Thermal Physics
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Module No # 11
Lecture No # 54
The 2nd Latent Heat Equation

Hello and welcome back to another lecture of this NPTEL lecture series on thermal physics. Now for today's lecture we will be talking about thermodynamics near triple point.

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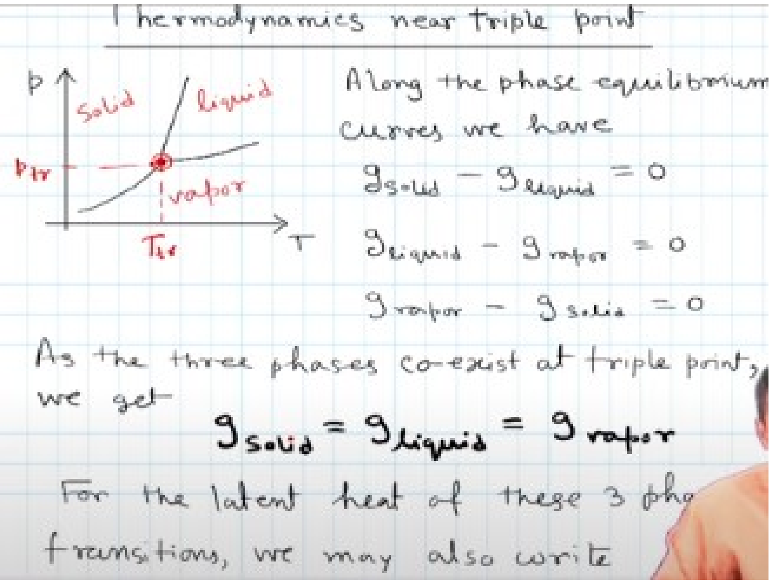

Thermodynamics near triple point

Along the phase equilibrium curves we have

$$g_{solid} - g_{liquid} = 0$$
$$g_{liquid} - g_{vapor} = 0$$
$$g_{vapor} - g_{solid} = 0$$

As the three phases co-exist at triple point, we get

$$g_{solid} = g_{liquid} = g_{vapor}$$

For the latent heat of these 3 pha
transitions, we may also write

Or rather we will start with this and we will go into little more different topics. So what happens in thermodynamics near triple point? We have already defined triple point where three phases do coexist. Actually it need not be solid, liquid and vapour phase because we will see later like in the next lecture that there could be many different phases in solids called the electron phases. Like in certain cases liquid also can have multiple phases for example for liquid crystals this is the system that go becomes liquid crystal.

They might have two different types of liquid phases as well but for a triple point all three phase I mean three different phases must coexist. Now just for the sake of simplicity as it is the most common case the triple point is an intersection of the 3 phases solid, liquid and vapour phases.

So this means this curve is the sublimation curve this is the melting curve and this is the boiling curve so these three curves will meet at this particular junction.

Now because these are first order phase transition we are discussing so along this curve for example along this particular curve g solid will be equal to g liquid so g solid minus g liquid is equal to 0. Similarly for this particular curve g liquid minus g vapour is equal to 0 and along this particular curve g vapour minus g solid is equal to 0. That means the specific Gibbs energies along of the 2 coexisting phases along this curve is equal and that is the definition of this phase equilibrium curve.

And as we remember these curves are defined by the Clapeyron equation where Clapeyron equation starts with the assumption that two phases have equal Gibbs energy. So at the triple point where three phases can coexist we must have g solid is equal to g liquid is equal to g vapour. Now if we want to calculate the latent heat for this three phase transition.

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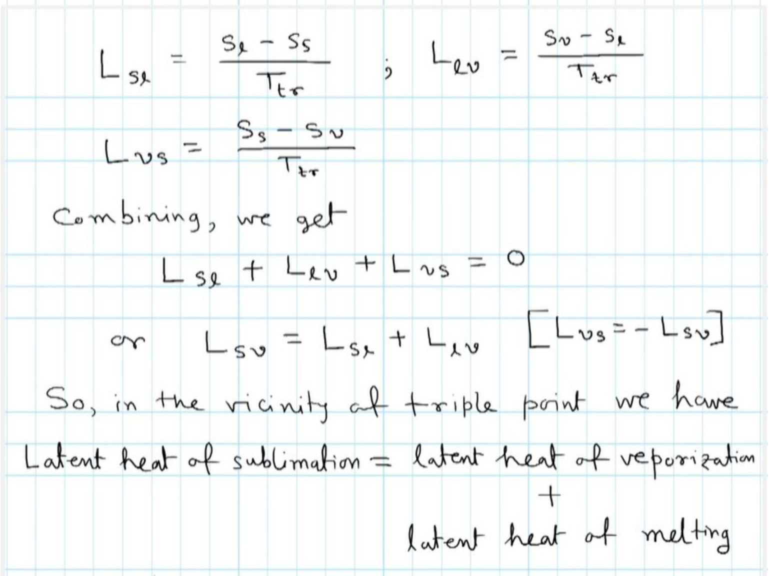

$$L_{sl} = \frac{s_l - s_s}{T_{tr}} \quad ; \quad L_{lv} = \frac{s_v - s_l}{T_{tr}}$$

$$L_{vs} = \frac{s_s - s_v}{T_{tr}}$$

Combining, we get

$$L_{sl} + L_{lv} + L_{vs} = 0$$

$$\text{or} \quad L_{sv} = L_{sl} + L_{lv} \quad [L_{vs} = -L_{sv}]$$

So, in the vicinity of triple point we have

Latent heat of sublimation = latent heat of veporization + latent heat of melting

We may also write L s or L solid liquid that means going from solid to liquid is s liquid minus s solid divided by temperature of triple point. Because see the transition temperature from solid to liquid will solid to liquid transition will vary according to this particular curve here. So it will have different temperatures at different points but at or around triple point let us say varying some a point very close to the triple point the temperature may be approximated as t r.

So what is t r? T r is t t r is this temperature and p t r is the pressure the corresponding pressure right so going by this convention we have s l minus s s divided by t r. Similarly l liquid vapour is s v minus s l divided by t r and l vapour solid that means going from solid to vapour to solid that is basically condensation opposite process of sublimation it will be s s minus s p divided by t of t r. Now combining if we just add them through we get L s l + L s l + L of L v + L of v s = 0.

So that means if we just change the side of this one for example so we can write L s v is equal to which is equal to minus of L v s which is equal to minus of L s v so we see L s v is equal to L of s l plus L of l v. So in the vicinity of triple point we have latent heat of sublimation this is precisely the sublimation where solid the first phase is solid from the second phase is vapour. So solid from solid to vapour is sublimation is equal to latent heat of vapourization which is this one actually liquid to vapour and plus latent heat of melting solid to liquid.

So actually I mean I should have probably flipped the order of this to go I mean to make it equivalent to this particular statement.

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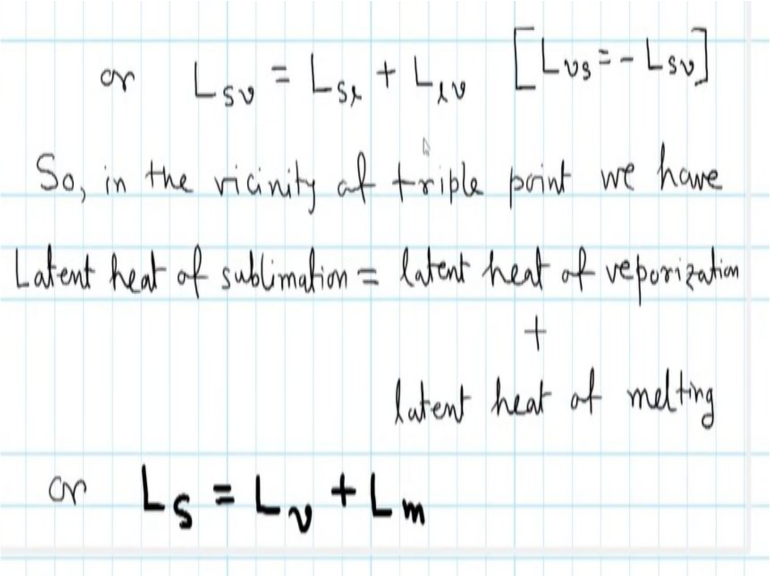

or $L_{sv} = L_{sl} + L_{lv}$ $[L_{vs} = -L_{sv}]$

So, in the vicinity of triple point we have

Latent heat of sublimation = latent heat of veporization

+

latent heat of melting

or $L_s = L_v + L_m$

But I hope you understand that latent heat of sublimation is equal to latent heat of vapourization and plus latent heat of melting or L s = L v + L m. So typically when we talk about you know sublimation we talk about latent heat of sublimation only not the condensation. Similarly when we talk about vapourization we talk about latent heat of vapourization and not condensation.

Latent heat of melting and not latent heat or freezing although they are just equal only the sign is reversed.

So heat is going from 1 phase to the other or phase 1 to phase 2 or phase 2 to phase 1 but the numerical value is the same. Generally this is the convention that we use in our discussion so L s is equal to L v plus L m right. So this is an important relation but please remember this relation is valid only around I mean only exactly at or around the triple point temperature. Because if we; go far from here for example if we are somewhere here this relation is not valid.

Somewhere so we can assume that there is a tiny circle just around the triple point so if we; are in the vicinity of the triple point not may not be exactly at the triple. But at least in the vicinity of the triple point this particular relation is a valid relation. So we with this relation we go to our next thing that is we will solve some problems from the classroom problem set.

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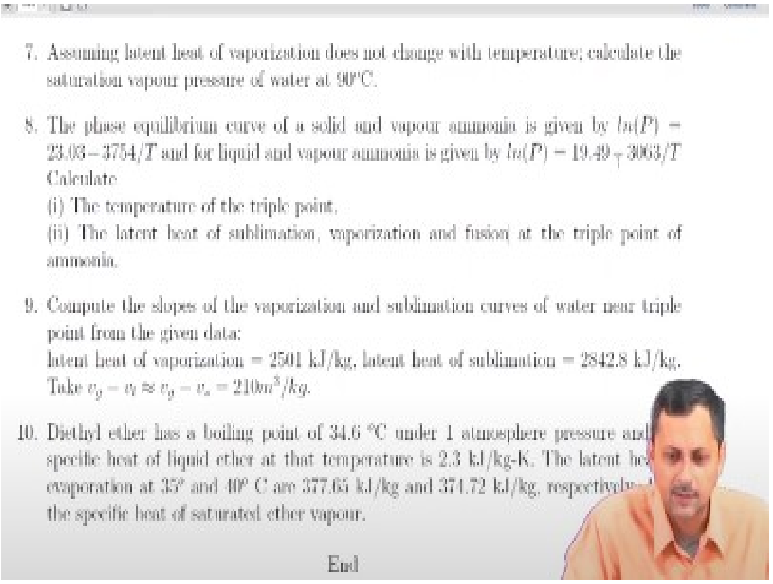

7. Assuming latent heat of vaporization does not change with temperature; calculate the saturation vapour pressure of water at 90°C.

8. The phase equilibrium curve of a solid and vapour ammonia is given by $ln(P) = 23.03 - 3754/T$ and for liquid and vapour ammonia is given by $ln(P) = 19.49 - 3063/T$ Calculate
(i) The temperature of the triple point.
(ii) The latent heat of sublimation, vaporization and fusion at the triple point of ammonia.

9. Compute the slopes of the vaporization and sublimation curves of water near triple point from the given data:
latent heat of vaporization = 2501 kJ/kg, latent heat of sublimation = 2842.8 kJ/kg.
Take $v_g - v_l \approx v_g - v_s = 210 m^3/kg$.

10. Diethyl ether has a boiling point of 34.6 °C under 1 atmosphere pressure and specific heat of liquid ether at that temperature is 2.3 kJ/kg-K. The latent he evaporation at 35° and 40° C are 377.65 kJ/kg and 374.72 kJ/kg, respectively the specific heat of saturated ether vapour.

End

So where were we have already solved problem number up to problem number 7 in the last lecture so we will have two more problems to solve for, today lecture. The first problem is the phase equilibrium curve of a solid and vapour ammonia is given by ln p is equal to 23.03 minus 70, 3754 divided by T you can identify this form as the Young's law because where latent heat is supposedly not a function of temperature.

And similar form for liquid and vapour ammonia is given by ln p is equal to 19.49 minus 3063 by T calculate the temperature of the triple point, the latent heat of sublimation and vapourization and fusion means actually melting at the triple point of ammonia. So basically this two curves are given one is for the solid vapour and another is for the liquid vapour equilibrium line.

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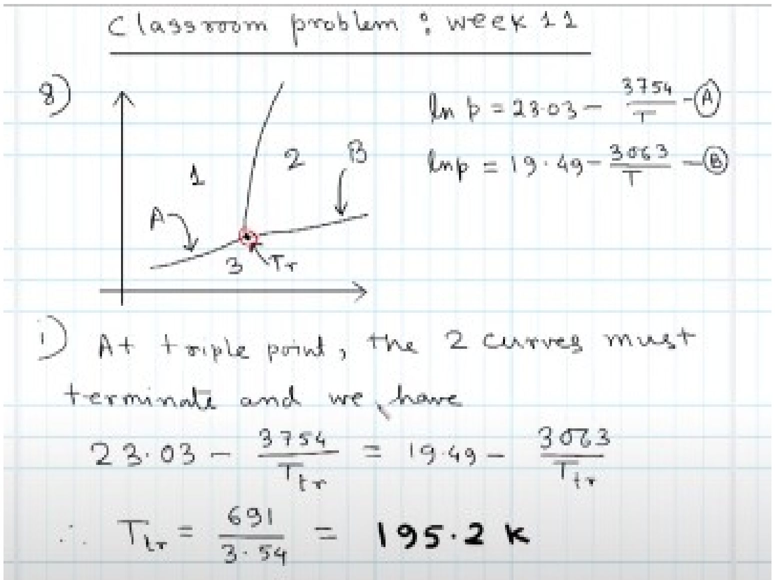

Classroom problem : week 11

8)

$\ln p = 23.03 - \frac{3754}{T}$ — Ⓐ

$\ln p = 19.49 - \frac{3063}{T}$ — Ⓑ

1) At triple point, the 2 curves must terminate and we have

$$23.03 - \frac{3754}{T_{tr}} = 19.49 - \frac{3063}{T_{tr}}$$

$$\therefore \; T_{tr} = \frac{691}{3.54} = 195.2 \text{ K}$$

So let us start with this these 2 curves A, and B are given the equation of A is ln p is equal to 23.03 minus 3754 by 3 T to and for B it is ln p is equal to 19.49 minus 3063 divided by T. So at the triple point the 2 curves must terminate and we have so here these 2 curves are meeting. So at the triple point we must have this curve A = curve B so we equate this 2 sides. With writing T is equal to T of t r that is the temperature of the triple point and by simple calculation we get T of t r is equal to 195.2 Kelvin.

Now the next part is we need to find out the three latent heats one for melt fusion means melting actually the other one is vapourization and the third one is sublimation. Now these two are already given so these two curves are given so we can straight forward calculate the sublimation, melting of sublimation and melting point of vapourization from this two curves A and B.

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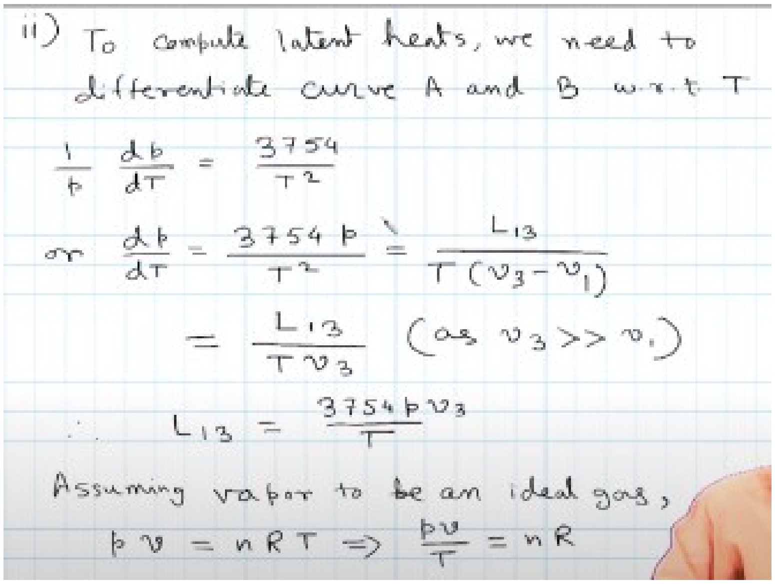

ii) To compute latent heats, we need to differentiate curve A and B w.r.t T

$$\frac{1}{p}\frac{dp}{dT} = \frac{3754}{T^2}$$

or $$\frac{dp}{dT} = \frac{3754\,p}{T^2} = \frac{L_{13}}{T(v_3 - v_1)}$$

$$= \frac{L_{13}}{T v_3} \quad (\text{as } v_3 >> v_1)$$

$$\therefore \quad L_{13} = \frac{3754\,p v_3}{T}$$

Assuming vapor to be an ideal gas,

$$pv = nRT \Rightarrow \frac{pv}{T} = nR$$

So we first in order to do that we first differentiate the two curves from curve a we get 1 by p d p d T is equal to 3754 divided by T square. Now rearranging we get d p d T is equal to 3754 p by T square which will be now d p d T according to the Clapeyron equation is l of 13 divided by T times v 3 minus v 1 right. So this is the standard form of Clapeyron equation we just equated it with this particular value. So if we rearrange this so and then then what happens you understand that v 3 is the vapour phase in this case this phase is the vapour phase.

So the volume of the vapour phase is lot more as compared to the volume of solid phase and the specific volume of solid phase and liquid phase. So that means we can always approximate v 3 to be much greater than v1 and this relation may be written as L 13 divided by T v 3. So if we rearrange this so we start from this relation so basically we equate this one and this one and we can write L 13 is equal to 3754 p v 3 divided by T.

Now here we have to make an assumption that the vapour to be an ideal gas. So this is not a very bad assumption that because the foundation of Kirchhoff's law which gives the, this 2 equations curve A, and B which actually assumes that the vapour is an ideal gas. So we have p v = n R T so p v by T should be equal to n R. So basically this quantity p v 3 by T should be simply equal to n R which is a constant now n being the number of moles here.

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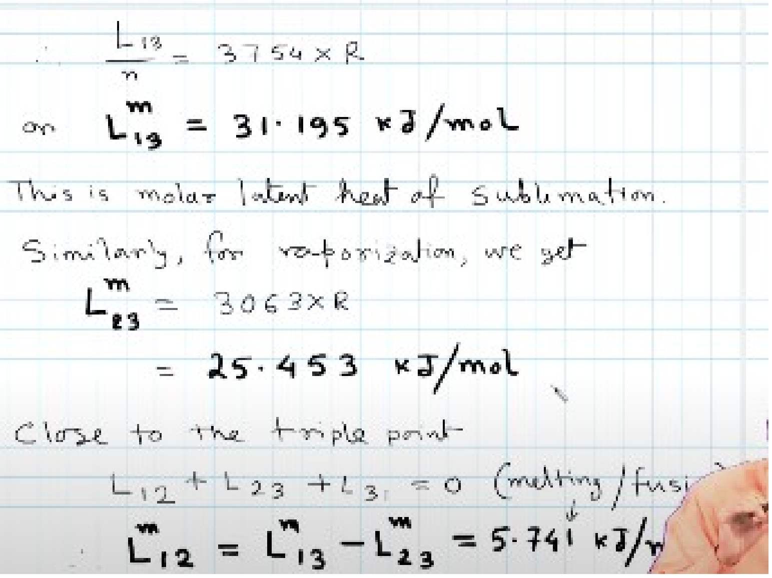

$$\frac{L_{13}}{n} = 3754 \times R$$

or $L^{m}_{13} = 31.195$ kJ/mol

This is molar latent heat of sublimation.

Similarly, for vaporization, we get

$$L^{m}_{23} = 3063 \times R$$

$$= 25.453 \text{ kJ/mol}$$

Close to the triple point

$L_{12} + L_{23} + L_{31} = 0$ (melting / fusi

$$L^{m}_{12} = L^{m}_{13} - L^{m}_{23} = 5.741 \text{ kJ/}$$

So if we substitute for that we get L 1 3 by n = 3754 times R which gives and this L 1 3 by n gives you the latent heat per mole. So basically the molar latent heat so molar latent heat is 31 point molar latent heat for 13 should be sublimation going from phase 1 to phase 3 will be 31.195 kilo joules per mole. So this is the molar latitude of sublimation. Similarly for the vapourization we can also do the similar treatment because the approximation that vapours phase specific volume is much more compared to the liquid phase specific volume also valid.

So we simply have latent heat of the specific latent heat of boiling will be that constant which is 3063 in this case times R which will be 25.453 kilojoules per mole. Now these 2 the curve equations are given so we are good to go. Now for the third we have to use the relation that L 1 2 + L 2 3 + L 3 1 = 0 close to the triple point. Now these are typically this equation has been derived for this one the specific what you call the specific latent heat per unit volume also.

But we can anyway divide all 3 of this by number of moles and we can also see that this relation will be equally valid for molar latent heat right. Because it is just a scale factor right between the specific latent heat and molar latency these are all we have discussed that in the when we discuss latent heat itself. So that scale factor is equal for a single component system where there is only one component in the represented in a phase diagram.

This scale factor is fixed so we can very well write L 1 to m = L1 2 m = L 1 3 m – L 2 3 m by rearranging this equation. And so the latent heat the latent heat of fusion will simply be the difference of latent heat of these 2 and it will be 5.741 kilojoule per mole. But please remember this value is only around the triple point temperature which is 195.2 all these 3 values are only around that particular value. So with this we move to the next problem for the class.

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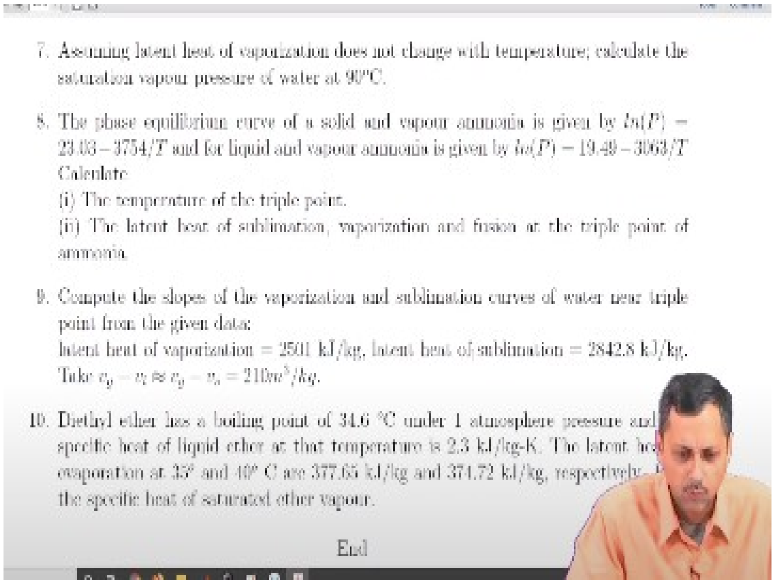

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End

And this problem is this problem 9 compute the slope of vapourization and sublimation curve of water near triple point from the given data. Latent heat of vapourization is 2501 kilojoules per kg latent heat of sublimation is 2842.8 kilo joules per kg. And we can take v g minus v l which is approximately equal to v g – v s = 210 meter cube per kg. So these are the values that have been provided also this is the, these are the values which are easily available from the, steam table for water.

So actually these are taken from steam table only so latent heat of vapour and the values once again these are given close to the triple point.

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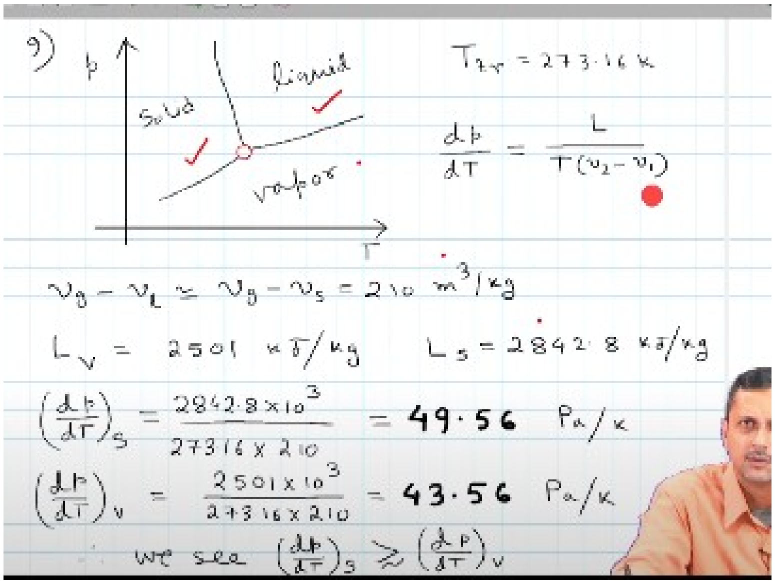

9)

$T_{tr} = 273.16\ K$

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

$v_g - v_L \simeq v_g - v_s = 210\ m^3/kg$

$L_v = 2501\ kJ/kg \quad L_s = 2842.8\ kJ/kg$

$$\left(\frac{dp}{dT}\right)_s = \frac{2842.8 \times 10^3}{27316 \times 210} = 49.56\ Pa/K$$

$$\left(\frac{dp}{dT}\right)_v = \frac{2501 \times 10^3}{27316 \times 210} = 43.56\ Pa/K$$

we see $\left(\frac{dp}{dT}\right)_s \gtrsim \left(\frac{dp}{dT}\right)_v$

So what we have to do is we have to compute the slope of these two curves. So basically which two curves this one and this one not this one not the other one. And please remember for water the solid liquid, curve has a negative slope because water the volume specific volume reduces in melting that we have discussed already. So d p d T is equal to L divided by T v 2 minus v 1 right Now v g minus v l is approximately equal to v g – v s = 210 meter cube per kg.

So and Lv L s values are given so that means d p d T for the sublimation curve will be simply by putting these numbers L s divided by T times which is 273 point please remember that triple point temperature is 273.16. And we have to put 210 here for the volume difference and we get 49.56 Pascal’s per Kelvin. Similarly for the vapourization curve this one this particular curve the slope near triple point should be 43.56 Pascal’s per Kelvin.

And what do we see here that once again the sublimation curve has a slightly higher slope as compared to the vapourization curve but they are pretty close to the values are pretty close to each other.

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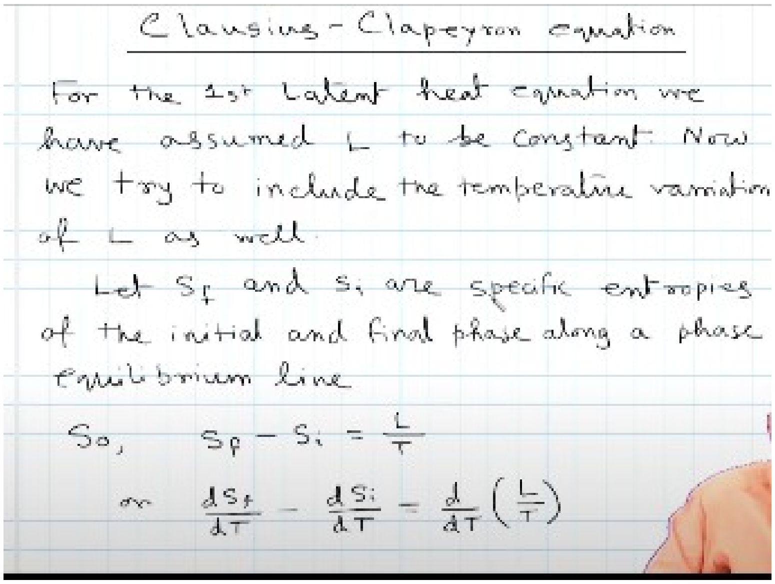

Clausius - Clapeyron equation

For the 1st latent heat equation we have assumed L to be constant. Now we try to include the temperature variation of L as well.

Let S_f and S_i are specific entropies of the initial and final phase along a phase equilibrium line

So, $S_f - S_i = \frac{L}{T}$

or $\frac{dS_f}{dT} - \frac{dS_i}{dT} = \frac{d}{dT}\left(\frac{L}{T}\right)$

So with this we move to our next topic which is the second latent heat equation classed Clausion Clapeyron equation. Now for the first latent equation we have assumed that latent heat l does not change with temperature. Now what we used that for we used the standard form that S f - S i = L by t. Right and that, we used this particular form to calculate the slope of the phase equilibrium line.

So here we are going to estimate through this equation how much does latent heat change as a function of temperature right. So if we start once again from here S f - S i = L by T. Now along the phase equilibrium line see these are all specific entropy is latent heat also a specific quantity that means given in either in per moles or per kg. So volume is immaterial here so these are already scaled by volume.

Now along the phase equilibrium line pressure is fixed so the pressure is always the saturated vapour pressure. So if we are talking about temperature change we might as well talk about the complete derivative instead of the partial derivative. So if I take derivative with respect to t because here along the phase equilibrium line when I say along the phase equilibrium line there is always a definite relation between pressure and temperature.

So we might as take this derivative as a complete derivative not a partial derivative with respect to temperature. So we have d s f d T minus d s i d T is equal to d d T of l by T.

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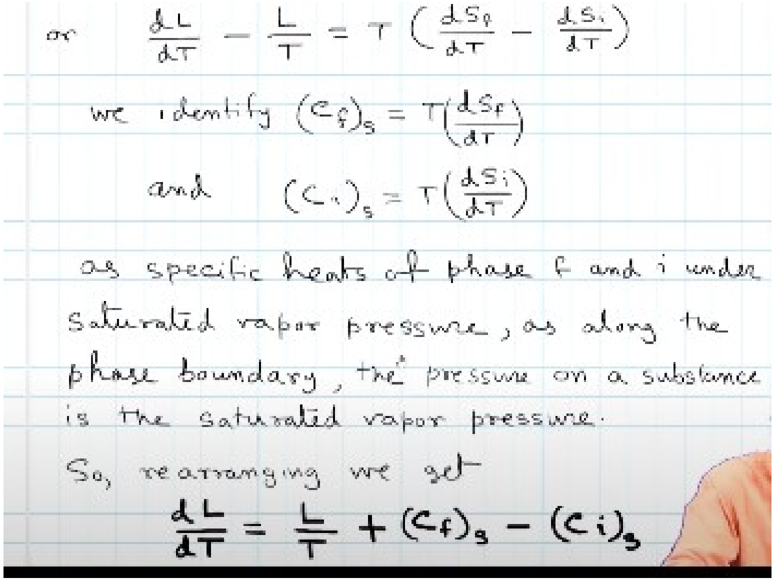

or $\frac{dL}{dT} - \frac{L}{T} = T\left(\frac{dS_f}{dT} - \frac{dS_i}{dT}\right)$

we identify $(C_f)_s = T\left(\frac{dS_f}{dT}\right)$

and $(C_i)_s = T\left(\frac{dS_i}{dT}\right)$

as specific heats of phase f and i under saturated vapor pressure, as along the phase boundary, the pressure on a substance is the saturated vapor pressure.

So, rearranging we get

$$\frac{dL}{dT} = \frac{L}{T} + (C_f)_s - (C_i)_s$$

And then you know this will be d l d T so this basically will give you l there will be a 1 d 1 by T d l d T term. Assuming that the latent heat also changes with temperature and there will be minus L by T square term right because 1 over t will give you minus 1 over T square. So l and now after rearranging we get d L d T minus l by T is equal to t times d s f d T minus d s i d T. Now we have to identify these two terms you remember this two terms are nothing but the specific heat of the final phase and specific heat of the initial phase at I mean under saturated vapour pressure.

So this s actually the represents not anything else but the word saturated vapour pressure saturated. So c f and c i are the saturated vapour pressures and we can write d L d T minus l by T is equal to s minus c i s. Now so this is one form of the second latent heat equation which is called the Clausius Clapeyron equation. Now so for the solid the solid vapour or liquid vapour transition the latent the specific heat we are talking about these are somewhat close to the saturated specific heat.

We have derived here these were somehow correlated to I mean they are very closely resembled by the C p the specific heat measured at constant pressure. But for the solid liquid transition experimentally it has been seen that this specific heats they are pretty much deviated from the measured value of specific heat at constant pressure.

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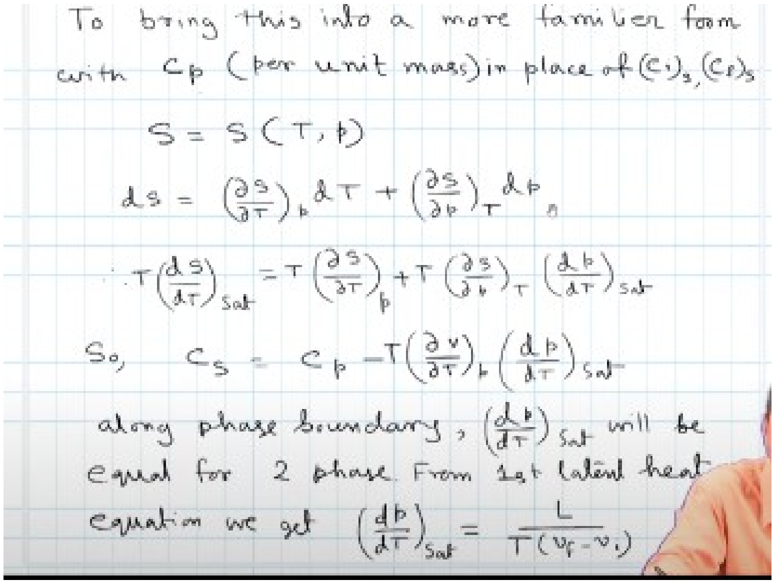

To bring this into a more familier form with c_p (per unit mass) in place of $(c_i)_s$, $(c_f)_s$

$$S = S(T, p)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp$$

$$\therefore T\left(\frac{ds}{dT}\right)_{sat} = T\left(\frac{\partial s}{\partial T}\right)_p + T\left(\frac{\partial s}{\partial p}\right)_T \left(\frac{dp}{dT}\right)_{sat}$$

So, $c_s = c_p - T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{dp}{dT}\right)_{sat}$

along phase boundary, $\left(\frac{dp}{dT}\right)_{sat}$ will be equal for 2 phase. From 1st latent heat equation we get $\left(\frac{dp}{dT}\right)_{sat} = \frac{L}{T(v_f - v_i)}$

So it is let us try to correlate the quantity c i s and c s s with a more common quantities like c i p and c f p. That means specific heat of initial and the final stage under constant pressure condition that is what we are more familiar with right. So let us start with S = S of T and p so d s is equal to del s del dp dT plus del s del p T d T d, d p right. Now that is exactly what I was trying to tell you that this one along the phase equilibrium line T and p they have a definite relation.

So that is why it is sufficient only to take the full derivative with respect to temperature. Anyway so **s** T d s d T sat is equal to so for if we just try to rearrange this we will get T d s del s del T p plus T del s del p T dp dT sat. Now so this is my c s this is equal to c p - now S there is a del s del p we can substitute it with minus del v del T p from the Maxwell's relation and there is a dp dT set. Now along the phase boundary this dp dT sat will be to equal for two phases.

So if we have because this gives you the condition for phase equilibrium line from the first latency equation. So what we can do is we can substitute for L by T v f minus v i from the first latent heat equation into this equation.

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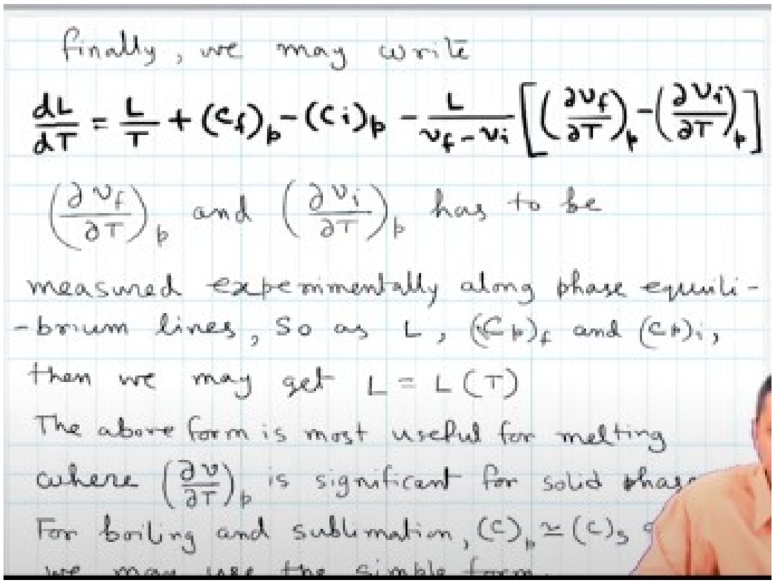

finally, we may write

$$\frac{dL}{dT} = \frac{L}{T} + (c_f)_p - (c_i)_p - \frac{L}{v_f - v_i}\left[\left(\frac{\partial v_f}{\partial T}\right)_p - \left(\frac{\partial v_i}{\partial T}\right)_p\right]$$

$\left(\frac{\partial v_f}{\partial T}\right)_p$ and $\left(\frac{\partial v_i}{\partial T}\right)_p$ has to be measured experimentally along phase equilibrium lines, so as L, $(c_p)_f$ and $(c_p)_i$, then we may get $L = L(T)$

The above form is most useful for melting where $\left(\frac{\partial v}{\partial T}\right)_p$ is significant for solid phas

For boiling and sublimation, $(c)_p \simeq (c)_s$

we may use the simple form.

And finally we may write d L d T is equal to L by T c f p minus c i p minus L by v f minus v i times del v f del T p minus del v i del T p. So this is a rather complicated looking relation and I mean frankly it is not very user friendly. So the previous form which we have derived here is a lot more user friendly form. If we only we have to believe that the specific heats under saturated vapour pressure are you know it somewhat closely resembles the specific heat measured under constant pressure condition.

But as I said for solid liquid equilibrium there is a considerable deviation and we have to come we have to revert back to c p at the specific heat at constant pressure values. So del v f del T and del v i del T in this equation has to be measured experimentally along the phase equilibrium line. So as similarly L c p f and c p i also have to be measured experimentally. Then from if we only know all these parameters experimentally then only we can express L is equal to L of T.

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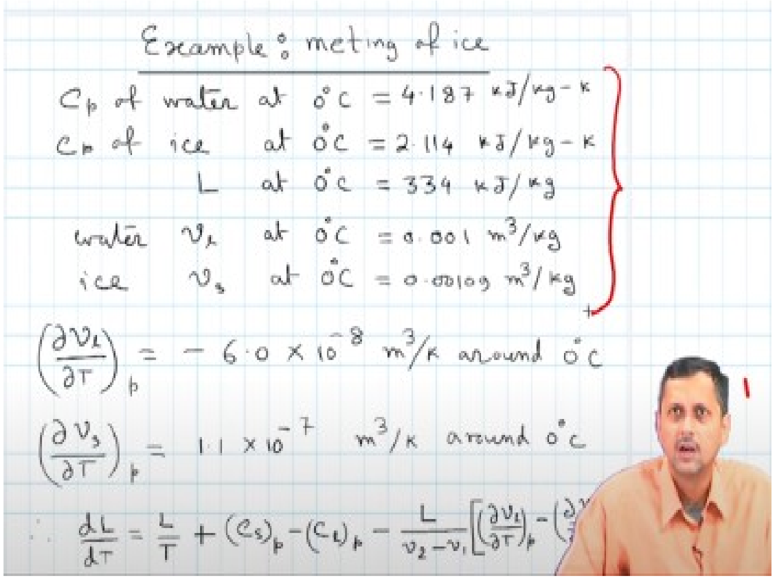

Example: meting of ice

C_p of water at $0^\circ C = 4.187$ kJ/kg-K

C_p of ice at $0^\circ C = 2.114$ kJ/kg-K

L at $0^\circ C = 334$ kJ/kg

water v_l at $0^\circ C = 0.001\ m^3/kg$

ice v_s at $0^\circ C = 0.00109\ m^3/kg$

$$\left(\frac{\partial v_l}{\partial T}\right)_p = -6.0 \times 10^{-8}\ m^3/K \text{ around } 0^\circ C$$

$$\left(\frac{\partial v_s}{\partial T}\right)_p = 1.1 \times 10^{-7}\ m^3/K \text{ around } 0^\circ C$$

$$\therefore \frac{dL}{dT} = \frac{L}{T} + (C_s)_p - (C_l)_p - \frac{L}{v_2 - v_1}\left[\left(\frac{\partial v_l}{\partial T}\right)_p - \left(\right.\right.$$

So let us take two examples one is the melting of ice now what happens for melting of ice? We have c p of water is at 0 degree centigrade which is so? So let us just compile the data so c p of water at 0 degree centigrade is 4.187 kilo joules per kg per k. C p for ice at 0 degree centigrade is 2.114 kilojoules kg k L at 0 degree centigrade is 334 kg k per kilo joules per kg. So this L is the latent heat of melting we are talking about.

So water the v L and v s these are available from the steam table. So actually this 2 or rather all this relations or all these values are readily available from the steam table but some values are not and that has to be measured. These ones for example del v del T at p is equal to minus 6 into 10 to the power minus 8 meter cube around 0 degree centigrade. Once again the minus sign is because the water is heavier as compared to this one the compared to ice.

So del v L del T is or rather not only that and please remember between 0 and 4 degree centigrade if you there is a something called the anomalous expansion of water. So the water density increases as you increase the temperature so that is why del v L del T around 0 degree centigrade is a negative quantity. And del v s del T around 0 degree centigrade is 1.1 into 10 to the power minus 7 meter cube per kelvin.

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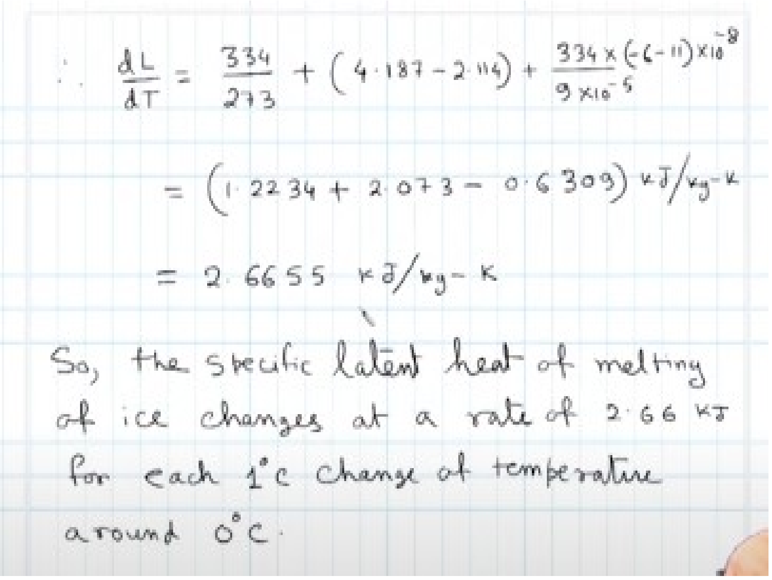

$$\therefore \frac{dL}{dT} = \frac{334}{273} + (4.187 - 2.114) + \frac{334 \times (-(-11)) \times 10^{-8}}{9 \times 10^{-5}}$$

$$= (1.2234 + 2.073 - 0.6309) \ kJ/kg\text{-}K$$

$$= 2.6655 \ kJ/kg\text{-}K$$

So, the specific latent heat of melting of ice changes at a rate of 2.66 kJ for each 1°C change of temperature around 0°C.

So if we put all this together then we get the final form of d L d T which is equal to I mean we have to put all these numbers together we get d L d T is equal to 2.6655 kilojoules per kg. So that means the specific latent heat of melting of ice changes for every 1 degree centigrade of temperature change around 0 degree centigrade the specific heat of sorry the latent heat of melting changes by 2.66 kilo joules per kg k rate right.

Now let us compare it with the actual value l is 334 so if I go from 0 degree centigrade to 1 degree centigrade it will be instead of 334 it will be what is it 336.66 kilo joules per kg. Or if we go to let us say instead of and this is positive so as we increase the temperature the latent heat increases. So if we go to -1 degree centigrade and try to compute the latent heat at of melting at that temperature it will be 330 so it will be 330 1.4 kilojoules per kg.

So it is not a very big deviation but it is a considerable deviation. So it is by effect I mean roughly 1% change in latent heat so which is significant. And in order to get the correct result we have to measure we have to know all these parameters some of these are already available in steam table and some we have to know from the experimental data right.

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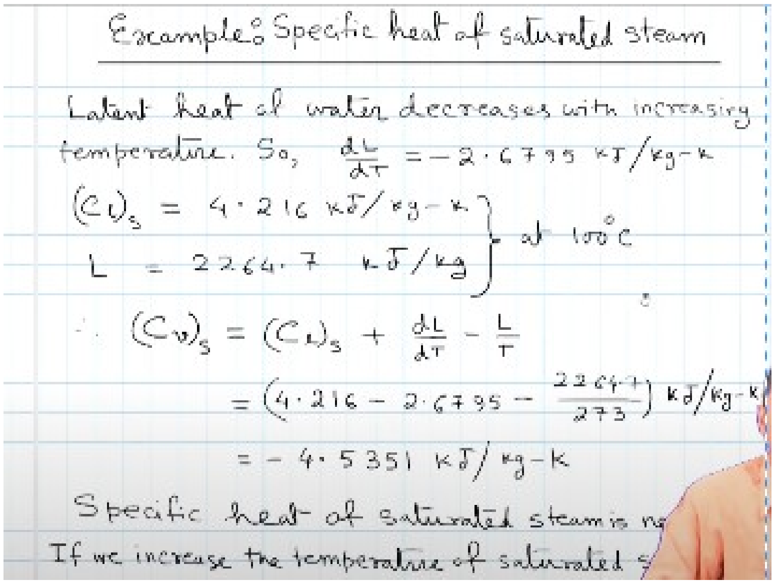

Example: Specific heat of saturated steam

Latent heat of water decreases with increasing temperature. So, $\frac{dL}{dT} = -2.6795$ kJ/kg-K

$$\left.\begin{array}{l}(C_l)_s = 4.216 \text{ kJ/kg-K} \\ L = 2264.7 \text{ kJ/kg}\end{array}\right\} \text{at } 100°C$$

$$\therefore (C_v)_s = (C_l)_s + \frac{dL}{dT} - \frac{L}{T}$$

$$= \left(4.216 - 2.6795 - \frac{2264.7}{273}\right) \text{kJ/kg-K}$$

$$= -4.5351 \text{ kJ/kg-K}$$

Specific heat of saturated steam is n

If we increase the temperature of saturated s

So the second and the last example for today's lecture is specific heat of saturated steam. Now latent heat of water decreases with increasing temperature. So we have so here the value of d L d T is already given all we have to do is we have to find out the specific heat at 100 degree centigrade of the saturated steam. So d L d T is given as minus 2.6795 kilojoules per kg. So c l s is equal to 4.216 kilojoules per kg k, l is 22644.7 kilo joules for kg k both at 100 degree centigrade.

These are once again the values which are available from steam table so c v s if we put and please remember this is a liquid vapour transition. So we can directly use the simple form of the Clausius Clapeyron equation we do not have to use the complicated where all this volume change with specific volume change with temperature and all are involved. So we simply calculate C v s is equal to c l s plus d L d T minus L by T put this values this one is 4.216 this one is minus 2.6795 and l by T is simply this I mean this number here.

So if we compute everything we get a value of minus 4.5351 kilojoules per kg k so that means specific heat of saturated steam is negative.

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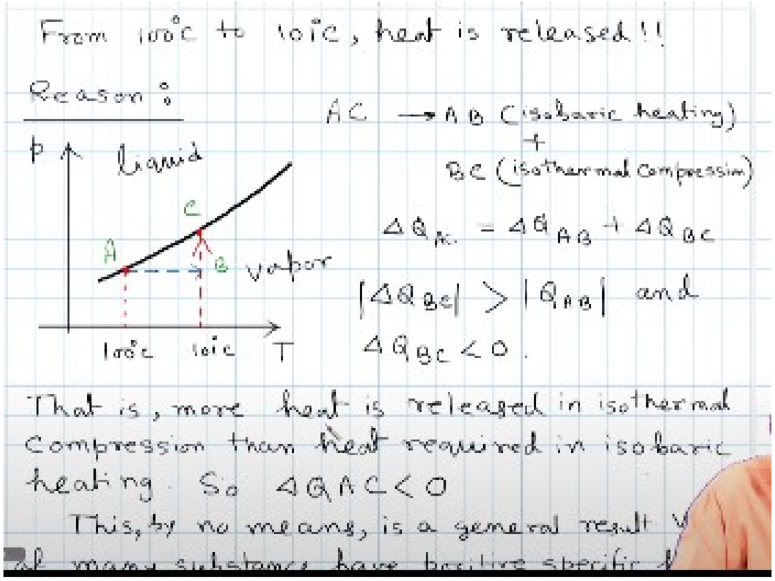

From 100°C to 101°C, heat is released!!

Reason:

AC → AB (isobaric heating) + BC (isothermal compression)

$\Delta Q_{AC} = \Delta Q_{AB} + \Delta Q_{BC}$

$|\Delta Q_{BC}| > |Q_{AB}|$ and $\Delta Q_{BC} < 0$.

That is, more heat is released in isothermal compression than heat required in isobaric heating. So $\Delta Q_{AC} < 0$

This, by no means, is a general result

So that means if we increase the temperature of the saturated steam heat will 100 from let us say from 100 degree to 101 degree centigrade heat is released. Now this is something very counter-intuitive because we you know we do not experience that we are trying to increase the temperature of something and heat is coming out of it. That is something that is very unusual I mean not very unusual I would say but it is very counter intuitive at this point at this moment.

So let us try to examine the reason so once again we try to focus on this liquid vapour equilibrium line in this p-T diagram so we have liquid phase here we have vapour phase here. So this is let us say this is the curve so let us say this point A represents 100 degree centigrade and point C represents 101 degree centigrade all right. So in order to go from A, to C my mistake here it should be A, C so AC is equal to AB plus BC.

So we just break it into 2 parts now we are free to do that I mean we are just assuming that we are I mean you know represent or rather breaking this quasi-static path into 2 other quasi-static processes. One is an isobaric heating that is taking place along A B at constant pressure and the other one is a, isothermal compression that is taking place exactly at this temperature 101 degree centigrade from B to C.

Now so the total heat that is required in this process Q AB can be represented as this should be a C once again C right Q AC is equal to delta Q AB plus delta Q BC right. So that is the total heat that is required now you might argue that so I can go from A, to C and heat requirement might be different yes you are right. That is also a possibility but we are just trying to explain the situation here so let us assume that this is the only way we can go from A to C.

So delta Q BC is greater than the mod of delta Q BC the mod of this change is experimentally found to be greater than the or rather amount of heat absorbed the magnitude of amount of heat that is absorbed. Or released during this process is found to be greater than the magnitude of heat that is required for this particular process and also Q delta Q BC is less than 0. Now this is something that you can even understand from if you remember in lecture 35.

There was a general I mean heat conduction has been calculated for many general processes from there if you simply look at the expression for isobaric sorry isothermal. If you look at the process for isothermal compression you will realize that heat has to be the heat has to come out during this process. Go back to this expression try to find it yourself if you do not understand why let us post a problem question in the forum and we can discuss that.

But it is very rather easy to if you simply investigate this relation you will understand why this has to be a negative quantity? So that is now what happens is so this quantity experimentally it has been found that this is the quantity of heat required in this process is more as compared to this process and this is negative. So even if this one is positive the total heat requirement delta Q AC is less than 0.

And this is once again it is not a general result in certain cases we can have you know water is one example. But there are other examples also where we can have saturated the specific heat of saturated vapour could be negative under over a small or a relatively large temperature scale. But once again this is not a general result and we can have many substances for which, has the positive specific heat for saturated vapour.

So that is where we will stop today for the next lecture we will discuss something called the Gibbs phase rule and second order phase transition thank you.