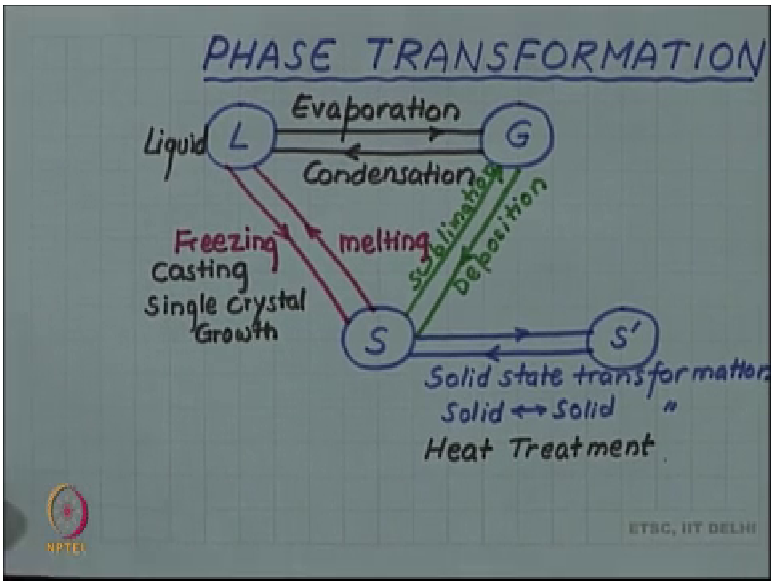
Introduction to Materials Science and Engineering
Prof. Rajesh Prasad
Department of Applied Mechanics
Indian Institute of Technology, Delhi

Lecture - 89
Phase Transformation

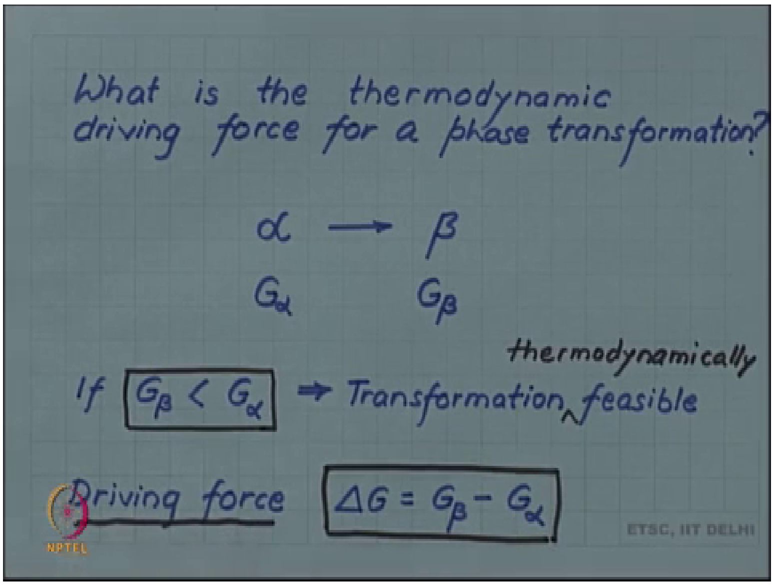
(Refer Slide Time: 00:08)



So, we will discuss today the topic of Phase Transformation. With phase transformation is a transformation from one phase to another phase. For example, a liquid phase shown here by L, this is liquid this can evaporate into a gas phase. So, we have a transformation evaporation, the gas can also condense back into liquid. So, we have condensation. A liquid can freeze into a solid. So, we have freezing, or a solid can melt into liquid, we have melting. A solid can directly sublimate into gas a process called sublimation, or a gas can condense back into solid.

We can call this deposition and a very important class of transformation is one in which one solid phase transforms into another solid phase. So, we can have a solid solid transformation, solid state transformation sometimes known as solid solid transformation. Some of these transformations are technologically very important. So, for example, freezing is used in casting which is a very important engineering a process, for fabricating many components, you also in the modern semiconductor industry, there is a single crystal growth and, solid solid transformation we will see is used very much in a process called heat treatment.

(Refer Slide Time: 03:52)



What is the thermodynamic driving force for a phase transformation?

$$\alpha \longrightarrow \beta$$

$$G_\alpha \qquad G_\beta$$

If $\boxed{G_\beta < G_\alpha}$ ⇒ Transformation thermodynamically feasible

Driving force $\boxed{\Delta G = G_\beta - G_\alpha}$

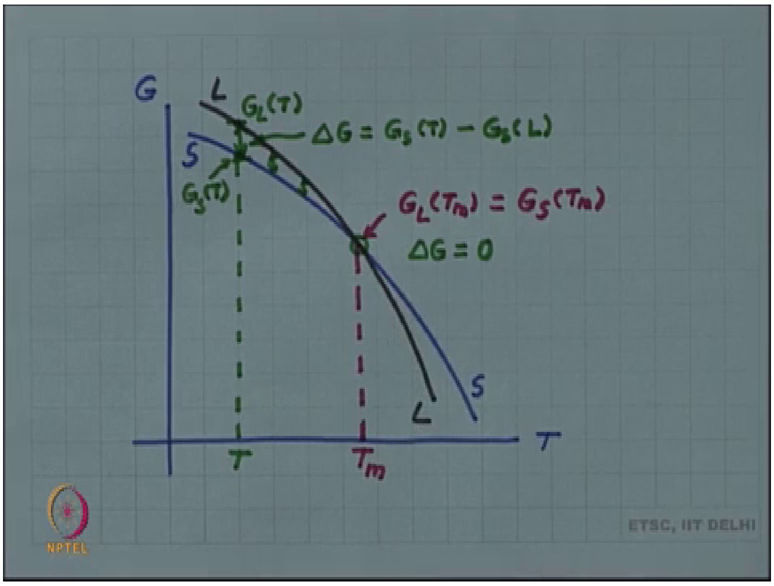
ETSC, IIT DELHI

Let us now look at the question that what is the driving force, the thermodynamic driving force of a phase transformation, by driving force we mean that when a phase alpha is transforming into beta, then the free energy of the two phases will be different. So, the alpha phase has a free energy G alpha whereas, the beta phase has a free energy G beta.

The difference between these two phases control the phase transformation, the phase transformation will be thermodynamically feasible. So, the transformation is thermodynamically feasible, only if the final product phase G beta has a lower free energy than the starting phase alpha. This is an important condition for phase transformation to occur at constant temperature and pressure.

So, this difference so since beta has to have lower free energy than alpha for transformation to happen, lower is G beta in comparison to G alpha higher is the driving force. This is what we mean by the driving force. So, the driving force is the difference between the free energy of the two phases, this difference is what we call the driving force.

(Refer Slide Time: 05:38)



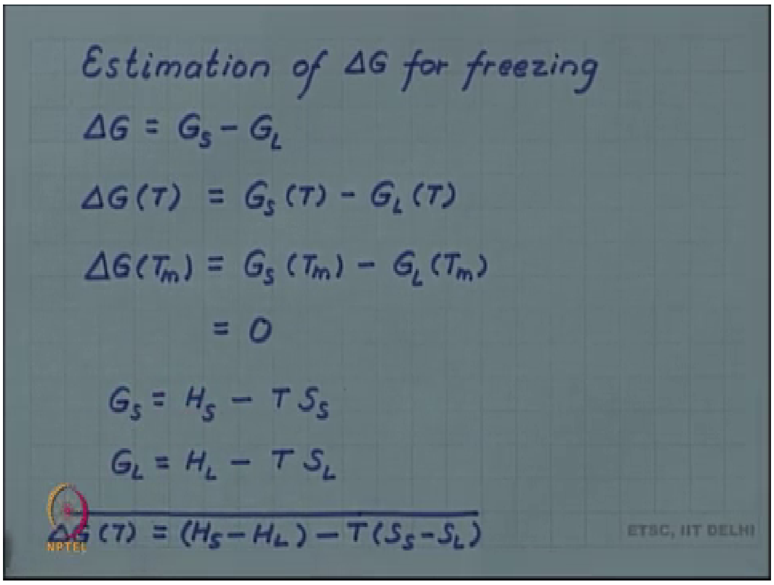
Let us look at what the free energy curves look like. So, here I have drawn free energy as a function of temperature for two different phases. So, the one phase shown in black, let us say represents the liquid phase whereas, the other phase represented in blue is the solid phase. So, we are talking of a solid liquid phase transformation here, you can see that the two free energy curves are intersecting at a given temperature. So, at that temperature the two phases have the same free energies.

So, this is the temperature which is called the thermodynamic melting point. So, at the melting point the 2 free energy G alpha and G beta are equal free energy of the liquid phase, at the melting point it is same as free energy of the solid phase at the melting point. Below the melting point one can see that the solid phase has a lower free energy than liquid phase.

So, liquid can transform into solid below the melting point, where as solid will melt into liquid above the melting point. So, if we have some transformation temperature, represented by this green vertical T, then at that transformation temperature the liquid phase has a higher free energy whereas, the solid phase has a lower free energy.

So, the difference between the two phases, this difference is what will be the driving force delta G G S T minus G S L. We can see that this driving force is actually a function of temperature. So, if T was closer to the melting point it is value the driving force value will be lower and exactly at the melting point the driving force is actually 0, delta G because the 2 free energies are the same the driving force is 0 at the thermodynamic melting temperature. So, that is why for actually freezing to happen some amount of under cooling is essential.

(Refer Slide Time: 08:56)



Estimation of ΔG for freezing

$$\Delta G = G_S - G_L$$

$$\Delta G(T) = G_S(T) - G_L(T)$$

$$\Delta G(T_m) = G_S(T_m) - G_L(T_m) = 0$$

$$G_S = H_S - T S_S$$

$$G_L = H_L - T S_L$$

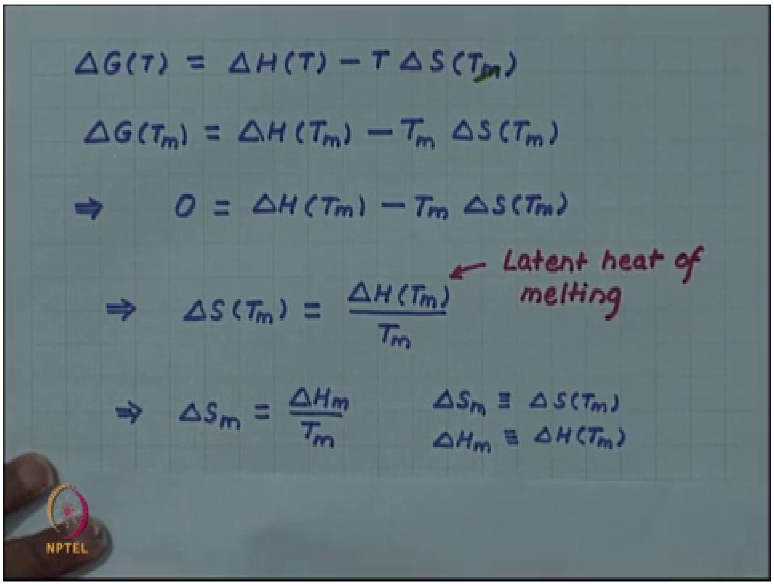
$$\Delta G(T) = (H_S - H_L) - T(S_S - S_L)$$

Let us now have an estimate of the in this free energy difference, or the driving force for freezing. So, by definition this driving force is free energy of solid minus the free energy of liquid. Since all these quantities are functions of temperature, we write them as delta G as a function of temperature T is equal to G S as a function of temperature minus G L as a function of temperature.

Now, if we evaluate this at the melting point, then we have an expression like delta G T m is equal to G S T m minus G L T m what we have seen, that G S and G L are equal at the melting point. So, this free energy difference delta G T m is 0. Now, at any given temperature we can write as G S is equal to H S minus T S and, similarly G L is equal to H L minus T S L.

If we take the difference, then the difference is the free energy change delta G which will be H S minus H L minus T times S S minus S L.

(Refer Slide Time: 10:20)



$$\Delta G(T) = \Delta H(T) - T\,\Delta S(T_m)$$

$$\Delta G(T_m) = \Delta H(T_m) - T_m\,\Delta S(T_m)$$

$$\Rightarrow \quad 0 = \Delta H(T_m) - T_m\,\Delta S(T_m)$$

$$\Rightarrow \quad \Delta S(T_m) = \frac{\Delta H(T_m)}{T_m}$$

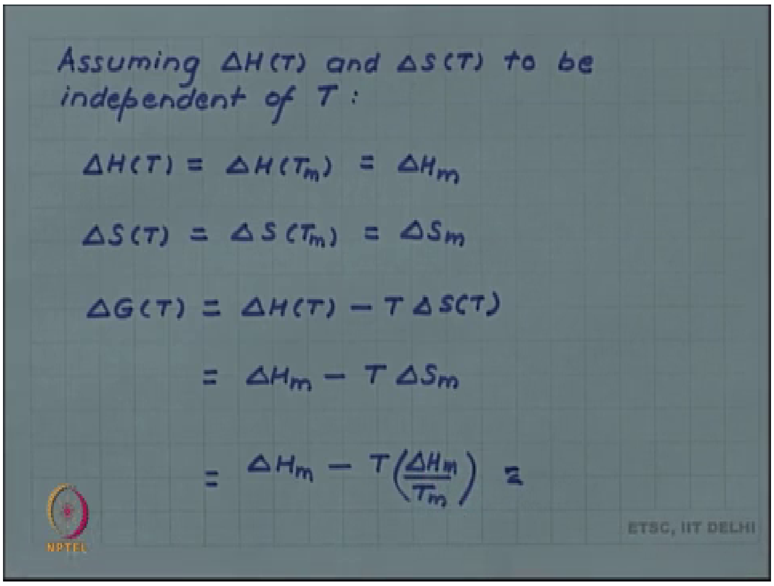
← Latent heat of melting

$$\Rightarrow \quad \Delta S_m = \frac{\Delta H_m}{T_m} \qquad \Delta S_m \equiv \Delta S(T_m) \quad \Delta H_m \equiv \Delta H(T_m)$$

So, this we can write as delta H evaluated at T minus T times delta S evaluated at T. If we evaluate these quantities at the melting point, then we have delta G T m is equal to delta H T m minus T m delta S T m, but we have seen delta G T m is 0. So, we can write 0 is equal to delta H T m minus T delta S T m.

So, if we rearrange we see that the entropy of melting, the entropy change upon the transformation upon freezing at the melting point is nothing, but enthalpy of melting divide by T m. And this enthalpy of melting is nothing, but what we commonly call a latent heat of melting, we simplify the notation by writing delta S T m, as simply delta S m and delta H T m simply as delta H m. So, we get delta S m is equal to delta H m by T m.

(Refer Slide Time: 11:52)



Assuming $\Delta H(T)$ and $\Delta S(T)$ to be independent of T:

$$\Delta H(T) = \Delta H(T_m) = \Delta H_m$$

$$\Delta S(T) = \Delta S(T_m) = \Delta S_m$$

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

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

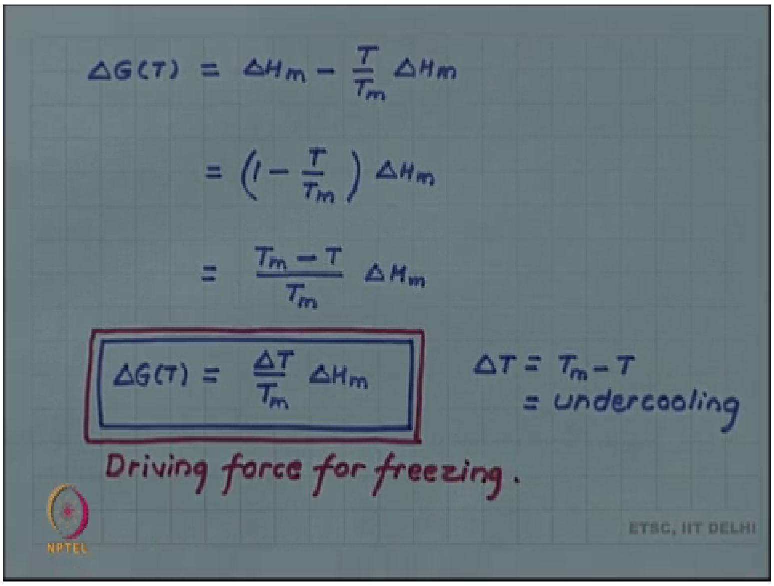
$$= \Delta H_m - T\left(\frac{\Delta H_m}{T_m}\right) \cong$$

If, we now make an assumption that the variation of delta H and delta S as a function of temperature is T, they are not varying rapidly. And effectively they are independent. If you make this assumption we can assign the value of delta H T equal to that at the freezing temperature delta H m.

And similarly delta S m can be assigned to delta S T, with this assignment and with this assumption, we can rewrite our free energy difference delta H T is delta H T minus T delta S T has simply delta H m delta H T is now, equated to delta H m and delta S T is also equated to delta S m.

So, we have delta H m minus T delta S m. So, we have already shown that delta S m is nothing, but delta H m by T m entropy of freezing, or entropy of melting is equal to enthalpy of melting divided by the melting point.

(Refer Slide Time: 13:06)



$$\Delta G(T) = \Delta H_m - \frac{T}{T_m}\Delta H_m$$

$$= \left(1 - \frac{T}{T_m}\right)\Delta H_m$$

$$= \frac{T_m - T}{T_m}\Delta H_m$$

$$\boxed{\Delta G(T) = \frac{\Delta T}{T_m}\Delta H_m}$$

$\Delta T = T_m - T$
$= \text{undercooling}$

Driving force for freezing.

ETSC, IIT DELHI

So, if we now continue with this derivation, we start with this delta H m minus T by T m delta H m, we simply collect the term delta H m. So, we have an expression like this, which we can now write in this way T m minus T the difference between the melting point and actual freezing temperature, this is what is called under cooling. So, we have write written that as delta T T m minus T under cooling and we get the expression delta G T is equal to delta T by T m times delta H m.

This is the final express which is useful approximation because, see we have made certain approximation and the approximation wall that the enthalpy, difference and the entropy difference do not vary as a function of temperature and are constant and, their value is equal to their value at the freezing temperature. With this assumption we find that in the free energy change, as a function of temperature is linearly dependent upon temperature, more is the under cooling more is delta G T.

So, this is what we were seeing, in the drawing which we had that more is the under cooling, more is the difference delta G; however, the curve was linear. So, essentially our approximation is making these curves as straight lines. So, it is a straight line approximation. So, it will be true for certain degree of under cooling, but not very high under coolings.

So, close to the melting point for small under cooling we can have this linear approximation for the driving force. So, essentially what we have derived is the driving force for transformation. And we have taken as an example although this will be applicable for any transformation; we have taken as an example of freezing so, driving force for freezing.