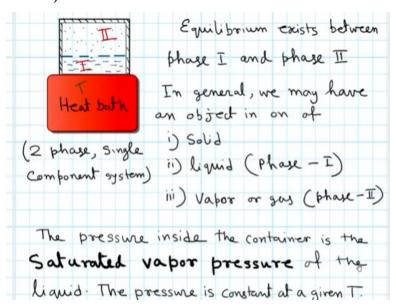
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Module No # 11 Lecture No # 51 Equilibrium Between Phases: The Clapeyron Equation

Hello and welcome back to eleventh week lecture of this NPTEL lecture series on thermal physics. So this week we are going to discuss equilibrium between phases so basically which is call phase transition.

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Now what is equilibrium? Equilibrium is you see if we have a heat path on top of that if we have a closed vessel only the bottom part of the vessel is diathermic the rest of the vessel is nicely insulated. Now if we have the situation and it is placed on the heat bath I mean it does not have to be a very high temperature but some fixed temperature. So heat bath temperature let us say T and then what happens is?

Once we evacuate this chamber I have not shown it completely but there should be some process to evacuate this chamber. Once this chamber evacuated and sealed and only the liquid is kept inside certain amount of liquid vapour will make it is way into the empty space and it will create and it will create a equilibrium condition in which some part will be in the liquid phase, which

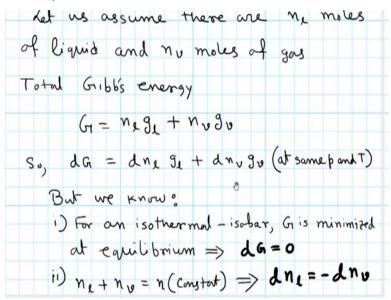
we call phases one and some part of the material will be in vapour phase which we call phase 2. We can have a object either in solid or liquid or vapour phases.

As we all know also we have other phases like plasma phase and there are different type of ordered phase disorder phase which is discussed during the context of you know conduct matter physics. But right now we are talking about simple thermodynamic system in which we keep ourselves in the discussion of solid, liquid and vapour or gas phase. Now what is the difference between vapour and gas phase? We have talked about this during the discussion on real gases.

And we have seen that there is a critical point that do exist below this critical point the gas can be vapour can be liquefied I mean a gas can be liquefied by applying pressure compression which is called a vapour. And above this critical point it cannot be you know brought back to the I mean it the gas or vapour whatever the gas cannot compressed to liquid and we call it gas. So this we have already seen but right now we will just treat vapour and gas in kind of equal footing.

So the pressure inside the container is where in this particular case will be the saturated vapour pressure which is a function of the temperature of the heat path. So if we change the temperature of the heat path the saturation vapour pressure will also change that means a new equilibrium will exist. But for a given temperature the pressure that is the saturated vapour pressure is constant.

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Now let use examine the specific gives free energy for this particular system so let us assume that the specific gives energy per mole or per kg whichever way we want to look at it is just that matter of definition. Whether we want to express something in per mole unit or some per kg unit depending on our convenience we sometime define something in terms of per mole sometimes we define per kg. And they are absolutely inter I mean the inter conversation between them are absolutely easy and arithmetic in nature.

So let us assume that we have n l mole of the liquid phase and n v mole of the gas phase Or vapour phase and corresponding specific gives energies are g l and g v now total gives energy will be G is equal to n l g l plus n v g v. Now if we assume that there are some fluctuations around the phase boundary that means some part of the liquid has gone into gas or either from phase 1 to phase 2 or from phase 2 to phase 1 certain amount has come back and that happens at the equilibrium.

Mean it is now us I mean although we from a macroscopic scale we just see that the liquid amount and the gas the vapour proportion is changing but in reality it is a dynamic process the molecule keep crossing between the vapour phase crossing the interface vapour to liquid and liquid to vapour and vice versa so this keeps happening. So let us say one such mass exchange between the liquid and vapour phase leads to a small variation in G which can be given as d n l g l plus d n v g v.

Which happens at exact I mean the same pressure and temperature so it is a fixed pressure temperature situation. So g l and g v that means the specific gives energies does not change now because it is in equilibrium and we know for an isothermal isobaric process that gives free energies is already at this minimal so for equilibrium. So we have d G is equal to 0 which will also we have to keep in mind that n l plus n v is equal to n.

Which the total number if moles or also we can absolutely express this relation in terms of the masses like ml g l plus m g m v g v is also an acceptable form because in only thing is those g l and g v will be specific gives energy per kg anyway per unit mass. So even there also we will have an m l plus m v is equal to m the total mass of the substance so whatever we do we do not

change it is a close system we do not change the total amount of material that have been enclosed.

Whether it is a liquid phase or in a gas phase does not matter the total mass that is total number of moles which is given by this relation will be constant. So that means d n l is equal to minus d n v so in a similar manner we express in terms of mass. So by comparing by putting this and applying this condition into this initial equation over here what do we get?

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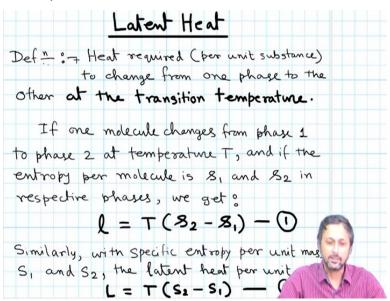
So we get g l is equal to g v so basically we put this term will be g l minus g v d n l is equal to 0 so d n l is not equal to 0 because we are you I mean the fluctuation is real it has happened so g l has to equal to g v so the conclusion from this is in a single component system it has 2 phases. For example you know it has liquid phase and gas phase it could have been solid and liquid it could have been solid or solid and gas together under certain condition. But it is 2 phase system of a single component as in single material we will come back to this terminology of component and you know phases once again when we will be discussing gives phase rule.

But it is single component system equilibrium is established if and only if the specific gives energies of different phases which are coexisting phases are equal. So this is true for any of the single component I mean any of the phases for the single component system and the change in temperature will establish a. So what happens now? If we go to the now let us come back here now we have a temperature fixed temperature T.

Now let us say we change this temperature from T to T prime so what happens a new equilibrium is established and if this new equilibrium corresponds to a new saturated vapour pressure also it will correspond to new values of the specific gives energies g l and g v. So it is not only with temperature not only the saturation vapour. Saturated vapour pressure changes but also the values of the specific gives energy also changes.

But at the interface where the phases are I mean where the 2 materials are or sorry when the 2 materials are guest distinct only condition is value of specific gives energy in this phase and in this phase has to be equal.

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Now let us discuss the concept of latent heat what is latent heat? Latent heat is the heat required to change from one phase to the other at the transition temperature. I mean of course actually at the transaction temperature is probably an over statement because whenever we talk about change of phase change from one phase to the other it has to be at the transition temperature. So probably I should correct this particular statement over here anyway but I hope u understand whatever we are trying to tell you.

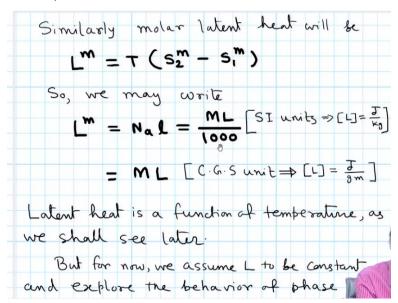
Now if one molecule changes from phase 1 to phase 2 at temperature t and if the entropy per molecule is s 1 and s 2 so we are talking about molecular level here molecular entropies S 1 and S 2 just like we have discussed about the transport properties when we discussed about discuss

the transport properties we talked about the amount of momentum or amount of energy that has been carried by individual molecule.

Similarly each molecule carries a certain amount of entropy association with it so basically it is the molar entropy divided specific molar specific entropy divided by the Avogadro number that will give you the entropy per molecule. As molar entropy is a constant so entropy per molecule is also a constant given temperature is fixed. So, 1 is nothing but T times s 2 minus s 1 because 1 is the heat that is T d s T delta s.

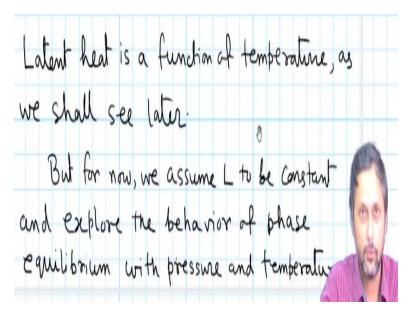
So it s going from phase 2 to phase 1 so it is 1 is equal to T times s 2 minus s 1 similarly if the specific entropy is given in the units of per I mean given per unit mass then we can write L is equal to T times s 2 minus s 1 I am just using a slightly different notation.

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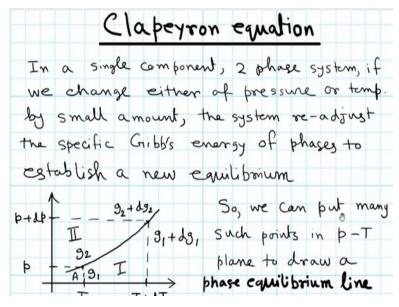
And similarly if we are using for latent molar latent heat then L m will be T times s 2 m minus s 1 m. So we may write L m which is the molar latent it is equal to N a times the latent heat per molecule which is once again M L divided by thousand where m is expressed in the in m is expressed in kg's that is the molar mass in kg's 1000 is there for to compensate for this kg unit. And or if it is expressed in I mean latent it is expressed in joules per gram then we have L m is equal to m times 1 and if the latent is it is expressed as joules per kg then we have M L divided by 1001 extra factor.

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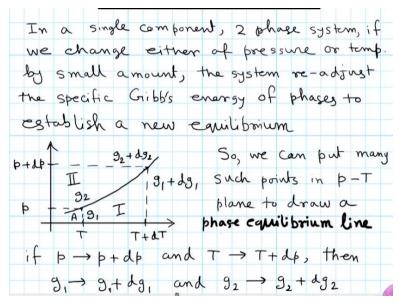
So latent heat is also a function of temperature although it is I mean we will see that later but for some small temperature range we can consider latent heat to be constant. So we assume latent to be constant from now and what and we try to see what is the behavior of the phase equilibrium in terms of pressure and temperature?

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So this is there is a equation that is called the Clapeyron equation or latent heat equation the first latent equation that actually talks about the that gives you the locus of the phase equilibrium line between two different phases the two coexisting phases.

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So in a single component system let us say we have in this temperature pressure p t diagram we have point a, and b, a, is at the temperature t and pressure p whereas b is as at a temperature t plus dT and at a pressure p plus dp. So let us say the gives energy of this 2 phases are right let us say g 1 and g 2 and that is at point b is g 1 plus dg 1 is equal to g 2 plus dg 2. Now we have already seen that g 1 has to be equal to g 2 so that means dg 1 has to be equal to dg 2.

Because along this phase equilibrium line that any the latent sorry the specific gives energy of these 2 coexisting phases must be equal to each other right. So if dg is a g 1 is equal to g 2 those infinite decimal change in those will has to be equal to each other.

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along phase equilibrium line, we have
$$g_1 + dg_1 = g_2 + dg_2$$
 or $dg_1 = dg_2$ [as $g_1 = g_2$]

as $dg = vdp - sdT$ ($v, s \rightarrow specific volume and entropy$)

So, we may write

 $v_1dp - s_1dT = v_2dp - s_2dT$

(p, T is same for both the phases at a given print)

reastranging: $dp = \frac{S_2 - s_1}{v_2 - v_1}$

Remembering $L = T(S_2 - s_1)$, we get

 $dp = \frac{L}{dT} = \frac{L}{T(v_2 - v_1)}$ [Clapeyron equations]

Now remember that d = v d p - S dT and we did not write this exact expression but we wrote

in terms of the g is actually d g d g=V d p - S dT and that was the differential from of gives

function. Now once we do that and once we bring everything in everything down in terms of the

specific volume and specific entropy and specific gives energy then we can write d = v d p - S

d T. So now starting from this relation which is d g 1 = d g 2 we can write v 1 d p - s 1 d T = v 2

d p-s 2 d T.

Please remember pressure and temperature remains constant sorry not constant but pressure and

temperature at the variable of interest in this case. So but for and along the phase coexistence line

the pressure and temperature of both the phases are equal for a given at one given point so that is

why we write v1 but we write d p similarly we write d t in both sides we do not write p 1 T 1 and

p 2 d 2 because p 1 T 1 and p 2 d 2 along the phase equilibrium line is essentially constant is

essentially equal.

So if we rearrange this we get d p d T = T 2 - T 1 sorry s 2 - s 1 divided by v 2 - v 1. Right now

remember what is latent heat is 1 is equal to T times s 2 minus s 1 this is the specific latent heat

so we can rearrange so we can substitute for s 2 minus s 1 in this equation and we can write d p d

T is equal to 1 by T v 2 minus v 1 so this differential equation gives you the locus of the phase

boundary between 2 existing phases in terms of the specific volumes and latent heat.

Now this equation is called Clapeyron equation or the first latent equation. There in certain

books it is wrongly mentioned as Clausius Clapeyron equation it is not Clausius Clapeyron

equation it is pure Clapeyron equation. There is second latent equation which also takes into

account the variation of latent heat with temperature that is called the second latent equation or

Clausius Clapeyron equation.

So please do not get confused this is simply Clapeyron equation or the identity first latent

equation. So, now as we have learned about this particular equation which gives you the locus of

the phase equilibrium line in p, T temperature diagram p, T indicator diagram let us try to solve

some problem and try to understand what is the implication of this equation.

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NPTEL On-line Certification Courses Thermal physics

Classroom problems: Week 11

- If it takes 3 minutes to boil a kettle of water which was initially at 20°C, how much longer will it take to boil the kettle dry?
- 2. Calculate the change in melting point of ice at 273K when the pressure is increased by 2 atms. 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?
- In a sealed container small amount of a liquid is in equilibrium with its vapour. The vapour pressure of a substance is 3,000Pa 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 Pa?

So we have classroom problem for week 11. So there are few like some problems I have listen here will be in this lecture we will be solving the first 3 problems and we will get an idea of how to use this Clapeyron equation and also the first problem is about the fundamental definition of latent heat. Let us start from the first problem. If is it takes 3 minutes to boil a kettle of water which was initially at 20 degree centigrade how much long will it take to boil the kettle dry?

So this is the problem where okay and by the way the end of this problem said that there is certain important data set that has been given.

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Important data for water:

In solid phase:

Specific volume: $0.00109 \ m^3/kg$ (almost constant with temperature)

Melting point: 273 K 1 atm. $(1.0135 \times 10^5 \text{ Pa})$ pressure

Specific latent heat of melting: 334 kJ/Kg (changes slightly with temperature)

In liquid phase:

 $C_p = 4.2 \text{ kJ } kg^{-1}K^{-1}$ (changes slightly with temperature)

Specific volume: $0.00100 \ m^3/kg$ at 273 K (changes slightly with temperature)

Boiling point: 373K under 1 atm. $(1.0135 \times 10^5 \text{ Pa})$ pressure

Specific latent heat of boiling: 2264.705 kJ/Kg

In vapour phase:

 $C_p = 1.09 \text{ kJ } kg^{-1}K^{-1}$

Specific volume: $1.674 \text{ } m^3/kg$ at 373 K (changes rapidly with temperature)

For example in solid phase the specific volume at which is almost constant for water actually. So for other material we have to supply I mean if you have a problem to solve you need to get the value in the problem itself. But in the water because we keep visiting that or we keep solving problem where different data of water is needed where water is involved and so many of such problems do exist.

Actually it is better to give this the important data for water in a tabulated form that is what exactly what I did so in solid phase in water the specific volume is given which is almost constant with temperature melting point is 273 Kelvin at one atmosphere and let us go back to this equation. It essentially tells you that as there it is locus of dP dT so if you change temperature will change and vice versa.

So that means whenever you mention the melting point or boiling point for the fact of any phase transition temperature you should also mention the corresponding pressure otherwise it makes no sense. So when we say 0 degree centigrade 273 Kelvin the melting of ice takes place at 273 Kelvin it essentially means it is under 1 atmosphere or 1.0135 into 10 to the power 5 Pascal's pressure.

Similarly the specific latent heat of melting is 330 kilojoules per kg which changes slightly with temperature we will see that later. In liquid phase C p the value of C p is given as 4.2 kilojoules per k g inverse per calorie inverse k g inverse per Kelvin inverse. Specific volume is 0.00100 meter cubed per kg at 273 Kelvin which changes slightly with temperature once again boiling point is 373 Kelvin under one atmosphere specific.

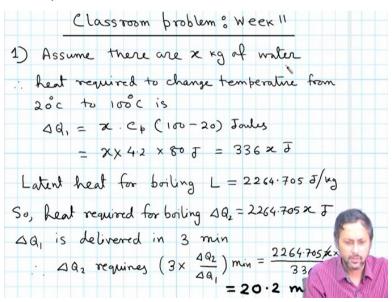
Latent heat f boiling is 264.7005 kilojoules per kg now in vapour phase C p in given and specific volume which is 1.674 meter cube per kg at 373 Kelvin that changes rapidly with temperature. So we will keep revising these parameters for water so for now I just give you a brief idea of the number. Now for this particular problem we need to use the latent heat for boiling under 1 atmosphere by the way this is also under 1 atmospheric pressure I should mention that.

Because are we; change the pressure the temperature changes and also the latent heat changes slightly. So this is 2264.7 kilojoules per kg. Now if we go to the problem how does this problem work? So let us go up it is said that 3 minutes to boil it takes 3 minutes to boil the kettle of water

which was initially at 20 degree centigrade that means initially the mass is not specified it takes three minutes for whatever amount of electric power we have given to that kettle to star boiling the water which was initially at 20 degree centigrade.

That means the water that was initially at 20 degree centigrade reaches 100 degree centigrade at a time of 3 minutes. So how much longer it will take to boil the kettle dry so that means if there are certain mass of water totally mass at 100 degree centigrade needs to evapourate that means the latent heat will come into action.

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So let us assume there are x kg of water so heat required that to change the temperature from 20 degree centigrade to 1000 degree centigrade is delta Q 1 is equal to x times C p times 100 minus 20 joules. Because it is constant pressure process everything in a cattle when we try to boil water it happens under atmospheric pressure. So we need to use C p value which is also listed in the table 4.2 this is 8 minus joules that is 336 x joules x.

So let us say so if you want I can actually change this to m because it looks better I do not why I have used x so m actually sounds better m and m, right. Now this I the amount of heat that goes in to the water in three minutes time now the same m amount of water if at 100 degree centigrade if we try to evapourate this because this is latent heat. So it will take this latent heat multiplied by m joules of heat in order to completely evapourate right.

So Q 1 is delivered in 3 minutes so by simple arithmetic deduction we get Q 2 requires 3 times

the delta Q 2 I mean Q 2 divided by Q 1 number of minutes. So I am just you know I will just

change I anywhere so this masses cancel and we get approximately 20.2 minutes. So we did this

problem without knowing the mass of water. And that is absolutely not needed because whatever

the water let us say we have a small kettle where we have 200 ml of water this takes 3 minutes.

So that means 20 in 0 minutes approximately the kettle will be dry and if we really have a large

kettle where we have let us say 50 liters of water. Even if and assuming that even that kettle

takes 3 minutes from 20 degree 100 degree centigrade it will also takes 20 minutes to become

completely dry. So it does not matter of mass of water but actually what actually matter is the

calculation based on the ratio of the 2 heats where the masses will nicely cancel out.

The next problem what we have here is calculate the change in melting pint of ice at 273 Kelvin

when the pressure is increased by 2 atmosphere how much pressure change is required to change

the melting point by 1 degree centigrade? So we have 2 parts into the problem the part one we

need to calculate the change in melting point was initially 273 Kelvin when the pressure is

increased by 2 atmospheres.

Now 1 atmosphere is 1.0135 or 013 let us say Pascal's so 2 atmosphere is 2 times many Pascal's

so and there is second part that requires to change the so to calculate the pressure if we want to

change the melting point by 1 degree Centigrade.

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2) Clapeyron equation
$$\frac{dP}{dT} = \frac{L}{T(V_{\ell} - V_{s})} \quad \text{(for Solid} \rightleftharpoons \text{liquid)}$$
i) $dP = 2$ atm (ideally we need to integrate!)
$$dT = \frac{T(V_{\ell} - V_{s})}{L} dP$$

$$= \frac{273 \left(0.001000 - 0.00109\right)}{L} \times 2 \times 1.013 \times 10^{5} Pa$$

$$= -0.0149 \text{ K}$$
The negative sign indicates that the

So ideally we need to solve this problem we need integrate this Clapeyron equation. But here we will see that because small changes 1 degree centigrade or 2 atmospheres. So these are tiny changes as compared to the value of 273 Kelvin or 10 to the power 5 you know one atmosphere pressure okay actually 2 atmosphere is not very tiny change in terms of Pascal's but we will see that application of this will give you to some extent good idea.

So d p d T is equal to L by T v l minus v s so this is for the solid liquid transition. Now the values of v l and v s we can get from the table similarly L given assuming that the L is constant we can also get that from the values that has been given below the problem. So once we put that and we put d p is equal to 2 atmosphere we get d T is equal to T times $(v \cdot l - v \cdot s)$ by L times d p. So we put 273 temperature for L we put 334 into 10 to the power 3 and $v \cdot l - v \cdot s$ is this meter cubed per kg which is 0.001000 minus 0.00109.

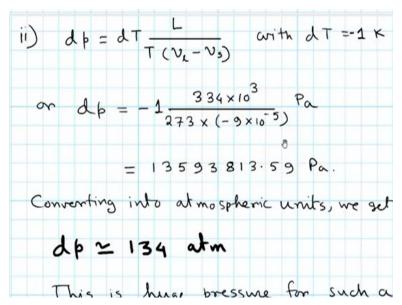
And we see finally get a negative temperature that means increasing the pressure actually reduces the melting point of ice and that is something that probably we all know because that is why because ice the volume of ice decreases on melting. So ice occupies more volume than water that is precisely the reason why ice floats on water because ice is lighter than water and this is the reason why we press on ice the melting point decreases.

You must have learn or you must have heard of this thing that in order to move a heave truck on ice actually that is routinely done by our Indian army on extreme Himalaya condition. If you

have been on winter or spring you must have seen that military trucks are moving whereas all other vehicles are halted. And if you notice carefully you see that every military vehicle has a long chin that is wined around its wheel.

There is a technique for hat then they know how to do it so that chain actually puts some extra pressure at the point of contact makes the ice to melt so that the truck can proceed. So this equation actually tells you that because ice reduces the volume in melting point decreases as a function of applied pressure right.

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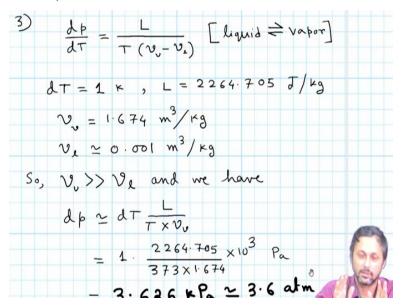


Now for the second part we have to compute how much pressure do need if we want to change the melting point by 1 Kelvin. Now it will be the negative change of course buy anyway the sign does not matter because we are only interested in magnitude. So we put dT is equal to minus 1 Kelvin once again v 1 minus v s has to be computed which will be minus 9 into 10 to the power minus 5. Put everything and we will get a huge value in Pascal convert into atmospheric pressure and you will get it will be 134 atmosphere.

So this is the huge pressure for such a small change of 1 Kelvin and also let me tell you strictly telling this type of simplified calculation do not hold true for such a huge change in pressure because this is really huge. So in principle we cannot put really dp is equal to this but we need to integrated it more in a more careful manner considering the variation of you know latent heat and of course we cannot really consider t as a constant any more.

So there are more other parameters that we have to keep in mind but I will show u later that even this approximate calculation for water is not actually that bad we will come to that slowly. So for the last problem of the day we have a similar problem under what pressure the boiling point of water will rise by 1 degree centigrade? So now we are going from solid liquid transition to liquid vapour transition.

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And in liquid vapour transition exactly the same rule applies dp dT is equal to L by T v minus v l but this is a liquid vapour transition as opposed to the solid liquid transition. Now d T is once again 1 Kelvin just like here we have dT is equal to 1 Kelvin. L is equal to L has different value 2264.7 joules per kg v v is 1.674 meter cubed per kg where as v l is equal to 0.01 meter cube per kg. So we see v v is much greater than v l and we have dp approximately equal to dT times L by T into delta v v if we put the number we get t is 3.6 atmosphere.

So here when we increase pressure the boiling point increases but when we are talking about solid liquid transition in ice when we increase pressure the melting point decreases. But again that is a different issue although that is a property of water alone I mean it is a very kind of anomalous property of water. But what I am trying to focus here is the value it is 3.6 atmosphere as supposed to 134 atmosphere.

So almost 2, order of magnitude more when we compare the amount of pressure needed in order to manipulate the melting point buy one Kelvin and boiling point by 1 Kelvin. So it basically says that liquid vapour transition or rather the solid liquid transition is lot stiffer as compared to the liquid vapour transition. We will come to that when we will be discussing phase diagram but for now we will stop here for today's lecture. In the next lecture we will be talking about first order transition and how the different properties changes across the first order transition until then good bye.