

Thermal Physics
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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.

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Integral form of Clapeyron equation

$$\frac{dP}{dT} = \frac{L}{T(v_2 - v_1)} \quad \text{--- (1)}$$

In case of liquid \rightleftharpoons vapor phase equilibrium, we have seen in the last problem that $v_v \gg v_{liq}$ in general.

So, for liquid-vapor phase transition we may write

$$\frac{dP}{dT} = \frac{L}{T v_v} \quad \text{--- (2)}$$

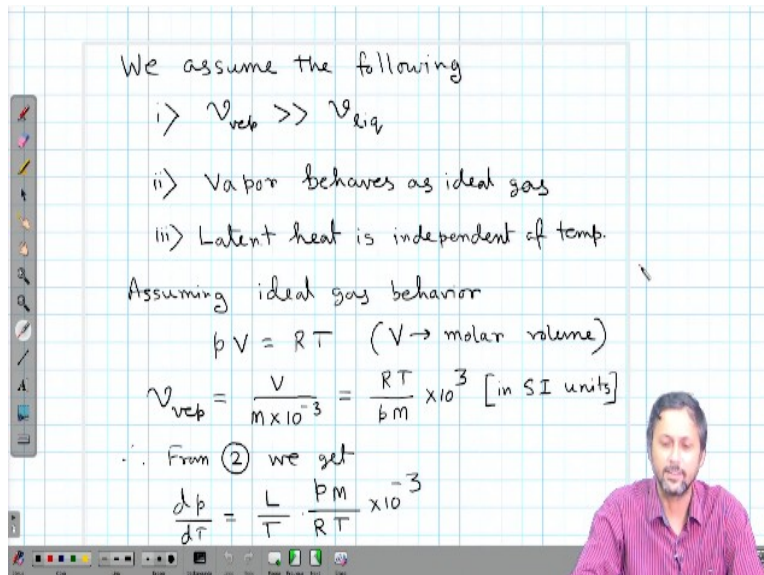
We may try to integrate it now!

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.

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We assume the following

- i) $v_{\text{vap}} \gg v_{\text{liq}}$
- ii) Vapor behaves as ideal gas
- iii) Latent heat is independent of temp.

Assuming ideal gas behavior

$$pV = RT \quad (V \rightarrow \text{molar volume})$$

$$v_{\text{vap}} = \frac{V}{m \times 10^{-3}} = \frac{RT}{p m} \times 10^3 \text{ [in SI units]}$$

\therefore From (2) we get

$$\frac{dp}{dT} = \frac{L}{T} \cdot \frac{p m}{RT} \times 10^{-3}$$

So then what we do we can write $pV = RT$ and V vapour is equal to V divided by capital p . So, what is this $pV = RT$? 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 RT 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.

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re-arranging we get

$$\frac{dp}{p} = \left[\frac{mL}{R} \times 10^{-3} \right] \frac{dT}{T^2}$$

or $\frac{dp}{p} = \frac{L^m}{R} \frac{dT}{T^2}$

$$\ln p = -\frac{L^m}{RT} + B \quad \text{--- (3) (B constant)}$$

Eqn (3) is known as **Young's law** for phase boundary. This equation provides the locus of vapor-liquid equilibrium in p - T plane.

also, we may write

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{L^m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{--- (4)}$$

Now rearranging and simplifying little bit further we get dp/p is equal to mL/R into 10 to the power minus 3 dT/T^2 right. Now what is this mL into 10 to the power -3 that means mL 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 dT/T^2 integrating we get $\ln p$ is equal to minus L^m by RT 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 these known limits where between T_1 and T_2 temperature and corresponding to p_1 and p_2 pressure we can simply write $\ln p_2$ by p_1 is equal to minus L_m by R times $1/T_2$ minus $1/T_1$ 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.

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It has been found experimentally that latent heat also changes with temperature in a linear manner

$$L^m = a + bT$$

So, we rewrite (2) as

$$\frac{dp}{dT} = \frac{a+bT}{RT^2} p$$

integrating, $\ln p = \frac{b}{R} \ln T - \frac{a}{RT} + B$

or $\ln p = k \ln T - \frac{m}{T} + B - (5)$

This is known as the Kirchhoff's law

This has better agreement with experiment

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 $a + bT$. 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 $T^2 v$. So if we do that we get dp/dT is equal to $a + bT$ divided $R T^2$ times P , so basically not in equation 2 directly. But in equation this equation here I have substituted for L is equal to $a + bT$.

And after this integration then if we integrate we get $\ln p$ is equal to $k \ln T$ 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.

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The screenshot shows a presentation slide with the following text:

2. Calculate the change in melting point of ice at 273K when the pressure is increased by 2 atm. How much pressure change is required to change the melting point by 1°C ?

3. Under what pressure the boiling point of water will raise by 1°C ?

4. In a sealed container small amount of a liquid is in equilibrium with its vapour. The vapour pressure of a substance is $3,000\text{Pa}$ at 300K and the latent heat of vaporization is 50 kJ/mol .

i) The volume of the container is doubled isothermally. What is the new pressure inside?

ii) At what temperature the vapour pressure will reach $15,000\text{ Pa}$?

The diagram shows two identical cylinders on stands, both labeled 'T' for temperature. The left cylinder contains a small amount of liquid and is labeled 'V' for volume. A green arrow points to the right cylinder, which contains a larger amount of liquid and is labeled '2V' for volume.

5. Liquid He has a boiling point of 4.2K under 1 atm. pressure. But under pressure ($\sim 1\text{ mm of He}$) it boils at 1.2K . Calculate the average latent

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 $2V$. 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 $50\text{ kilo joules per mole}$.

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Classroom problems : Week 11

4) i) $V \rightarrow 2V$
 $p \rightarrow ?$ } Pressure will not change

The pressure inside is the saturated vapor pressure. If the volume increases, more liquid will evaporate to maintain pressure.

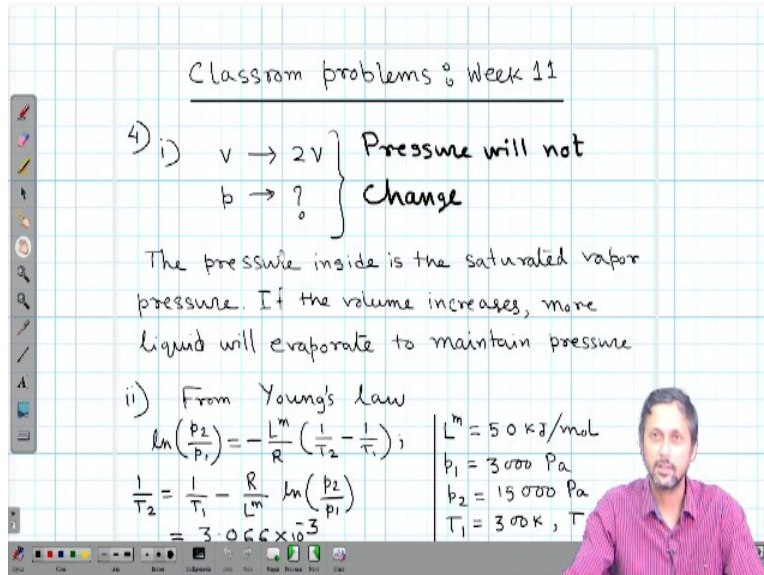
ii) From Young's Law

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{L^m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right);$$

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{L^m} \ln\left(\frac{p_2}{p_1}\right)$$

$$= 3.066 \times 10^{-3}$$

$L^m = 50 \text{ kJ/mol}$
 $p_1 = 3000 \text{ Pa}$
 $p_2 = 15000 \text{ Pa}$
 $T_1 = 300 \text{ K}$



Now in order to solve this problem the first problem is we have V to $2V$ the volume changes from V to $2V$ 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 evaporate 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 evaporated 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.

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$$\frac{a_1}{b} = \left[\frac{L^m}{R} \times 10^{-3} \right] \frac{1}{T^2}$$

$$\text{or } \frac{dp}{p} = \frac{L^m}{R} \frac{dT}{T^2}$$

$$\therefore \ln p = -\frac{L^m}{RT} + B \quad \text{--- (3) (B constant)}$$

Eqn (3) is known as **Young's law** for phase boundary. This equation provides the locus of vapor-liquid equilibrium in p - T plane.

also, we may write

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{L^m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{--- (4)}$$

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

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i) $v \rightarrow 2v$
 $b \rightarrow ?$ } Pressure will not change

The pressure inside is the saturated vapor pressure. If the volume increases, more liquid will evaporate to maintain pressure.

ii) From Young's law

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{L^m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right);$$

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{L^m} \ln\left(\frac{p_2}{p_1}\right)$$

$$= 3.066 \times 10^{-3} \text{ K}^{-1}$$

$$T_2 \approx 326 \text{ K}$$

$L^m = 50 \text{ kJ/mol}$
 $p_1 = 3000 \text{ Pa}$
 $p_2 = 15000 \text{ Pa}$
 $T_1 = 300 \text{ K}, T_2 = ?$

So we have L^m which is 50 Joules per mole we have P_1 which is 3000 Pa which is 15000 Pa we have T_1 which is 300 Kelvin now the question is what is T_2 ? So we start from this equation we simply right $1/T_2$ is equal to $1/T_1$ after rearrangement we write $1/T_2$ is equal to $1/T_1$ 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 $1/T_2$ is equal to 3.033×10^{-3} . So the unit here should be Kelvin inverse which gives you it should be $T_2 = 326$ Kelvin.

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5. Liquid He has a boiling point of 4.2K under 1 atm. pressure. But under a reduced pressure (~ 1 mm of Hg) it boils at 1.2K. Calculate the average latent heat in the range.

6. A pressure cooker is fitted with a petcock of mass 140gm on an exhaust nozzle of cross section 4mm^2 . What is the boiling point of water inside?

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?

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5) p vs T graph showing liquid-vapour equilibrium line. Points: $T_1 = 4.2 \text{ K}, p_1 = 760 \text{ mm}$ and $T_2 = 1.2 \text{ K}, p_2 = 1 \text{ mm}$.

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{L^m}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

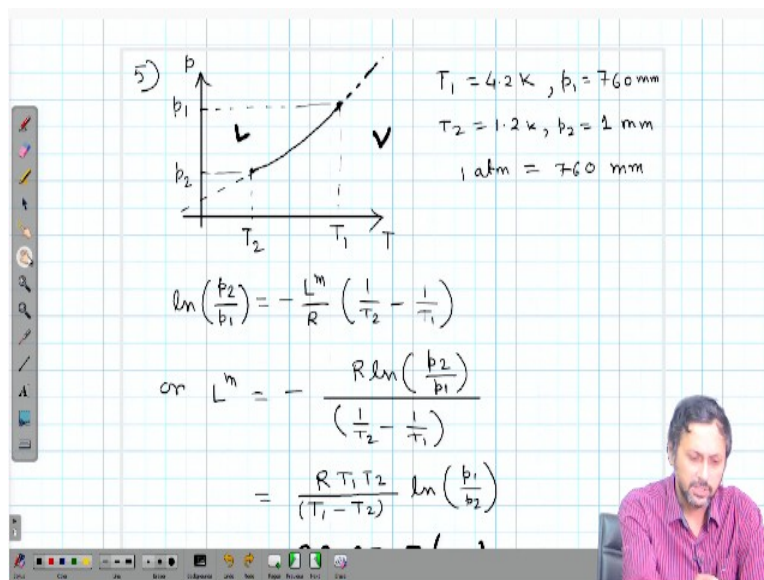
$$\text{or } L^m = -\frac{R \ln\left(\frac{p_2}{p_1}\right)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

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.

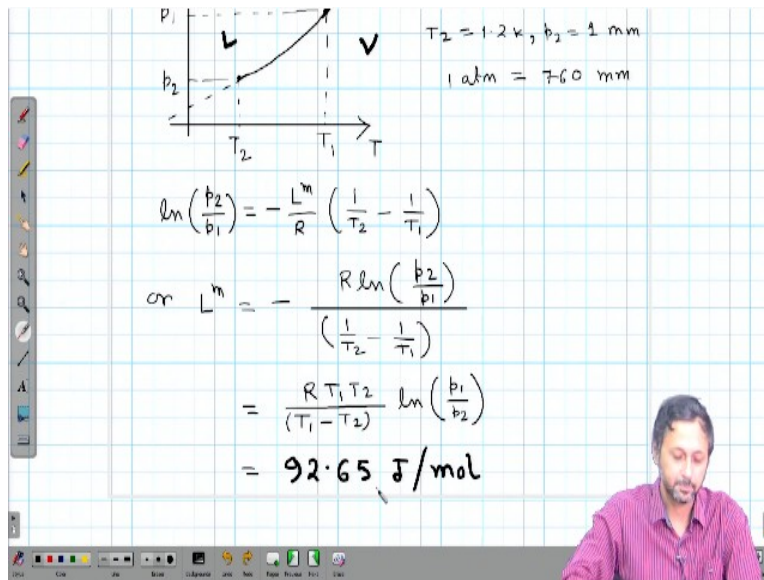
So it should be p_1, p_2, T_1, T_2 right, so that means corresponding to 4.2 Kelvin we have 760 mm of course the slope is not very evident but it should be there should be good amount of slope and at $T_2 = 1.2$ Kelvin we have 1 mm of pressure. Now 760 mm 1 atmosphere of in mercury scale is 760 mm I hope you are familiar with this concept if not please go back and read your school physics textbook where it is clearly mentioned.

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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 do? 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 .

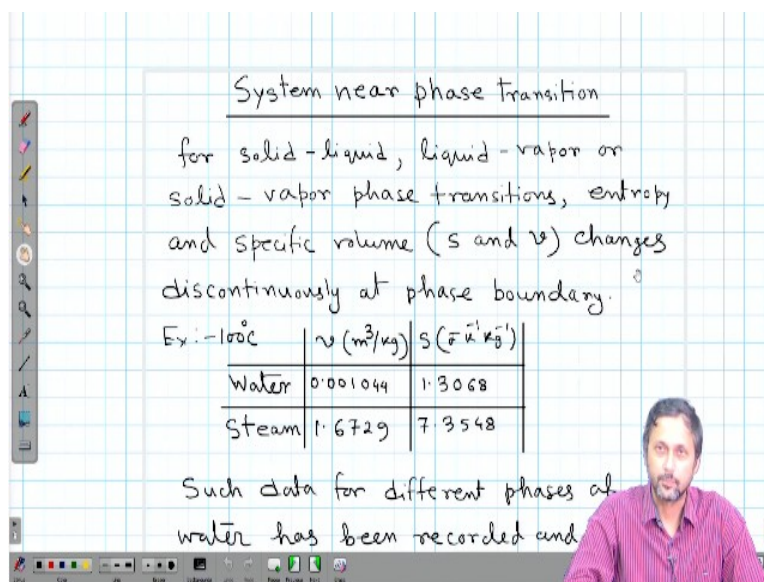
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Which is after arrangement $R T_1 T_2$ divided by $T_1 - T_2$ $\ln p_1$ by p_2 and we do not need any unit conversion, because p_1 and p_2 already there coming as a ratio. So whatever unit conversion we do it will cancel nicely we do not need that 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 1.2 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.

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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 0.0010044 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 whereas 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.

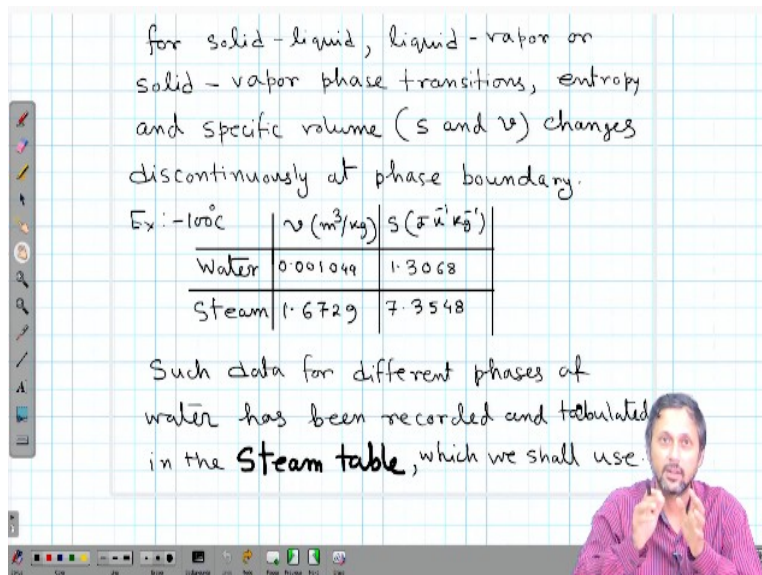
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for solid-liquid, liquid-vapor or solid-vapor phase transitions, entropy and specific volume (s and v) changes discontinuously at phase boundary.

Ex: -100°C

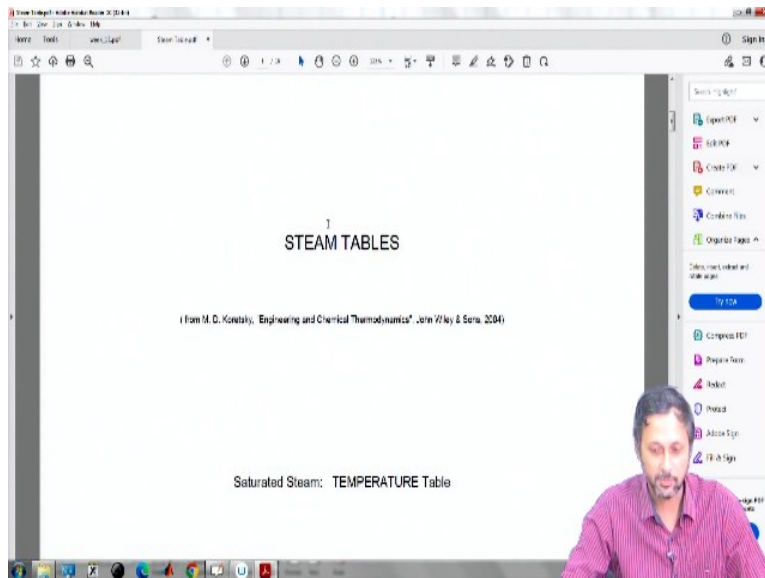
	v (m ³ /kg)	s (kJ/kg·K)
Water	0.001044	1.3068
Steam	1.6729	7.3548

Such data for different phases of water has been recorded and tabulated in the **Steam table**, which we shall use.



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.

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

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2
TABLE B.1 Saturated Water: Temperature Table

T °C	P MPa	v_f m ³ /kg	v_g m ³ /kg	u_f kJ/kg	u_g kJ/kg	h_f kJ/kg	h_{fg} kJ/kg	h_g kJ/kg	s_f kJ/kg·K	s_{fg} kJ/kg·K	s_g kJ/kg·K
0.01	0.6113	0.001000	206.132	0.00	2375.3	2375.3	0.00	2391.3	0.0000	9.1562	9.1562
5	0.8721	0.001000	167.119	20.07	2381.5	2382.2	20.09	2401.6	0.0761	9.0466	9.1227
10	1.0137	0.001000	166.577	41.86	2374.3	2374.9	41.86	2397.7	0.1519	8.9465	9.0984
15	1.7081	0.001001	77.025	82.08	2351.1	2356.0	82.08	2368.9	0.3268	8.7969	9.1237
20	2.3385	0.001002	57.769	93.94	2319.9	2402.9	93.94	2404.1	0.5066	8.5706	9.0771
25	3.1691	0.001003	41.559	104.96	2284.9	2490.6	104.97	2492.3	0.6873	8.3005	9.0078
30	4.2461	0.001004	31.993	125.77	2250.9	2418.0	125.77	2430.5	0.8689	8.0104	8.8793
35	5.6219	0.001006	25.149	148.00	2217.7	2423.4	148.00	2418.6	1.0513	7.7078	8.7591
40	7.3837	0.001008	19.823	187.52	2185.5	2430.1	187.54	2406.7	1.2353	7.3948	8.6301
45	9.5934	0.001010	15.259	199.41	2146.4	2435.6	199.42	2394.4	1.4209	7.0784	8.4993
50	12.559	0.001012	11.012	209.90	2104.2	2440.5	209.91	2381.7	1.6081	6.7595	8.3676
55	16.535	0.001015	8.069	220.10	2059.9	2445.1	220.10	2369.0	1.7979	6.4384	8.2363
60	21.641	0.001017	5.971	251.06	2002.5	2450.0	251.11	2356.5	1.9906	6.1161	8.1067
65	28.023	0.001020	4.417	272.00	1941.1	2455.1	272.03	2344.3	2.1864	5.7935	7.9789
70	35.991	0.001023	3.254	282.02	1876.5	2460.5	282.06	2332.6	2.3854	5.4700	7.8534
75	45.838	0.001026	2.361	312.07	1802.9	2475.9	312.01	2321.4	2.5876	5.1464	7.7300
80	57.991	0.001029	1.697	334.94	1747.4	2482.2	334.88	2309.6	2.7930	4.8228	7.6100
85	73.834	0.001032	1.228	355.02	1703.6	2488.4	355.00	2298.0	2.9999	4.5000	7.4934
90	94.339	0.001036	0.901	375.02	1671.7	2494.5	375.00	2287.2	3.2081	4.1781	7.3800
95	120.84	0.001040	0.662	397.56	1642.7	2500.6	397.54	2277.2	3.4181	3.8580	7.2700
100	155.38	0.001044	0.508	419.81	1617.5	2506.5	419.82	2267.9	3.6306	3.5400	7.1634
105	199.80	0.001047	0.394	440.00	1595.3	2512.3	440.13	2259.3	3.8459	3.2259	7.0600
110	255.36	0.001052	0.302	461.12	1575.0	2518.1	461.27	2251.2	4.0644	2.9159	6.9600
115	324.86	0.001056	0.230	482.26	1556.4	2523.7	482.46	2243.6	4.2864	2.6100	6.8634
120	412.13	0.001060	0.180	503.45	1539.5	2529.2	503.60	2236.6	4.5119	2.3179	6.7700
125	519.31	0.001065	0.140	524.72	1524.0	2534.6	524.86	2230.5	4.7411	2.0300	6.6800
130	648.80	0.001070	0.110	546.00	1509.9	2540.0	546.20	2225.3	4.9741	1.7479	6.5934
135	799.91	0.001075	0.089	567.24	1497.7	2545.0	567.67	2220.9	5.2119	1.4700	6.5100

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.

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TABLE B.3 Saturated Water–Solid–Vapor

T °C	P kPa, MPa	\hat{v}_f m³/kg	\hat{v}_g m³/kg	\hat{u}_f kJ/kg	$\Delta \hat{u}_{fg}$ kJ/kg	\hat{u}_g kJ/kg	\hat{h}_f kJ/kg	$\Delta \hat{h}_{fg}$ kJ/kg	\hat{h}_g kJ/kg	\hat{s}_f kJ/kg K	$\Delta \hat{s}_{fg}$ kJ/kg K	\hat{s}_g kJ/kg K
0.01	0.6113	1.0008	206.153	-333.40	2708.7	2375.3	-333.40	2834.7	2501.3	-1.2210	10.3772	9.1562
0	0.6108	1.0008	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	1357.964	-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	0.04694	1.0861	2415.201	-389.45	2725.8	2336.4	-389.45	2839.0	2449.5	-1.4394	11.5908	10.1412
-30	0.03810	1.0858	2945.228	-393.23	2726.8	2333.6	-393.23	2839.0	2445.8	-1.4550	11.6965	10.2213
-32	0.03090	1.0854	3601.823	-396.98	2727.8	2330.8	-396.98	2839.1	2442.1	-1.4705	11.7733	10.3028
-34	0.02499	1.0851	4416.253	-400.71	2728.7	2328.0	-400.71	2839.1	2438.4	-1.4860	11.8713	10.3857
-36	0.02016	1.0848	5430.116	-404.40	2729.6	2325.2	-404.40	2839.1	2434.7	-1.5014	11.9704	10.4700
-38	0.01618	1.0844	6707.022	-408.06	2730.5	2322.4	-408.06	2839.0	2431.0	-1.5168	12.0714	10.5557
-40	0.01296	1.0841	8366.396	-411.70	2731.3	2319.6	-411.70	2838.9	2427.2	-1.5321	12.1768	10.6428

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

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TABLE B.4 Superheated Water Vapor												
$P = 10 \text{ kPa}$												
T °C	\hat{v} m³/kg	\hat{u} kJ/kg	\hat{h} kJ/kg	\hat{s} kJ/kg K	T °C	\hat{v} m³/kg	\hat{u} kJ/kg	\hat{h} kJ/kg	\hat{s} kJ/kg K	T °C	\hat{v} m³/kg	\hat{u} kJ/kg
sat	16.73	2454.0	2583.9	8.1501	sat	3.240	2453.9	2583.9	7.5009	sat	1.6960	2506.1
50	16.890	2440.0	2591.8	8.1740	100	3.416	2511.6	2692.5	7.6967	100	1.6996	2506.9
100	17.146	2452.5	2601.5	8.4479	150	3.666	2595.6	2798.1	7.9400	150	1.9384	2595.7
180	18.813	2587.0	2713.9	8.6881	200	4.256	2693.8	2877.6	8.1870	200	2.1723	2686.0
200	21.825	2661.5	2873.8	8.9037	250	4.821	2736.0	2978.0	8.3988	250	2.6060	2733.7
280	34.136	2726.0	3077.3	9.1602	300	5.264	2811.3	3078.8	8.5372	300	2.8398	2810.4
300	38.445	2812.1	3075.5	9.2812	400	6.200	2904.4	3278.9	8.9541	400	3.1006	2907.0
400	51.893	2960.9	3273.5	9.6076	500	7.124	3113.9	3486.6	9.1545	500	3.5075	3118.2
500	55.679	3123.2	3483.9	9.8077	600	8.029	3302.2	3706.1	9.3177	600	4.0278	3301.9
600	40.235	3202.5	3705.4	10.1610	700	8.681	3479.5	3928.5	9.4506	700	4.6860	3475.2
700	44.911	3479.6	3928.7	10.4028	800	9.064	3653.7	4158.9	9.5822	800	4.9577	3663.8
800	49.838	3663.8	4158.1	10.6581	900	10.628	3849.0	4396.3	10.0087	900	5.4125	3848.8
900	54.141	3858.0	4398.4	10.9258	1000	11.721	4052.0	4640.5	10.3584	1000	5.8753	4051.8
1000	58.757	4053.0	4643.8	11.0022	1100	12.674	4257.4	4901.1	10.6998	1100	6.3378	4257.2
1200	67.372	4297.5	4901.2	11.2057	1200	12.867	4457.9	5147.7	10.8602	1200	6.7296	4467.7
1300	67.997	4467.9	5147.9	11.4050	1300	14.521	4683.6	5406.6	10.9382	1300	7.2893	4683.3
1400	72.693	4683.7	5408.7	11.5810								
$P = 100 \text{ kPa}$												
T °C	\hat{v} m³/kg	\hat{u} kJ/kg	\hat{h} kJ/kg	\hat{s} kJ/kg K	T °C	\hat{v} m³/kg	\hat{u} kJ/kg	\hat{h} kJ/kg	\hat{s} kJ/kg K	T °C	\hat{v} m³/kg	\hat{u} kJ/kg
sat	0.60523	2583.9	2769.8	7.1271	sat	0.19399	2583.9	2769.8	6.9393	sat	0.46146	2583.6
120	0.89584	2578.9	2768.8	7.2295	150	0.47084	2584.5	2753.9	6.9908	150	0.53422	2584.9
200	1.05834	2584.4	2570.5	7.3088	200	0.71039	2690.7	2690.5	7.3113	200	0.71039	2690.5
250	1.10580	2712.1	2671.0	7.7085	250	0.79630	2795.7	2697.6	7.5165	250	0.79630	2795.7
300	1.20486	2808.6	2671.8	7.9805	300	0.87529	2906.7	2696.3	7.7022	300	0.87529	2906.7
400	1.54039	2966.7	3276.5	8.2217	400	1.02151	3068.5	3275.0	8.0229	400	0.77203	3068.4
500	1.78139	3129.7	3487.9	8.5132	500	1.19960	3130.6	3486.0	8.3259	500	0.59631	3129.2

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 ΔQ is equal to ΔH and in case of a phase transition ΔQ 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 ΔT 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.

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T °C	P MPa	v m³/kg	h kJ/kg	s kJ/kg·K	h_g kJ/kg	s_g kJ/kg·K	h_{fg} kJ/kg	s_{fg} kJ/kg·K	h_{gg} kJ/kg	s_{gg} kJ/kg·K
0.01	0.001013	0.001000	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5	0.00712	0.001000	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
10	0.01227	0.001000	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
15	0.01705	0.001001	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
20	0.02339	0.001002	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	0.03169	0.001003	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
30	0.04246	0.001004	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
35	0.05623	0.001005	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40	0.07387	0.001006	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
45	0.09594	0.001010	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50	0.12350	0.001013	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
55	0.15688	0.001015	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
60	0.19641	0.001017	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
65	0.24353	0.001020	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
70	0.29967	0.001023	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
75	0.36629	0.001025	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
80	0.44483	0.001029	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
85	0.53684	0.001032	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
90	0.64387	0.001035	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
95	0.76854	0.001040	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
100	0.10135	0.001044	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
105	0.12082	0.001047	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
110	0.14289	0.001050	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
115	0.16806	0.001055	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
120	0.19683	0.001060	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
125	0.22921	0.001065	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
130	0.27000	0.001070	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
135	0.31930	0.001075	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
140	0.36735	0.001080	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
145	0.41454	0.001085	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00
150	0.47000	0.001090	0.001	0.00	0.00	0.00	0.00	0.00	0.00	0.00

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,

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We recall that

$$S = -\left(\frac{\partial g}{\partial T}\right)_p ; \quad v = \left(\frac{\partial g}{\partial p}\right)_T$$

That is the **1st derivative** of Gibbs function changes **discontinuously** across these transitions (crystallization/melting, boiling/condensation, sublimation/condensation). This is why these are called the **1st order phase transition**.

The Gibbs function changes its slope but remains continuous.

Now we recall that S is equal to minus $d g / d T$ at p or $\partial g / \partial T$ at 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 are 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 crystallize 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 is a 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 evaporates 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 ∂g . I should write with small

g dg is equal to $\left(\frac{\partial g}{\partial T}\right)_P dT$ plus $\left(\frac{\partial g}{\partial P}\right)_T dP$. 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.

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Specific heat, on the other hand, is written as

$$C_X = T \left(\frac{\partial S}{\partial T} \right)_X \quad [X \rightarrow P \text{ or } V]$$

as S is discontinuous, C_X **diverges** to ∞ at transition temperature (where both phases co-exist), but stays finite in individual phases

Similarly, the elastic modulus

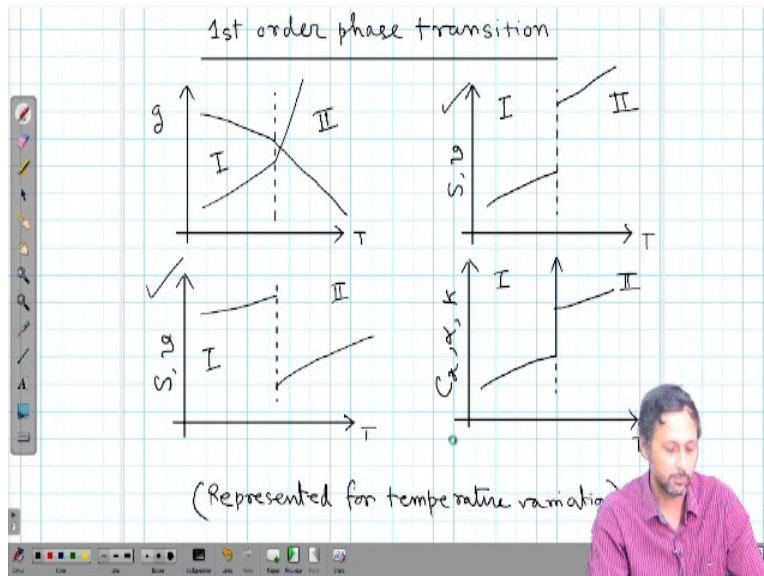
$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{and} \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

diverges across 1st order phase transition

Now next is specific heat what happens to specific heat? Specific heat is the first derivative of entropy. So $T \left(\frac{\partial S}{\partial T}\right)_X$ with some quantity X constant X could be pressure or volume or anything, so X is a conserved quantity and $\left(\frac{\partial S}{\partial T}\right)_X$. 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 α that it these are also the first derivative of ΔV 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.

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If we try to plot the parameters important parameters like you know the Gibbs function the enthalpy, the 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 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 C_p .

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 sum remains continuous in terms of the Gibbs function and the quantities like the second derivative of Gibbs function.

So basically $\frac{\partial S}{\partial T}$ is essentially the second derivative of this function similarly α and κ 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 these 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 lecture or the next lecture with his upcoming we will discussing about the second latent heat equation thank you.