**Phase Equilibria in Materials (Nature and and Phase Properties of Materials - II)**
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Lecture – 03
Phase Stability in Materials

Today, we start the lecture number 3 of Phase Equilibria course. So, just I will give you a recap of what we did in the last class.

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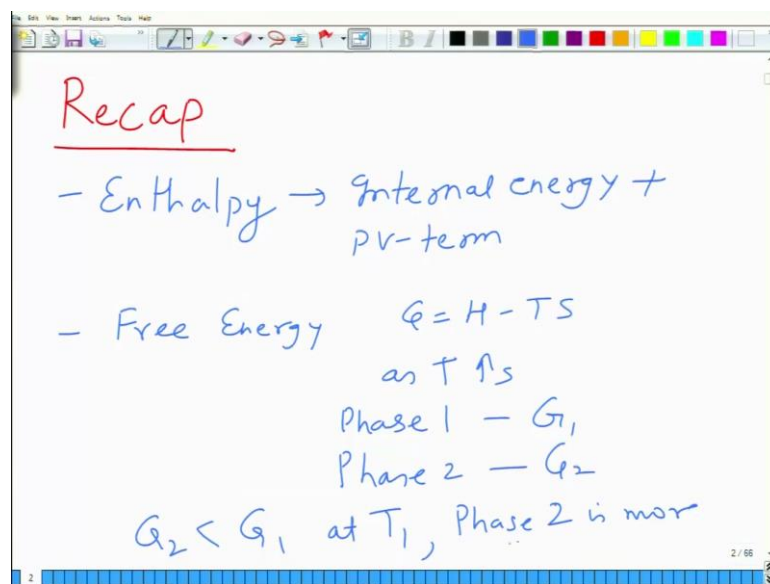
In the last lecture, we learnt about the principles of Enthalpy which consists of internal energy and a PV term. And this Enthalpy is basically the heat content of the of the materials and enthalpy of; for example, liquids is higher than that of solids or enthalpy of gases is higher than the higher than the liquids and then we talked about this free energy and free energy is nothing but $G = H - TS$ where S is the entropy, entropy is a measure of randomness in the system.

So, it is the relative competition between these two quantities as the function of temperature, for most material system and the competition between enthalpy and entropy determines which phase will have lower free energy as compare to another. So, basically what happens is that as we increase the temperature; as temperature increases, so let us say you have phase 1 with free energy G_1, phase 2 has free energy G_2 and these G_1 and G_2 terms will include enthalpy and entropy terms one. So, enthalpy will increase as the

temparature increases, entropy will also increases as the temperature increases, but since entropy term goes as negative, it is the competition between two will win.

So, which will allow which will prevail, so for instance if $G_2 < G_1$ at certain temperature T_1, then phase 1, phase 2 is more stable. So, you will find the system will drive towards having phase 2 as the stable phase. And then, we came to concept of equilibrium. The concept of equilibrium was, so if this is the free energy and this is let us say atomic configuration, so you can have free energy structure like this.

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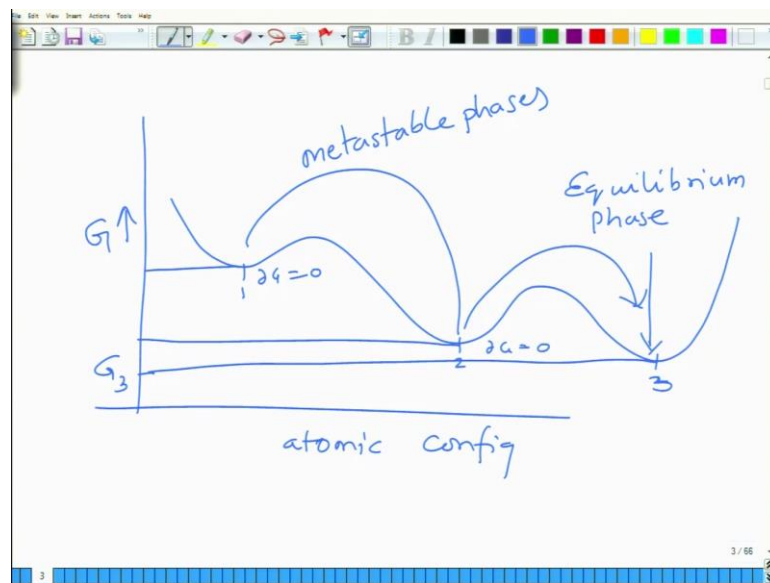
So, you can see that there are local minimas. So, this is for example 1, this is 2, this is 3 and you can see that, they have corresponding minimas and you can see that state 3 has lowest free energy, but there are local minimas. So, this local minimas correspond to what we call as metastable phases and this is the equilibrium phase.

So, although metastable phases also have $\partial G = 0$ at the minimum, if you provide sufficient time and energy, this will, the atomic movement will happen in such a way, so that it goes from this to that and then this to this. So, this is the stable equilibrium phase if you allow sufficient time for the system to achieve equilibrium. So, this is what we discussed in the last lecture. In the today's lecture, we will talk about what makes a phase stable. So, question that we will answer.

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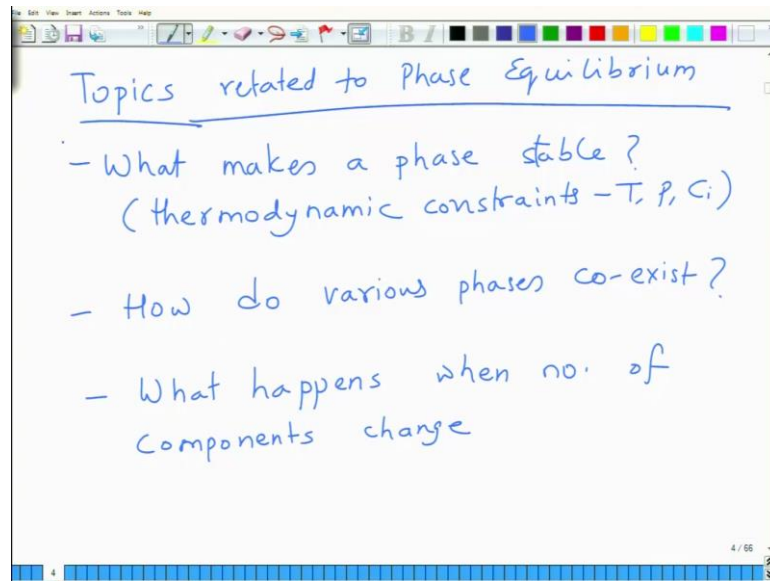
What makes a phase stable given that, constraints are so, thermodynamic constraints are typically T, P and C_i. where C_i is the composition of i'th species.

And, how do various phases co exist? This, we will see later on in more detail, but these are the question that we need to answer in phase equilibrium, topics related to I would say phase equilibrium ok. And then, what happens, when number of components change in a system and then and so, all of this requires little bit thermodynamic framework. So, that is what we will do in remaining lectures.

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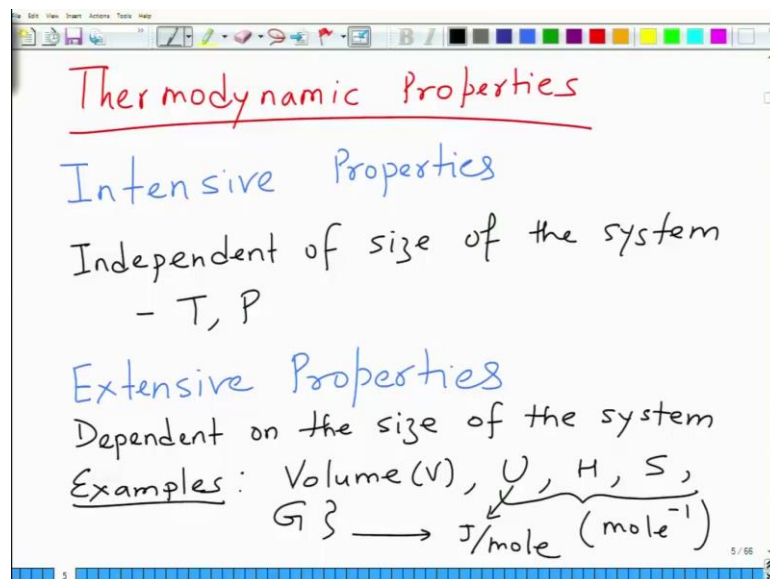
So, let us first look at the thermodynamic properties. There are two properties which we normally encoun[ter]-, talk about; one is called as intensive properties, intensive properties are those which are independent of size of the system.

Size could be for example, mass and what are these properties? These properties are variables such as, temperature and pressure. On the other hand, we have another thing called as extensive properties which are determined whose magnitude depends upon the size of the system. So, for example, so these are you can say dependent upon the size of the system. So, examples are in this case, example could be for example, volume. Volume depends upon the size of the system, internal energy U or enthalpy H and entropy S or free energy G and all of these units; you can see they are determined in. So, whatever the value is, so for example, you can have internal energy; you can have Joule/mole. So, they are basically did their molar quantities, as a result they are expressed as mole^{-1}, ok.

So, they are basically expressed in the form of per unit mass. Of course, volume has it is own unit in terms of meter cube or whatever. So, most of these thermodynamic quantities are expressed in terms of mass of the system.

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Now, let us look at the, how the phase changes happen. So, as you go for example, let us say I go from temperature $T_1 \rightarrow T_2$ and this is the condition that $T_2 > T_1$ then the phase 1

has free energy which is $G_1 \rightarrow G_1'$ ok. The free energy decreases as a function of temperature and phase 2 is another one which has a free energy $G_2 \rightarrow G_2'$, ok.

Now, in terms of thermodynamics if at T_1, $G_1 < G_2$, then phase 1 is stable and if at T_2, $G_1 > G_2$, then phase. So, I would say basically $G_1' > G_2'$. So, at T_2, $G_1' > G_2'$, then phase 2 is stable. Now, phase transformation if you, so, when you go from phase 1 to phase 2

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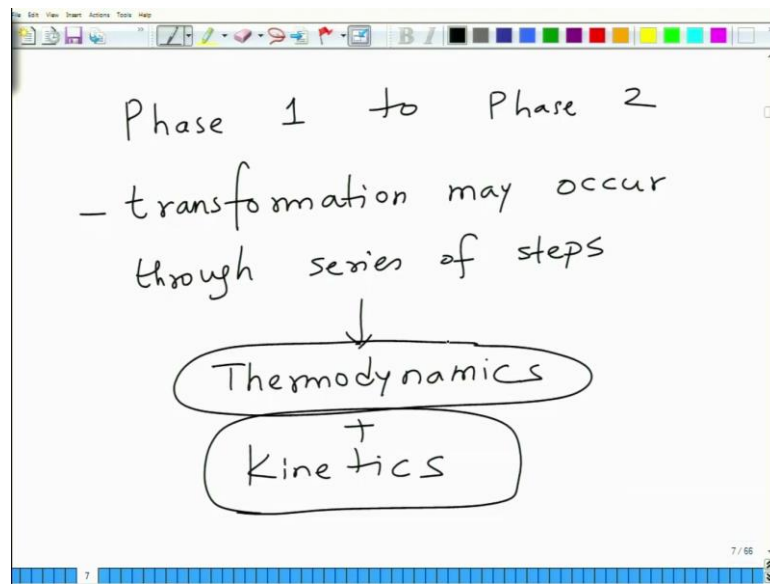
It may not be a continuous transformation, the transformation may happen, may occur through series of steps which may involve formation of a few metastable faces on the way.

So, you need to provide sufficient time. So, all the thermodynamics tells you that phase 2 will be more stable if it is energy is lower at higher temperatures as compare to phase 1. The route to achieve phase 1 to phase 2 is not determined only by thermodynamics, but also by kinetics. So, phase transformation is basically determined by both thermodynamics and kinetics. So, we will not dwell into the kinetic aspects in this course. We will only determine with the existence of equilibrium phases at a certain, at a given condition of thermodynamics constraints. So, without, so we will only look at what kind of phases will exist if you define temperature, pressure and composition for a given system.

So, let us just look at the thermodynamic aspects of it. Now, let us move to the next topic. The next topic is, we first consider within this thermodynamic framework, what happens in Single Component Systems.

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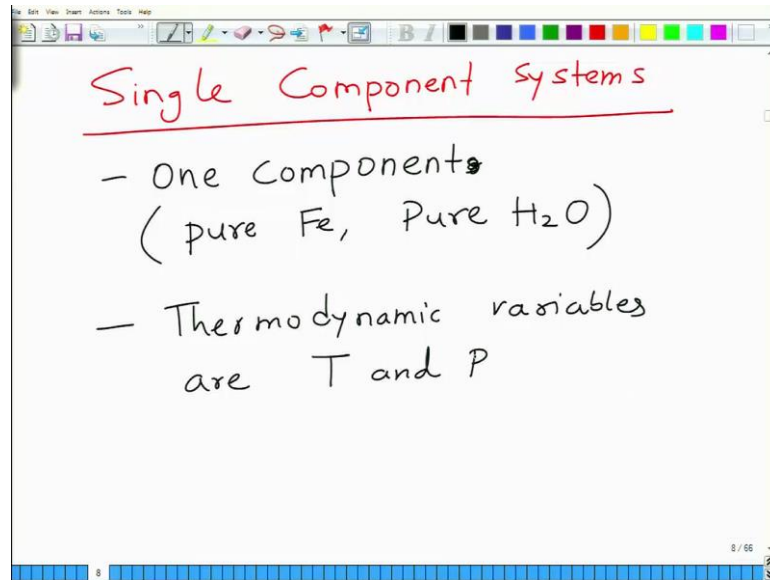
A Single Component System basically, what it means is that you have only one component.

This could be pure iron or pure H_2O, ok. So, these could be the examples. So, basically in this case since you have only one component the thermodynamic variables are temperature and pressure. These are the two important variables that we have and we will see some example of this. So, let us see, so basically, what we what we do is that we want to predict the phase stability as a function of temperature and pressure for single component system. So, let us first look at how the free energy varies as a function of temperature.
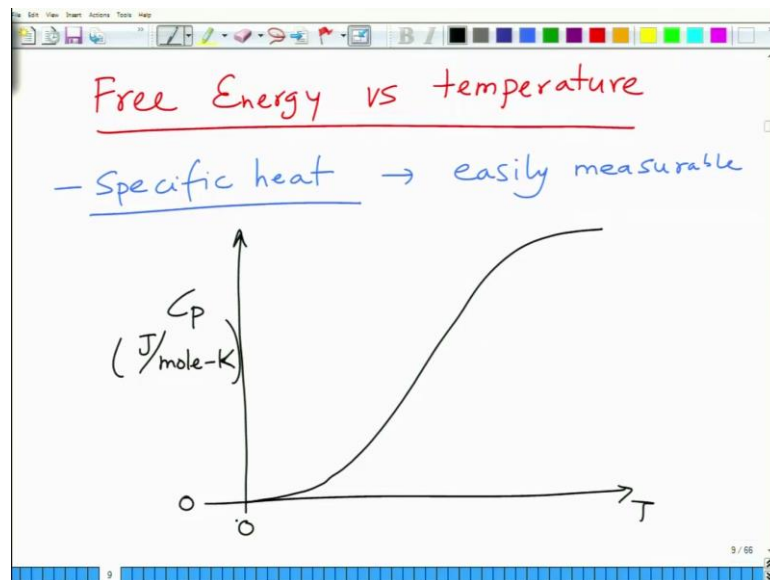
Now, in this regard, first we would like to define the Specific heat, Specific heat, ok. Specific heat is, now specific heat is something which is easily measured. It is a measurable quantity and it is known for most substance.

So, when you plot a specific heat as a function of temperature T, then specific heat for the unit of this will be Joule/mole-Kelvin, ok. So, a specific heat of most substance goes as something like that, ok. So, start from 0, this is the variation of specific heat will be and what is the specific heat.
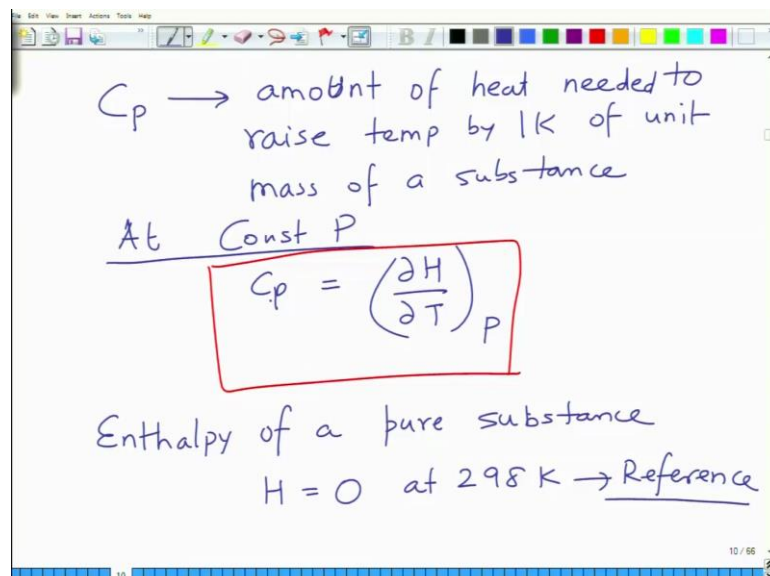
Specific heat is basically, amount of heat that is needed to raise the temperature of a substance or temperature of one gram or unit mass of a material by one Kelvin. So, basically you are all aware of what is C_P, C_P is the specific heat at constant pressure. So, amount of heat needed to raise temperature by one Kelvin of unit mass of a substance or material ok. So, at constant pressure, C_P is defined as,

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

So, this is the question that you have for, this comes from basic thermodynamics. Now, another thing that we need to notice; enthalpy of pure substance, H = 0 at 298K. This is what is taken as a reference level. If H = 0 at 298K for a pure material taken as reference level, then all you need to do that, you need to integrate if you want to find out the variation of H as a function of temperature, you need to integrate C_P.

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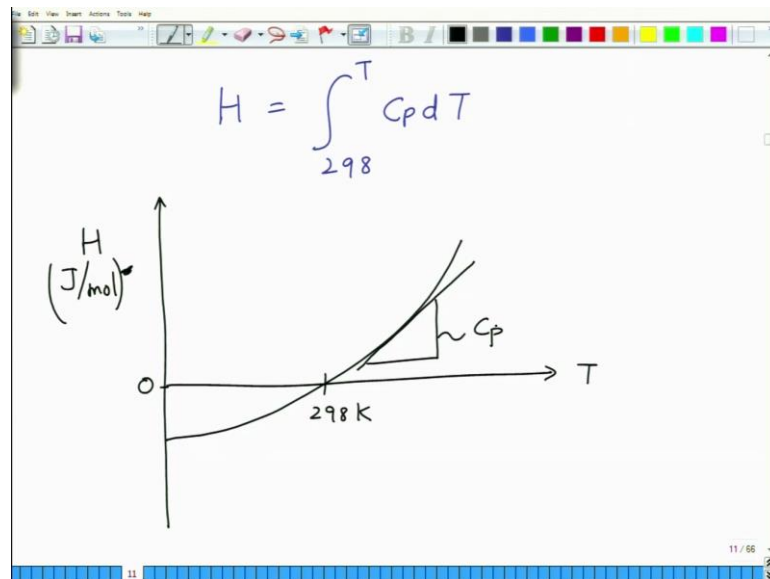
So, if you, so for finding enthalpy the H will become,

$$H = \int_{298}^{T} C_P dT$$

And when we plot this as a function of temperature, so this is H, this is T. So, H is basically Joule/mole and this is let say 0 Kelvin and the behavior of this is something

like, so at 298 Kelvin, H is 0 and the slope of this is basically you can say a C_P. So, this is what is the, this is what is about enthalpy.

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Now, let us look at the variation of entropy. Now, we know that C_P from the basic you need to know this much of basic thermodynamic,

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

because you know, $dS = \frac{dQ}{T}$

and Q for all practical purposes if PV term is small, you can take Q as H. So, basically this will become the same as what we saw. So, basically what you have done is, you have replaced dH by dQ ignoring the PV term. So, as a result, your, here you had, so this will become $C_P = \left(\frac{TdS}{dt}\right)$, TdS is nothing but dQ, dQ is nothing but dH. So, we are following the same definition, right.

So, since, at, now by definition at 0 K, S = 0. So, then if you just integrate this expression, the above equation,S will become,

$$S = \int_0^T \frac{C_P}{T} dT$$

This is the expression for entropy that you will obtain from the basic thermodynamic equation and if you plot this, the plot will look something like that.
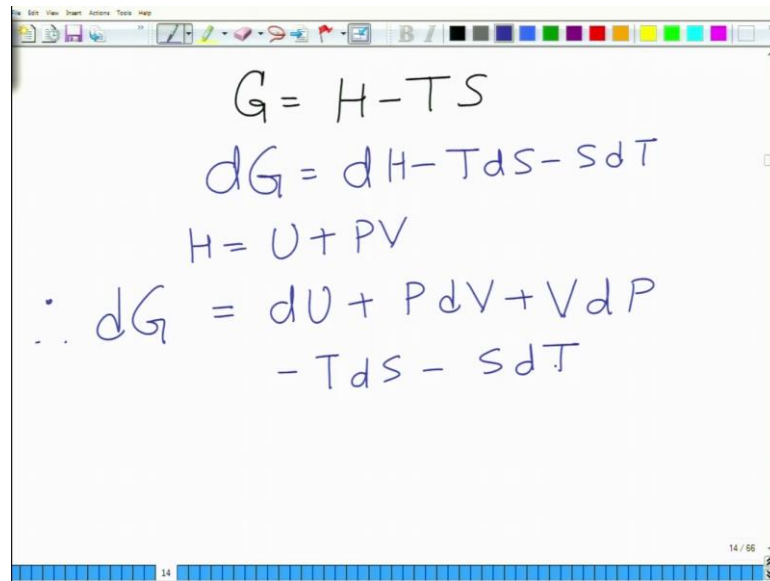
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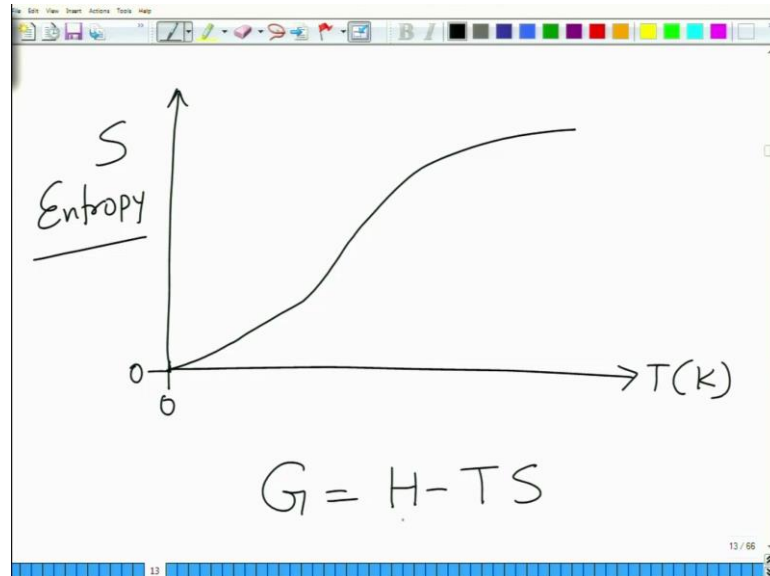
So, this is 0, 0, T in Kelvin, we have entropy,ok and ok. So, this we will follow behavior we have something like this ok. So, this is the variation of entropy. So, entropy increases as the temperature increases. We can see both of them, the enthalpy also increases as a function of temperature and the entropy also increases as a function of temperature but in the free energy equation,

$$G = H - TS$$

The enthalpy increases and this term will decrease because S is also increasing as a function of temperature. So now, we know that

$$G = H - TS$$

Expand upon it further,

$$dG = dH - TdS - SdT$$

and we know that

$$H = U + PV$$

So, replace this then,

$$dG = dU + PdV + VdP - TdS - SdT$$

Now, for a system,- now this is the expression that you get.

So, now for a system with fixed mass and composition, we write

$$dU = dQ - dW$$

Since, $dQ = TdS$ or $dS = \dfrac{dQ}{T}$ by definition of second law

$$dU = TdS - PdV \ (for \ a \ closed \ system, W = PV)$$

dW = Pd V for a closed system. We can say W = P V ok. Now, if that is the case then

$$dG = TdS - PdV + PdV + VdP - TdS - SdT$$

. So, we cancel this, we cancel this and what we obtain at the end is

$$dG = VdP - SdT$$

This is the basic thermodynamic equation that we have. So,

$$At\ canstant\ pressure\ dP = 0$$

and hence $dG = -SdT$ or you can write alternatively,

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

So, this is the variation of free energy as a function of temperature and you see that this is -S. So, free energy, since as the temperature increases, the entropy increases, the free energy will decrease as a function of temperature. So, this is a very important relation that you obtain.

Decrease of energy as a function of temperature at constant pressure, ok.
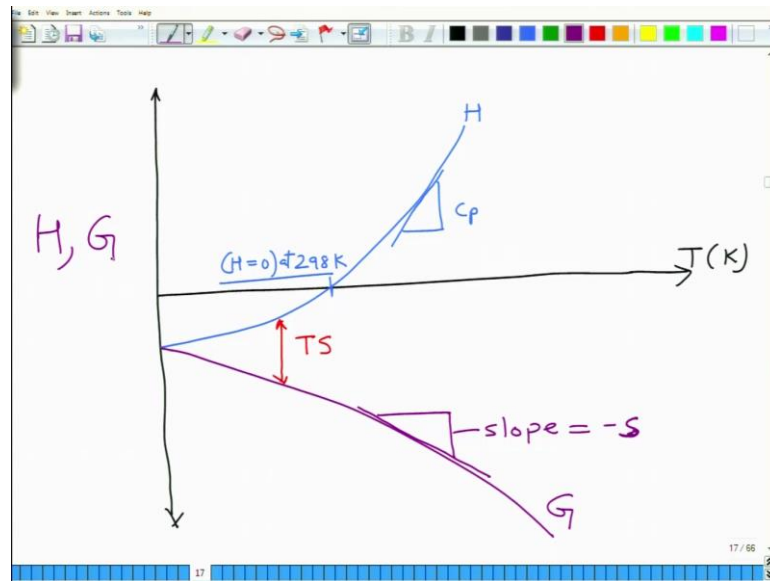
So now, let us plot, let us make a plot. So, this is 0, now this is T at Kelvin. So, we want to plot both H and G, the H for a given phase will vary like this. This is the variation of H and the slope of this of course, will be nothing but C_P and this is, you know you can say 298 K when H = 0 at 298 K. And the free energy goes as like this and the difference between these two is nothing but you can say TS. This is the difference, the TS. So, this plot that we have shown is of G and the slope of this is nothing but what will the slope = −S as we wrote in the previous slide. So, we can see that as a function of temperature although the enthalpy, so here you can write H, G, so, as the function of temperature the enthalpy increases because of increasing TS term, the free energy decreases as a function of temperature and the slope is −S. So, let us just look the example of liquid to solid.
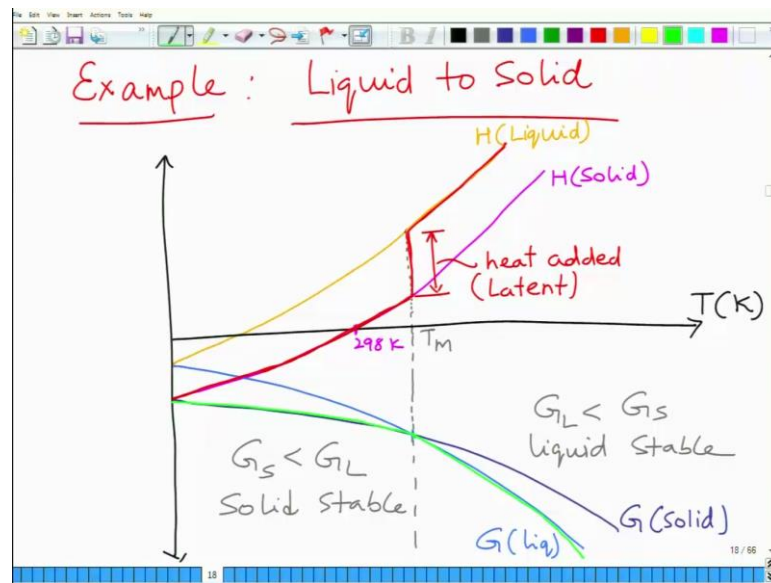
So, I again make a plot in this fashion and we will plot both. So, let say if I first draw the free energy for a solid phase, free energy for a solid phase would be like this. So, this is 298 K, this is H for solid, alright and then free energy for liquid would be, sorry enthalpy. So, this is enthalpy of solid and enthalpy of liquid would be higher than that of solid. So, if I now plot the enthalpy of liquid, enthalpy of liquid would go in a very similar fashion like this. And the free energy of two phases; so, for the first phase the free energy would be, so if I take the free energy; it would be like this ok.

And for a second phase, the term would be like this. So, now, if I look at it in a different, so, what I have drawn here is, this is free energy of let us say the solid phase, G_S and this is G_L and here it is H liquid ok. Now, what we see from this plot is, first let us look at the free energy. What happens with the free energy is that, free energy of both solid and liquid phases decrease as a function of temperature; however, we see that at this particular temperature, let us say this particular temperature is some transition temperature let us say in this case T_M, which is the melting point, we see that below the melting point, the free energy of solid phase is lower, but above the melting point, free energy of liquid phase is lower which means solid is stable in this regime. So, we can say in this regime $G_S < G_L$. So, we can say solid stable in this regime, $G_L < G_S$, we can say this is liquid stable regime. And what happens corresponding changes in the entropy, the entropy on the other hand sorry the enthalpy, you can see that at this temperature the overall entropy curve follow something like that. It follows in the fashion like this upto

this point. Then, at melting point there is sudden jump and then it continues. So, this is what is the overall change in the enthalpy and you can see at T_M, at this point there is no change in temperature all the heat that is added, so, this is the heat that is added, ok. See this is heat added this is basically the heat that is added for solid to convert into liquid right and this is basically the latent heat as we call it. So, at, when this heat is added, the bonds are broken, the solid is converted into liquid without raising the temperature of the material.

So, temperature of the material does not raise at this point, it remains at T_M which is called as a melting point and free energy curve on the other hand if you want to plot in a different way, the free energy curve up to this point, the free energy of the system continuous like this. And after this point, the free energy of continue, system continues like. So, this is the overall free energy of the system. First it follows the track of solid and at melting point it starts falling the track of liquid phase. So, this is what we have discussed in this lecture as to how the phase stability, how the phase formation happens and at what, as a function of temperature, how is the stability of these two phases governed with respect to corresponding changes in the free energy and the enthalpy. So, we will stop here. In the next lecture, we will we will further the discuss this and we will also discuss some more concepts related to change in the pressure of the system.

Thank you.