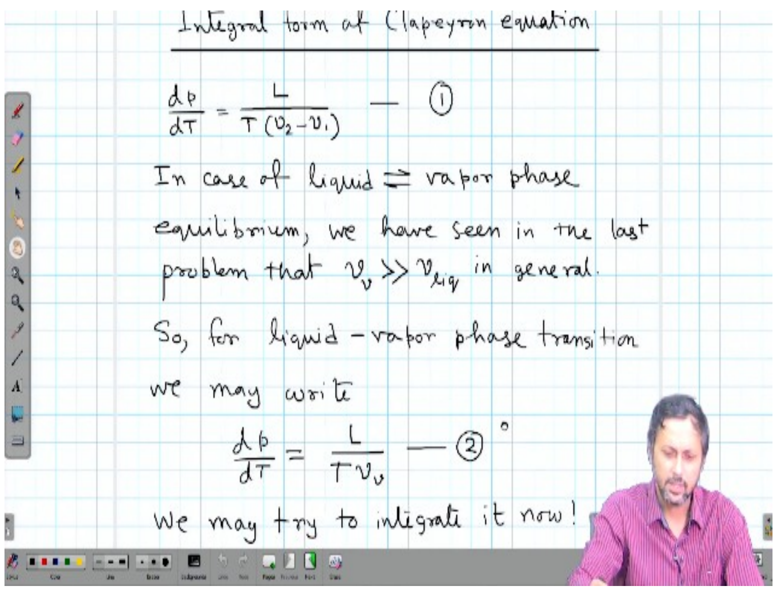
Thermal Physics
Prof. Debamalya Banerjee
Department of Physics
Indian Institute of Technology - Kharagpur

Module No # 11
Lecture No # 52
Topic – 1st Order Phase Transition along Liquid-Vapour Equilibrium

Hello and welcome back to another lecture of this NPTEL lecture series on thermal physics. Now in the last lecture we have introduced Clapeyron equation which defines the locus of the phase boundary between any two phases during a phase transition process. And today we will be discussing about the general properties of certain parameters or general properties of a system across a phase transition or near to the phase transition point. But before that let us try to focus on Clapeyron equation little more before we move on from here.

(Refer Slide Time: 01:02)

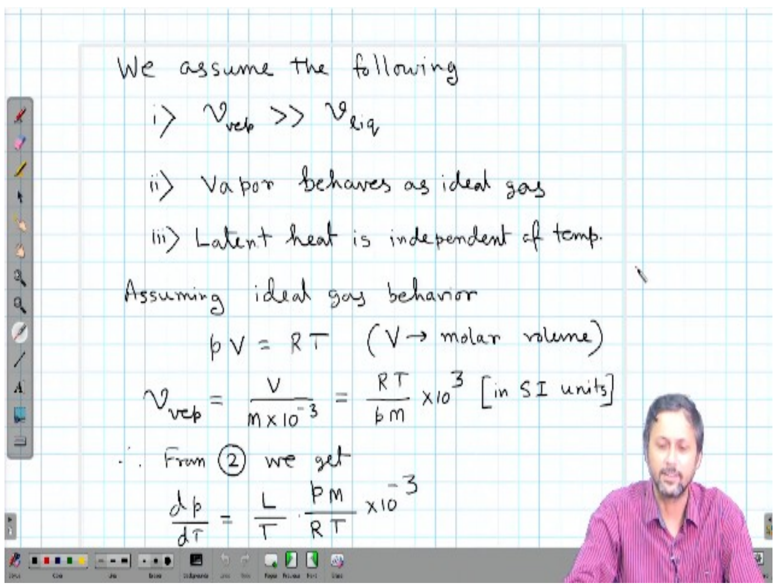


So let us start from this Clapeyron equation which is dP dT is equal to L by T v 2 minus v 1 which is also called the first latent heat equation. We have seen in the last problem of the last lecture that if we have a liquid vapour phase transition the specific volume of vapour phase is typically much higher as compared to the specific volume of the liquid phase. And we can in principle write and we can always have v vapour is much greater than v liquid there is a general procedure general feature.

So, except there of course there are certain cases which we will explore little bit later that, under certain circumstances we can have the volume the specific volume of 2 phases really close to each other but in general this is the scenario. Now, if we rewrite under this approximation if we rewrite the Clapeyron equation we can write dp dT is equal to L divided by T V v right. And now it is in a form which is integrable right I mean okay in principle this one is also integrable.

But this is little more difficult to handle because we have to have incorporate the different parameters I mean the temperature variation or pressure variation of v 2 and v 1 here we have only one volume and also please remember that because it is the volume of the vapour phase and if we assume of course it is an approximation that the vapour phase behaves like an ideal gas okay.

(Refer Slide Time: 02:46)



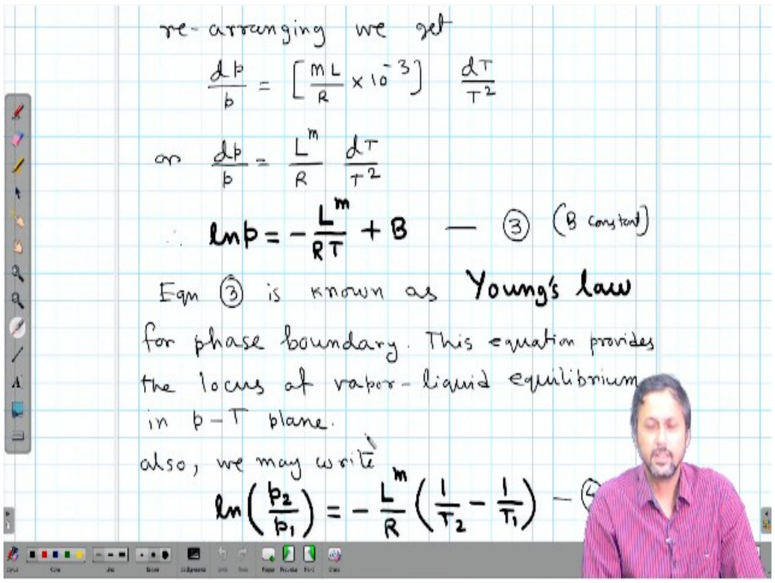
So then what we do we can write p V = R T and V vapour is equal to V divided by capital. So, what is this p V = R T? In this case V is the molar volume right, now the conversion from molar volume to the specific volume is v vapour is equal to V divided by m which is the molar mass in kg into 10 to the power minus 3, which once again we can substitute for this V and write R T by p times M into 10 to the power 3 right.

Now, in order to get to this point we have to make certain assumption, the first assumption of course is v vapour is equal to v liquid which is justified in most of the cases. Also we have to assume that the vapour behaves as an ideal gas and the latent heat is independent of temperature.

Which we will see that is not the case truly and we will have a second latent heat equation which is where which will discuss the temperature variation of the latent heat.

But for now let us focus on the first latent heat equation assuming the latent heat is constant and the vapour in question is behaves like an ideal gas we can write dp dT is equal to L by T p M divided by R T into 10 to the power -3.

(Refer Slide Time: 04:20)



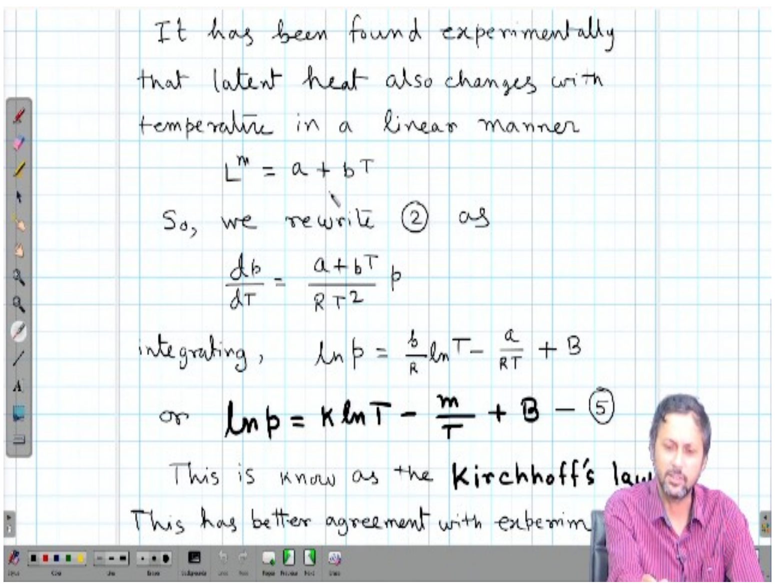
Now rearranging and simplifying little bit further we get d p by p is equal to into m L by R into 10 to the power minus 3 d T by T square right. Now what is this m L into 10 to the power -3 that means m L divided by 1000 this is nothing but, L I mean the molar latent heat which we can write as L superscript m. So L m divided by R d T by T square integrating we get ln p is equal to minus L m by R T plus B where B is some arbitrary integration constant.

Now this equation 3 is known as the Young's law for phase boundary and this equation provides the locus of the vapour liquid equilibrium plane, an equilibrium line in the P T plane. Please remember the pressure that we are talking about here is the saturated vapour pressure because, as we are moving along the phase equilibrium line. So we are actually every time along the phase equilibrium line the liquid is in equilibrium with its own vapour.

And that is why the pressure in question, the pressure in this particular equation is nothing but the saturated vapour pressure. Now we can also get rid of this B and we can write if we perform this integration between this known limits where between T 1 and T 2 temperature and corresponding to p 1 and p 2 pressure we can simply right ln p 2 by p 1 is equal to minus L m by R times 1 minus T 2 minus 1 by 1 by T 2 minus 1 by T 1 right. So this is also another form of the Young's Law of course here we do not have this indefinite the arbitrary constant B.

Now it turns out that this rule I mean this law is not so nice when it comes to you know for actual experimental data it fits for a limited range of temperature and pressure. But in order to gain get the variation over a wider range of temperature and pressure we need to consider the variation of latent heat as a function of temperature as well.

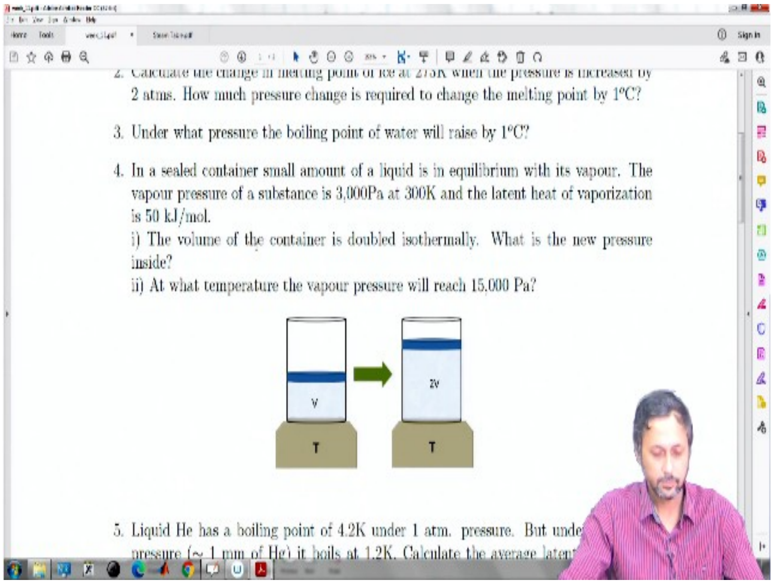
(Refer Slide Time: 06:57)



And typically it has been found that the latent varies in a linear manner. So we can model this as L m is equal to a plus b T. So if rewrite put this one in and rewrite equation 2 where is equation 2 just a minute equation 2 which is dp dT is equal to L by T V v. So if we do that we get dp dT is equal to a plus b T divided R T square times P, so basically not in equation 2 directly. But in equation this equation here I have substituted for L is equal to a plus B T.

And after this integration then if we integrate we get ln p is equal to k lnT minus T by m plus B which is called the Kirchhoff's Law. So this generally has this particular functional form has a better agreement with the experimental results. Anyway, so let us but we will focus primarily on this Young's Law on this particular form which is rather simple to use and try to use this in order to solve some simple problems. So let us move to classroom problems set so sorry this is the steam table which we will come back.

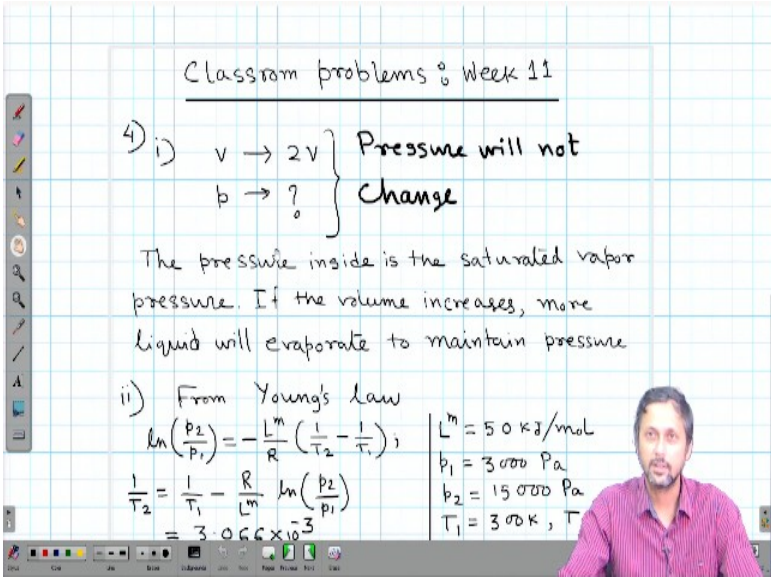
(Refer Slide Time: 08:26)



So this is the classroom problem set of week 11 in Problem 11. It says that in a sealed container small amount of liquid is in equilibrium with its vapour. So we have in this container there is a tiny bit of liquid present here which I tried to draw here and the rest is vapour. And we have a movable piston which seals the container now and it is placed on a heat path at fixed temperature T.

Now let us somehow by some external work we have moved this piston outside, so that the volume has changed from V to 2 V. So what is the new pressure inside? So this is the first question and the second question is at what temperature the vapour pressure will reach 15000 Pascal’s? So the initial pressure inside at this initial point the vapour pressure is 3000 Pascal’s at 300 Kelvin and the latent heat of vapourization is 50 kilo joules per mole.

(Refer Slide Time: 09:41)

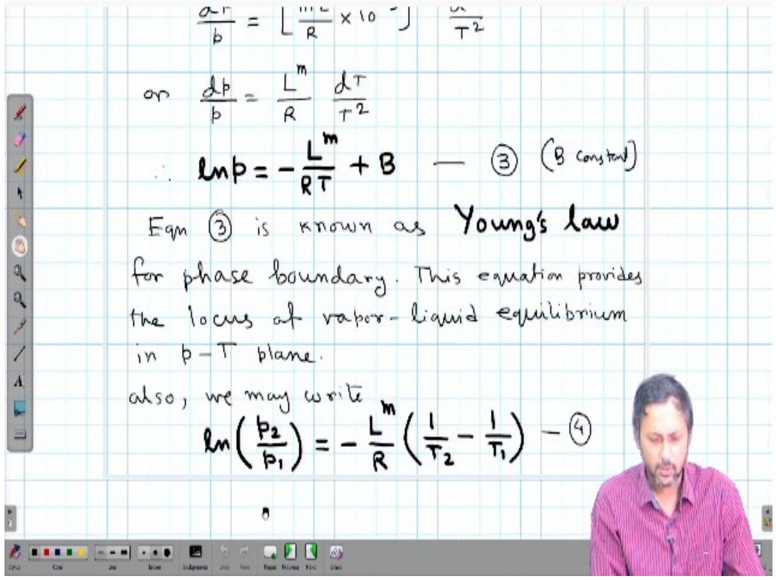


Now in order to solve this problem the first problem is we have V to 2 V the volume changes from V to 2 V at fixed temperature that I also should mention here that the temperature is not changing, what should be the new value of P? So the answer is the pressure will not change in this particular system why? Because the pressure inside once again as I have mentioned already is the saturated vapour pressure inside the cylinder.

So if we change the volume as long as there is a smallest amount of liquid left inside it will evapourate completely to maintain the pressure at the saturated vapour pressure the temperature is not changing please keep in mind. So that means the saturated vapour pressure will also not change. Now if we keep expanding the cylinder at some point entire liquid will be evapourated in to gas phase or vapour phase then it will start behaving differently.

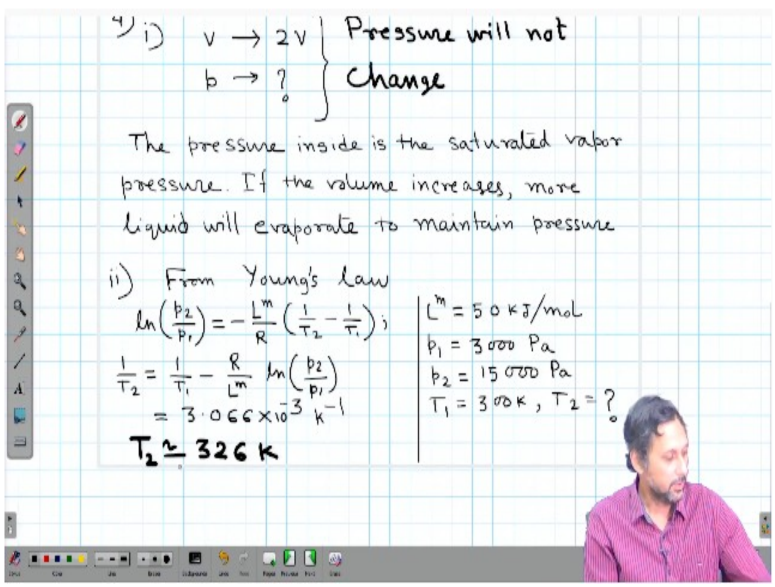
Then with further expansion the pressure will drop and things will start happening, but as long as there is even a tiny bit of liquid left inside this container the pressure will not change please keep that in mind.

(Refer Slide Time: 11:06)



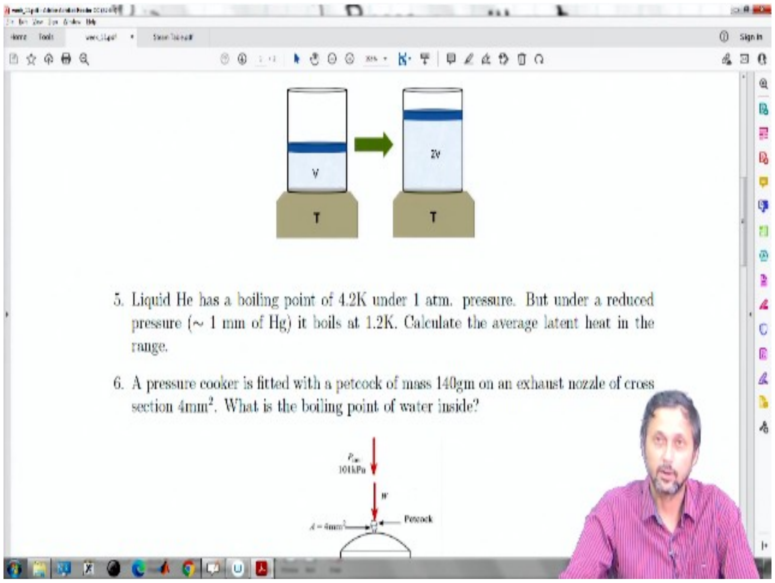
For the second part we simply need to use Young's Law in its integral form which is this one actually.

(Refer Slide Time: 11:11)



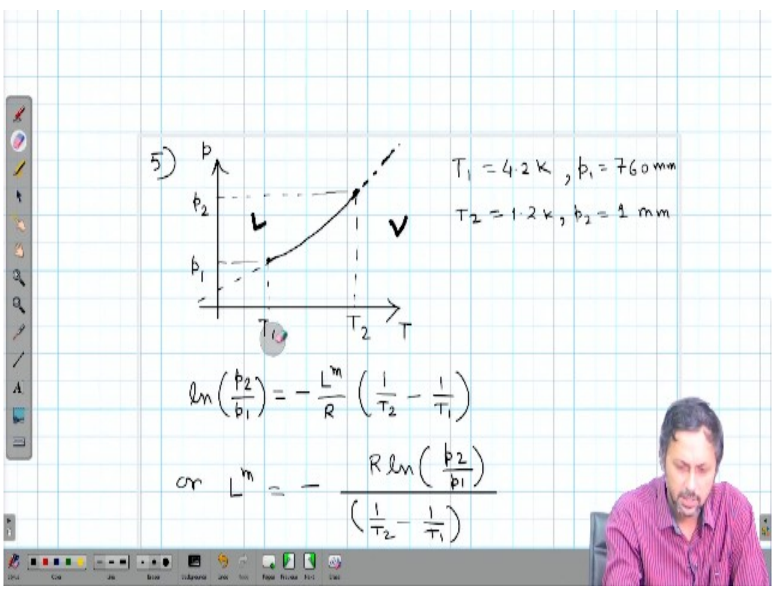
So we have L m which is 50 Joules per mole we have P1 which is 3000 Pa which is 15000 Pa we have T 1 which is 3000 Kelvin now the question is what is T 2? So we start from this equation we simply right 1 over T 2 is equal to 1 over T 1 after rearrangement we write 1 over T 2 is equal to 1 over T 1 minus L R by L m ln P 2 by P 1 putting these values of p 1 and p 2 and R and L m and T 1 gives you 1 over T 2 is equal to 3.033 into 10 to the power minus 3. So the unit here should be Kelvin inverse which gives you it should be T2 = 326 Kelvin.

(Refer Slide Time: 12:12)



So this is problem number 4 for you next we have problem number 5, liquid Helium has a boiling point of 4.2 Kelvin under 1 atmosphere pressure which is a standard cryogenic temperature reference temperature that we all use in our low temperature labs. But under a reduced pressure of 1 millimeter of mercury here please understand this unit this is given as 1 millimeter of mercury it boils at 1.2 Kelvin calculate the average latent heat in this particular range. Now, how does this problem sound?

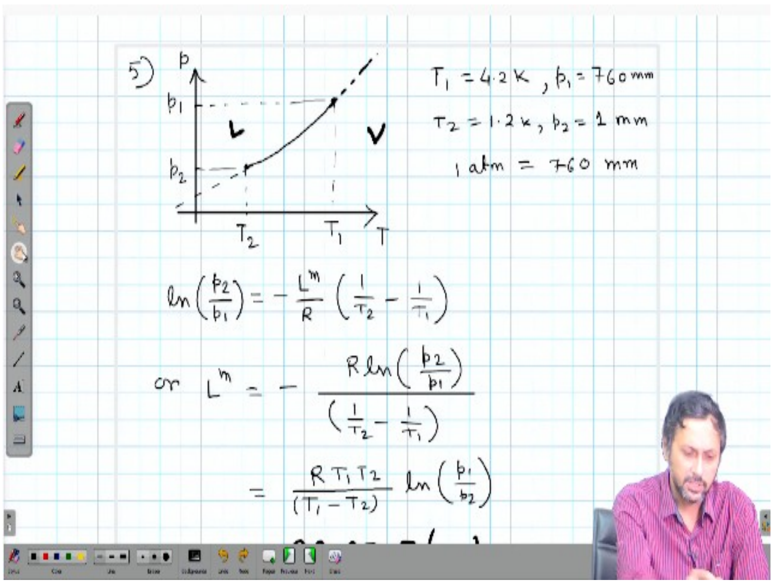
(Refer Slide Time: 12:51)



The problem is basically this we have along this liquid vapour equilibrium line this side we have liquid this side we have vapour along this liquid vapour equilibrium line and please remember this line actually continues in does not terminate here. So it goes on we just 2 points the first point is p 1 T 1 and the second point is p 2 T 2, T 1 = 4.2 Kelvin corresponding to it should be drawing is wrong.

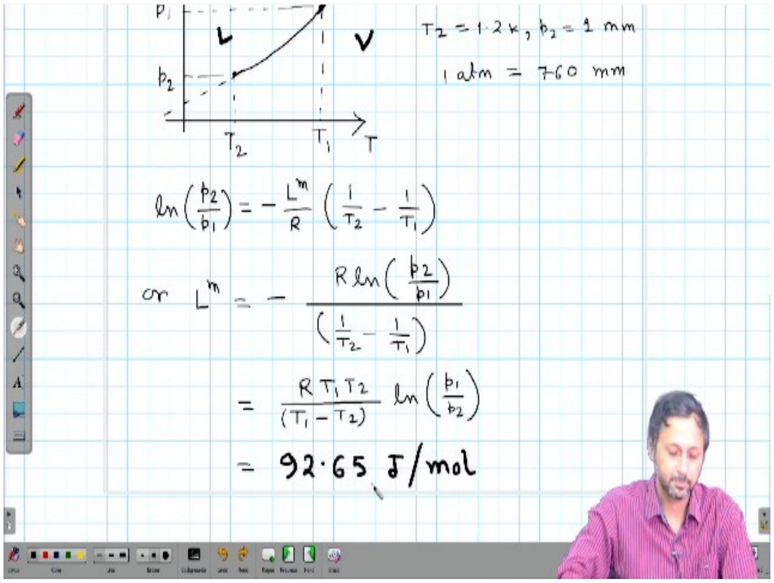
So it should be p 1 p 2, T 1 T 2 right, so that means corresponding to 4.2 Kelvin we have 760 mm of course the slope is not very evident but it should be there should be good amount of slope and at T 2 = 1.2 Kelvin we have 1 mm of pressure. Now 760 mm 1 atmosphere of in mercury scale is 760 mm I hope you are familiar with this concept if not please go back and read your school physics textbook where it is clearly mentioned.

(Refer Slide Time: 14:28)



And then we can use the integrated form of this Clapeyron equation which is Young's Law once again assuming that and here we need to calculate the average latent heat. So that means what do we d? We write ln p 2 by p 1 is equal to minus L m by R 1 over T 2 minus 1 over T 1 we rearrange and write L m is equal to R ln p 2 by p 1 divided by 1 by T 2 minus 1 by T 1.

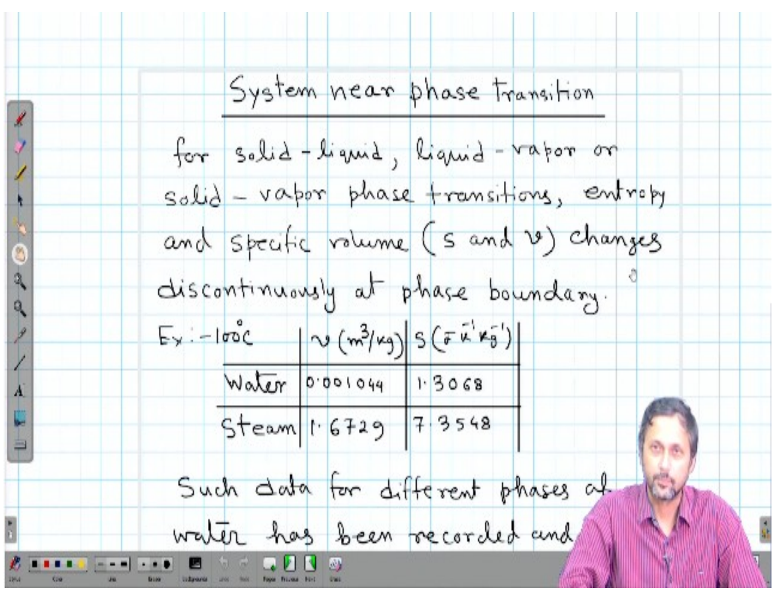
(Refer Slide Time: 14:52)



Which is after arrangement R T 1 T 2 divided by T 1 – T 2 lnp 1 by p 2 and we do not need any unit conversion, because p 1 and p 2 already there coming as a ratio. So whatever unit conversion we do it will cancel nicely we do not need that actually and after putting values we get 92.65 Joules per mole. So this is the average specific heat in the range between T 2 and T 1 that means l.2 Kelvin to 4.2 Kelvin this is the latent heat of not the specific heat the latent heat of liquid helium right.

Now the other problems which are there we will revisit those in the next lecture may be so because before that we need some more discussion.

(Refer Slide Time: 15:45)

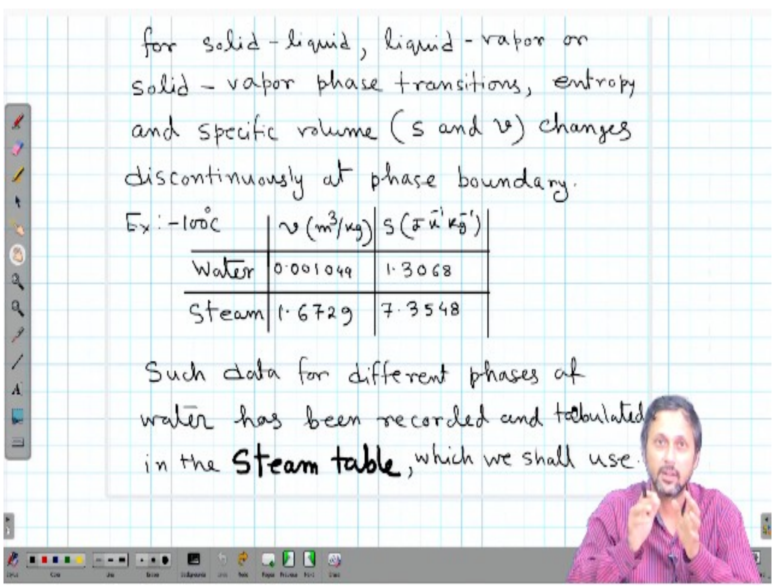


So let us continue with system what happens to a system near its phase transition? Now, for solid liquid or liquid vapour or solid vapour phase transition it is experimentally observed that the specific volume and entropy the specific entropy that changed discontinuously at the phase boundary. So let us take an example at water for, So I should write water at 100 degree centigrade I will correct it here I should write water here it is already mentioned.

So if you look at the values of V the specific volume and specific entropy for water and steam at 100 degree centigrade. We see the specific volume is 00.0010044 if you remember the value at it should be 0, 0 actually my mistake it should be this is fine because it is 0.00100 at 0 degree centigrade not 100 degree centigrade my mistake. So this is fine and the same for steam is 1.6729 where as for the specific entropy for water liquid phase is 1.3 whereas that for the steam is 7.3.

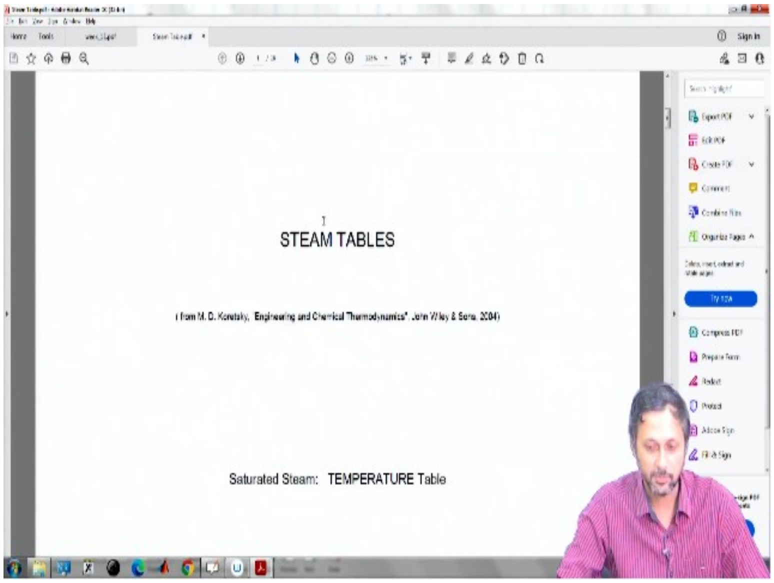
So there is a huge discontinuity and both are measured exactly the same temperature and same pressure. So this is I have not mentioned it but this is 100 degree centigrade and 1 atmosphere pressure maybe I should mention that and nothing else, right.

(Refer Slide Time: 17:58)



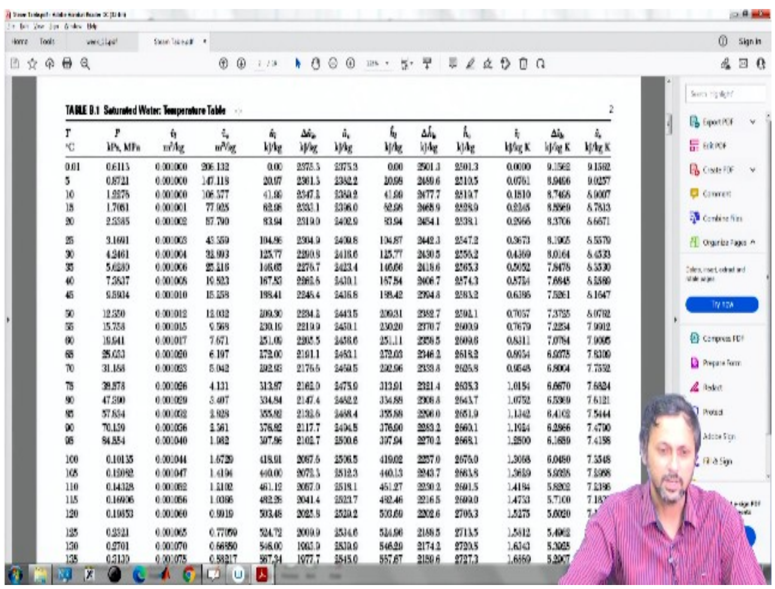
So this difference and for water particularly this such data at different phase of water has been tabulated and recorded and tabulated in a table called the steam table which we shall use later.

(Refer Slide Time: 18:19)



So let us quickly have a look at a steam table, so this is the steam table.

(Refer Slide Time: 18:20)



The first table itself is a saturated water temperature table this is the most useful table for us at present. Of course there are other tables like the next table is saturated water at different pressure.

(Refer Slide Time: 18:39)

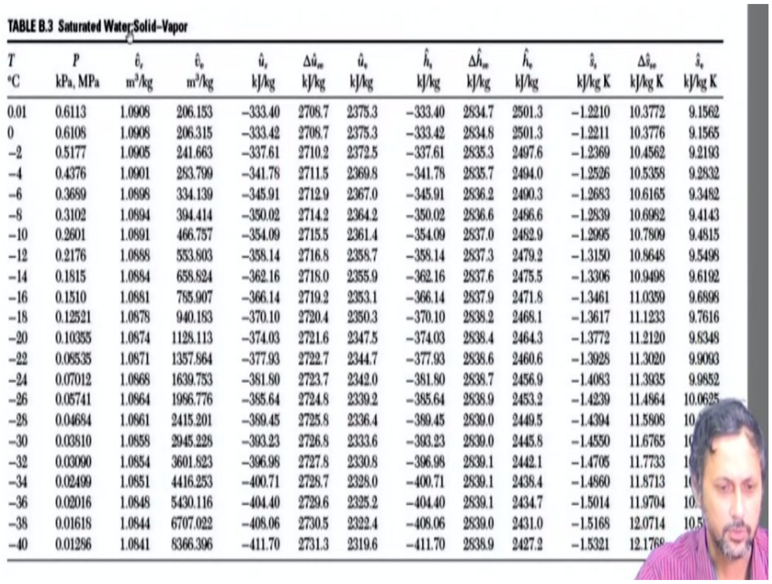
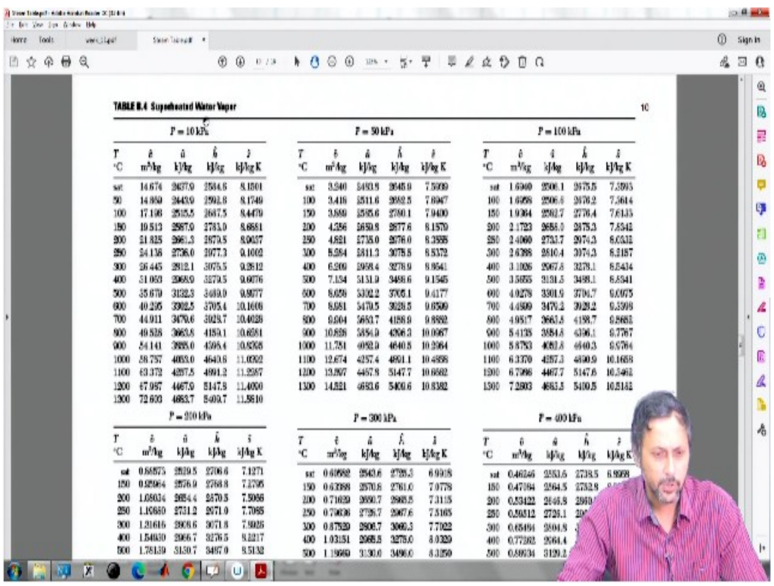


TABLE B.3 Saturated Water: Solid–Vapor

T °C	P kPa, MPa	$\hat{v}_s$ m³/kg	$\hat{v}_v$ m³/kg	$\hat{u}_s$ kJ/kg	$\Delta\hat{u}_{sv}$ kJ/kg	$\hat{u}_v$ kJ/kg	$\hat{h}_s$ kJ/kg	$\Delta\hat{h}_{sv}$ kJ/kg	$\hat{h}_v$ kJ/kg	$\hat{s}_s$ kJ/kg K	$\Delta\hat{s}_{sv}$ kJ/kg K	$\hat{s}_v$ kJ/kg K
0.01	0.6113	1.0908	206.153	−333.40	2708.7	2375.3	−333.40	2834.7	2501.3	−1.2210	10.3772	9.1562
0	0.6108	1.0908	206.315	−333.42	2708.7	2375.3	−333.42	2834.8	2501.3	−1.2211	10.3776	9.1565
−2	0.5177	1.0905	241.663	−337.61	2710.2	2372.5	−337.61	2835.3	2497.6	−1.2369	10.4562	9.2193
−4	0.4376	1.0901	283.799	−341.78	2711.5	2369.8	−341.78	2835.7	2494.0	−1.2526	10.5358	9.2832
−6	0.3689	1.0898	334.139	−345.91	2712.9	2367.0	−345.91	2836.2	2490.3	−1.2683	10.6165	9.3482
−8	0.3102	1.0894	394.414	−350.02	2714.2	2364.2	−350.02	2836.6	2486.6	−1.2839	10.6982	9.4143
−10	0.2601	1.0891	466.757	−354.09	2715.5	2361.4	−354.09	2837.0	2482.9	−1.2995	10.7809	9.4815
−12	0.2176	1.0888	553.803	−358.14	2716.8	2358.7	−358.14	2837.3	2479.2	−1.3150	10.8648	9.5498
−14	0.1815	1.0884	658.824	−362.16	2718.0	2355.9	−362.16	2837.6	2475.5	−1.3306	10.9498	9.6192
−16	0.1510	1.0881	785.907	−366.14	2719.2	2353.1	−366.14	2837.9	2471.8	−1.3461	11.0359	9.6898
−18	0.12521	1.0878	940.183	−370.10	2720.4	2350.3	−370.10	2838.2	2468.1	−1.3617	11.1233	9.7616
−20	0.10355	1.0874	1128.113	−374.03	2721.6	2347.5	−374.03	2838.4	2464.3	−1.3772	11.2120	9.8348
−22	0.08535	1.0871	1357.864	−377.93	2722.7	2344.7	−377.93	2838.6	2460.6	−1.3928	11.3020	9.9093
−24	0.07012	1.0868	1639.753	−381.80	2723.7	2342.0	−381.80	2838.7	2456.9	−1.4083	11.3935	9.9852
−26	0.05741	1.0864	1986.776	−385.64	2724.8	2339.2	−385.64	2838.9	2453.2	−1.4239	11.4864	10.0625
−28	0.04684	1.0861	2415.201	−389.45	2725.8	2336.4	−389.45	2839.0	2449.5	−1.4394	11.5808	[illegible]
−30	0.03810	1.0858	2945.228	−393.23	2726.8	2333.6	−393.23	2839.0	2445.8	−1.4550	11.6765	[illegible]
−32	0.03090	1.0854	3601.823	−396.98	2727.8	2330.8	−396.98	2839.1	2442.1	−1.4705	11.7733	[illegible]
−34	0.02499	1.0851	4416.253	−400.71	2728.7	2328.0	−400.71	2839.1	2438.4	−1.4860	11.8713	[illegible]
−36	0.02016	1.0848	5430.116	−404.40	2729.6	2325.2	−404.40	2839.1	2434.7	−1.5014	11.9704	[illegible]
−38	0.01618	1.0844	6707.022	−408.06	2730.5	2322.4	−408.06	2839.0	2431.0	−1.5168	12.0714	[illegible]
−40	0.01286	1.0841	8366.396	−411.70	2731.3	2319.6	−411.70	2838.9	2427.2	−1.5321	[illegible]	[illegible]

And we have saturated water and solid vapour you know it is a solid vapour equilibrium data.

(Refer Slide Time: 18:50)



And also we have super heated water data but we will be using and we will come to that maybe later on. We will be primarily using the saturated water as a function of temperature table. So in this left most side we have temperature in degree centigrade then we have pressure, we have volume of the specific volume of the liquid phase, specific volume of the vapours phase, internal energy of the liquid phase, internal energy of the vapour phase the difference of this to which is also listed here.

Similarly enthalpy of these 2 phases and the difference entropy of these 2 phases and the difference the latent heat is not given but as long as you know the entropy difference and the temperature. You can easily compute the latent heat not the latent heat the specific heat, and the latent heat is nothing but the enthalpy difference. So that is why because you know if you remember in a constant pressure, constant temperature process the amount of heat that is observed is equal to their change in entropy.

So delta Q is equal to delta H and in case of a phase transition Delta Q is nothing but the latent heat L, so L is nothing but the specific enthalpy. So if you find in a question specific enthalpy is given do not be confused. This specific enthalpy change which is given here this is nothing but the latent heat. So from this table we can readily get the latent heat data and from this change in specific heat we can very easily compute the C p data. This temperature table, so these are all under 1 atmosphere pressure with temperature the pressure also changes my mistake.

But anyway for this given pressure and temperature you can very easily compute the specific heat value from this table. So if we look at it, all this important data has been tabulated and we can use this data over and over again in order to see whether our calculations are right. So we in one of the previous lectures we have already computed the change in pressure. If you want to you know, what you call if you want to increase the boiling point by 1 degree centigrade?

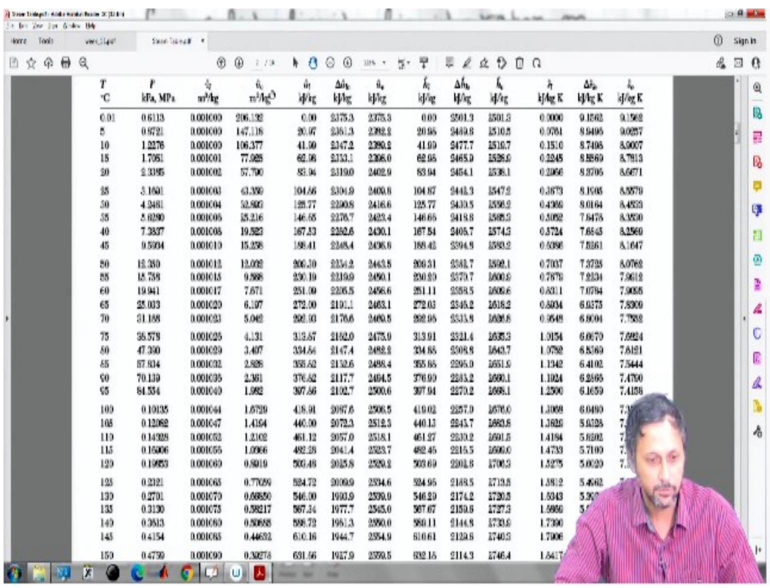
So let us around 100 degrees centigrade, so let us say if you want to go from 100 degree centigrade. At 100 degrees centigrade the pressure is 0.10135 mega Pascal's when it is on the left shifted manner it is in kilo Pascal's when it is right shifted it is in mega Pascal's. So it is 100 degrees centigrade and 105 degrees centigrade, so that means a 5 degree temperature change corresponds to a 0.12082 MPS.

So the difference between these 2 pressures will give you the actual pressure change that is experimentally measured in order to change the boiling point of water from 100 degree centigrade 105. So you can do one thing you can compute this and see and you can use you know the Clapeyron equation in order to compute and you take delta T is equal to 5 and see if you get the same pressure change from there.

We can actually it is a good practice to I mean it will be a good exercise to compare and see how does it tally with the standard steam table. This steam table is given to you use it if you have any questions if you do not understand how to use the steam table please ask in the forum we week's lecture where we will be using the steam table and you will have a lot better idea on how to use it?

So we will come back to steam table again, so all I am trying to tell you that volume and entropy here it is listed for water but for any known material around the liquid vapour transition the volume and entropy changes discontinuously.

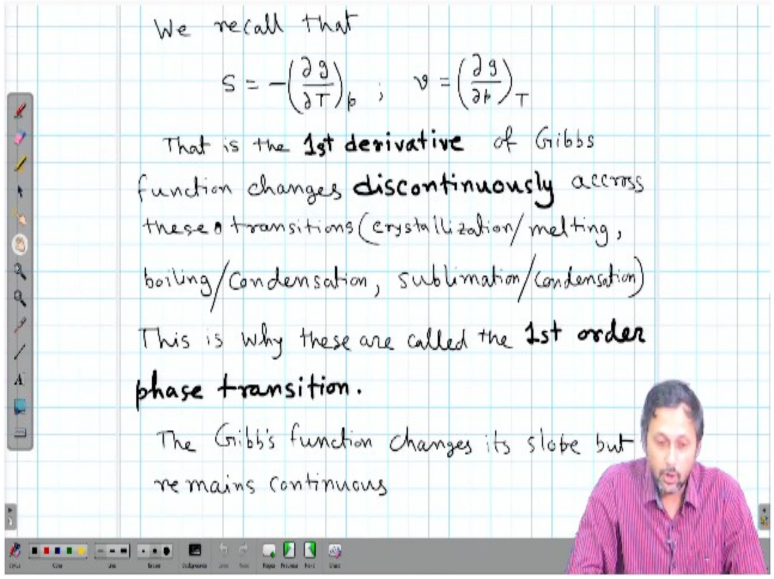
(Refer Slide Time: 23:22)



Now if that happens so it is obvious from here also you see this volume is given here so V L, V V. At any given temperature, so liquid the vapour can exist all the way down to the triple point of water which will come back later on what is triple point? What is the significance of this temperature? But look at this column number 3 and 4 you can see there is always a discontinuity similarly column I mean this Delta S value which is given in the last but one column you this is never zero but you always get a good finite value here.

So that means there is a discontinuity at all this transition points. So that is for water and let me tell you the same story goes for any other material,

(Refer Slide Time: 24:04)



Now we recall that S is equal to minus d g d T p or del g del T p that means this is the temperature derivative of the Gibbs free energy at fixed pressure. Similarly volume is the pressure derivative of Gibbs free energy at fixed temperature. So that means, the first derivative of the Gibbs functions changes discontinuously across this transition. What is these transitions crystallization melting or boiling condensation or sublimation condensation?

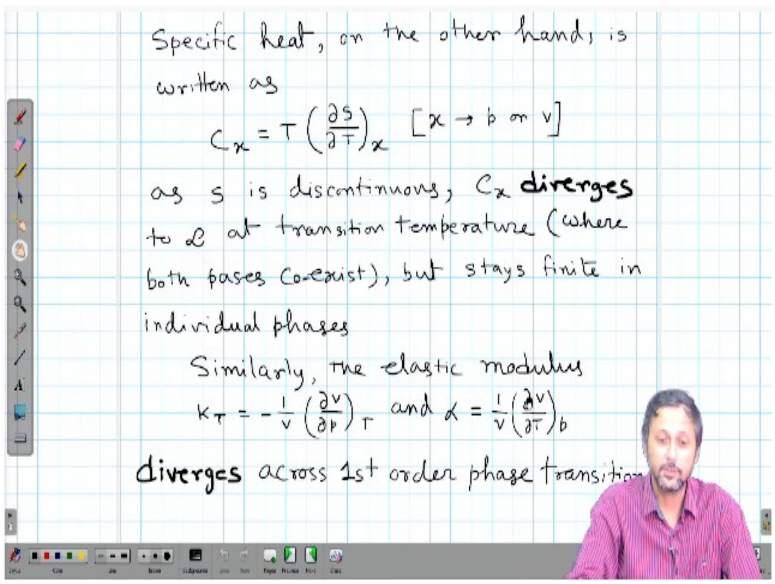
Crystallization is the opposite of melting if we heat up ice it will melt if we cool down liquid water, it will crystalline into ice form it will freeze right. So I should actually say not crystallization but freezing but I hope you understand so it should be freezing similarly we have boiling and condensation this 2 opposite reaction similarly there is something called sublimation and condensation which is probably something that you already know what is sublimation?

When a solid directly evapourates into vapour what happens for naphthalene or camphor these are sublimation, will come back to that in the next lecture. So this is why these are called and because this first derivative of the Gibbs energy changes discontinuously these are called the first order phase transition. So that immediately tells you if there is a second order phase transition that the second derivative of Gibbs energy should change discontinuously precisely that is the case which we will visit towards the end of this week's discussion.

So the Gibbs function changes its slope, but it remains continuous Gibbs function definitely changes its slope. Because if you recall what is dg is equal to del g Del I should write with small g dg is equal to del g del T P d T plus del G del T p dT. So if this should you be p T dp right, so if this one is changing discontinuously I mean this one is changing definitely dg will change, but surprisingly although these two changes discontinuously this one changes but in a continuous manner.

So that actually tells you something that when this one changes in a positive way this one should change in a negative way and vice versa, so that the combination is somehow continuous.

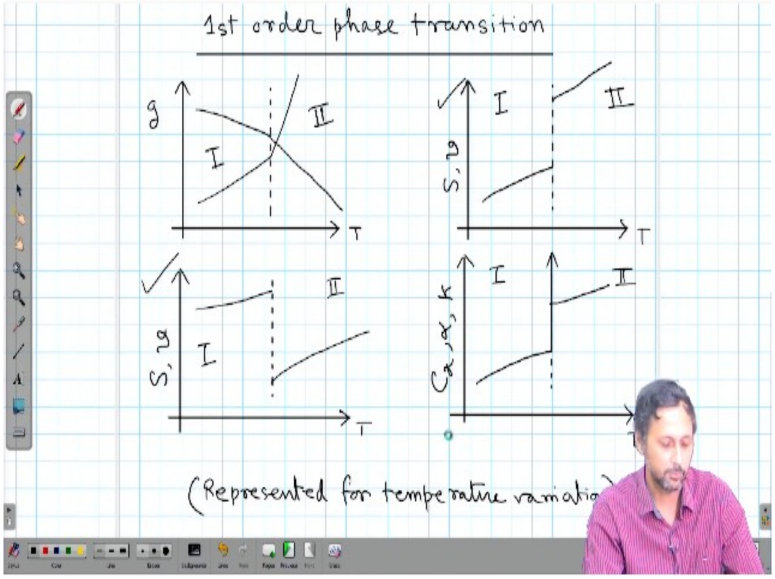
(Refer Slide Time: 27:07)



Now next is specific heat what happens to specific heat? Specific heat is the first derivative of entropy. So T del S del T with some quantity X constant X could be pressure or volume or anything, so X is a conserved quantity and del S del T. So now as this is the second derivative I mean S is already discontinuous then what happens is? C actually diverges to infinity at the transition temperature but remains finite in the individual phases.

So at the phase boundary where these 2 phases coexists the quantity like C x also the elastic modulus like k T and alpha that it these are also the first derivative of Del I mean volume with respective pressure or volume with respective temperature. Just because just like entropy volume is also discontinuous, so the first derivative of volume at the phase boundary will diverge and go to infinity so keeping all this in mind keeping these things in mind.

(Refer Slide Time: 28:20)



If we try to plot the parameters important parameters like you know the Gibbs function the end specific entropy, the specific volume, the elastic coefficient and the specific heat, the general trend is as follows. The Gibbs function changes I mean it could be a change like this it could be a change like this, whatever but it there will be a definite slope change at the boundary point. So if the slope here is like this, the slope there will be like this. So there is a definite slope change at the boundary similarly for v S and v 1.

If one goes like this if one increases the other decreases or vice versa. So I have given it could be like this also it could be like this also depending on, but together they should not have the same type of change. So if one changes you know in a positive manner the other should decrease. So that, the total sums remains continuous in terms of the Gibbs function and the quantities like the second derivative of Gibbs function.

So basically del S del T X is essentially the second derivative of this function similarly alpha and K T these are also second derivative of a function. They will diverge to infinity so this will go to infinity at the transition temperature phase transition temperature and then but it will remain continuous in this 2 phases 1 and 2. Here we try to depict the phase transition phenomena of phase transition as a function of temperature only because this is how we try to visualize.

We generally visualize the phase transition, that is where we stop today in the next lecture we have 3 more lectures for this week there we will try to cover almost all the discussion regarding phase transition and in tomorrow's lecturer or the next lecture with his upcoming we will discussing about the second latent heat equation thank you.