Thermal Physics

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Module No # 11
Lecture No # 53
Phase Diagram and Triple Point

Hello and welcome back to another lecture of this NPTEL lecture series on thermal physics. Now in the last lecture we talked about the applications of Clapeyron equation which is also called the first latent heat equation. And at the end of the lecture I said we will be discussing a second latent equation in the next lecture. But then I realized that, we have to have actually there is a long way to go before we go to the second latent heat equation.

We first need to discuss what is a phase diagram? Then there is relevant discussion that has to be covered before we can eventually go to the second latent heat equation. For today's lecture, let us start with the problem set the classroom problem set.

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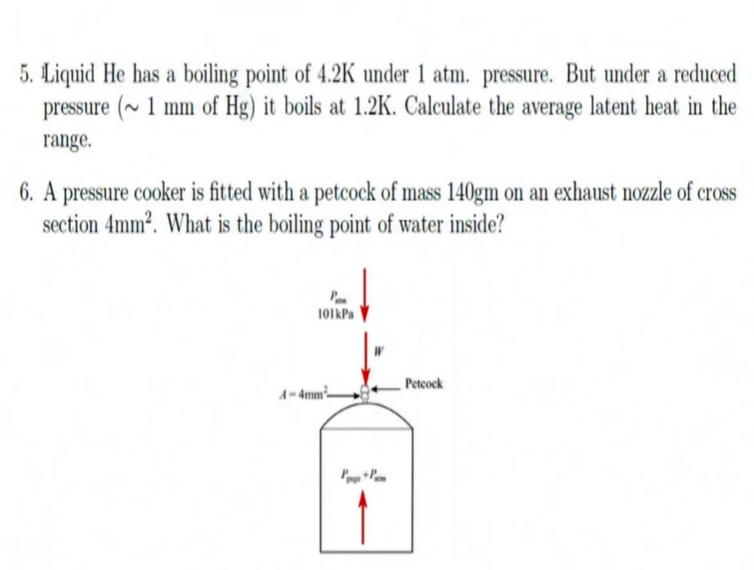

5. Liquid He has a boiling point of 4.2K under 1 atm. pressure. But under a reduced pressure (~ 1 mm of Hg) it boils at 1.2K. Calculate the average latent heat in the range.

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?

We have finished up to problem number 5 completed up to problem number 5 in the last lecture now we will complete problem number 6 and 7 today now 6 is a slightly conceptually more challenging.

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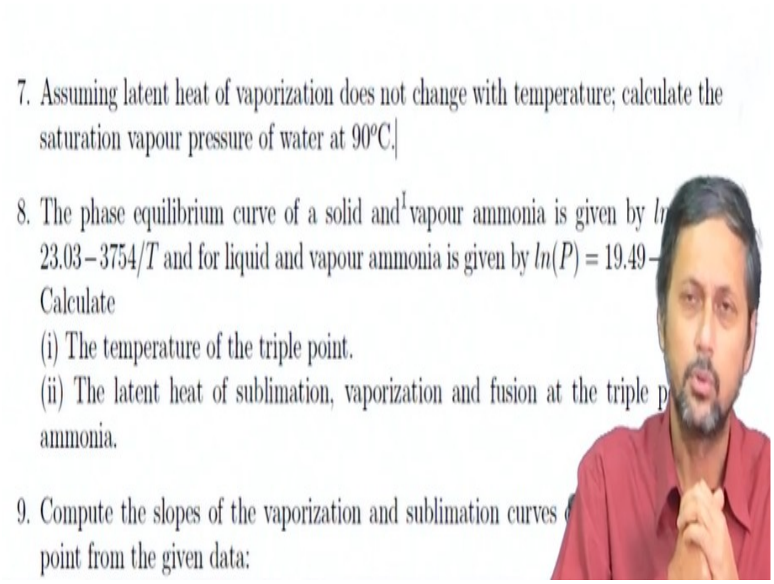

7. Assuming latent heat of vaporization does not change with temperature; calculate the saturation vapour pressure of water at 90°C.

8. The phase equilibrium curve of a solid and vapour ammonia is given by l
$23.03 - 3754/T$ and for liquid and vapour ammonia is given by $ln(P) = 19.49-$
Calculate
(i) The temperature of the triple point.
(ii) The latent heat of sublimation, vaporization and fusion at the triple p
ammonia.

9. Compute the slopes of the vaporization and sublimation curves
point from the given data:

So, let us come to scroller number 7 which is basically the same thing the concept is more or less the same but we will start with problem number 7. That says assuming latent heat of vapourization does not change with temperature, calculate the saturation vapour pressure of water at 90 degree centigrade. So the situation is the following we have typically we know under 1 atmosphere pressure the water boils at around 100 degree centigrade exactly at 100 degree centigrade this is the steam point.

Now if we reduce the pressure on water then water should boil at a lower temperature. Now and this is something that we have already read in our, you know school level physics books. That if you go to a hills it cooking takes longer because water will boil at a lower temperature and other things so this today we will get an example where this will be demonstrated mathematically.

So far we know that the boiling point decreases but how much to what extent it decreases what the actual value is or rather this is a I mean slightly you know different way of looking at it. We will try to find out the pressure at which it will the boiling point will reduce to 90 degree centigrade that means a 10 degree reduction.

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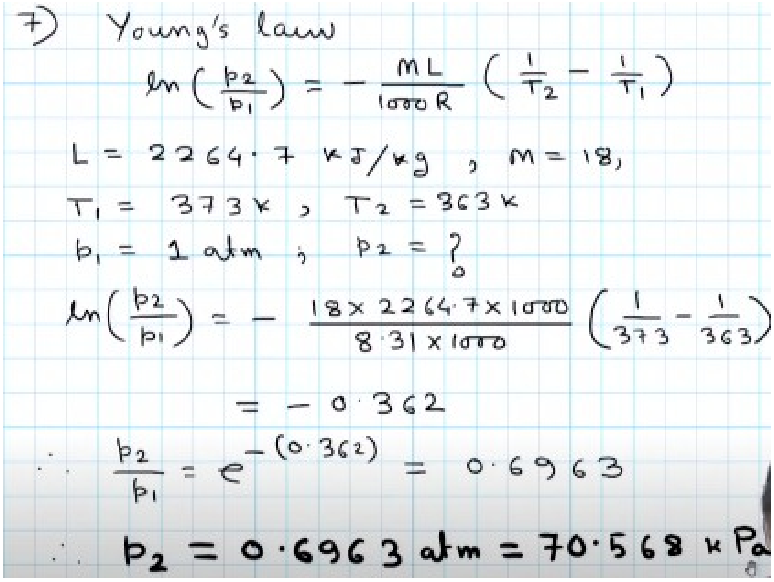

7) Young's law

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{ML}{1000R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$L = 2264.7$ kJ/kg , $M = 18$,

$T_1 = 373$ K , $T_2 = 363$ K

$p_1 = 1$ atm ; $p_2 = ?$

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{18 \times 2264.7 \times 1000}{8.31 \times 1000}\left(\frac{1}{373} - \frac{1}{363}\right)$$

$$= -0.362$$

$$\therefore \frac{p_2}{p_1} = e^{-(0.362)} = 0.6963$$

$$\therefore p_2 = 0.6963 \text{ atm} = 70.568 \text{ kPa}$$

So let us start we will once again start from Young's law which is long p 2 minus p 2 by p 1 is equal to minus m l 100 by r sorry m l divided by m l divided by 100 r times 1 by T 2 minus 1 by T 1. So basically it is the integral form between the 2 limits T 1 and T 2 corresponding to 2 pressure p 1 and p 2. Now in the question the problem statement itself it has been said that assume that latent heat does not change. If latent heat does not change that means L remains constant right.

So we take 2264.7 kilojoules per kg which is the value exactly at the 100 degree centigrade m is equal to 18 that we know. T 1 is equal to 373 Kelvin that is the normal boiling point of water under 1 atmosphere pressure and T 2 is 10 degrees lower that is 363 Kelvin p 1 is equal to 1 atmosphere what is the value of p 2? So simply we put p 2 by p1 we compute the right hand side of this relation by putting the values of different parameters and we get l on p 2 by p 1 is equal to minus 0.362 which if I just from there if we try to compute p 2 by p 1 then we get 0.6963.

So that means p 2 is 0.6960 atmospheres or almost 0.7 atmospheres. So if one atmosphere is our normal pressure if we reduce the pressure by 30% then water will boil at a reduced temperature. I mean 10 degrees less temperature. So in terms of pascals kilo pascals the value is 70.567 kilopascals right. So this is problem number 6 problem number 7 for you straight forward. Now of course this is a huge reduction 70% less atmospheric pressure is typically that we do not experience but 10 to 10 to 15% less pressure is not very abnormal at higher altitude.

So that means just by simple deduction may be with the boiling point of water will reduce by 5 degree centigrade even that is significant. So if we have you know cooking temperature instead of 100 degree Centigrade's if we have somewhere close to 95 degree centigrade it takes significantly longer time. Now one way of encountering this problem is by using a pressure cooker what happens inside a pressure cooker?

So let us go back to problem number 6 here. So this is a sim the schematic construction of a simple pressure cooker and we also use it when I mean for normal I mean household cooking as well. Primarily because it saves lots of fuel lots of energy and thereby reducing the cost and also it helps you know cook things like for example potato or meat for example it takes much lesser time as compared to normal cooking.

Now what is the principle of pressure cooker? In pressure cooker what happens is we have a vessel right.

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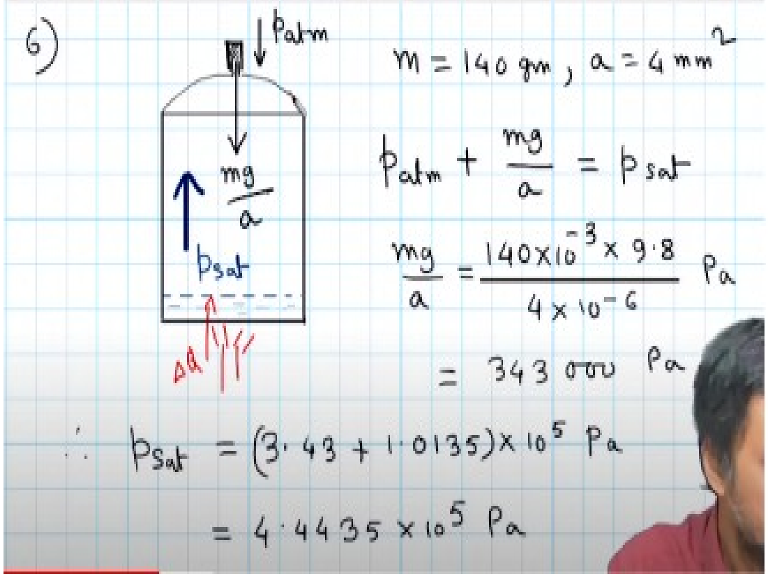

6)

$m = 140\ gm,\ a = 4\ mm^2$

$$p_{atm} + \frac{mg}{a} = p_{sat}$$

$$\frac{mg}{a} = \frac{140\times10^{-3}\times 9.8}{4\times10^{-6}}\ Pa$$

$$= 343\,000\ Pa$$

$$\therefore p_{sat} = (3.43 + 1.0135)\times10^{5}\ Pa$$

$$= 4.4435\times10^{5}\ Pa$$

So let us go to the problem that we have solved then we will try to explain. So we have a vessel a closed vessel we all know how a pressure cooker looks like. So we have some liquid inside this liquid boils and this liquid for most of the time for household cooking at least it is water. Of course if we have a thing similar to the pressure cooker in our labs also that is called an autoclave. Now in an autoclave we sometimes we have different types of liquid present anyway.

So now we have this one this container this vessel and on top of that there is a nozzle we all know there is a petcock. So which makes this hissing sound we call it whistle sometime so this is actually in a technical term it is called a petcock now petcock is placed on a nozzle. So this is the safety valve of a pressure cooker. So the idea is because it is a closed vessel as the temper I mean the pressure inside will build up.

So is essentially due to this phase equilibrium because the pressure is building up inside so the water will start boiling at a much elevated temperature. Now if we keep it completely closed then it will be like you know it will be like a super pressurized cell and if we keep putting energy because we are you know putting it on the flame. So there is a flame here so we have some sort of a flame here so that means we are continuously putting energy I mean heat delta A inside.

And as this delta Q builds up it will you know it will make the internal I mean it will increase the temperature as well as the pressure. So if there is no release mechanism the pressure will eventually reach a point where it will be a super heated super saturated steam and then if the whole thing might explode. Now to avoid such situation and to make this process a controlled one we have this petcock placed here.

Now what does the petcock do? Petcock has a given weight and this nozzle here it has a finite I mean a given cross section area. Now that nozzle that means there is a finite pressure so this weight of this pressure repeat is mg and the area of the nozzle is a. So the pressure inside is mg plus mg divided by a of course there is an atmospheric pressure that is acting on this petcock. So the total pressure is p atmosphere + m g + m g by a downwards which has to be equal to the saturated vapour pressure p sat at a given temperature. And sorry that is where this balance is achieved.

This will be the maximum temperature till which it will be allowed the water will be allowed to go. Beyond that the saturation vapour pressure becomes more as compared to this combination and this petcock will be pushed up and vapour will be released from here that is when we will we hear the whistle. So this is the mechanism of a pressure cooker. Now the problem that has been given to us it says the petcock mass is 140 milli 140 gram and the exhaust nozzle cross section is 4 millimeter square what is the boiling point of water inside?

And we will see that only this two parameter along with the standard parameters of water determines the boiling point. So once again we come back to this relation that p atmosphere +m g by a is equal to p sat. So m g by a is 140 into 10 to the power minus 3 into 9.8 divided by 4 into 10 to the power minus 6 Pascal's which is 343000 Pascal's. Now total so, p sat will be this plus the atmospheric pressure which is one 1.0135 Pascal into 10 to the power 5 Pascal's. So all; together the saturated pressure the maximum saturated pressure that is allowed inside is 4.4435 into 10 to the power 5 Pascal's.

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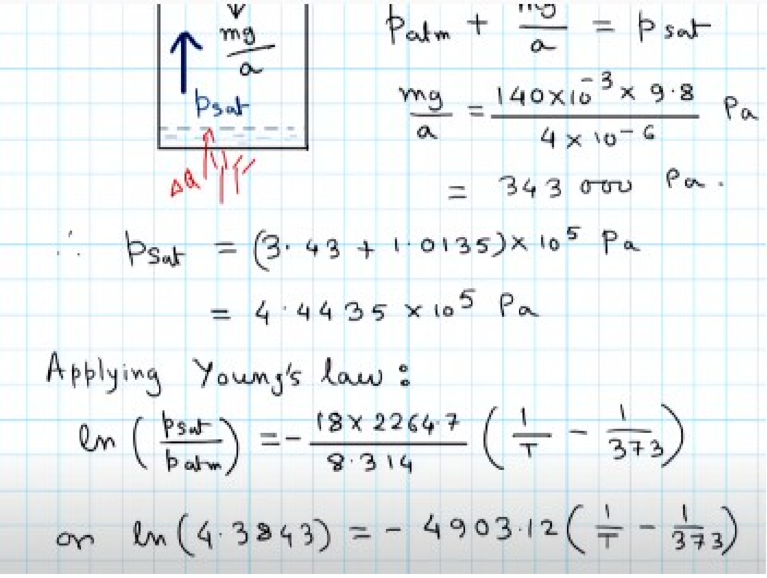

$$p_{atm} + \frac{mg}{a} = p_{sat}$$

$$\frac{mg}{a} = \frac{140\times10^{-3}\times 9.8}{4\times10^{-6}}\ \text{Pa}$$

$$= 343000\ \text{Pa}.$$

$$\therefore\ p_{sat} = (3.43 + 1.0135)\times10^{5}\ \text{Pa}$$

$$= 4.4435\times10^{5}\ \text{Pa}$$

Applying Young's law:

$$\ln\left(\frac{p_{sat}}{p_{atm}}\right) = -\frac{18\times 2264.7}{8.314}\left(\frac{1}{T}-\frac{1}{373}\right)$$

$$\text{or}\quad \ln(4.3843) = -4903.12\left(\frac{1}{T}-\frac{1}{373}\right)$$

Now once again we come back to young's law what which is once again simplification assuming that the latent heat does not change with temperature. So we have relation loan of p sat by p atmosphere so we need to have a reference point for this type of integration. And in this case the reference point is the atmospheric pressure and 100 degree centigrade temperature right. So 373 we substitute 373 for the reference temperature p atmosphere for the reference pressure and this is the temperature we would like to find out.

So this basically this is the temperature corresponding to 4.44 into 10 to the power 5 Pascal's of pressure for water vapour equilibrium.

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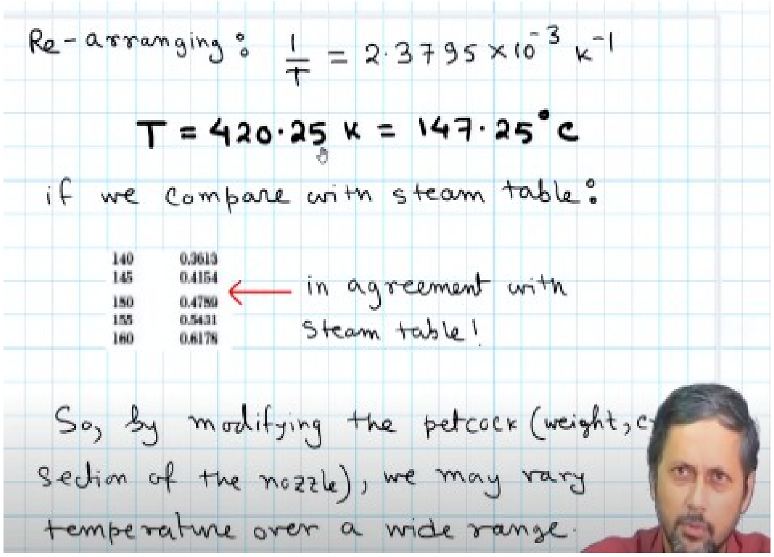

Re-arranging : $\frac{1}{T} = 2.3795 \times 10^{-3}\ K^{-1}$

$T = 420.25\ K = 147.25^{\circ}C$

if we compare with steam table :

140	0.3613
145	0.4154
150	0.4780
155	0.5431
160	0.6178

← in agreement with Steam table!

So, by modifying the petcock (weight, c section of the nozzle), we may vary temperature over a wide range.

So we solve this solution ispretty straight forward and finally we get 420.25 Kelvin which is 147.25 degree centigrade. So inside a pressure cooker the water boils at a much elevated pressure or elevated temperature and also at a much elevated pressure. Now if you take this pressure cooker to the mountains where the atmospheric pressure is reduced by let us say 15 10 to 15% from the plane land as compared to the plane land.

Then what modification we need to do we instead of adding the atmospheric pressure directly we have to add maybe a 0.90% of this value to this. So similarly so, correspondingly the value of p sat will be reduced. And instead of 147 we might get a pressure of I do not know just roughly guessing maybe 130, 135. But that is also high much higher as compared to the normal boiling point of water under one atmosphere condition.

So that is why it takes less I mean less energy to cook the food. Because the cooking has been done at a much elevated temperature also it takes i mean it you know. It is easy to you know soften hard materials like potato or some meat or some other for example tapioca these things they it becomes easier for the pressure cooker I mean to cook in a pressure cooker now. So now this is a very rough crude calculation where we have assumed that the latent heat does not change with temperature.

Now the values of the experimentally measured values have been tabulated in steam table as we have said in the last class. So just out of curiosity let us have a look at the steam table so I have just taken a screenshot of this the actual steam table which is here.

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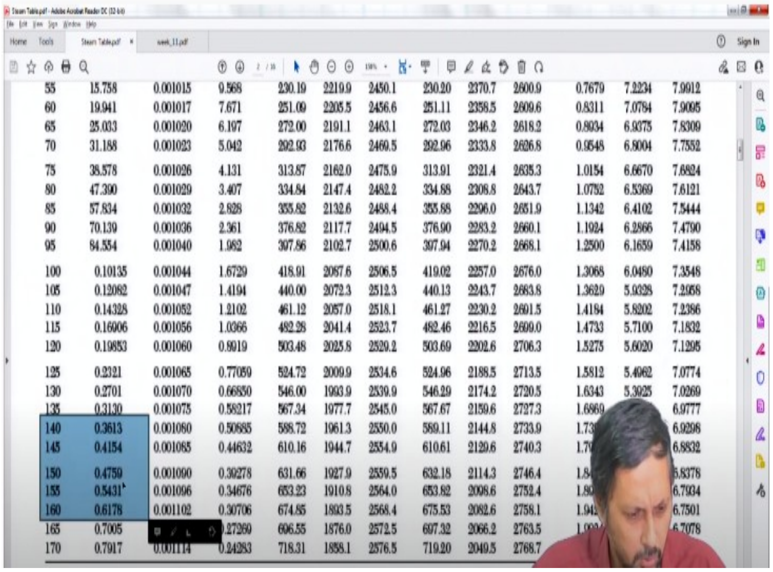

55	15.758	0.001015	9.568	230.19	2219.9	2450.1	230.20	2370.7	2600.9	0.7679	7.2234	7.9912
60	19.941	0.001017	7.671	251.09	2205.5	2456.6	251.11	2358.5	2609.6	0.8311	7.0784	7.9095
65	25.033	0.001020	6.197	272.00	2191.1	2463.1	272.03	2346.2	2618.2	0.8934	6.9375	7.8309
70	31.188	0.001023	5.042	292.93	2176.6	2469.5	292.96	2333.8	2626.8	0.9548	6.8004	7.7552
75	38.578	0.001026	4.131	313.87	2162.0	2475.9	313.91	2321.4	2635.3	1.0154	6.6670	7.6824
80	47.390	0.001029	3.407	334.84	2147.4	2482.2	334.88	2308.8	2643.7	1.0752	6.5369	7.6121
85	57.834	0.001032	2.828	355.82	2132.6	2488.4	355.88	2296.0	2651.9	1.1342	6.4102	7.5444
90	70.139	0.001036	2.361	376.82	2117.7	2494.5	376.90	2283.2	2660.1	1.1924	6.2866	7.4790
95	84.554	0.001040	1.982	397.86	2102.7	2500.6	397.94	2270.2	2668.1	1.2500	6.1659	7.4158
100	0.10135	0.001044	1.6729	418.91	2087.6	2506.5	419.02	2257.0	2676.0	1.3068	6.0480	7.3548
105	0.12082	0.001047	1.4194	440.00	2072.3	2512.3	440.13	2243.7	2683.8	1.3629	5.9328	7.2958
110	0.14328	0.001052	1.2102	461.12	2057.0	2518.1	461.27	2230.2	2691.5	1.4184	5.8202	7.2386
115	0.16906	0.001056	1.0366	482.28	2041.4	2523.7	482.46	2216.5	2699.0	1.4733	5.7100	7.1832
120	0.19853	0.001060	0.8919	503.48	2025.8	2529.2	503.69	2202.6	2706.3	1.5275	5.6020	7.1295
125	0.2321	0.001065	0.77059	524.72	2009.9	2534.6	524.96	2188.5	2713.5	1.5812	5.4962	7.0774
130	0.2701	0.001070	0.66850	546.00	1993.9	2539.9	546.29	2174.2	2720.5	1.6343	5.3925	7.0269
135	0.3130	0.001075	0.58217	567.34	1977.7	2545.0	567.67	2159.6	2727.3	1.6869	[illegible]	6.9777
140	0.3613	0.001080	0.50885	588.72	1961.3	2550.0	589.11	2144.8	2733.9	[illegible]	[illegible]	6.9298
145	0.4154	0.001085	0.44632	610.16	1944.7	2554.9	610.61	2129.6	2740.3	[illegible]	[illegible]	6.8832
150	0.4759	0.001090	0.39278	631.66	1927.9	2559.5	632.18	2114.3	2746.4	[illegible]	[illegible]	[illegible]
155	0.5431	0.001096	0.34676	653.23	1910.8	2564.0	653.82	2098.6	2752.4	[illegible]	[illegible]	6.7934
160	0.6178	0.001102	0.30706	674.85	1893.5	2568.4	675.53	2082.6	2758.1	[illegible]	[illegible]	6.7501
165	0.7005	[illegible]	0.27260	696.55	1876.0	2572.5	697.32	2066.2	2763.5	[illegible]	[illegible]	6.7078
170	0.7917	0.001114	0.24283	718.31	1858.1	2576.5	719.20	2049.5	2768.7	[illegible]	[illegible]	[illegible]

So let us say around 147 so basically I took a screenshot of this part so there is no data for 147 but there is a data for 145 there is a data for 150. And we see I have just taken it here so you see the values are 0.41 so this means basically this is in mega Pascal's so 415.4 kilo Pascal's to 455.9 kilo Pascal's. And what have we got? We got 4 so it will be 444 kilo Pascal's right so this is nothing but 444.35 kilo Pascal's right.

So this is somewhere between these 2 numbers 415 and 475 so that means and the temperature is also intermediate to one 145 and 150. So we will be somewhere here which is in agreement general agreement with the steam table.

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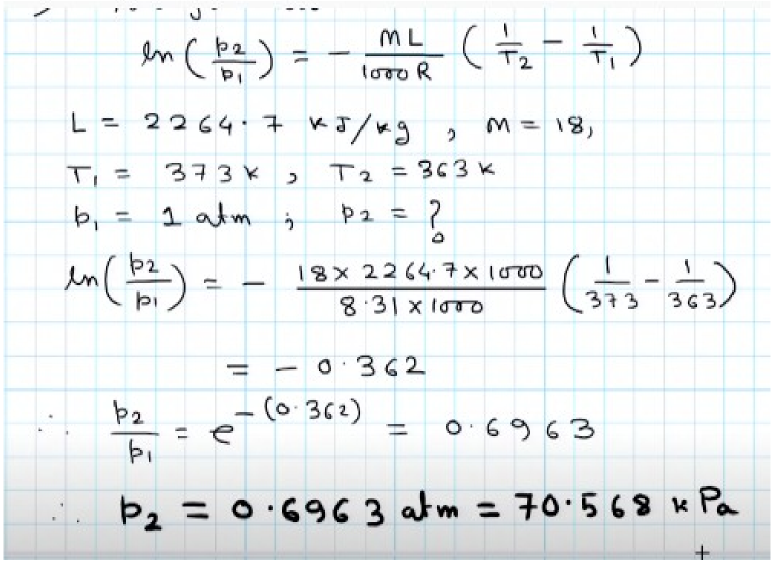

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{ML}{1000R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$L = 2264.7$ kJ/kg , $M = 18$,

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$$= -0.362$$

$$\therefore \frac{p_2}{p_1} = e^{-(0.362)} = 0.6963$$

$$\therefore p_2 = 0.6963 \text{ atm} = 70.568 \text{ kPa}$$

Now just out of curiosity let us check what happens what we did in the last problem also. We have 70.56 kilo Pascal's pressure corresponding to our calculation is 70.568 kilo Pascal's pressure compared to a temperature of 90 degree centigrade.

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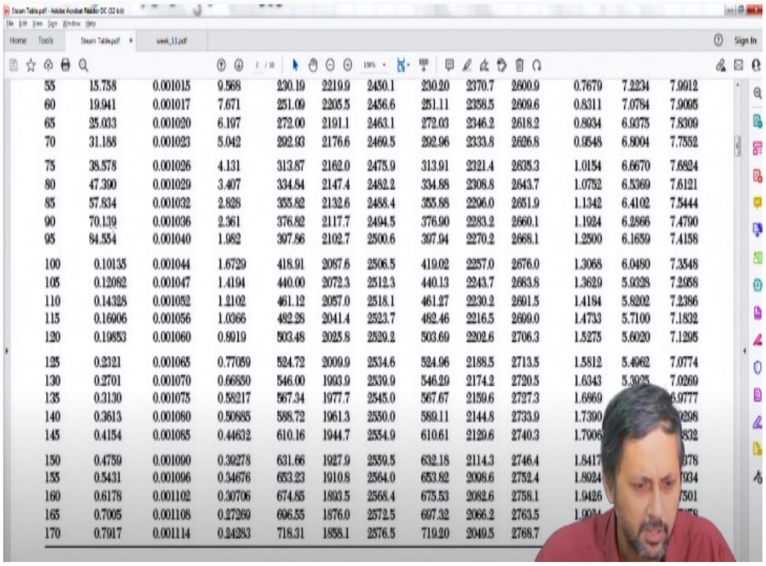

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110	0.14328	0.001052	1.2102	461.12	2057.0	2518.1	461.27	2230.2	2691.5	1.4184	5.8202	7.2386
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120	0.19853	0.001060	0.8919	503.48	2025.8	2529.2	503.69	2202.6	2706.3	1.5275	5.6020	7.1295
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140	0.3613	0.001080	0.50885	588.72	1961.3	2550.0	589.11	2144.8	2733.9	1.7390	[illegible]	[illegible]
145	0.4154	0.001085	0.44632	610.16	1944.7	2554.9	610.61	2129.6	2740.3	1.7906	[illegible]	[illegible]
150	0.4759	0.001090	0.39278	631.66	1927.9	2559.5	632.18	2114.3	2746.4	1.8417	[illegible]	[illegible]
155	0.5431	0.001096	0.34676	653.23	1910.8	2564.0	653.82	2098.6	2752.4	1.8924	[illegible]	[illegible]
160	0.6178	0.001102	0.30706	674.85	1893.5	2568.4	675.53	2082.6	2758.1	1.9426	[illegible]	[illegible]
165	0.7005	0.001108	0.27269	696.55	1876.0	2572.5	697.32	2066.2	2763.5	[illegible]	[illegible]	[illegible]
170	0.7917	0.001114	0.24283	718.31	1858.1	2576.5	719.20	2049.5	2768.7	[illegible]	[illegible]	[illegible]

So let us check from the steam table for 90 degree Centigrades we have 70.139 kilo Pascal's whereas we have come calculated p 70.568 kilo Pascal's. So once again this calculation also what we have got by using Young's law which is once again a simplification assuming I mean given that the latent. We do not consider the temperature dependence of latent heat but this is in general in good agreement with the experimentally actual experimentally measured values.

So now that what does it tells you? That at least in the temperature range where we are dealing with at within this range the latent heat does not vary. Latent heat of liquid water does not vary much with temperature. So but of course there are some variations which are also significant that we will see in future.

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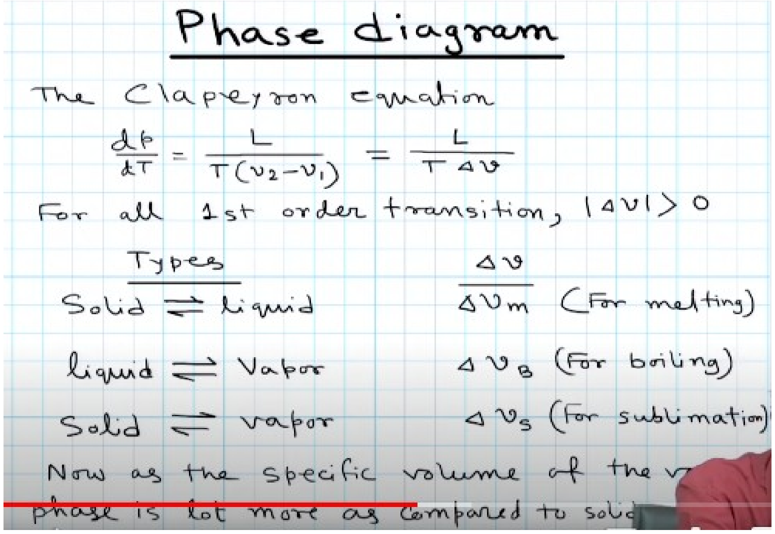

Phase diagram

The Clapeyron equation

$$\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)} = \frac{L}{T\Delta v}$$

For all 1st order transition, $|\Delta v| > 0$

Types	Δv
Solid $\rightleftharpoons$ liquid	Δv_m (For melting)
liquid $\rightleftharpoons$ Vapor	Δv_B (For boiling)
Solid $\rightleftharpoons$ vapor	Δv_S (For sublimation)

Now as the specific volume of the v
phase is lot more as compared to soli

So now let us move on from here so let us discuss a concept called the phase diagram. Once again we start from the Clapeyron equation which has been the master equation for all our discussion d p d T is equal to L by T v 2 minus v 1 or l by T delta v. Now for all of this first order phase transition that we have discussed so far delta v the mod I mean the magnitude of this change has been greater than equal to 0.

I mean I am not saying whether it is reducing or increasing but at least there is a, what I am going to say is there is a finite volume change across the phase transition because this is the definition. So across first order phase transition the volume the specific volume and specific entropy does change discontinuously.

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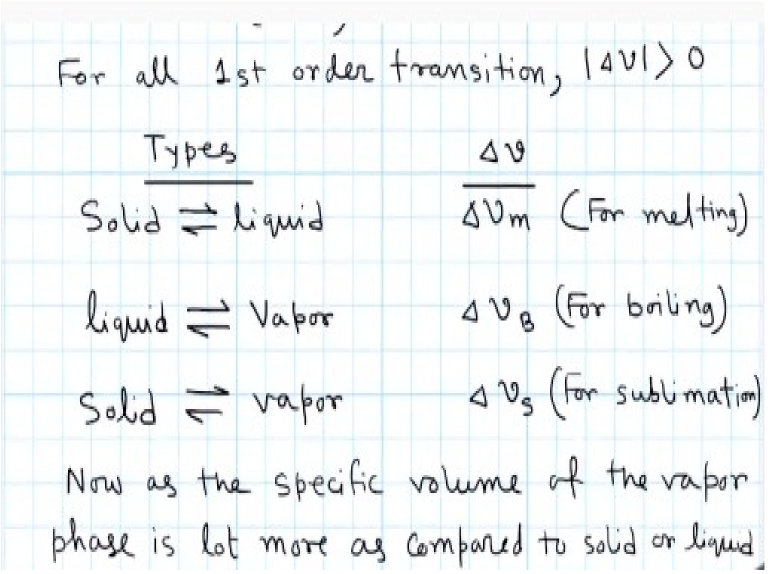

For all 1st order transition, $|\Delta v| > 0$

Types	Δv
Solid $\rightleftharpoons$ liquid	Δv_m (For melting)
liquid $\rightleftharpoons$ Vapor	Δv_B (For boiling)
Solid $\rightleftharpoons$ vapor	Δv_s (for sublimation)

Now as the specific volume of the vapor phase is lot more as compared to solid or liquid

So now let us focus on the 3 types of transitions that we have dealt with so far one is the solid liquid transition which we can also call the melting or freezing transition. And let us write delta v as delta v m corresponding to this transition. Similarly we have a liquid vapour transition and we write this the volume change as delta v b, b is for boiling m is for melting. And similarly there is a solid vapour transition where we write this as delta v s where s stands for sublimation.

Now what is sublimation? Sublimation is going from directly from solid phase to the vapour phase that we experience for example with Naphtholene or camphor we will explain that why it happens in some materials and for other materials it does not happen we will explain that now. Now let us remember that the specific volume of the vapour phase is typically much higher for as compared to the volume specific.

Volume of the liquid phase and the solid space and this is true for in general for all substances in all temperatures not at all temperatures. But typically if we are you know within I mean along the phase equilibrium line for most of the temperature and pressure regime this is generally true what does it mean that means?

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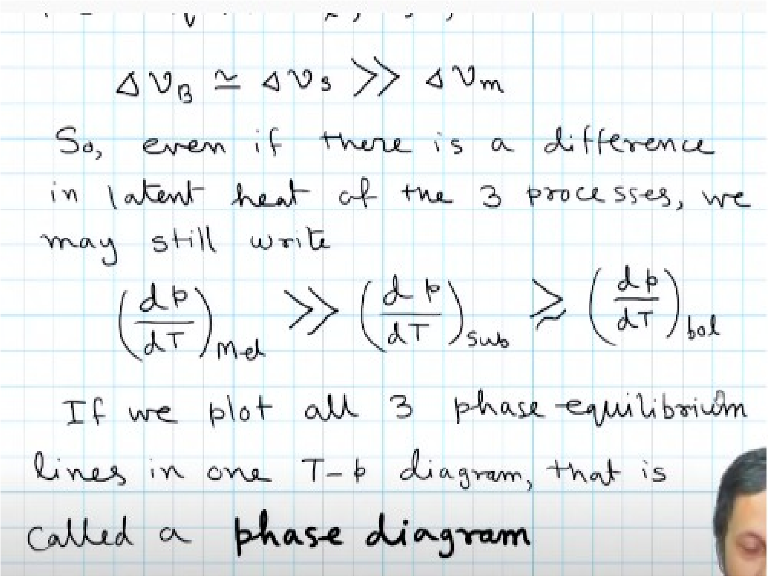

$\Delta v_B \simeq \Delta v_s \gg \Delta v_m$

So, even if there is a difference in latent heat of the 3 processes, we may still write

$$\left(\frac{dp}{dT}\right)_{Mel} \gg \left(\frac{dp}{dT}\right)_{Sub} \gtrsim \left(\frac{dp}{dT}\right)_{bol}$$

If we plot all 3 phase-equilibrium lines in one T-p diagram, that is called a **phase diagram**

That means so v v that means the specific volume is much greater than v l and v s and we can also say that you see v l minus v v. When we have for right for boiling we have v l minus vv and for sublimation we have v s minus v v. This 2 so delta v b and delta v s will be comparable and both of them; will be much higher as compared to delta v m. So basically delta v m the change in specific volume in a melting freezing transition will be much less as compared to a boiling transition or a sublimation transition that is what i am trying to establish here.

Now although the specific sorry the latent heat of these 3 transitions will be different. But this difference will be overwhelming as compared to that; and we can very easily write that for dp dt the slope that we have.

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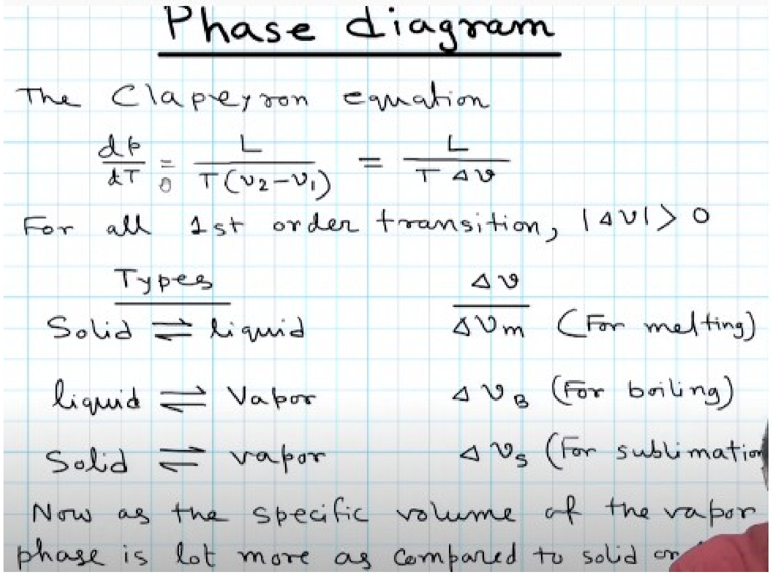

Phase diagram

The Clapeyron equation

$$\frac{dp}{dT} \underset{0}{=} \frac{L}{T(v_2-v_1)} = \frac{L}{T\Delta v}$$

For all 1st order transition, $|\Delta v| > 0$

Types	Δv
Solid ⇌ liquid	Δv_m (For melting)
liquid ⇌ Vapor	Δv_B (For boiling)
Solid ⇌ vapor	Δv_s (For sublimatio

Now as the specific volume of the vapor phase is lot more as compared to solid or

So basically if the denominator is less then the value of dp dT will be more now as for melting transition this will be much less compared to the 2 other transitions the slope dp dT for a melting transition will be lot higher as compared to the boiling freezing or boiling condensation or sublimation condensation transition. So now mathematically dp dT melting is much greater than dp dT sublimation which will be little bit higher in slope as compared to the boiling transition but comparable not very much different.

Now if we try to plot all these 3 phase equilibrium lines into one t p diagram we get something called a phase diagram.

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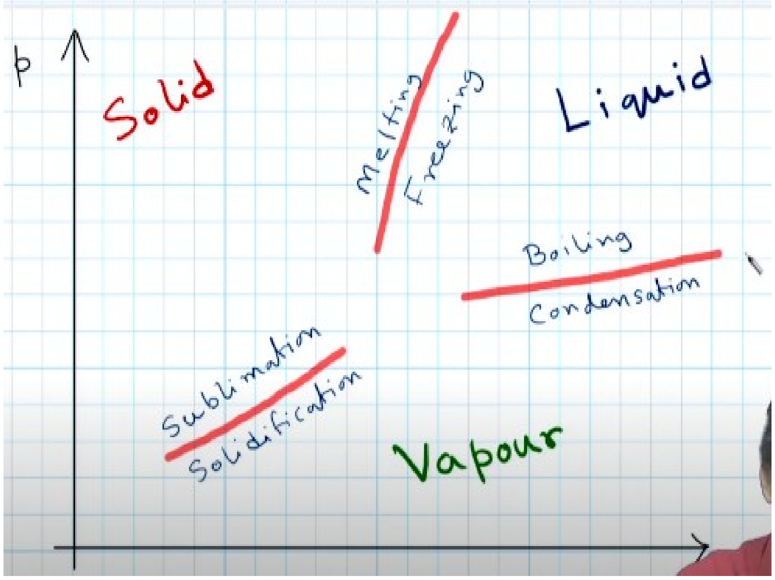

So how does a phase diagram look like? A phase diagram so we see that the melting curve will have a lot stiffer slope as compared to the boiling or the sublimation curve which will have comparable slope. But sublimation curve will have a slightly more slope there are reasons for that and this also been experimentally verified. So if we plot I mean if we represent those in one single diagram definitely this portion will be of solid will represent the solid phase.

This portion over here will represent the liquid phase this portion over here will represent the vapour phase. So vapour will have equilibrium with solid through this line or with liquid through this line similarly solid will have equilibrium with liquid through this line. Or with vapour through this line andliquid have equilibrium with solid with through this line along this line or through to with vapour along this line.

So there are 3 different lines of 2 of similar slope and one much steeper slope they consist i mean they are when represented together this is called a phase diagram. Now this picture this diagram what i have given you is by far being is complete. So we have to see what happens where does this line to terminate? So we just have represented these 3 lines without knowing much about what happens to the both ends in to these lines.

Now it so happens that see the solid phase must be continuous similarly the vapour phase and the liquid phase must be continuous among itself. So from that continuity principle itself by just by pure physical consideration we can conclude that all these 3 lines should meet in a single point. And that point is called the triple point of a substance which is unique for every substance and that is the point where all 3, phases solid, liquid and vapour can really coexist.

Now for the sublimation curve it has been found experimentally also and there are theories that also tell you that as t test goes to 0 the vapour pressure goes to 0 vapour pressure on a solid material goes to 0. So that means this curve will actually go towards origin now for the melting freezing curve which is a solid liquid equilibrium curve for most of the substance it goes on indefinitely.

And there is no theoretical bound till what pressure and what temperature it can be extended. For most of the solids or most of the experimental data except for things like there are certain examples exceptions which we will discuss later on this line goes on indefinitely. And for the liquid vapour equilibrium curve it should actually terminate somewhere one side should be at the triple point the other side should be terminated in a liquid in a critical point.

Now what is the critical point that we have already discussed if you remember the experiments on carbon dioxide when we discussed real gas there was a concept of critical point. So that same critical point comes into this phase diagram as well so this curve the boiling condensation curve should terminate in a critical point.

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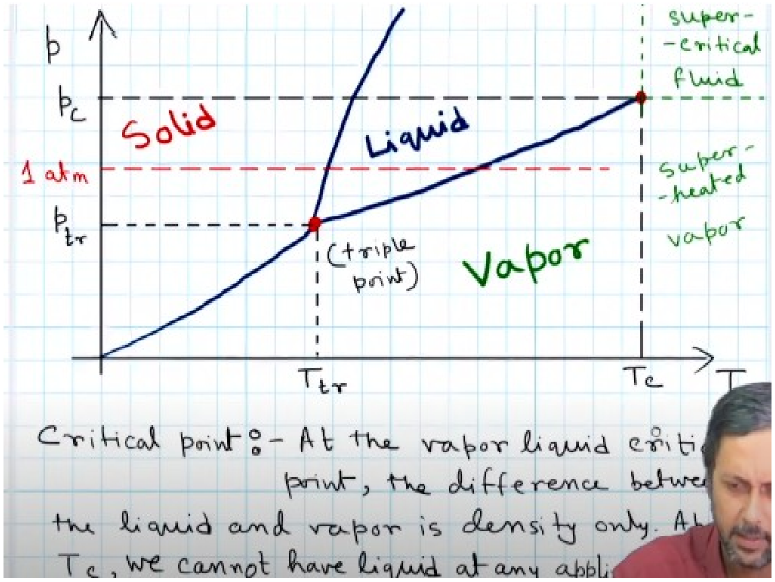

Critical point :- At the vapor liquid criti
point, the difference betwe
the liquid and vapor is density only. A
T_c, we cannot have liquid at any appli

So this is the final representation of a phase diagram for a typical substance once again where we have solid in this portion the solid liquid solid vapour equilibrium that is the sublimation curve that goes on to the 0 I mean towards the origin. The liquid vapour curve gets terminated at the critical point for a temperature of T c and a pressure of p c. Now above this critical point we do not have a defined vapour or liquid phase we can have super critical fluid

Or we can have super heated vapour that sometimes we have like ideal gas that we have already seen. But the physics around and beyond critical point is not very simple so we cannot cover that in this particular course there will be I mean there are these topics a lot much advanced. Similarly the solid liquid curve it goes off goes and goes on indefinitely and most of the curves for most of these substances solid melts to you know expand in volume.

So that is why the slope is positive so that is why we have a positive slope and this one this one looks like this. Of course for materials like water and there are few others example the slope will be negative which will be coming back very soon? Now the triple point is uniquely defined and this is given as T of t r and p of t r we will also there are some interesting properties of triple point which will we will discuss in brief.

Now typically what we can do is we can place this red line corresponds corresponding to red vertical horizontal line corresponding to one atmosphere pressure on a phase diagram. Now what is the significance of this means? If the one atmosphere line is above the triple point that means under atmospheric pressure the substance in question will go from solid phase to liquid phase and from liquid phase to vapour phase.

So there will be 2, temperature corresponding to melting and boiling under atmospheric pressure. Now if it so happens that this one atmosphere line is below the critical point that means let us say it is somewhere here right let us say this one is the line in question so what happens? We can see that solid can directly go into vapour phase and this is exactly what we know as sublimation. We have seen that for certain material you know like camphor or Naphtholene these are the most common example or solid carbon dioxide.

Solid carbon dioxide directly evaporates it does not at least under atmospheric condition it does not go to a liquid phase why? Because the dry eyes I am talking about. Because the critical the triple point is lying the triple point pressure is above the normal atmospheric pressure so that is why it directly sublimates so reverse process is also true. If the triple point is less than the atmospheric pressure so solid so the vapour phase can directly condense it into solid phase that if the triple point is more than the atmospheric pressure the other way it is not true.

So for water we have or for many of the solids we have liquid phase and vapour phase in under atmospheric pressure only. But even for those substances if we reduce the pressure substantially we can actually observe sublimation in any object any solid material. So and now let us focus on this critical point what is the critical point?

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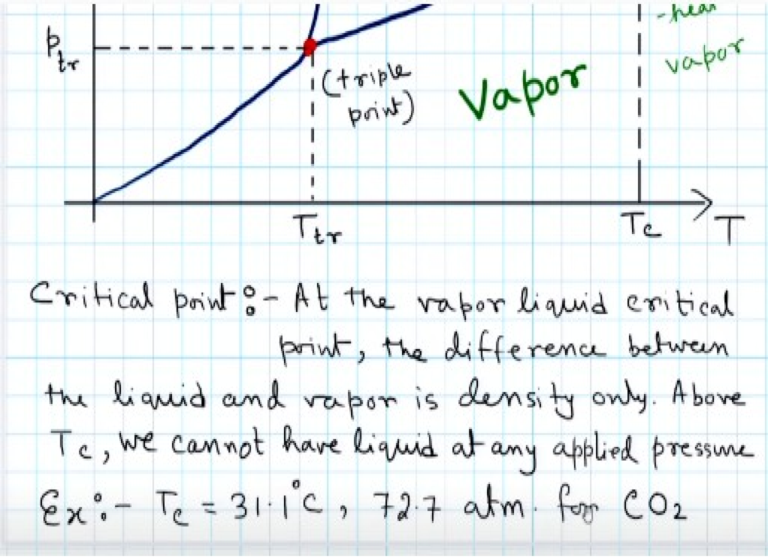

Critical point:- At the vapor liquid critical point, the difference between the liquid and vapor is density only. Above T_c, we cannot have liquid at any applied pressure

Ex:- $T_c = 31.1°C$, 72.7 atm. for CO_2

This vapour liquid critical point the difference between the liquid and so; the vapour is actually pure density. And the physics near as I have already mentioned the physics around this critical point is very complicated cannot be dealt with very easily a certain order parameter and other things has to be defined. Now one example we have already encountered that for carbon dioxide T c is equal to 31.1 degree centigrade and p c is equal to 72 atmosphere I should write p c here 72 atmosphere for carbon dioxide.

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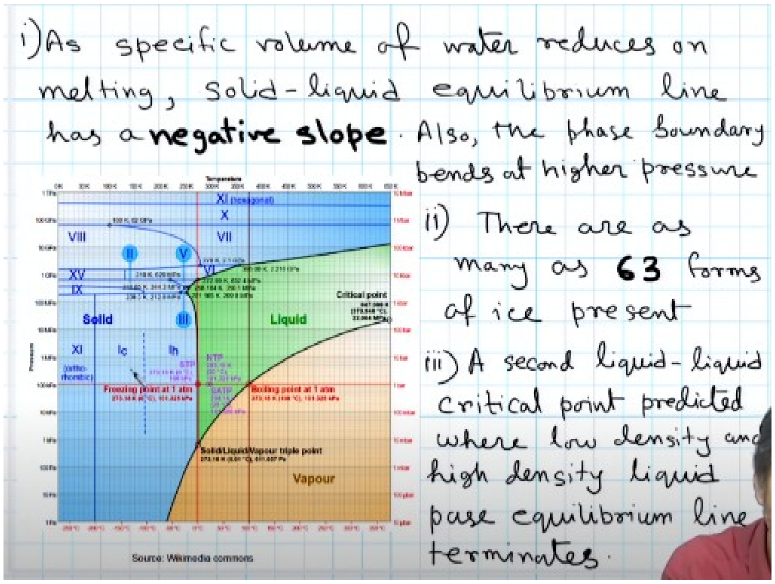

i) As specific volume of water reduces on melting, solid-liquid equilibrium line has a **negative slope**. Also, the phase boundary bends at higher pressure

Source: Wikimedia commons

ii) There are as many as **63** forms of ice present

iii) A second liquid-liquid critical point predicted where low density an high density liquid pase equilibrium line terminates.

So let us focus on the phase diagram of water and in water what happens is? As water reduces the volume reduces on melting the solid liquid equilibrium line has a negative slope. So in this particular right so let us focus on the phase diagram of water and in water what happens is as water reduces the volume reduces on melting the solid liquid equilibrium line has a negative slope. So in this particular scale because the pressure if you look at the pressure scale it is in logs logarithm actually.

So it is starting from 1 Pascal this is one atmosphere and it goes all the way to 100 Giga Pascal's so it looks almost like a straight vertical line but actually there is a slight negative slope right. Now this solid phase of ice is really complicated the ice we know typically these are the hexagonal ice phase I H given by I H. But there are cubic phase orthorhombic phase and there are altogether as far as I know 63 different forms of ice present.

But we do not see them normally it only appears under either very low temperature or extremely high pressure or both. So that is why the water phase diagram is one of the most complicated phase diagram for the known compounds known compounds or elements. So one critical point so; the triple point is here which isat a temperature of 273.16 kelvin will come to that we have the normal freezing point.

So this red line is the one atmosphere line so if this is the 1 atmosphere line it corresponds to the ice point and the steam point here the liquid vapour equilibrium curve that terminates at a critical point here and also there is a second critical point. The liquid-liquid critical point that has been theoretically predicted where also in some experiment there is evidence of existence of this critical point which is around 225 Kelvin.

So there the 2 different types of liquid phases the low density liquid and the high density liquid that phase line terminates. So once again let me tell you that water phase diagram is one of the most complicated phase diagrams. And when we say that certain things are easy we say that this is clear as water but let me tell you water is extremely complicated system to study.

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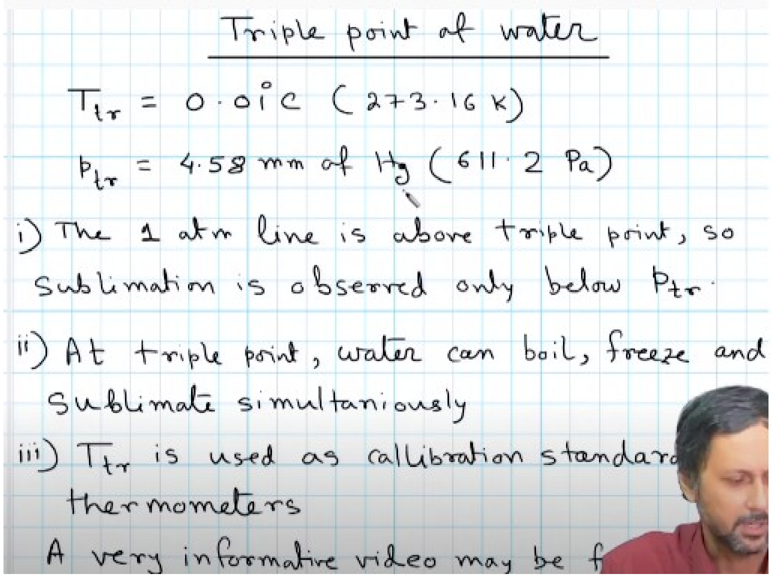

Triple point of water

$T_{tr} = 0.01°C$ (273.16 K)

P_{tr} = 4.58 mm of Hg (611.2 Pa)

i) The 1 atm line is above triple point, so sublimation is observed only below P_{tr}.

ii) At triple point, water can boil, freeze and sublimate simultaniously

iii) T_{tr} is used as callibration standar thermometers

A very informative video may be f

So the triple point of water is at 0.01 degree Centigrade which is 273.16 kelvin and at a pressure of 611.2 Pascal corresponding to 4.58 millimeters of marker. So the 1 atmosphere line is above the triple point so we do not see sublimation at normal atmospheric pressure. Only if we bring this pressure below this triple point pressure we can we will see water the ice directly goes into the vapour phase.

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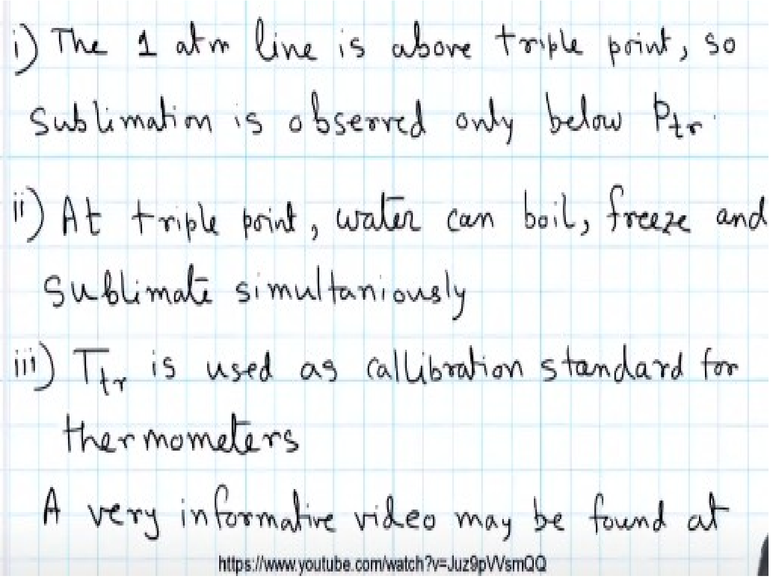

i) The 1 atm line is above triple point, so sublimation is observed only below P_{tr}.

ii) At triple point, water can boil, freeze and sublimate simultaniously

iii) T_{tr} is used as callibration standard for thermometers

A very informative video may be found at

https://www.youtube.com/watch?v=Juz9pVVsmQQ

Now the statement here is actually true for any substance that at the triple point water can boil freeze and sublimate simultaneously. It is sounds very counter intuitive but this is actually possible. And triple point is used as a calibration standard for many thermometers the standard thermometers. And I think we have discussed all of that during the when we discussed thermometer.

Now if you want to see how the triple point I mean water near triple point behaves there is a beautiful video that is by one of the academic institution only I do not remember the name exactly the description is given in this link. Where you can actually see these phenomena where water boils freezes and sublimate simultaneously at the triple point temperature and pressure. So that is where we stop in today's lecture today so we have discussed about phase transition the phase diagram.

We have discussed about triple point and other properties of the phase diagram. Now in the next lecture we have to you know discuss certain some more thermodynamic properties or thermodynamic principle that occurs around the triple point only then we can go into the discussion of the second latent heat equation. So see you again in the next lecture bye.