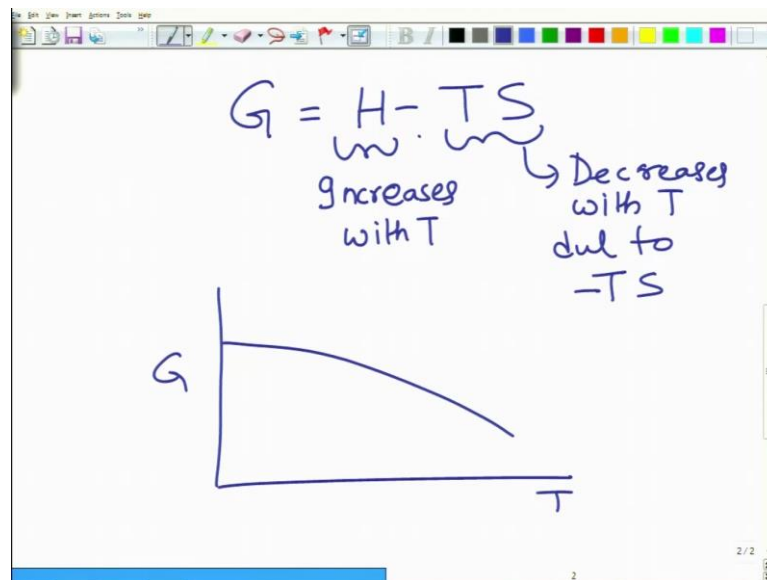


Phase Equilibria in Materials (Nature and Properties o)
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Lecture – 04
Effect of Temperature & Pressure on Single Component System

So, welcome again in this lecture number 4. And here we will continue talking about the previous lecture. In the previous lecture, we looked at the variation of various, we looked at the definition of thermodynamic properties, what intensive extensive properties are, and how do thermodynamic properties vary as a function of temperature. For example, we looked at the variation of specific heat as a function of temperature which typically increases as a temperature goes up, then we look at the variation of enthalpy as a function of temperature, enthalpy being dependent on the specific heat, it also increases as a function of temperature and then we looked at a entropy, entropy generally increases with temperature.

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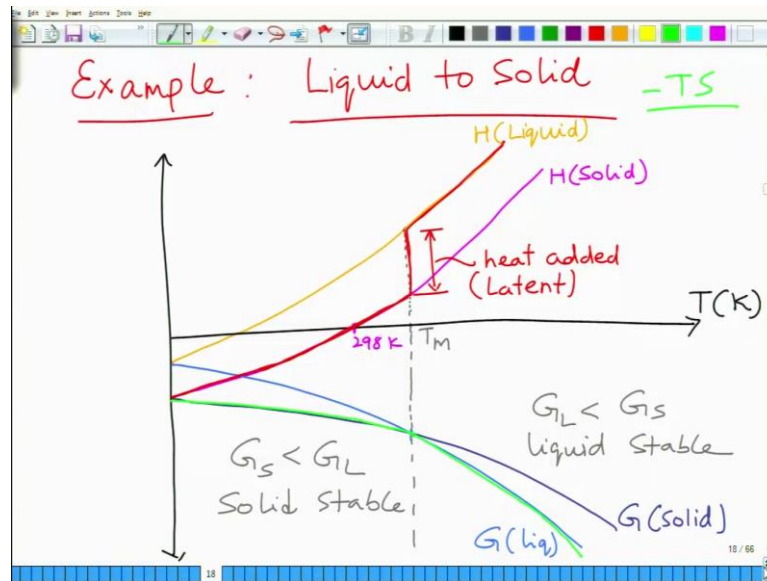
However, the overall term G ,

$$G = H - TS$$

and so one increases and this term becoming; so, this increases with temperature and this decreases with because of negative sign, due to $-TS$ term. As a consequence of this the

free energy, if you plot free energy as a function of temperature, the free energy tends to decrease as a function of temperature. So, it is the relative change of free energy of various phases with temperature that determines which phase will be stable and which phase will not be stable at a given temperature. So, this is what we did. So, we looked at for example, this if I change the slide.

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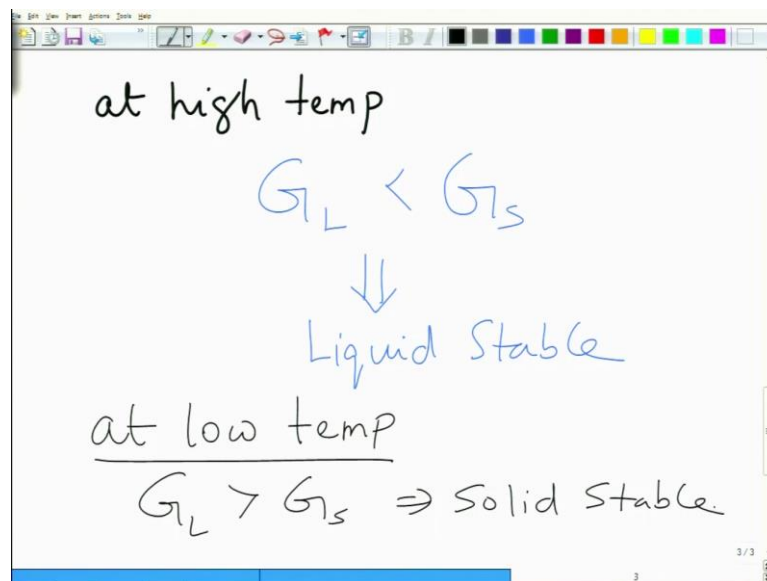
We looked at the example of liquid to solid. So, what we saw was that transformation is happening from liquid to solid as you change the temperature, as you increase temperature and enthalpy of both the phases increases as a function of temperature. And if you, so, this is for example, the orange one is the enthalpy of liquid, the magenta one is enthalpy of solid. If you look at the corresponding changes in the free energy the blue one is the curve representing free energy of liquid, and the dark blue one as the free energy of solid. You can see that below a certain temperature T_M the free energy of solid phase is, like smaller than free energy of liquid, as it is a solid is more stable phase. Whereas, at higher temperatures $G_L < G_S$ and as a consequence liquid phase is stable at higher temperatures.

And if you see the corresponding changes in the enthalpy, the enthalpy shows a sudden jump at this temperature T_M , which suggests that the heat is added in the form of latent heat of melting; however, there is no temperature change. And basically at this point if

we calculate specific heat; specific heat is $\partial H / \partial T$ and specific heat would be infinity. So, basically addition of extra heat does not lead to any change in the temperature.

And if you look at the TS term, that TS term is $-TS$ alright. So, TS term is minus and as you increase the temperature, the TS term for liquid drops much faster as compared to solid, because liquid will have higher entropy as compared to solid. So, that is why you see that the free energy for liquids, liquid phase which is the light blue curve drops much more faster as compared to the free energy of the solid. And this tells me that basically what I was able to tell you is that if I summarize, at high temperature $G_L < G_S$, making liquid stable. Whereas, at low temperature, $G_L > G_S$ which means solid was stable.

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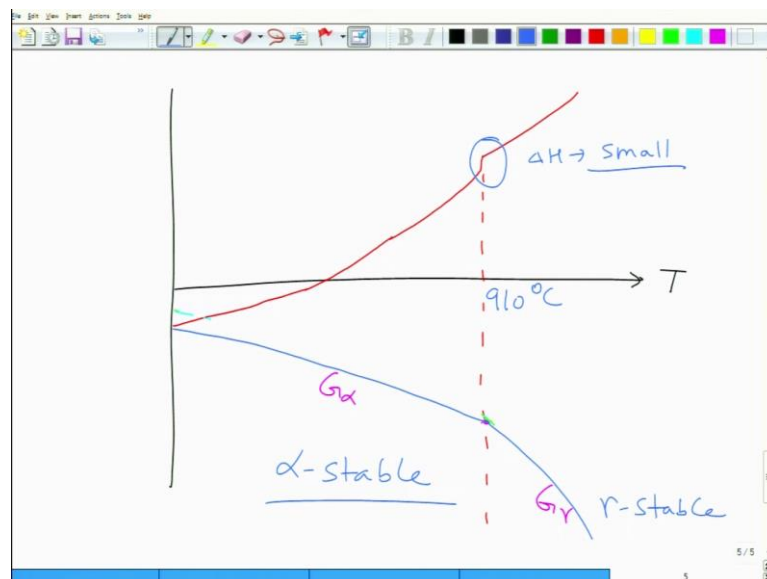
So, this was the take home message for free energy variation as a function of stability.

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Material Systems
- Example \rightarrow Fe
At lower temp ($T < 910^\circ\text{C}$)
Solid Pure Fe \rightarrow BCC- α -Fe
At higher temp ($T > 910^\circ\text{C}$)
Solid FCC- $(\gamma$ -Fe)

If you look at the material systems, in single component, then the most common example is of iron; pure iron. So, pure iron is, at low temperature, pure iron is BCC structured, we call it α -Fe, ok, let us say lower temperature. At higher temperature, so, lower temperature would be $T < 910^\circ\text{C}$ and this would be $T > 910^\circ\text{C}$, it becomes FCC structured γ -Fe ok. Now, this basically tells that if you compare for example, the free energy and enthalpy now here.

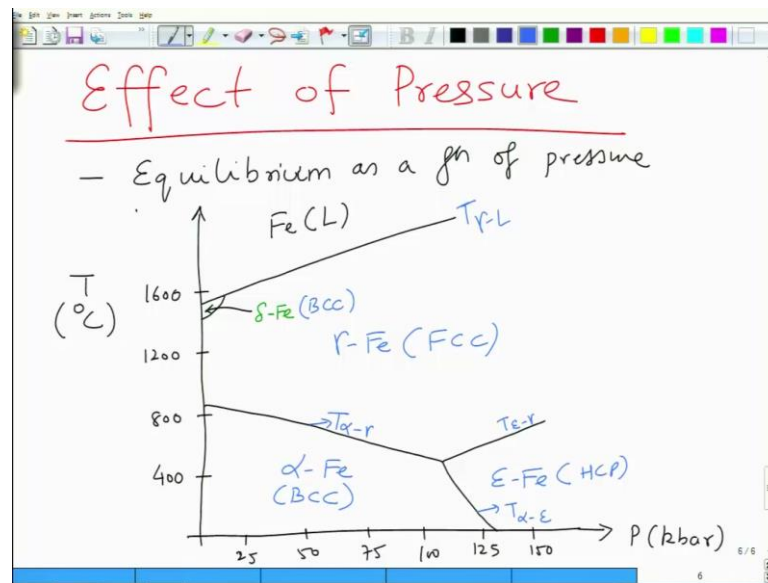
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So, the free energy; if I plot the enthalpy first overall change in the enthalpy so, this goes through 0 at 298K and then at certain point there will be changed in, there will be minor change in enthalpy, before it increases further because you know this is a solid to solid transformation, both of them are solid. So, this is also solid and this is also solid. And at this temperature correspondingly you will have a transition so, your free energy of, if I plot the free energy, so, free energy up to this point, it will be corresponding to, so upto this point it will correspond to α -phase and then beyond this point it will be, it will suddenly change the shape at this point. So, this will be G_α and this will be G_γ if you wanted to plot the individual plots, the γ will continue to be like that. And may be α will continue to be like that and γ will somewhere like this. So, these would be the individual plots. Let me let me put the blue color here. So, this is how they would have been, but if you just want to plot a single, if you just want to plot a single line, single line will tell you that; initially choose the color; initially it would be for α and then it prefer γ .

So, in this phase at 910°C this would be γ stable and this point it would be α stable; however, unlike solid to liquid transformation, this ΔH will be small it will not be very large. Because all you have is, you have a solid to solid transformation from BCC to FCC phase. As a result the change in enthalpy is not very high, because the internal energy is, as far as the internal energy is concerned both of these are solid phases. So, there will not be huge change in the internal energy as far as ΔH is concerned. So, this is how the curve is going to look like for something like iron.

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Now, let us look at another effect of another thermodynamic parameter called as pressure ok. So, this is what we want to here is basically equilibrium as a function of pressure and its effect on, so, and its effect on phase, presence of different phases ok. So, let us make a plot of what we call as; we make a plot of plot of iron ok. So, iron is a very nice system to study this. So, this is temperature axis, this is pressure axis, let us say pressure is in kilobar, temperature is in °C. So, let us make 400 800 1200 1600; this is 400, this is 800, this is 1200 and this is 1600.

And the line is, this line is something like that alright. So, this would be nearly 125 this would be about 150 this would be about 100. So, it should be 25 50 75 100 125, 150 they not be equal (Refer Time: 10:55) just draw these 2 little differently 50 and 75; now they are more equally distributed. So, what you have here is on the y axis we have temperature on the x axis we have pressure, temperature is plotted up to about 1600 degree centigrade or even higher and pressure is plotted again up to 150 kilobar or so.

And at high temperatures the iron is stable in the form of liquid phase. At, in this regime, this regime is basically δ -Fe (BCC) within this regime, we have γ -Fe which is FCC structured, δ is again BCC and then we have α -Fe at this lower temperature, BCC and then we have ϵ -Fe which is HCP. So, this is the pressure temperature phase diagram of iron, single component pure iron, what we see is that at lower pressures, so, what we have here is at lower pressure the iron transforms to, α -Fe transforms to γ -Fe. α is

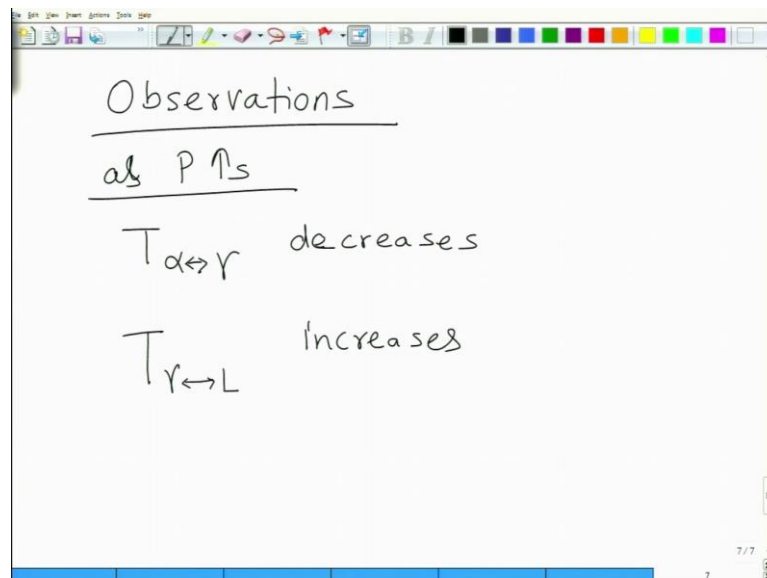
BCC structured γ is FCC structured at 910K, before it transforms and then subsequently $\gamma - Fe$ transforms to $\delta - Fe$ which transforms to liquid phase at high temperature 1500 and something, is the melting point of iron.

What you see here interestingly is that, as you change the pressure beyond atmospheric pressure the phase boundaries, the the transition temperature change. So, this is for example, the temperature corresponding to $T_{\gamma-L}$, this is $T_{\alpha-\gamma}$. These are called as phase boundaries. This is $T_{\alpha-\varepsilon}$ and this is $T_{\varepsilon-\gamma}$.

So, there are various phase boundaries here. We look at the cases of for example, $T_{\alpha-\gamma}$ and $T_{\gamma-L}$. We see that $T_{\alpha-\gamma}$ decreases as the pressure increases ok whereas, $T_{\gamma-L}$ increases as the pressure increases. So, you see the difference for the transition from, for phase transition from α to γ phase. Both are solid phases ok. From, for phase transition from α to γ phase as you increase the pressure the phase transition temperature decreases.

On the other hand, for transition from γ solid phase to liquid phase the phase transition temperature goes up as the pressure increases. And we will see why this happens in the next few minutes.

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Now, the observations are as pressure increases $T_{\alpha-\gamma}$ decreases, but $T_{\gamma-L}$ increases. And of course, at very high pressure what we obtain is a different phase which is $\varepsilon - Fe$.

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At constant temperature
 $dG = dH - TdS - SdT$

$\left(\frac{\partial G}{\partial P}\right)_T = V$

as \rightarrow $P \uparrow, G \uparrow$

So at, from the free energy relations, at constant temperature, you can obtain this from the free energy expression that we wrote. So, we wrote

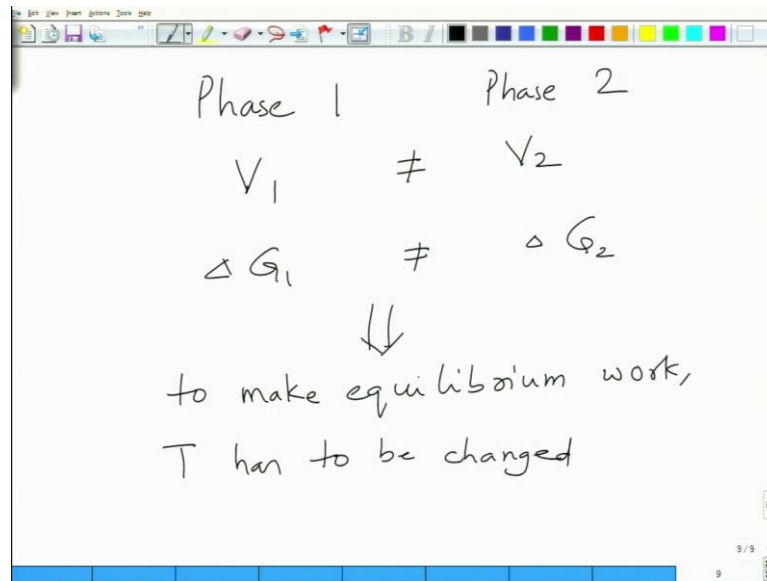
$$dG = dH - TdS - SdT$$

and if you expand this further at constant temperature, you will make certain terms equal to 0 at constant temperature what happens is that

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

So, basically as pressure increases G also increases. And the slope of ∂G by ∂P is the volume. So, this suggests that, what it says that, what it says, you can see from here is, as the pressure changes, ∂G by ∂P is equal to volume, so, as the pressure changes the G will change.

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You have two phases phase I and phase II. V is nothing but the molar volume ok. So, we can say this is the molar volume. Now suppose you have 2 phases and for though both of these phases $V_1 \neq V_2$, that free energy changes as the function of pressure, but $V_1 \neq V_2$.

So, what will happen? If V_1 is not equal to V_2 which means the free energy change for both phases is not similar. Which means $\Delta G_1 \neq \Delta G_2$. Which means if these phases had to exist in equilibrium, for phases to coexist in equilibrium, the free energy changes for both of these must be equal, but they are not equal. So, in order to make them equal what will now happen is that, to make equilibrium work, you have to, temperature has to be changed.

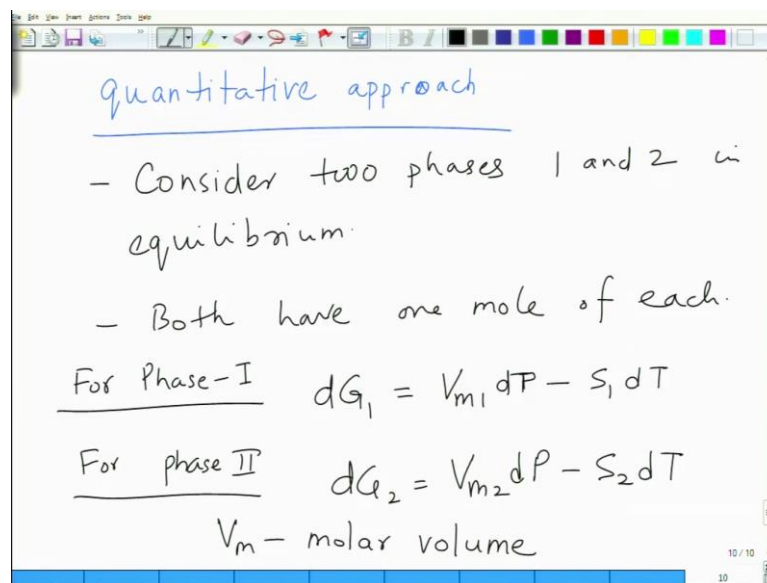
So, this is a problem in specially, when the phase volumes are very different. So, molar volume of two phase is V_1 and V_2 they are different to each other. As a result, when you change the free energy as a function of pressure, the changes in the free energy are not similar.

And if the changes in the free energy are not similar which means one is, one phase going to be stabler than another phase, that will create a problem at equilibrium because at equilibrium both, if these phases, if these two phases have to coexist with each other at a certain temperature and pressure, at a certain pressure then temperature also has to be changed. So, that is why you see in this plot, at these lines the phase boundaries, both the phases coexist.

So, at this line both the phases coexist, at this line both the phases coexists. And this temperature is decreasing, this temperature increasing because the molar volumes of 2 phases are different. As a result, to maintain the equilibrium because, remember at this point the free energy of both the phases are equal.

So, as you change the pressure the molar volumes have changed. As a result, the free energies of both phases are not same. So, to maintain the similarity of free energy changes, you need to change the temperature and in this case the temperature increases at this pressure, in this case for example, the temperature the temperature decreases as we increase the pressure by the same amount. So, let us see this in this in more quantitative framework. So, basically we are going to define this now in, what we call as quantitative framework ok.

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So, you consider phase, let us say I and II in equilibrium ok. So, and assume both have 1 mole of each alright. So, the incremental change in the free energy; so, I can write

$$\text{For Phase I} \quad dG_1 = V_{m1} dP - S_1 dT$$

$$\text{For Phase II} \quad dG_2 = V_{m2} dP - S_2 dT$$

where V_m is the; we say V_m is the molar volume. So, V_m is basically the molar volume.

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If 1 and 2 are in equilibrium
 $G_1 = G_2$
 $dG_1 = dG_2$
At Equlbm $V_{m1} dP - S_1 dT = V_{m2} dP - S_2 dT$
 $\left(\frac{dP}{dT}\right)_{eq} = \left(\frac{S_1 - S_2}{V_{m1} - V_{m2}}\right)$
 $= \frac{\Delta S}{\Delta V}$

So now assume if I and II are in equilibrium; if I and II are in equilibrium which means

$$G_1 = G_2 \text{ and then } dG_1 = dG_2$$

If that is the case, then I just equate the 2 equations. So,

$$\text{At equilibrium } V_{m1} dP - S_1 dT = V_{m2} dP - S_2 dT$$

And if you rearrange the terms what you will get is

$$\left(\frac{dP}{dT}\right)_{eq} = \left(\frac{S_1 - S_2}{V_{m1} - V_{m2}}\right)$$
$$= \frac{\Delta S}{\Delta V}$$

The change in the entropy of 2 phases and the change in the molar volume of 2 phases.

So, basically what we see in this equation is, you can determine the change in temperature if the pressure is changed and the molar volume change is not equal to 0.

Now how to now calculate delta S?

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For both phases
 $G_1 = H_1 - TS_1$
 $G_2 = H_2 - TS_2$
 $\Delta G = G_2 - G_1 = \Delta H - T\Delta S$
 at eq/bm $\Delta G = 0$
 $\Delta H = T\Delta S$
 $\Delta S = \frac{\Delta H}{T}$
 $\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_c \Delta V}$ Clausius Clayperon Eqn

So, delta S can be calculated very simply, we know that for both phases

For both phases $G_1 = H_1 - TS_1$ and $G_2 = H_2 - TS_2$

So, you can write $\Delta G = G_2 - G_1 = \Delta H - T\Delta S$

And we know that At equilibrium $\Delta G = 0$

Change in enthalpy $\Delta H = T\Delta S$

$$\Delta S = \frac{\Delta H}{T}$$

where ΔH the change in enthalpy the enthalpy of transformation. And so, this will make my equation read as

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_c \Delta V} \quad \text{Clausius clayperon equation}$$

So, this is a important expression which allows you to calculate the change in the temperature, when the pressure of a system is varied and if you have ΔV which is not 0, when the 2 phases have different molar volume then to maintain the equilibrium, what is the change in temperature that is required.

This equation is called as Clausius Clayperon equation. It is a very important equation as far as phase transitions are concerned. So, we can see that if a molar volume change is

negative and if pressure is, dP is positive then dT will be negative. If your ΔV is positive, if your ΔV , if ΔV is 0 then; obviously, dT will be 0 as well, but if ΔV is positive then V is positive then dT will also be positive. So, we can see the temperature, the temperature to maintain the equilibrium will increase or decrease depending upon the sign of ΔV as if dP is positive. So we will see the ramifications of this equation on the iron phase diagram as we saw earlier on the 2 phase boundaries in the next class.

So, in summary I would just say in this class, in this lecture, what we have learnt is the effect of thermodynamic variables on changes in the free energy for, as far as single, as far as phase transformation in single component systems is concerned. So, at a certain transition temperature the transformation happens as a function of temperature, below that temperature, free energy of one phase is lower and above that temperature, free energy of over another phase is lower making the 2 phases stable in different regime. And then we looked at the effect of pressure which is related to, which in most cases is related to change in the molar volume, which has its own repercussion on the change in the temperature as well, transition temperature as well. So, we look at that in more detail the next class.

Thank you