Heat Treatment and Surface Hardening - II

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Lecture - 07

Effect of pressure on phase transformation temperature and concept of equilibrium between condensed and vapor phase

Hello everyone. Let us get to the lecture number-7.

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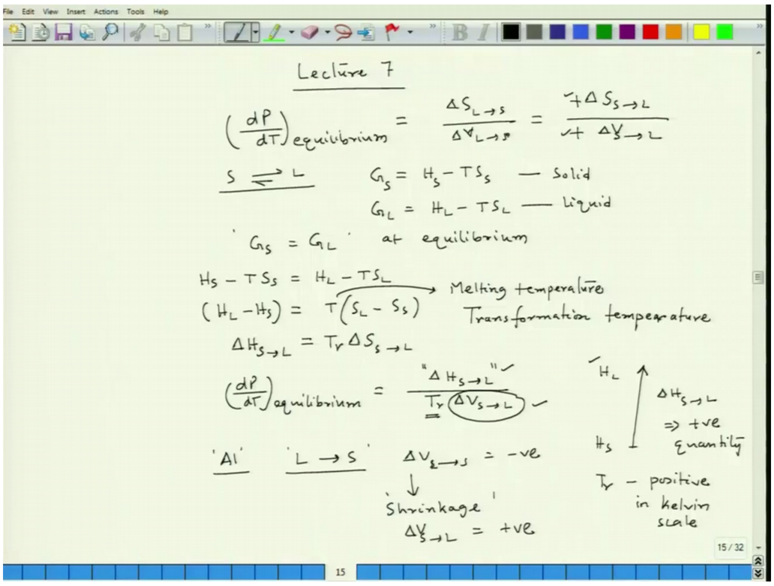

Lecture 7

$$\left(\frac{dP}{dT}\right)_{equilibrium} = \frac{\Delta S_{L\to S}}{\Delta V_{L\to S}} = \frac{+\Delta S_{S\to L}}{+\Delta V_{S\to L}}$$

$S \rightleftharpoons L$

$G_S = H_S - TS_S$ — Solid

$G_L = H_L - TS_L$ — Liquid

$G_S = G_L$ at equilibrium

$H_S - TS_S = H_L - TS_L$ → Melting temperature

$(H_L - H_S) = T(S_L - S_S)$ Transformation temperature

$\Delta H_{S\to L} = T_r \Delta S_{S\to L}$

$$\left(\frac{dP}{dT}\right)_{equilibrium} = \frac{\text{"}\Delta H_{S\to L}\text{"}}{T_r \boxed{\Delta V_{S\to L}}}$$

H_L ↑ H_S $\Delta H_{S\to L}$ ⇒ +ve quantity

T_r – positive in kelvin scale

'Al' 'L → S' $\Delta V_{L\to S} = -ve$

↓

'Shrinkage'

$\Delta V_{S\to L} = +ve$

Now, in our last lecture, we ended with an equation, which is giving equilibrium between solid and liquid; and that time, we have written it like this is the equation we ended in our last lecture. Now, if we consider equilibrium between solid and liquid, then I can also write G equal to H minus T S for solid. And also I can write it for liquid as S L this is for solid, this is for liquid, both the equations are valid. G S equal to G L at equilibrium.

Now, I can write it as H S, S L, then H l minus H S equal to T S L minus S S, and these T in case of if it is solid and liquid transformation these T is nothing but melting temperature. And if I consider solid transforms to liquid, and if I consider liquid transforms to solid that time it will be the freezing temperature so that means, it is basically the transformation temperature, transformation temperature.

Now, I can write it as del H. Now, again here I am writing L to be the final state. So, I can write it as solid converting to liquid that means, this is melting I can write it as this T and here I am just simply mentioning R that means, transformation temperature, and del S solid to liquid. But here we have put liquid to solid, I simply change this notation as liquid which will be a minus because if this is the case positive, so then it will be minus and this minus sign is coming, because I am just reversed in the transformation. For our benefit, because we have taken solid to liquid and here it was liquid to solid, so I am just changing the notations. It will be also and this minus sign is nothing but change in direction of transformation. So, this would get cancelled.

Now, I can replace this equal to I can replace it. Now, what would be the value of del H is solid converting to liquid. Since, c p of liquid is higher than c p of solid. So, liquid would have higher enthalpy than solid. See, if I consider solid converting to liquid, so actually I have del H which is solid converting to liquid would be positive quantity. T r is a finite quantity; and that time, it is also all the time positive in Kelvin scale. Now, entire attention goes to this particular quantity.

Now, in some cases when the transformation is taking place from solid to liquid, volume can be negative that is a change of volume could be negative or the change of volume could be positive, both have a different consequence. For example, in case of aluminium, if liquid transforms to solid, then there is a volume contraction and that is mostly been absorbed that has been mostly observed in most of the cases. That means, the volume of solid the molar volume of solid is less than the molar volume of liquid. And in case of aluminium, if it solidifies, melting little below the melting point, and you know why it should be bit below the melting point because of interface nature interface because of the interface only.

So, now this liquid to solid transformation the volume change; that means liquid to solid is negative and that is why we get shrinkage in casting. So, in the reverse, when solid transforms to liquid the volume expands, so that case if we are considering solid to liquid so; that means, del v solid to liquid would be positive. So, both the terms are positive; that means, this is positive all the time, because enthalpy of liquid has to be higher than enthalpy of solid, and this one is also positive in case of aluminium.

So, then what would be the situation if we change the pressure a little bit, if we change the pressure let say. Once we change the pressure so that means, this gives me a slope of pressure slope of this pressure temperature plot. So, in this case, since all the quantities are positive, the slope is also positive, that means, if I try to plot pressure and temperature the slope would be positive.

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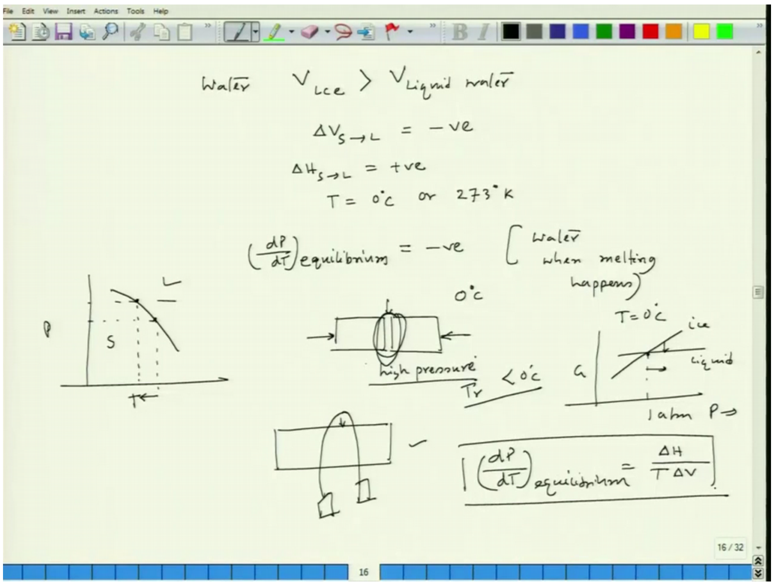

Water $V_{Ice} > V_{Liquid\ water}$

$\Delta V_{S \to L} = -ve$

$\Delta H_{S \to L} = +ve$

$T = 0^\circ C$ or $273^\circ K$

$\left(\frac{dP}{dT}\right)_{equilibrium} = -ve$ [Water when melting happens)

$$\left(\frac{dP}{dT}\right)_{equilibrium} = \frac{\Delta H}{T \Delta V}$$

But in case of water, ice has got volume of ice the molar volume of ice is more than molar volume of liquid water. So, hence that time the volume change, that means, del v solid to liquid you have that quantity to be negative, but del H solid to liquid is positive in case of water. And if we consider 1 atmosphere pressure, the melting point is T equal to 0 degree Celsius or 273 degree Kelvin actually it is 273.15 Kelvin. So, then I see that dP dT equilibrium is equal to negative quantity in case of water, when melting happens. What does it mean means that the system has to if it is a control system control volume system the system has to maintain its equilibrium.

Now, if pressure is increased, that means it has to reduces its transformation temperature since the slope is negative. So, the slope is negative means pressure and temperature the slope becomes like this. So, it is a negative slope. So, that means, if I this line indicates the equilibrium line. So, if I am here then if I change the pressure to higher pressure, I have to change the transformation point which is this is solid, this is liquid I have to change the transformation point and the transformation point sits too late that means, the temperature gets lowered.

What does it mean let say you have two ice blocks, and then you press them and if you are keeping it at 0 degree Celsius, if we press them then at this point we are having very high pressure and these pressure will take the melting point less than 0 degree Celsius. That means, the T transformation is less than 0 degree Celsius at this point at this local regions. So, if it is less than 0 degree that means it has to melt because the outside temperature is 0 degree.

Since, we have already seen that 1 atmosphere pressure, this is G, this is pressure and temperature if it is 0 degree Celsius, if we increase the pressure ice melts, ice melts. Now, if we now release the pressure, once you release the pressure that means the temperature melting temperature again goes back to 0 degree. So, what would happen, it would again solidify and that is what these particular block gets connected and this phenomena we always see.

Another interesting experiment you can do if you take a ice block you take a wire metal wire put it on the ice block, and then have a little weight at both of the ends of this iron wire and then leave it there. After sometime, we will see that this wire will go through but the ice is not get going to be going to be separated, they will not be in two halves. Because when it touches the ice surface, it gives a pressure melting point goes down melts, the wire goes through little bit in the depth direction. As it goes to the depth direction the top part again the pressure is released melting point goes back to 0 degree Celsius, it may it solidifies, because that local temperature is already low lower than 0 degree Celsius. So, now this way ice block can be connected, and this funny experiment can be done all those things can be possible. So, this is the effect of pressure on condensed system.

But now we are getting this does not tell me give whether this does not give me any idea that whether I have to do the heat treatment for this particular metal at a low pressure or high pressure or at a low temperature or high temperature. In order to know that concept of this particular equation needs to be known. And these equation in case of solid-liquid transformation, we call it Clapeyron equation.

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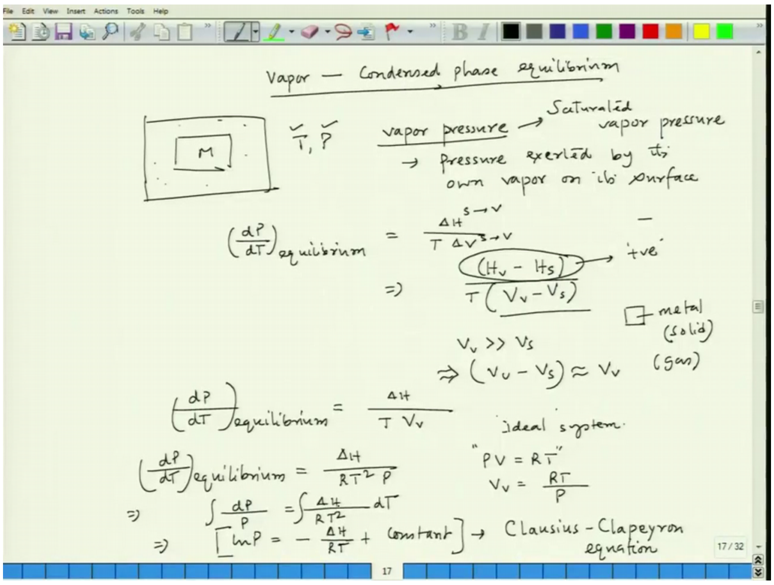

Vapor — Condensed phase equilibrium

$\check{T}, \check{P}$

vapor pressure → Saturated vapor pressure

→ pressure exerted by its own vapor on its surface

$$\left(\frac{dP}{dT}\right)_{equilibrium} = \frac{\Delta H^{s \to v}}{T \Delta V^{s \to v}}$$

$$\Rightarrow \frac{(H_v - H_s)}{T(V_v - V_s)} \quad \text{(}H_v - H_s\text{)} \rightarrow \text{'+ve'}$$

$$V_v >> V_s$$

$$\Rightarrow (V_v - V_s) \approx V_v$$

$$\left(\frac{dP}{dT}\right)_{equilibrium} = \frac{\Delta H}{T V_v}$$

ideal system.

"$PV = RT$"

$$V_v = \frac{RT}{P}$$

$$\left(\frac{dP}{dT}\right)_{equilibrium} = \frac{\Delta H}{RT^2} P$$

$$\Rightarrow \int \frac{dP}{P} = \int \frac{\Delta H}{RT^2} dT$$

$$\Rightarrow \left[\ln P = -\frac{\Delta H}{RT} + \text{constant}\right] \rightarrow \text{Clausius - Clapeyron equation}$$

Now, get to the system where we need to see what happens to this equation when we consider a vapor and condensed phase equilibrium. Let say I have a solid metal which is let say M, and if it is in a control volume at some temperature and pressure, the system would try to reach equilibrium. And if it is a pure metal, so then you have in this particular blank region, you have vapor of metal and the system would reach equilibrium. And the pressure exerted by this metal vapor on the metal surface, we call it vapor pressure. And remember this vapor pressure is coming due to the pressure exerted by its own vapor on its surface.

Now, these vapor pressures specific to temperature it reaches an unique quantity; and that time we call it saturated vapor pressure; that means, saturated vapor pressure indicates the equilibrium vapor pressure; and that time these two quantities are in equilibrium in sync with this particular system. Now, let us see what happens let us treat this particular system again the way we have created for solid-liquid gas.

Now, in this case, this equation would be again valid, which will be again can be written as del V. And let us say I consider solid to vapor and here also solid to vapor then can I not write it as H vapor minus H solid, I can write this, because here I am considering transformation from solid to vapor which is nothing but the sublimation. Also if we try to see this particular quantity, it would also be all the time positive because vapor phase has got a much higher C p than the solid phase, this is a positive quantity say that this quantity is positive. Now, coming to the this quantity here, if we have considered metal in solid and metal involve gas the gas volume of that metal would be much higher than molar volume of that gaseous metal would be much higher than the molar volume of solid metal. So, can I not write it as like this? So, that time, I can simply write V v minus V s, V v. So, the equation turns out to be dP dT equal to del H T V v.

So, now if I consider that the vapor is actually acting as ideal, ideal system means that interactions between its own molecules or atoms is negligible, then I can also get help from this particular equation which is gas law. Now, here I can convert this V v equal to R T P. So, if I replace this then become dP dT equilibrium equal to del H R T square P. I can do little treatment. So, if I integrate it, then I will get ln P equal to minus del H R T plus a constant, and these equation is called equation.

Now, here interestingly this temperature is nothing but the equilibrium temperature, this pressure is also equilibrium pressure, and this we can consider as a constant, for this is the enthalpy change for the transformation of a solid to vapor, and these pressure is nothing but then saturation vapor pressure. So, this pressure is saturation vapor pressure.

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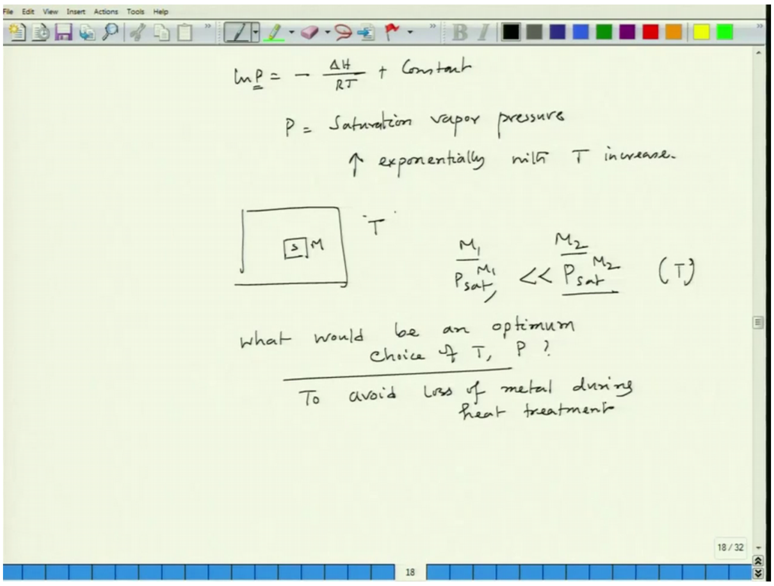

$$\ln \underline{P} = -\frac{\Delta H}{RT} + \text{Constant}$$

P = Saturation vapor pressure

↑ exponentially with T increase.

$$\frac{M_1}{P_{sat}^{M_1}} << \frac{M_2}{\underline{P_{sat}^{M_2}}} \quad (T)$$

what would be an optimum choice of T, P ?

To avoid loss of metal during heat treatment

So, now ln p equal to minus del H R T plus constant. Now, we see that these pressure which is saturation vapor pressure is increasing exponentially with an increase in temperature. So, if it increases exponentially with temperature increase. So, now you understand if I have a control volume, if I have a solid metal, then if I increase the temperature of this system, the vapor pressure would increase that saturation vapor pressure that it has to reach equilibrium that equilibrium vapor pressure of that its own vapor would go up exponentially. Means if something has got a very, very high vapor pressure; that means, saturation vapor pressure means that metal has a tendency to evaporate quickly. If we compare M 1 and M 2 and let say M 1 has got saturation vapor pressure M 1 and P saturation vapor pressure M 2 at a particular temperature T both the cases if this is very high then this one would evaporate much quickly quicker than this.

So, these concepts will be useful to see whether we need to do the heat treatment of that particular metal at low temperature or high temperature or high pressure or low pressure. So, this particular part that means, what would be an optimum choice of temperature and pressure to avoid loss of metal during heat treatment, this would be guided by this pressure.

Let us stop here, would discuss this particular question in our next lecture.

Thank you.