**Material and Energy Balance Computations**
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Lecture-44
Estimation of Physical Parameters-III

Welcome back, so we were continuing our discussion on estimation of physical parameters or physical properties and we will continue to do that. And we were at a very exciting time when we were about to look at how to calculate or what can be done about the latent heats, latent heat of fusion and latent heat of vapourization. And also I talked about a terminology called phase transition, the phase transformation. So, let us try to find out what that is and whether it is also associated with some sort of energy changes with it. So, we stopped the previous class over here just one second please.

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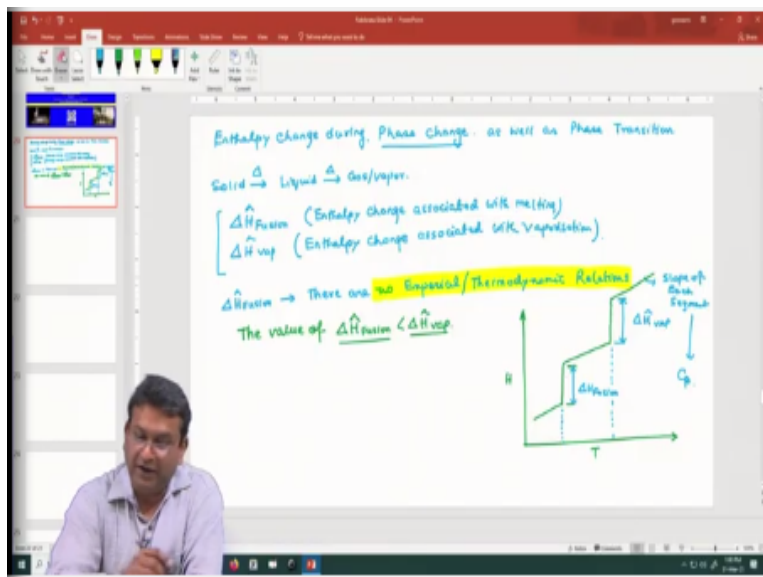
So, we stopped our previous class over here, so we started to talk about enthalpy changes the latent heat of fusion and latent heat of vapourization. Now latent heat of fusion, unfortunately there are no empirical or thermodynamic relations, nothing exists. So, there are no empirical or thermodynamic relation exists for latent heat of fusion. Essentially latent heat of fusion, so other important thing to note down is the value of latent heat of fusion is actually much lower than the value of latent heat of vapourization.

This is of course we can have a long discussion but I do not want to drag you into too many aspects. So, this is of course related to the fact that fusion is essentially a transition from one condensed phase to the other condensed phase like from a solid to a liquid or a water, solid to a liquid not water. So, the interaction between the molecules exists between solid and liquid and there is occasional or there is some change in volume.

So, this energy that is absorbed, so if you actually draw a enthalpy versus temperature plot, so you are supplying enthalpy. So, it will be something like this, it is actually much bigger and then plot. So, this is actually your latent heat of fusion and this is the latent heat of vapourization, what is important to note is that you keep on increasing enthalpy but the temperature does not increase. You know that this is where melting happens and this is where boiling happens.

In fact, the slope of each segment, what does it give? This gives the value of C_p because C_p is nothing but $\partial H/\partial T$. So, it is interesting, actually I have drawn it casually but one should be more careful that the slope in the vapour phase is actually the least because we have seen that C_p is 2.5R and here it is 3R, so this should be slightly higher and things like that. So, this is actually an interesting plot and if I again draw it to scale this will be, so let me try to do that instead of leaving too many mistakes like here.

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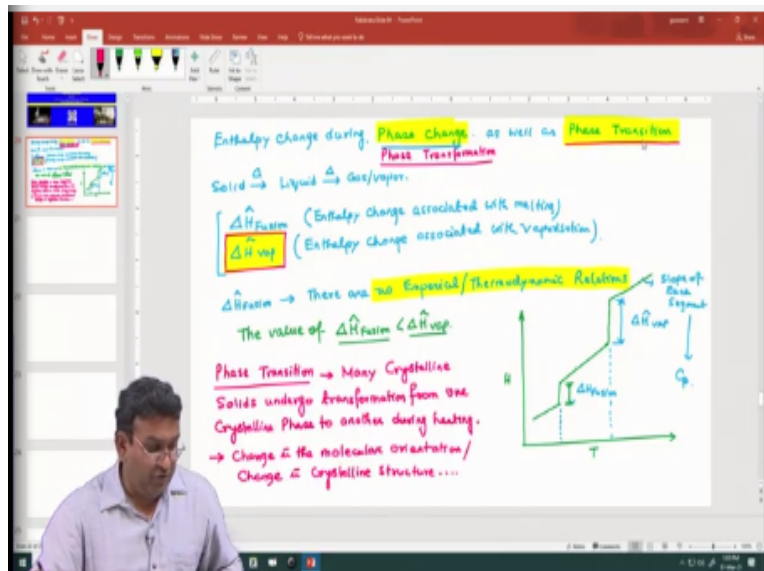
So, this will be more realistic if it looks something like this, so this is much, much smaller as compared to the latent heat of vapourization. Why latent heat of vapourization is much higher? Because during vapourization a large amount of internal energy needs to be supplied to the molecules, so that they can attain large amount of energy can completely overcome the cohesion and then can move around freely which is sort of a signature of a gas.

So, large amount of internal energy needs to be supplied or lot of enthalpy needs to be supplied which gets translated which aids the translation have kinetic energy of the molecules which sustains their Brownian motion and which allows them to overcome the intermolecular interaction, so this we understand. But there is another terminology that I have written here before I come into a formal expression for latent heat of vapourization.

This is very interesting latent heat of fusion we have nothing and for latent heat of vapourization we have a proper thermodynamic relation. So, I am coming to it, you will learn it in your thermodynamics but it is not a bad idea to have a knowledge about how it is. But before that I would like to spend some time on phase transition. So, what exactly is phase transition? So, phase transition, so melting, solidification we are writing as phase change or phase transformation one can write.

But phase change is a better terminology to avoid any ambiguity and confusion. So, what exactly is phase transition is many crystalline solids, you know about it, certain examples you know, many crystalline solids undergo transformation from one crystalline state phase to another during heating. So, this happens due to let us say change in the molecular orientation or change in crystalline structure something like that. So, heat of transition.

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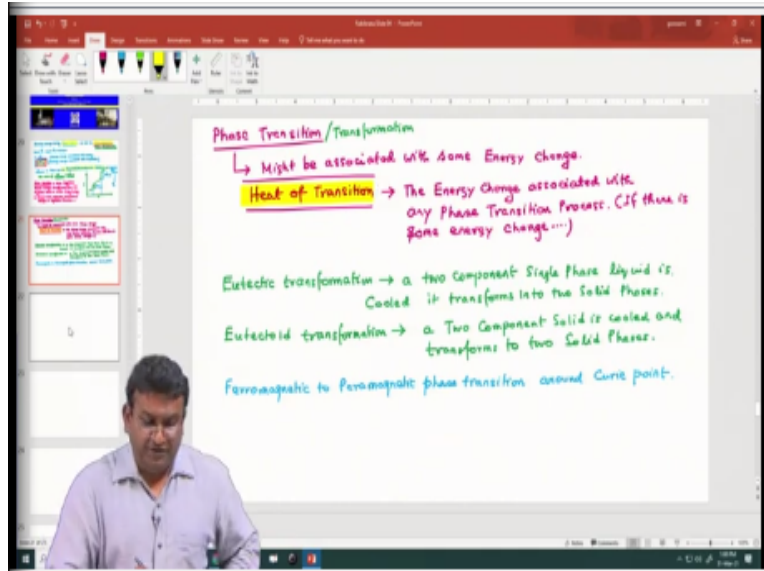
So, agreeing to the fact that we understand, giving some examples of this phase transition. Phase transition might be associated with some energy change. If there is some energy change associated with a phase transition that is called heat of transition, so which is called heat of transition. All transitions are not associated with energy change, so heat of transition is the energy change associated with any phase transition process.

If there are some energy changes or rather if there is some energy change associated. So, some examples maybe we should look into. So, some classical examples is people who will be studying metallurgy will come across lot of these examples. So, for example a very classical example is the eutectic transformation, this is also called phase transformation, I am sorry I should remove the word transformation from here. So, let us stick to phase change and let us use interchangeably phase transition or phase transformation at our level.

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So, one such example is eutectic transformation in which a two-component, these are some examples I am giving but 1 example that I will place all of you know. A two-component single phase liquid is cooled, and it transforms into two solid phases. Another similar transformation is eutectoid transformation, I know that most of you are grabbing them as a piece of information, hold on; I am going to tell something that all of you know.

So, eutectoid transformation which is essentially the same process but beginning with a solid. So, a two-component solid is cooled and transforms to two solid phases, you can check out in the internet and Wikipedia for getting more examples. You all know about the transition or the ferromagnetic to paramagnetic transformation or phase transition around curie point, so this is another example of phase transformation.

And in certain cases, phase transitions or phase transformations are associated with some change in energy and that counts as heat of transition. So, this is not a very important thing but for the sake of completeness I thought it is important that you know about this as well. So, next we come to heat of vapourization which is very important, and it is also very interesting how we calculate it.

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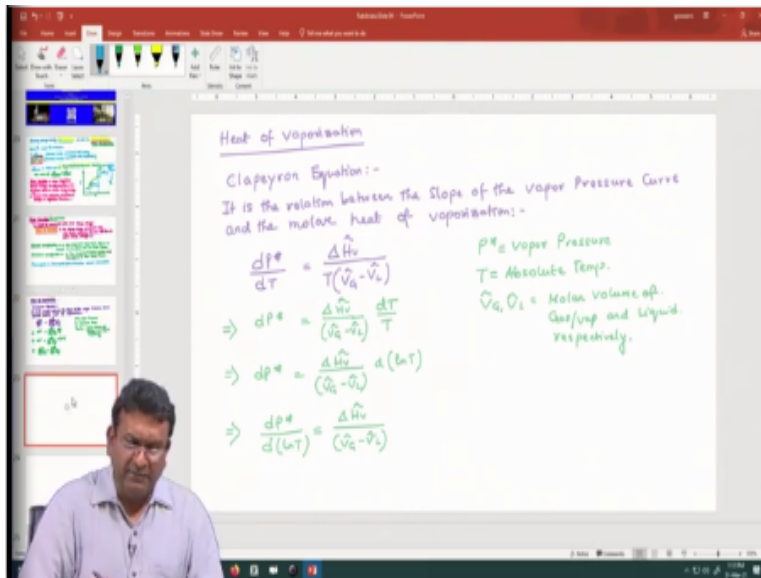
Because there is a precise thermodynamic relation. So, heat of vapourization, so it is essentially the heat required to vapourized a substance and it is always much large, so these things we know. And we now talk about what is known as the Clapeyron equation, this is an exact thermodynamic equation. It is the slope; it is a relation between the slopes of the vapour pressure curve.

And I know I am teaching to the second year, so I will take some time to figure out or make you understand what vapour pressure is? It is the relation between the slope of the vapour pressure curve and the molar heat of vapourization. So, how it goes? What we have is $dp^*/dT = \Delta Hv^\wedge/ (T (V_G^\wedge - V_L^\wedge))$. So, let us write down what are the constituent terms.

So, p^* is vapour pressure and had it been a real one to one online class, I would have checked how many of you know conceptually what is vapour pressure. I do not have an opportunity to do that, so if you have any doubt regarding vapour pressure, please ask me during the online interaction session, I will be happy to clarify your doubt. But I will spend some time on what exactly is vapour pressure?

T is absolute temperature, V_G and V_L molar volume of gas or vapour and liquid respectively. So, the other thing is that this equation the way you can write is that you can actually take it as $dp^*= \Delta H_v^\wedge/ (V_G - V_L) d(lnT)$. So, this becomes dp star, so in a textbook they will straight away write,

but there is no point some of you might actually get stuck up here and let us clarify, so it is d ln T.

Now let us spend the little bit of time on what is vapour pressure. So, you all know that some materials are volatile. So, if you open some acetone or alcohol or petrol for example in a room, it fills with smell. And you can take a drop of these organic liquids, put some on the surface and you see that soon it has evaporated away. In contrast if you let us say place a drop of water for example, it takes long time for it to evaporate.

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So, we all know that certain materials are more volatile, certain liquids are more volatile we all know that. Now how do you quantify what is more volatile and what is less volatile? The parameter to quantify what is more volatile and what is less volatile is vapour pressure. So, vapour pressure is defined as the pressure exerted by a vapour that is in thermodynamic equilibrium with it is own condensed phase.

That is liquidity at a given temperature in a it is a very easy concept closed system. This is at least I personally find it very interesting, that vapour pressure is formally defined for a closed system but when you tell something is more volatile, something is evaporating faster, you are essentially talking about an open system. So, parameter that is defined for closed system which you will understand right now is very conveniently used to explain behaviour of an open system and you all understand what a closed system and an open system is.

So, it is like this here we have let us say a chamber and you have some liquid. So, the vapour space above the liquid will contain what? It will contain atmospheric air and in addition how long? So, we know a little bit about equilibrium, when can we say that the vapour phase is in equilibrium with the liquid, of course the temperature has to be same to maintain thermal equilibrium.

But more importantly if no further molecule from the liquid phase can evaporate into the vapour phase. Or in other words the vapour phase now is saturated with molecules of this liquid. So, in simple terms means that the vapour phase is saturated with liquid molecule that means that it cannot hold more liquid molecule. So, what does it mean? Since the vapour phase cannot hold more liquid molecule, so therefore no liquid molecule will progressively evaporate, will subsequently evaporate.

Therefore, the vapour phase and the liquid phase are at equilibrium. So, just think of a situation when you introduce at a particular temperature fresh air, the vapour phase, so you can also measure let us say the pressure which is easy to do, so you can have a pressure indicator. So, when you introduce fresh air, it is not saturated with the molecules of liquid. So, what happens is some molecules from the surface evaporate. And what is more volatile?

More volatile is a component where the molecules have a higher tendency of evaporation. Something less volatile, it has lower tendency of evaporation. So, more volatile molecules for more volatile liquid, what will happen? More amount of liquid will go to the vapour phase quickly and it will get saturated. So, the pressure will be higher, so the vapour pressure will be higher.

For something where a smaller number of molecules go the tendency of the molecules to go or evaporate from the liquid phase to the vapour phase is less, the vapour pressure will be lower. This is what is vapour pressure in very simple terms. So, vapour pressure is an indication of a substrate tendency to vaporize, a substance with higher vapour pressure is often called volatile, so something that is volatile has higher vapour pressure, very interesting.

Again, to observe that whether something is volatile or not is actually an attribute for the liquid but that is defined in terms of vapour pressure, which is in the vapour phase, please remember these things. I am sure when you learn thermodynamics, you will learn about these things in great detail, but these are good pointers to sort of keep your eyes open. So, the atmospheric pressure boiling point of a liquid, this is also important.

The boiling point of a liquid at 1 atmospheric pressure is actually the temperature at which the vapour pressure equals atmospheric pressure. So, this is in a nutshell about vapour pressure. So, now let us come back to the Clapeyron equation again and what we have is let us pick up the original form of the Clapeyron equation.

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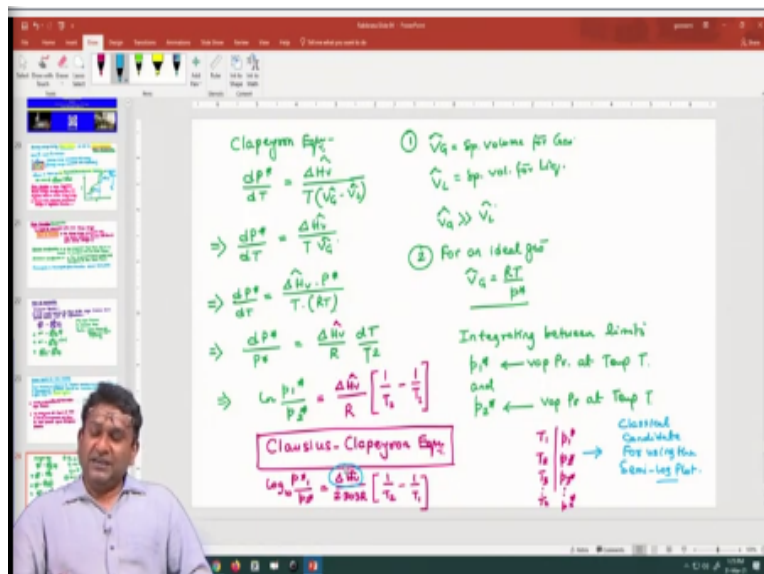
And what we have is $dp^*/dT = \Delta H_v^\wedge T$ divided by T into V G - V L. Now what are the simplifications we can do to the Clayperon equation? So, V G is the specific volume for gas and V L is the specific volume for liquid. So, it is obvious that V G is much, much greater than V L, so that is a simplification you can do. And therefore, the equation in with this simplification, now reduces to delta H v cap T V G cap.

Now the additional thing what you can do for an ideal gas? So, this is number 1, number 2 is for an ideal gas V G = RT by p star, because this is V G is the specific molar volume at saturation

when the pressure is equal to the vapour pressure. So, $V = nRT$ by p, so V_G is p in this particular case is p star. So, the equation subsequently now reduces to dP star dT = delta H_v cap into p star divided by T into RT.

So, this now you can arrange as dp star by p star = delta H_v into by R into dT by T square. And upon integration what happens is? We get ln, so if we integrate between 2 temperatures p_1, p_2 at which, so integrating between limits p_1 star and p_2 star, which is the vapour pressure at temperature T_1 and vapour pressure at temperature T_2? What we get is ln p_1 star by p_2 star = delta H_v cap by R into 1 by T_2, please be careful you are integrating 1 by T square, so minus sign comes out.

So, it is p_1 star by p_2 star and the temperature difference is 1 by T_2 - 1 by T_1, this is what is known as the Clausius-Clapeyron equation. So, essentially if you know for any substance, the vapour pressure at different temperature you can find out the delta H_v straightaway? So, let me also tell you that often you may encounter a situation where you have a data. Like you have several temperatures at which this type of data is given, so what do you do?

You will obviously plot p versus T and try to find out the slope. But look at the expression, so you can also convert this equation into $\log_{10} p_1^*/p_2^* = \Delta H_v^\wedge/2.303R \, (1/T_2 - 1/T_1)$. So, the only thing that I would like to highlight again we are running out of time is that, this is a classical candidate for using the semi log plot. And essentially the plot or the slope between p and $(1/T)$ will give you the ΔH_v. So, either graphically or based on values whatever is produced.

So, you need to do a graphical technique or some interpolation if multiple values are there. But all you need is essentially two sets of values, two temperatures at which the vapour pressure is defined and you can essentially find out the latent heat of vaporization. So, with that I stop today's lecture and we will see probably one more class before we do an extensive pick up a series of extensive tutorials where I teach you how to handle the steam table for enthalpy calculations. Thank you very much.