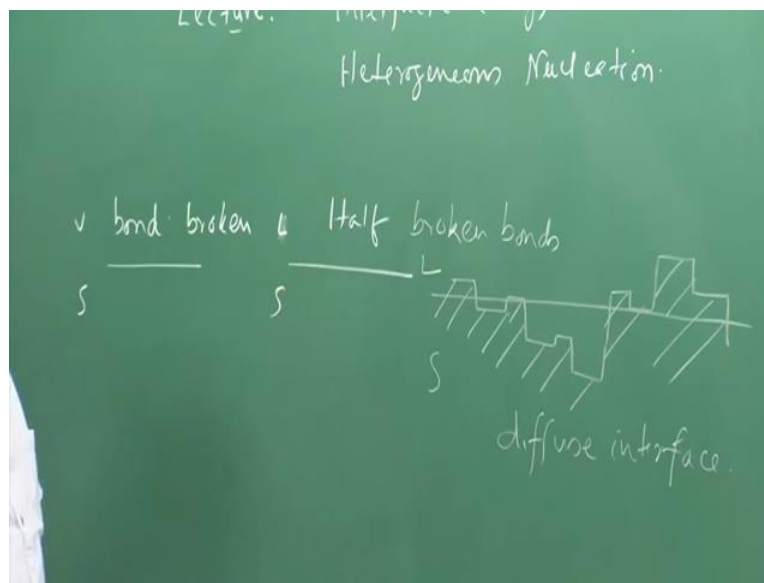


**Heat Treatment and Surface Hardening (Part-1)**  
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**Lecture Number 14**  
**Interfacial Energy**

Ok, so welcome to lecture 14 and lecture 14 we will complete our discussion on interfacial energy.

(Refer Slide Time: 00:40)



So in case of solid vapor we have calculated how to calculate interface energy or surface energy from the broken bond concept. And then in case of solid liquid, we have seen that we can use some empirical formula assuming that bonds are not completely broken it is a half broken.

And we have used one formula which is  $0.45 \Delta H_m$  which is the melting enthalpy divided by the Avogadro number. And then going through the same route that number of atoms per plane and getting the value of solid liquid interfacial energy. In case of solid solid interface energy we can also use some of those empirical formulas. Those formulas have come after doing calculations and experiments.

So we will come to that when we talk about solid solid transformation. Now whenever we are talking in this particular lecture we talk about the physical concept of interface energy. So where

from this energy is getting evolved from thermodynamic concepts or ideas. And then once we finish this, then we will get to the heterogeneous nucleation heterogeneous nucleation.

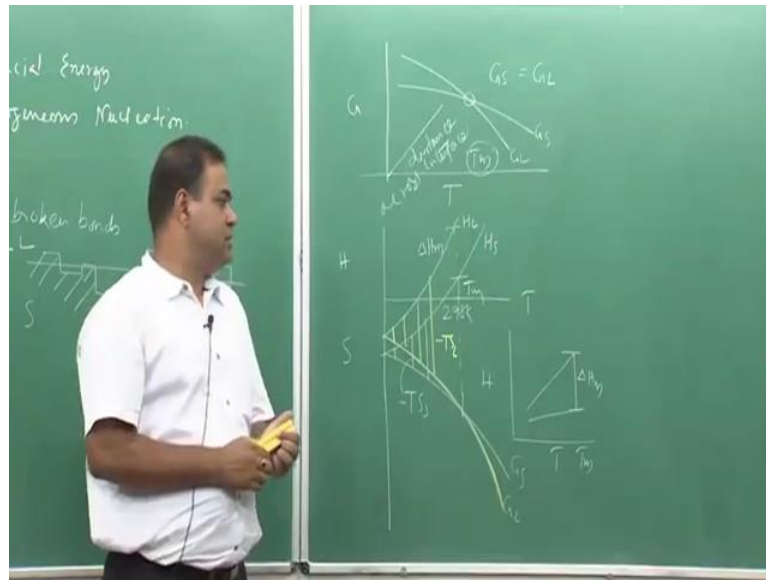
So first let us get to the interface energy. We have seen that the interface energy so it is actually in case of solid vapor. So all the bonds are broken, but in case of solid vapor the bonds are broken. In case of solid liquid solid half broken bonds. Now those are leading to some energy which is positive definitely because whenever we are considering broken bonds they are giving a sense of positive nature.

Now if we come to see the solid liquid or this, in case of solid vapor definitely it will be a kind of flat interface because all the bonds are broken. Now in case of liquid solid it may not be completely flat, there could be nature that solid to liquid transforms in a gradual (fash) fashion. So the interface could be instead of this flat it could be like this. So if we see this is the parting line, so interface could be like this.

In some portion some of the solid if we see this is the solid surface, this is the liquid surface. Some of the atoms in the solid they have gone into the liquid face and leaving rise this (truf) and some cases some of the portion they could not break open from the solid surface and they could not go to the liquid. So if we see this particular section, so these are the part of solid and interface is not flat.

And that time we call this interface as diffuse diffuse interface. Now at the same time we have done our exercise how to get to the information of free energy of liquid and free energy of solid from enthalpy of solid as well as enthalpy of liquid.

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And we have seen that if we try to draw the  $G$  as well as temperature, we have seen that this is my  $T_m$ , this is  $G_s$ , this is  $G_l$ . This is this we have seen.

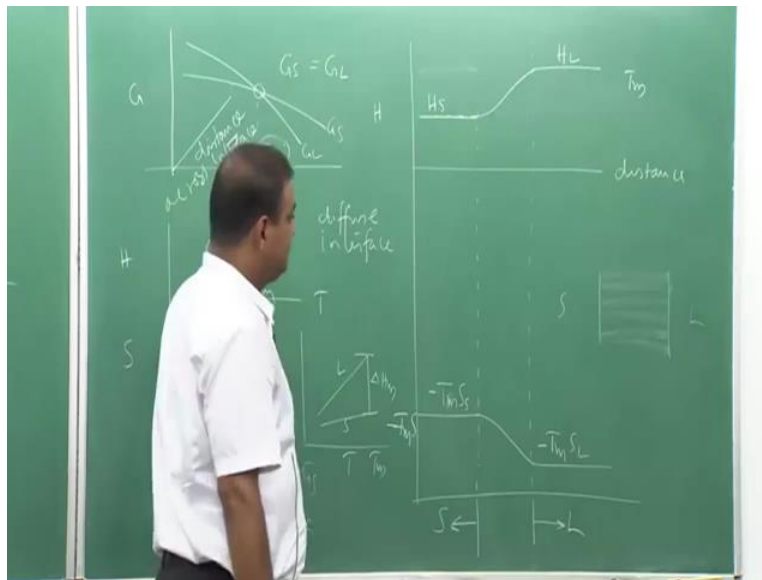
And we have seen that at this point  $G_s$  equal to  $G_l$ . Now if we try to see if we do another access and that access if we consider this the distance (access) access, distance across the interface, which is distance across the interface if we do another access. And if we try to see what is the situation there at along that particular line if we fix the temperature. So that means this  $T_m$  is fixed.

So then if we try to see the variation of  $G$  across this length would get some idea about the physical nature of the interface. And where from this positive factor of interface is coming into our picture. Now we have seen another information, what is that is basically if we see the  $H$  as well as  $S$  variation. We have seen that the and this across temperature, so then so we have seen that this information, this is 298 kelvin for  $H_s$  and this is  $H_l$ .

And  $H_l$  is higher than  $H_s$  and similarly this is  $S$ ,  $S_l$  and this is  $S_s$ . So solid interface sorry just reverse this solid this is solid, this is liquid. And now from that if we see the this is basically my  $\Delta H_m$  and this is  $G_s$  this is  $G_l$ . And here we are getting this  $G_s$  for example if we draw this  $G_l$  with fringe of  $G_l$  with yellow line. And these we are getting by deducting  $-T_s$  liquid term.

Similarly if I try to see how we are getting  $G_L$ , from  $H_S$  we are deducting  $T_S$  term. Now this is at melting point, so here  $G_S$  equal to  $G_L$ . Here also we have seen the variation of  $H$  across temperature, so this is liquid and this is solid. So there is a jump, which is  $\Delta H_m$  and this is my  $T_m$ . So at  $T_m$  also if a solid transforms to liquid so if we have both the existence of solid and liquid at  $T_m$ . So liquid entropy would be higher than the solid entropy. As well as liquid enthalpy would be higher than the solid enthalpy. And this is liquid, this is solid.

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Now if we try to plot them across distance, if I try to plot  $H$  as a function of distance across the interface and if we consider that the interface is diffuse. So that means, diffuse interface means the transformation the liquid atom and the solid atom they are not separated with the flat boundary rather in some portion liquid has percolated into solid and some portion solid had gone into the liquid.

So the transformation region of solid liquid, so if we consider this is the solid portion, this is the liquid portion, this is the solid, this is the liquid, within this zone. We have existence of both solid and liquid, so this interface is having a particular length. So it is not a single line it is there is a particular width of that particular interface.

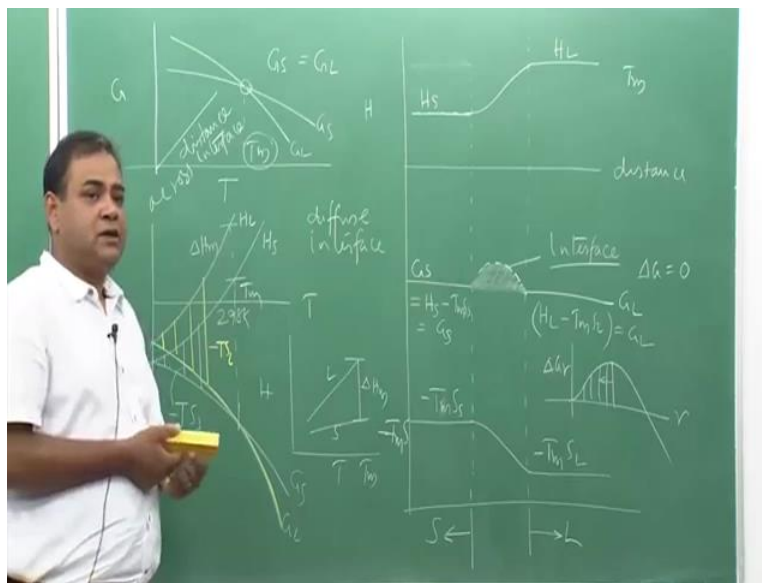
So now if I try to see how the variation of solid and liquid enthalpy distributes in this across this distance at  $T_m$ , this is I am doing at  $T_m$ . So that time we will see that, if this is my this is my

solid part let us do it here. If this is my solid part this is  $H_s$  and the liquid part would be this is liquid, this is completely liquid, this is completely (soi) solid and this is the interface region which has a specific width. And if we try to see, that the liquid enthalpy would be little higher but in between there is a gradual increase of solid enthalpy to liquid enthalpy, so this is like this.

Now similarly if we try to see what is the variation of  $S$ , or rather if I try to see what is the variation of  $-Ts$ . When I am talking about  $-Ts$ , this  $T$  is nothing but  $-T_m$ , because we are considering that entire this distribution thing is happening here at  $T_m$  and it is basically this point but across this access which is distance access. Now that time since we know that the solid entropy is higher than the liquid solid (entro) entropy is lower than the liquid entropy.

See if we multiply with  $T_m$ , both the thing would increase of the order of  $T_m$ . But if we put a minus sign, this  $T_s$  term for solid would be more than the  $T_s$  term of liquid, because we have consider a negative sign there. So at that time if this is my  $-T_s T_m S_s$  term, so the  $T_m$  is cell term would be lower than this. And the variation would be gradual from  $T_m S_s$  to  $T_m S_l$ . So the  $T_l$  is higher than  $T_s$  and that is why  $-T_m S_s$  would be higher than  $-T_m S_l$ .

(Refer Slide Time: 13:40)



Now if we see the variation of  $G_l$  across at this point so they are same they are same, so this is  $G_l$ , this is  $G_s$ . So both the things are same, because that is what we are getting equilibrium. But across interface at the same time if you see, that at this point would be  $H_s - T_m S_s$  and here  $H_l - T_m S_l$

SI is basically  $G_I$  and this is  $G_s$ . Now interestingly if we subtract  $T_s$  term from  $T$  term  $T_s$  term from  $H$  term you will see that across this interface, this  $G_s$  is not going to be  $G_I$ .

So they would have a positive energy hub. So this positive energy hub is coming due to the generation of interface. And this particular region is giving positive contribution if interface is formed. Now we can realize that even if at  $T_m$ , I have similarity we have same  $G_s$  and  $G_I$  term. Because we know that  $\Delta G$  equal to 0, but if there is an interface formation, that would have positive contribution.

And now if there is a positive contribution and if let us say some solid forms it cannot remain there because it is unstable formation, it is not possible it is not possible because there is a increase in free energy. So the transformation is not possible. So that means at melting point no nuclei is possible rather what would happen there as we have seen in our discussion, if you see this particular variation  $\Delta G_r$  as a function of  $r$ , those particular points would be always lying left side of this.

So that means as a function of  $r$ , there could be lot of solid like clusters, ok. But they cannot go beyond this, because all the cases I have positive contribution of in interface. And this interface has will not allow the free energy requirement for the nuclei formation stable nuclei formation. So now we can clearly see that interfacial energy is actually giving a positive contribution to the overall energy scenario.

We wanted to understand that particular situation that what is that interface energy, so what is the physical essence of interface energy. And this talks about the physical essence of interface energy. And this is from thermal dynamic principle and this is coming due to the difference between  $H$  and  $T_s$  term, ok. So now from what from the overall discussion of this we get to know how why interface is so critical.

And you might have notice in our previous calculations, we have solved one problem where we mention that if interface energy increases by 10 percent, what happens to the nucleation frequency or the nucleation rate. We have seen that the nucleation rate goes down to a great extent. Because this nucleation interface energy always acts positive towards the overall energy contribution but we need negative contribution.

So that means the negative contribution is coming from either you get rid of interface or you add volume free energy to it. So that would decrease the free energy but if you have interface creation that would always increase the free energy. So that is not a requirement for nucleation formation. So I think we will start our discussion on heterogeneous nucleation in our next lecture because once we start this we (would) would have to interrupt it in just two minutes time. So let us stop our discussion on this, but I would request you to go through those diagrams and I would also request you to plot yourself.

Either if you do not plot yourself, so you will it will not be a sufficient to understand the entire subject. So you when you solve you will have a lot of queries and get back with the queries so it will also give a lot of sense to plot this for the for this for this course at the same time we will have lot of interactions too, thank you very much will start our next lecture and in the next lecture will talk about heterogeneous nucleation, thank you very much.