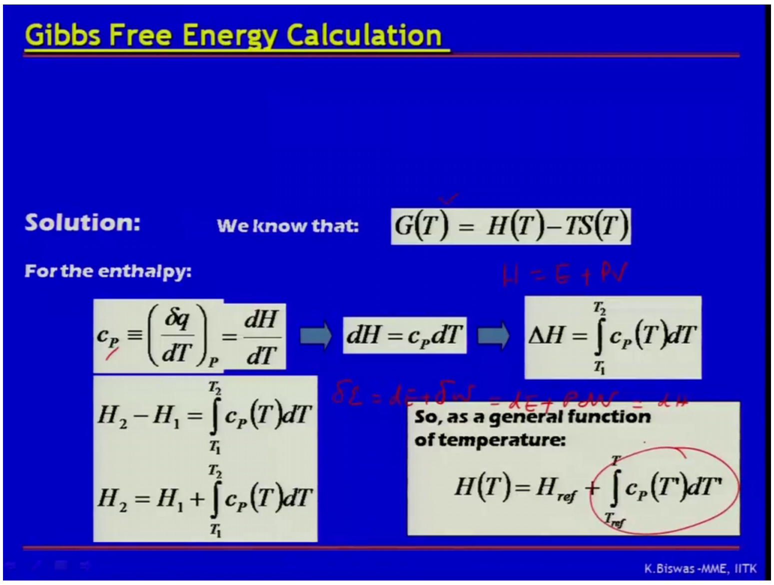
In the last lecture I just started discussing about the stability of the phases. So, as you know phase transformation involves change from one or more than one phases to other phases in the system. So that means, under certain experimental conditions the parent phases were unstable or metastable and that is why they have undergone changes. So, it (Refer Time: 00:41) on to the question which needs to be answered is that what is are the condition for stability of the phases for a particular set of experimental conditions. And that is what we have been discussing. So, in a nutshell, it is ask you a question about equilibrium conditions of the different phases.

If the phases are at equilibrium condition under certain experimental conditions they will not undergo any changes. Only when they are away from equilibrium the phases will undergo transformations. So, equilibrium in thermodynamics means all the 3 important conditions to be satisfied. First the system must be in mechanical equilibrium; that means, that energies of all the atoms whether it is a potential or kinetic together must be at the minimum level.

Second is a thermal equilibrium. And as I explained in the last lecture thermal equilibrium or the phases means that there is no net temperature gradient existing in the phases of the system. And the third conditions to be satisfied is known as chemical equilibrium; that means, for the chemical reactions taking place in the system both forward and the backward reaction rates must be equal. When all these 3 conditions are satisfied then only we call a system at thermodynamic equilibrium, please remember this. Because we always consider mechanical equilibrium to the main or the sole aspect for equilibrium in the very nascent manner. We never considered the thermal and chemical parts are important, but thermodynamically we are means all the 3 things to be satisfied.

Now, question is this, this is all fine in the aspect of you know theory, how we can put it in terms of mathematical formalism. And that is why we have to get into functions. And if you look at if you have studied thermodynamics even a small amount, but you will find in thermodynamics we define a function known as free energy. And these free energy tells you the available amount of the energy available amount of energy available rather to do work. So, in metallurgical thermodynamics we always consider Gibbs free energy to be the main parameter controlling the stability of the fields. And that way Gibbs free energy is defined is given on the screen, that is the Gibbs free energy is always marked with a letter called capital G.

(Refer Slide Time: 03:30)



Gibbs Free Energy Calculation

Solution: **We know that:** $G(T) = H(T) - TS(T)$

For the enthalpy:

$H = E + PV$

$$c_P \equiv \left(\frac{\delta q}{dT}\right)_P = \frac{dH}{dT} \Rightarrow dH = c_P dT \Rightarrow \Delta H = \int_{T_1}^{T_2} c_P(T)\,dT$$

$\delta Q = dE + \delta W = dE + PdV = dH$

$$H_2 - H_1 = \int_{T_1}^{T_2} c_P(T)\,dT$$

$$H_2 = H_1 + \int_{T_1}^{T_2} c_P(T)\,dT$$

So, as a general function of temperature:

$$H(T) = H_{ref} + \int_{T_{ref}}^{T} c_P(T')\,dT'$$

K.Biswas -MME, IITK

It is a function of both temperature and pressure a metallurgical system you all assume pressure to be at one atmospheric pressure. So, that is why I have written G as a function of temperature which is equal to H as a function of temperature minus T multiplied by S as a function of temperature. So, what are these parameters H is known as enthalpy of the system? Enthalpy means the basically is defined as like this it is low known as let me write down this is defined as H equal to E plus PV ok.

So, E is internalized system and P and V are the pressure and volume of the system. So therefore, H is nothing but the total energy of the system in the sense of internal energy plus dE pressure and volume term. An internal energy is obviously, transmission of the kinetic and the potential energy of the atoms. H can be re correlated because it is E plus PV is very difficult to measure experimentally.

So, that is why H is always correlated with a measurable quantity known as C P that is the specific heat at constant pressure. And C P as for as the first law of thermodynamics is given by del q by del T at constant pressure and constant pressure. If you know that is del q is nothing but del S del T how it comes is very simple this way we know that at first law of thermodynamics tell you del q is equal to del E plus P del w. So, remember these del is basically corresponds to the functions which are not state functions. And d correspond to the functions which are state functions. This is the way we differentiate them and these can written as dE plus PdV ok.

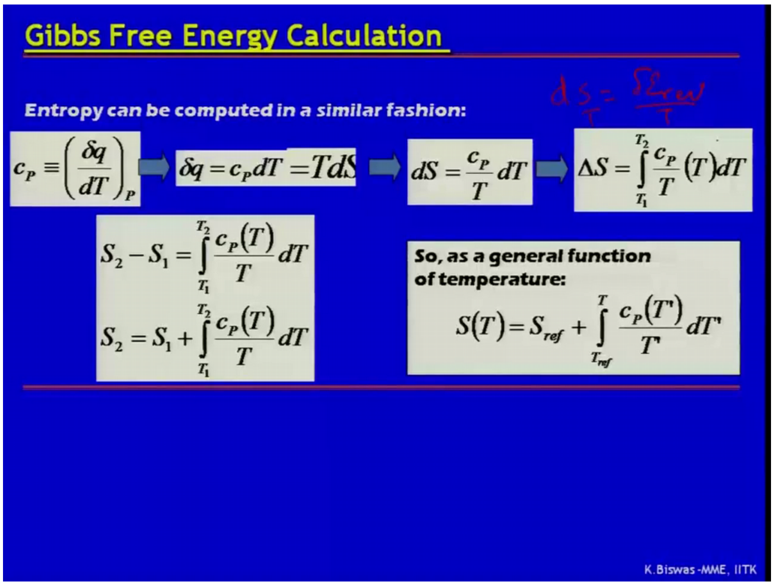
So therefore, at constant pressure is very constant pressure this is nothing but equal to dH, because if you differentiate the top equation H equal to E plus PV. So, del H is del E plus del PV PdV plus VdP. So, at constant pressure pdp dp is equal to 0; that means, is equal to dE plus PdV. So, that is why we get C P equal to del H by del T. So that means, del H is nothing but C P dT. So, this can be calculated by knowing the value of C P integrated over temperatures T 1 to T 2. In actual sense we measured H or enthalpy just by knowing the C P of the system. If you know the C P of the system very well we can calculate enthalpy of the systems very nicely.

Now, next term is known as enthalpy. Next term is known as sorry the entropy before I discuss that I like you tell you that we are never interested in calculating in thermodynamics the absolute values of the these functionals, like H or S or G. We are always interested to know the change or rather delta values of these functions. So, that is why H 2 minus H 1 is already shown you where it is a basically C P dT integrated over T 1 to T 2 or you can calculate H 2 as a function of H 1 plus these integral.

So, thus these are the routines formulae you should know to solve the problems in the course. So, as a general functions of a H function is temperature we always write H T as is equal to H reference plus cpdT indicated over T reference to any temperature T. Where a reference is a reference value that is normally taken as a enthalpy at a constant temperature, and pressure normally we take at 25 degree celsius temperature and 1 atmospheric pressure.

But remember these a reference has no meaning, because we never bother, we never will be interested to know absolute value of H, we will be always interested to calculated delta H. So, delta is nothing but at H T minus a difference. So that means, we are always interested to the calculate integral value which is shown in the function that is this one. So, that is what is a important when you know when you calculate the free energy functionals.

(Refer Slide Time: 07:57)



Gibbs Free Energy Calculation

$dS = \frac{\delta q_{rev}}{T}$

Entropy can be computed in a similar fashion:

$$c_P \equiv \left(\frac{\delta q}{dT}\right)_P \Rightarrow \delta q = c_P dT = TdS \Rightarrow dS = \frac{c_P}{T}dT \Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{c_P}{T}(T)dT$$

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{c_P(T)}{T}dT$$

$$S_2 = S_1 + \int_{T_1}^{T_2} \frac{c_P(T)}{T}dT$$

So, as a general function of temperature:

$$S(T) = S_{ref} + \int_{T_{ref}}^{T} \frac{c_P(T')}{T'}dT'$$

K.Biswas-MME, IITK

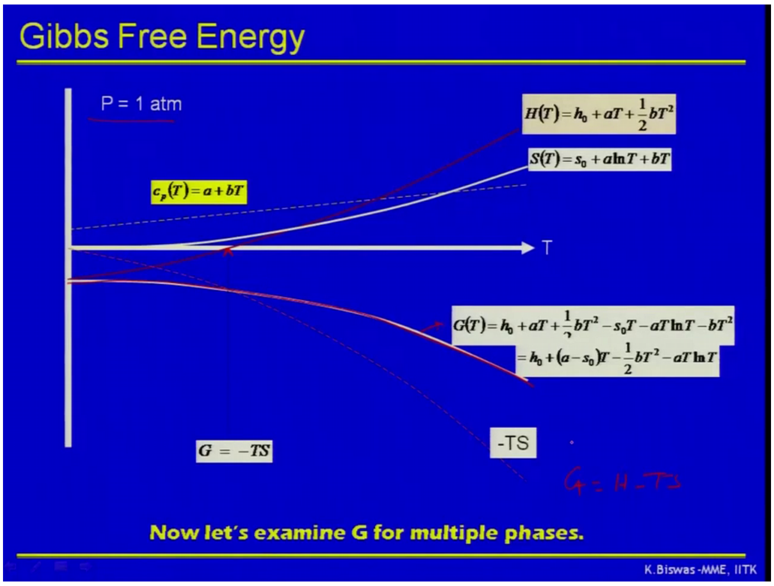
So now entropy is obviously, the second time S is known as entropy of the system. And remember entropy is always difficult concept for the students to understand. We will discuss about entropy later, what is the physical meaning of it first you have to understand what is what is the mathematical meaning of it. You know second law of thermodynamics defines entropy. And you know the second law of thermodynamics tells you that entropy is defined as like these dL is equal to del q reversible by temperature. So, where the change of entropy dS is given by del q reversible this is reversible heat, heat change divided by the temperature T. So that means, T this change is defined as a particular temperature T. This is the real definition of entropy directly originates from the second law of thermodynamics.

So, we can simply write down we know that this del q reversible sorry del q reversible is equal to T dS right. So, del q we know that C P is specifically equal to del P del q by del T at constant pressure; that means, del q equal to cpdT. So therefore, we can write down by connecting these 2 del q and these del q that cpdT is equal to TdS. So, how do you get that then? So, dS is nothing but C P y T. DT remember dS entropy is a state function that is why you use d not del, but q heat change is not a state function it is a part dependent function that is why we will use del. So, these are the very basic thing you should know from thermodynamics.

As I said you in the first lecture you must have some basic idea about thermodynamics. I am not going to go back on each of these things explain you of this last this situations. So finally, we can write down this way that entropy is nothing but entropy which is nothing but integral C P by T over T 1 to T 2. Again we are interest in calculate a change not interest in calculated the absolute value of entropy. And we can always write down the same equations like we have done in case of enthalpy.

So, finally, G is a function of enthalpy and entropy for a different values of temperature and pressure. When pressure is caused due to only a function of temperature for a pure materials right. So, by knowing C P I can calculate enthalpy and entropy of the both this parameters using these simple integrals or simple integrations. Rather once you know that you can actually do all kinds of stuff, all kinds of mathematics.

(Refer Slide Time: 10:41)



Gibbs Free Energy

P = 1 atm

$H(T) = h_0 + aT + \frac{1}{2}bT^2$

$S(T) = s_0 + a\ln T + bT$

$c_p(T) = a + bT$

$G(T) = h_0 + aT + \frac{1}{2}bT^2 - s_0T - aT\ln T - bT^2$

$= h_0 + (a - s_0)T - \frac{1}{2}bT^2 - aT\ln T$

$G = -TS$

-TS

$G = H - TS$

Now let's examine G for multiple phases.

K.Biswas-MME, IITK

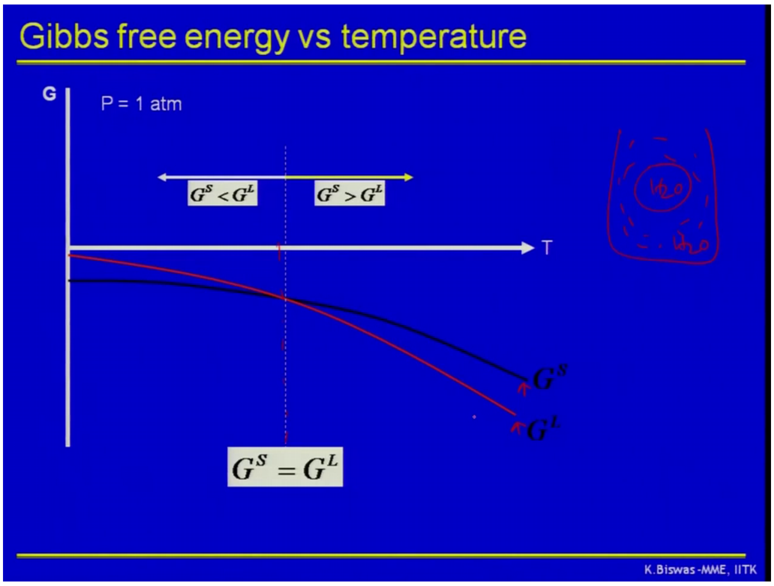
Let us do that, it is always better to use plots. Because plots will give you to the direct link between the physical meaning of the functions and the applicability. So, let us suppose I am plotting temperature on the x axis, and plotting this functions enthalpy entropy and free energy; obviously, free energy depends on the enthalpy entropy and the y axis. So, let us suppose C P most of that material C P can be approximated as a function of temperature like a plus bT, this is until fastward approximation one can actually keep on adding terms, but for simplicity we will assume C P is equal to a plus bT. It is nothing but a steady line you can see here the slope is b intercept is equal to a ok.

So now I integrate it the way it is functions are shown. So, H will be equal to H 0 plus at plus half bT square. I do not I do not want to do the maths, you do yourself in your problems you will get it know. So, this will look like this that is the red curve the white curve is basically entropy. Entropy is given as S 0 plus a log of T plus bT because the C P y T. So therefore,. So therefore, a log of T will become dT yT is log and integrated over certain temperatures. So, these are the values of the functions easily get. We can actually approximate this way. Now how do I get minus T s? Minus T s is nothing but S into T taken minus. So, that is what it looks like the dotted red line red curve is shown below. Now what is the G, G is nothing but H minus T s because T s I know, H I know. So therefore, I can know G and G is shown like this H 0 plus a minus S 0 T minus half bT square minus at log of T.

So, if I plot that this will look like these that white line which is see here is what is a G T. So, what you see from this curve it is basically it a curve with a negative slopes. This is obvious because entropy absolute values always positive, and G is given as H minus T S. So therefore, if I simply take differential of these the slope of the curve will be equal to minus entropy. So, that is why it has a negative slope and entropy is always positive value it cannot determined by negative absolute entropy that is why it has a negative slope. And this is why you should know very well. Now we can see here there is a cross over between minus T s and the G. That is where H is equal to T S. Because G H is equal to T s means the enthalpy and the entropic parts are equal, that is why this happens. Now I can write down this because H is equal to G of S G is equal to minus G S I am sorry I said wrongly.

So, here at this points this is nothing but G is equal to minus T s because H is considered to be 0 here you can see here H is 0 here on this point. This is lying on the temperature axis. So therefore, any point lying on the temperature axis for any of this functions value is 0. So, let us examine So, that is what is G looks like. So therefore, what you need to take away from the maths is from these plot always looks very done with only thing you should take a these curve G as a function of temperature at a fix pressure. It looks like this kind for a pure component. Remember we are not discussing about un pure components we are discussing about only pure components. Let us look at G are different phases what will look at because we are consist stability. So, stability means we have to compare different G values.

(Refer Slide Time: 14:20)



Gibbs free energy vs temperature

So, this is these are my 2 G. Red curve corresponds G of liquid ats the this is G of liquid you can see here this is G of solid. Let us consider for the sake of understanding in a beaker you have a ice as I shown you and you have water. And both are a H 2 O, this is solid H 2 O, this is liquid H 2 O. In a components no difference. And they are in touching they are actually in equilibrium.

Let us suppose if they are in equilibrium and if I plot a G of the solid and liquid there will be a cross over as you can see. It will come clear to you why this cross over is present, this is the cross over where G equal to G of solid equal to G of liquid, correct? So, at the point both the phases have same value of free energy. As I told you at the beginning of my lecture the G or the free energy or Gibbs free energy value dictate the stability of the phases; that means, by comparing the relative positions of the G as a function of temperature at a particular pressure, I can pearly clearly say which place will be stable which place will be unstable.

Let us do that now. So, at the cross over both are equal. And that is what going to happen at 0 degree celsius temperature one atmospheric pressure because at 0 degree celsius. Temperature atmospheric pressure both ice and water are stable or co exist. They will not there will be no net reactions, between ice and the water. There will be at mechanical thermal and chemical equilibrium. Because that is what is the equilibrium melting temperature of ice or freezing temperature of water at one atmospheric pressure. So, that is why at one atmospheric pressure G of S or G of the ice or G of the water or liquid will cross over, and that is cross over tells you they are equal.

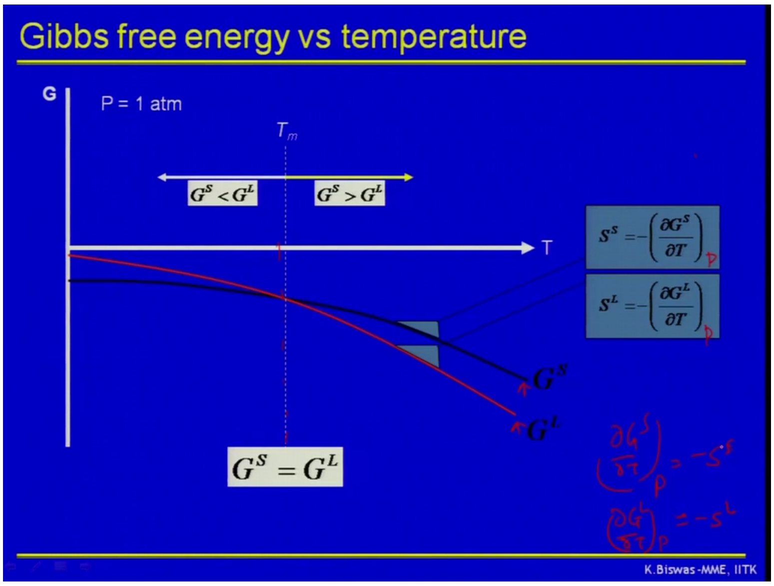
So that means, there is no net difference between the free energy of these 2 phases. Now below 0 degree celsius temperature or 273 kelvin G S is less than equal to less than G l; that means, the free energy of the solid is lower than free energy on the liquid. At you can see that free energy of solid is at the they are lying at the below the free energy of the liquid. So that means, below 273 k r G celsius ice is more stable than water; that means, if I cool down the water below 0 degree celsius water will slowly transform to ice.

That is a first phase transformation I have been telling you all S. So, that is very evident from the G, that is why you always think about Gibbs free energy. Gibbs you will come to know about Gibbs William Gibbs from many of the internet sources you was one of the great scientist in the field of thermodynamics in a material science. And this functionals puts down the theory in mathematical formalism in such a way you going to explain most of the observe phenomenon. Now if I go on the other side that is above 0 degree celcius temperature, we know above 0 degree celcius temperature water is more stable. Ice is melt down to water. How we can explain that? Is very clear from these 2 relative dispersion of these 2 curves G of solid is higher than G of liquid. So, as a G of solid high energy of liquid, liquid will be most stable, because the stable phase is we will always have lower, correct?

So, this is what you see very clearly on this plot. You do not have to do a rocket science to understand this it is very, very simple and very easily understandable in graphical form. That is why we always go for graphicalic representation of these equations. Mathematically most of the things are looks like little complex, but the moment you plot on a 2 dimensional (Refer Time: 18:28) as a function of a temperature the constant pressure things will very, very clearly understood.

So, these same thing I can do it I am that is I mentioned already. The temperature at which both the solid and liquid free energy is equal or known as the melting of solidification temperature, here it is written as Tm. Now if you look at the slopes of this curve, as I told you the slopes of this curve is again I just in the slide only I discussed.

(Refer Slide Time: 18:46)



Gibbs free energy vs temperature

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

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

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

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

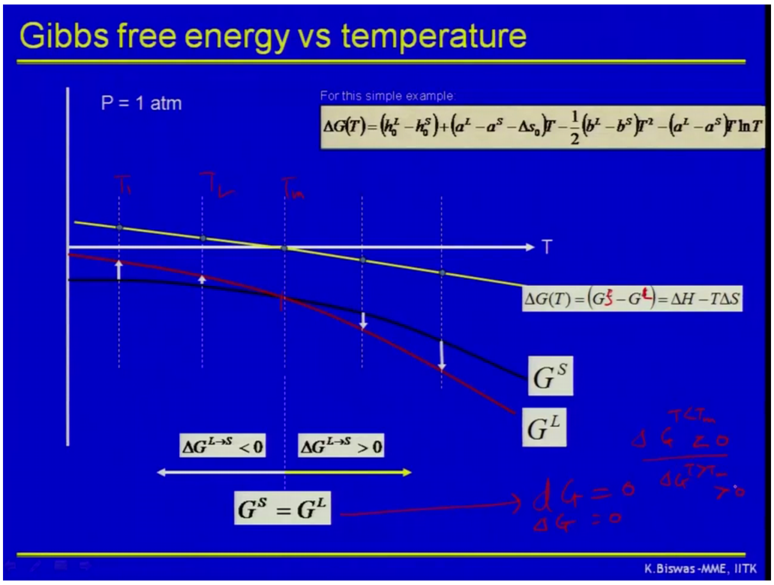
K.Biswas-MME, IITK

I am just showing you in detail So, that you understand it very clearly. This is not this is all entropy of the solid is equal to minus G S delta G of the G. This is the functional actually the first derivative of G S function of temperature. This is at one atmospheric pressure therefore, there is no need of writing P as a subscript because pressure is constant.

Similarly, entropy of those liquid is equal to this. So, rather I can write down G s T at constant pressure is nothing but minus S. And because S is always positive this slope is negative, because you have minus sign. And similarly G of liquid divided by R T first derivative of G of liquid it is some temperature is equal to minus or this is S as, sorry it is in S l. Entropy have only one thing solid liquid gas does not matter absolute value is always positive only third law of thermodynamics tells you the entropy of a pure crystalline solid and absolute 0 degree surface temperature is 0. At above the absolute 0 degree temperature any system will have a positive value of entropy.

Now can I do this thing in term of delta that is the change? Because I have been mentioning you that these change is what is we are interested change of this relative change of this functions not the absolute values. So, let us do that if I do that.

(Refer Slide Time: 20:31)



Gibbs free energy vs temperature

For this simple example:

$$\Delta G(T) = (h_0^L - h_0^S) + (a^L - a^S - \Delta s_0)T - \frac{1}{2}(b^L - b^S)T^2 - (a^L - a^S)T \ln T$$

$$\Delta G(T) = (G^S - G^L) = \Delta H - T\Delta S$$

K.Biswas-MME, IITK

So, let us consider these in terms of delta G. For a simple system let us what again everything G, I have already written there delta G will look like this. You please do not ask me to do the maths you can do yourself. Now delta G is nothing but G L minus G S that is equal to H delta H minus T delta S at a constant temperature, and a constant pressure.

Now, I have again plot a G of solid G of liquid there is a cross over here you can see here. So now, I consider a temperature any temperature these temperatures of course, this y dot O line is shown here this is the temperatures related to T 1. As a temperature delta G is nothing but the these difference shown by arrow delta G is d of l minus G of S ok.

So, these are all shown you here. At temperature T 2 this is what is the difference by arrow small arrow. So, arrow has got reduced numerical value of arrow. And at the melting temperature or solidification this is Tm this is vanished. There is no delta G that is equal to 0 basically. Now if I go to the other side what is happening? I have put arrow in the downward sign. There is a it is a reason behind it will come very clear to you now.

So, you can surely as you go away from the melting temperature on the right hand side again delta G is increasing, but the sign is changing. So, this is So, as G S equal to G L at a melting temperature. Below the melting temperature delta G here my delta G is G L minus G S, this thing you should not forget. That is though it is written delta G superscript l to S solid or water liquid water to solid ice. H is equal to less than 0, am I clear? Is very clear, because you can see here the G L is higher than the G S right, yes. Now let us see on the right side right side delta G is basically equal to positive. Why it is showing positive negative? Or am I doing some mistake? Let us correct it. I mean everybody can have mistakes. So, the way the delta G is defined between product minus front phase. So that means, G S minus G L it will be, I have written wrong. So, you can correct it in the actual. So, this is G S minus G L. So, if that is the case then delta G below T m.

Temperature less than Tm is less than or equal to 0, or less than 0 actually. And above the melting temperature or above Tm it is greater than is equal to 0. That is clear because this is G S is higher here then G L. So therefore, it is greater than or equal to 0. G S is lower here than the G L. So therefore, less than equal to 0. And add the melting temperature this is equal. So, this is how we can calculate. Let us explain it in detail manner this one. So, what we can understand from this very clearly, that above the melting temperature because delta G is 0 therefore, solid will never be stable, correct? There is no driving force available for the liquid to transform into solid.

On the other hand below the melting temperature there is it is less than equal to less than 0; that means, in our finite force available finite energy available to it. So, what is the meaning of negative and positive. Let me explain in thermo dynamics term. That is what problem we have already seen. Negative change of any function especially G in thermodynamics means you have available energy to you. System has energy available to it. Positive means system has no energy available to it. This is a (Refer Time: 24:18) used in thermodynamics. So that means, that below the melting temperature, there is a driving force available energy net energy available for the system to transform to solid.

On the other hand above the melting temperature above the Tm, there is no energy available for the system to transform the liquid to solid. So, this sin of delta G tells you the direction of transformations. At the melting temperature that is what is shown as dG or you can write delta G is equal to 0. So therefore, at the melting temperature there is no change of positive and negative change of free energy, this is vanishing. And because of this vanishing free energy change there will be no energy available for the system for transformation. But the system will not undergo any transformation. That is what happens at 0 degree celsius temperature and (Refer Time: 25:15) is very patient ice and water will co exist, they will never transform to each other. On the other hand below the melting temperature there is a negative sign of delta G, delta G is less than 0. And negative sign means there is a driving force available for the system to transform.

That above the melting temperature there is it is greater than 0; that means, there is no driving force available for the system to transform from liquid to solid. In a nutshell we should not spend more time on that in a nutshell the sign of delta G tells you the direction of transformation. If for a particular reaction suppose a plus b going to c, if the sign of delta G is negative in this direction a to b a plus b going to c that mean reactions will happen. If on the other hand the sign of delta G is positive reaction will not happen. These plot is telling you that answer. In a simple ice water analogy, I am giving you this concept that sign of delta G is going to dictate the direction of phase transformation. Finally, the answer of phase transformation direction with the solid (Refer Time: 26:44) transform to liquid or liquid transform to solid, can be obtained by simply calculating the delta G and plotting in this manner ok.

So now that is for very easy things can be done for the pure systems. What will happen you have an un pure system like alloy? Like or mixture of 2 phases or 2 components like, water with salt, coffee with sugar. When a 2 component mix together can I use the same analogy answer is no. So, this is what we are going to discuss in the next lecture whether can we calculate G and delta G of those systems and get the similar answer. Remember the conditions will be remaining same. The conditions of phase transformation directions will remain same. Things which we are going to change is how do you calculate the G H and S parameters for those systems. That will discuss in the next class.