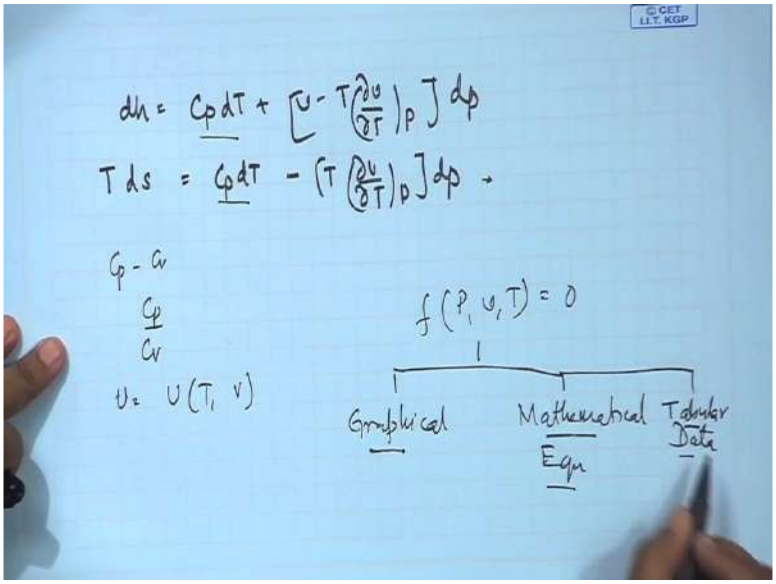
Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture 13
PvT Behaviour of gases

(Refer Slide Time: 0:32)



$$dh = C_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

$$T ds = C_p dT - \left[T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

$C_p - C_v$

$\frac{C_p}{C_v}$

$u = u(T, v)$

$f(P, v, T) = 0$

Graphical

Mathematical Eqn

Tabular Data

Hello everybody, to recall what we have done till now, we were using the Maxwell's equations to find out your entropy as a function of temperature and pressure the Tds equation is written down here. We had similar equations in terms of your T and v as well then we had also expressed enthalpy in terms of temperature pressure and we had also done this for several other properties if you recollect.

We had tried to predict Cp minus Cv, we had tried to predict Cp by Cv, we had tried to predict u as a function of T and v etc. Now in all these equations if you recollect, what do you find? We have used thermal data and volumetric data in order to predict these particular thermodynamic functions thermal data are those data which tell you how this function vary with temperature and volumetric data are those which tell you how these particular properties they vary with volume or density and pressure, right?

So as far as this part is concerned this either Cp or Cv etc, there also we have already discussed that more or less data is available for ideal gases as a result of which we would like to we would prefer to carry out this particular temperature change at very low pressure where we can use the data of ideal gases in order to predict the enthalpy change due to temperature change of gases the other part was to find out the dependence on pressure.

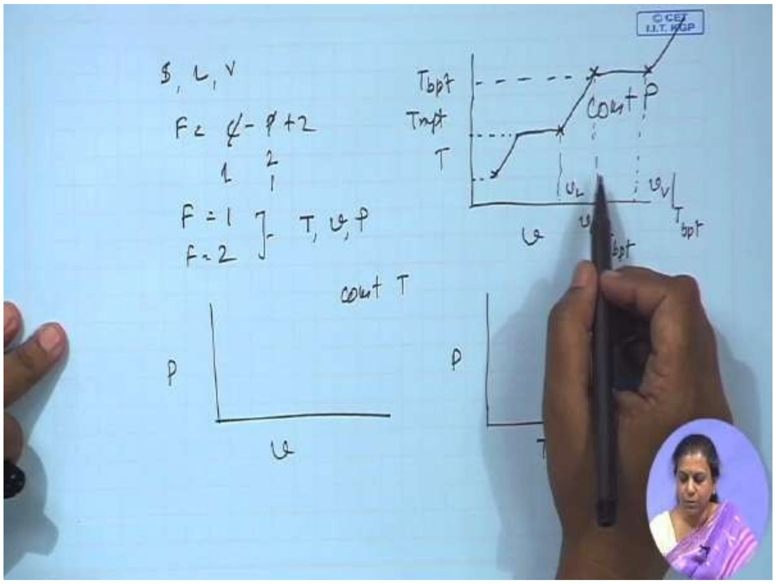
We find that this particular dependence it is a function or it depends upon the PVT Behavior of substances, right? Or in other words this is easy to evaluate provided we have a relationship of this form for the substance which we are going to consider, fine. And we find that these relationships they are available, plenty of them are available the reason for this plentiful availability is just that there is no particular relationship which is applicable over a wide range of conditions for different pure components as well as the mixtures.

We are going to discuss PVT Behavior of pure components in this class remembering fully well that mostly in thermodynamics we would be requiring to discuss or rather we will be dealing with thermodynamic properties of mixtures. So we will be doing PVT Behavior of pure gases a little amount about condensed phases and then after we complete fugacity we will be predicting or we will be discussing different mixing rules and combining rules to predict the thermodynamic properties of gaseous mixtures, right?

Now we know that this type of relationship they are available in different forms, one of them is a graphical representation, one of them is a mathematical equation we also have a third form which is as tables tabular data. So these are the 3 forms usually in which PVT Behavior of gases they are or rather sorry PVT Behavior of any particular substance it is available.

So we are first going to deal with graphical equations and our graphical representations and then we are going to deal with mathematical equations and as far as tables are concerned you are already aware of steam tables and several such tables are available we will not be discussing them in the process or in our course of learning of thermodynamics you may have to refer to several tables, so just be aware that PVT behavior of pure components in different phases are also available of tables the steam table is the most common example of it.

(Refer Slide Time: 4:32)



Now let us take up the graphical representations, for a pure substance it can exist in 3 forms it can be a solid, a liquid and a vapor state, right? And what are the properties that we can vary independently F in this particular case it is C minus P plus 2, C is one, so if P is 2 then in that case F becomes equal to1 if suppose P is 1, F becomes equal to 2, right? So therefore what can be and what are the variables that we have at hand? We have temperature of the gas we will prefer the molar volume because we would like to deal with intensive variables and the pressure of the gas.

So out of this we can vary 2 and keep the third one constant and try to find out the different variations. So for example we can generate curves of say T as a function of v, we can generate curves of say P as a function of v this will be at constant pressure and this will be at constant temperature. We can also have curves of P as a function of T at constant molar volume. So these are the 3 ways by which graphically the PvT Behavior of pure substances can be represented.

Let us take up the Tv behavior, so suppose we have taken up a substance say for a very low-temperature say minus 20 degrees centigrade we take up benzene for instance it remains solid under that temperature we keep on applying heat to it say the initial temperature or rather initial condition of existence of benzene is here for temperature is very low say minus 20 degrees centigrade benzene is in this particular case is solid, we start heating it what happens? Its temperature, it absorbs energy temperature increases along with that it expands.

So therefore even both of them they start increasing after that it is continues till the solid keeps on getting heated and it expands this keeps on continuing till we reach the melting point of the solid, at the melting point what happens? It changes to the liquid phase due to this change its volume increases but this change as all of us know occurs at a constant temperature. So therefore under this condition we find that they get a horizontal line which marks the fusion the process of fusion of the pure substance.

After that this fusion process continues till the point entire solid has melted and it forms the liquid during this entire time we find some amount of solid keeps on melting liquid form till at this particular point we find entire solid has melted and it is converted to the liquid phase, in this particular the volume corresponds to the molar volume of the liquid at the melting point and this particular temperature it is nothing but the melting point of the solid.

Now with the liquid we continue this heating process, again as the liquid gets heated the temperature keeps on increasing and along with that the volume also keeps on increasing, in this case possibly it is not clear from my particular figure but in this case the rise will be much steeper as compared to the rise in the case of the solid. So this continues as long as the liquid remains a liquid and it has not reached the boiling point then at one point it reaches the boiling point. So this is the T boiling point of the pure substance at the boiling point again the same thing occurs as the fusion this is the vaporization curve this curve continues till the entire liquid has vaporized and the pure component vapor is formed.

Once liquid has completely converted to the vapor again the temperature keeps on rising in this particular case. So therefore this part it corresponds to the volume of the vapor at the boiling point it is the T boiling point, right? This corresponds to the specific volume of the liquid at the T boiling point and we know there is a remarkable increase in the volume and due to this remarkable increase in the volume naturally it absorbs a good amount of latent heat.

Now this whole thing the entire heating process, what have I done? The entire heating process it is performed at constant pressure, say the pressure is 1 bar pressure, so what is this? This is basically an isobar on the Tv plot.

(Refer Slide Time: 9:31)

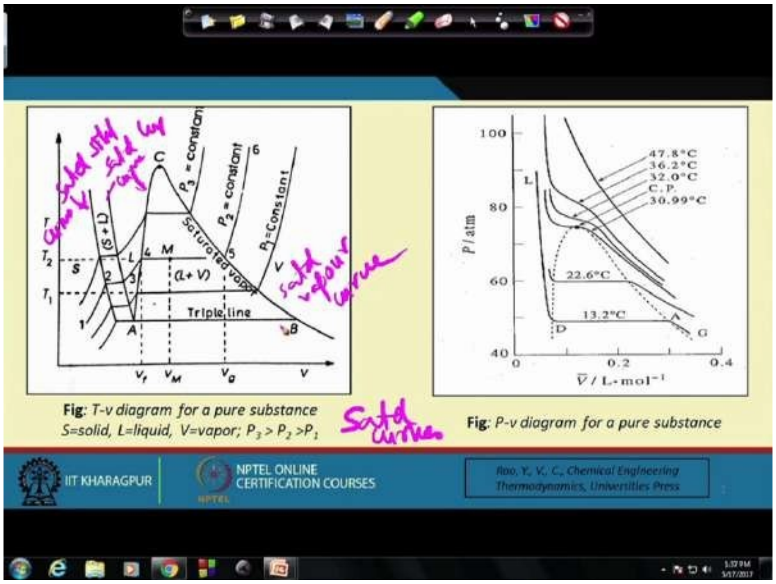


Fig: *T-v diagram for a pure substance*
S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$

Fig: *P-v diagram for a pure substance*

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

We can construct such isobars at different pressures, right? And this is what precisely I have done here. We have constructed isobars at different pressures at increasing pressures and we find that we get such identical curves as I have already shown.

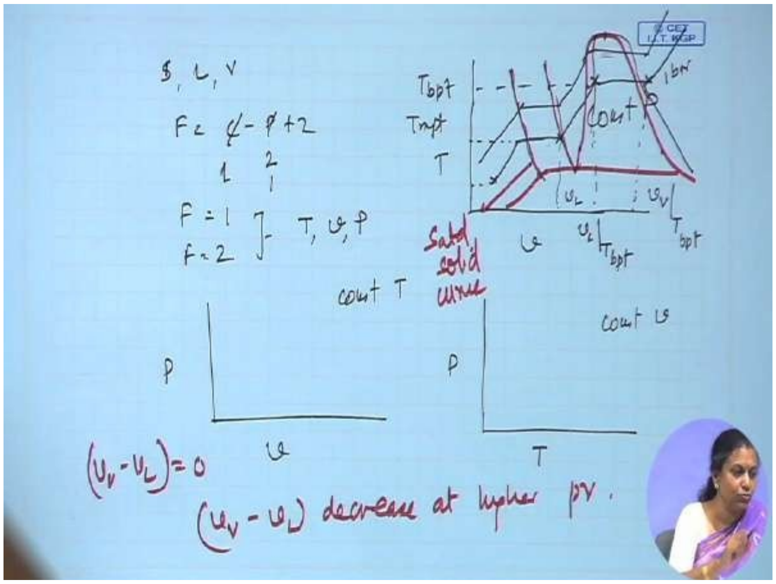
So the only difference between these curves is that we find that as we go for higher and higher pressure the solid liquid coexistence region that more or less remains the same what happens is the liquid vapor coexistence region that keeps on becoming lesser and lesser as we perform the experiment at higher and higher pressure. So therefore in this particular curve after that what we do? We have performed the experiments at different pressures and we have located the melting points and the boiling points etc.

And then we have joined the melting points boiling points at different pressures and these particular curves they are known as the saturated curves these curves which is the locus of the different saturation points at different pressures are known as the saturation curves. Now what do the saturation curves do? They join points at different pressure temperature conditions where 2 phases are in equilibrium it can be a solid liquid in equilibrium it can be a liquid vapor in equilibrium.

So therefore what is this curve? This particular curve this is a saturated curve with respect to the solid, what is this curve? This is a saturated liquid curve with respect to fusion, remember one thing we have 2 saturated liquid curves, one is with respect to fusion the other is with respect to boiling, right? So therefore this is a saturated solid curve this particular curve, right? This is a saturated liquid curve with respect to fusion, fine.

And this is a saturated liquid curve with respect to boiling and we have a saturated vapor curve here. Now we find that more or less the saturated liquid curve and the saturated solid curve with these 2 curves they are more or less parallel to each other while we find that the saturated liquid curve with respect to vaporization and the saturated vapor curve they gradually incline towards each other and finally they converge at a point.

(Refer Slide Time: 12:42)



So therefore on close observation what do we find? We find that the change in volume which I have marked here, so therefore in this particular way if we keep on making them at different pressures and then if we join these particular points then we get, I will do it with a different pen that will be easier for you. We can have this, we can have this then we can have this, we can have this, so therefore what do we find? We find that this is the saturated solid curve, saturated liquid curve with respect to the melting, saturated liquid curve with respect to vaporization.

Saturated vapor curve and we find that while these 2 lines they are more or less parallel to each other for this particular portion we find that Vv minus vL that keeps on decreasing at higher pressure , right? This keeps on continuing and as we go for higher and higher temperature also you will find that this keeps on decreasing till at some particular temperature we will find more or less that Vv minus vL this becomes equal to 0 and this particular point, in fact I have not drawn it as a point the drawing is not good.

(Refer Slide Time: 13:59)

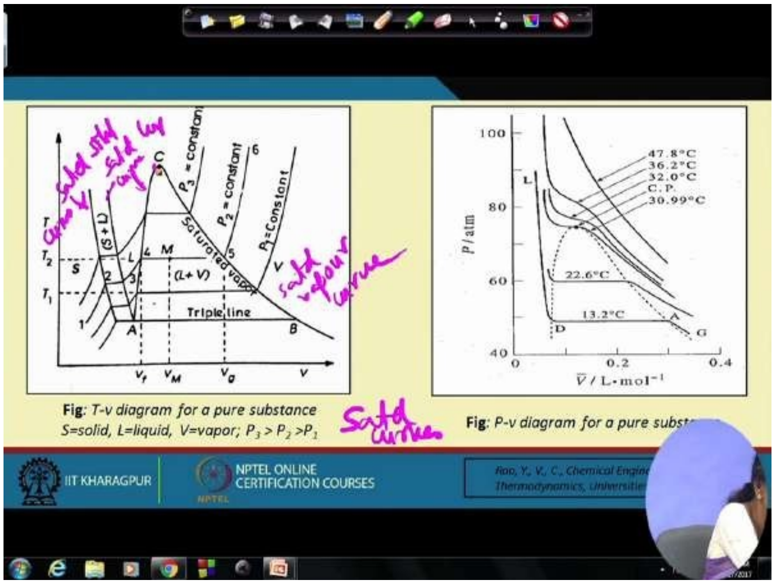


Fig: *T-v diagram for a pure substance S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$*

Satd curves

Fig: *P-v diagram for a pure subst*

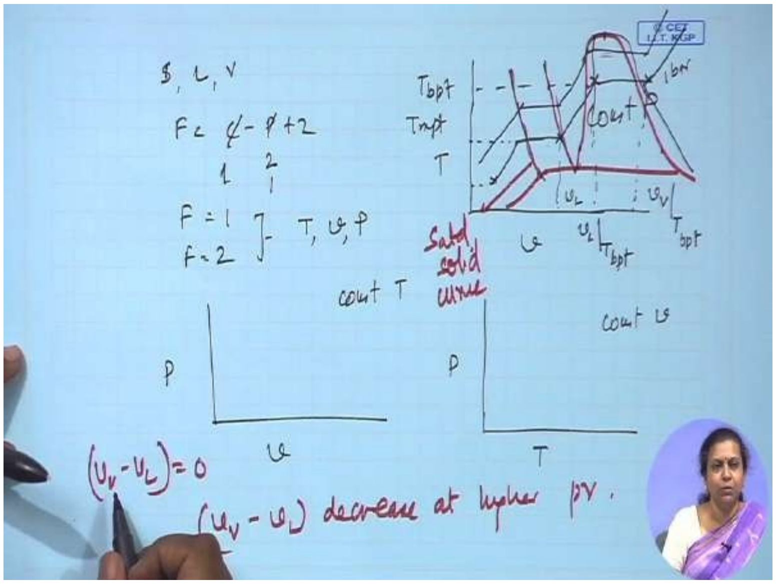
IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

Rao, Y., V., C., Chemical Engine
Thermodynamics, Universitie

If you find here you find at this particular point at this point more or less your change in molar volume becomes equal to 0.

(Refer Slide Time: 14:04)



S, L, V

$F = C - P + 2$

1 2
1

$F = 1$
$F = 2$] T, v, P

const T

const v

$(v_V - v_L) = 0$

$(v_V - v_L)$ decrease at higher pr.

Now when the change in molar volume becomes 0? What other thing happens? You know due to this particular change the substance it has to absorb latent heat and due to this change, absorption of latent heat there is volume expansion due to which the substance changes from the liquid state to the vapor state.

(Refer Slide Time: 14:30)

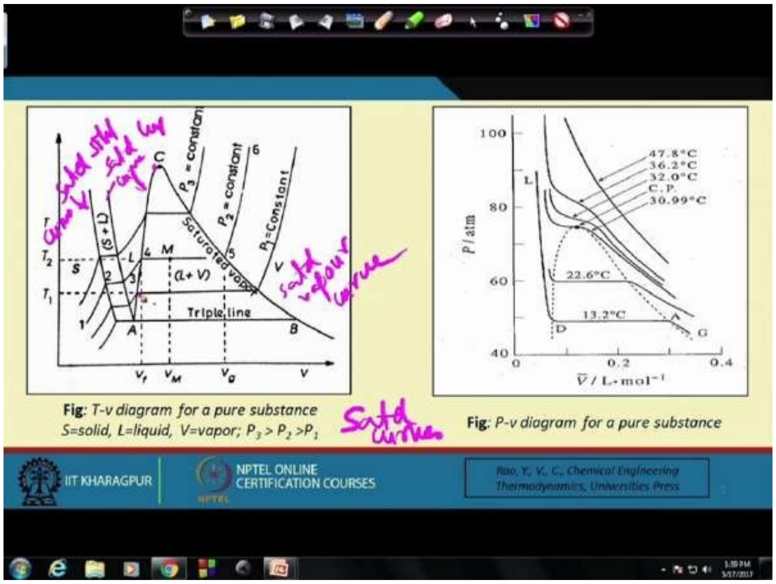


Fig: *T-v diagram for a pure substance S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$*

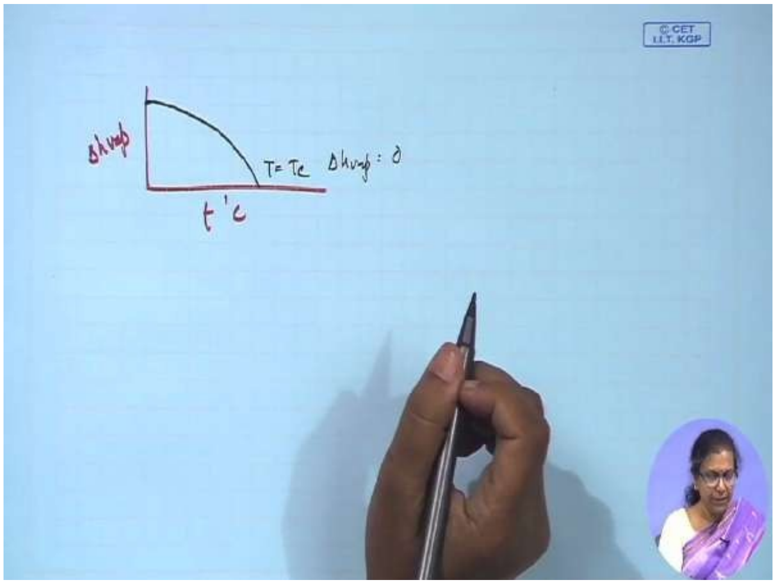
Fig: *P-v diagram for a pure substance*

Rao, Y. V., C., Chemical Engineering Thermodynamics, Universities Press

So therefore isn’t it quite natural that if we consider the portion of the curve here we find that Delta v the change of volume is much higher, here it is much lower.

So therefore it is quite natural that here the latent heat which the substance has to absorb in order to change from the liquid to the vapor state should be much higher as compared to the latent heat it needs to absorb at this pressure and therefore this should continue and here we believe the latent heat of vaporization that it has to absorb is going to be equal to 0.

(Refer Slide Time: 15:09)



Or in other words, suppose I plot delta h vaporization as a function of temperature then what is the curve which I expect? It should have a high latent heat vaporization to start with it keeps on decreasing and then at T equals to Tc we find delta h vaporization equals to 0, fine.

So therefore this was the temperature volume curve which we found out and what did we find? We find that mostly for our cases since we are dealing with solution liquid vapor substances we would like we would prefer to keep our discussion, since we are not dealing with physical methodology or solid state physics we will not be dealing with the solid state much.

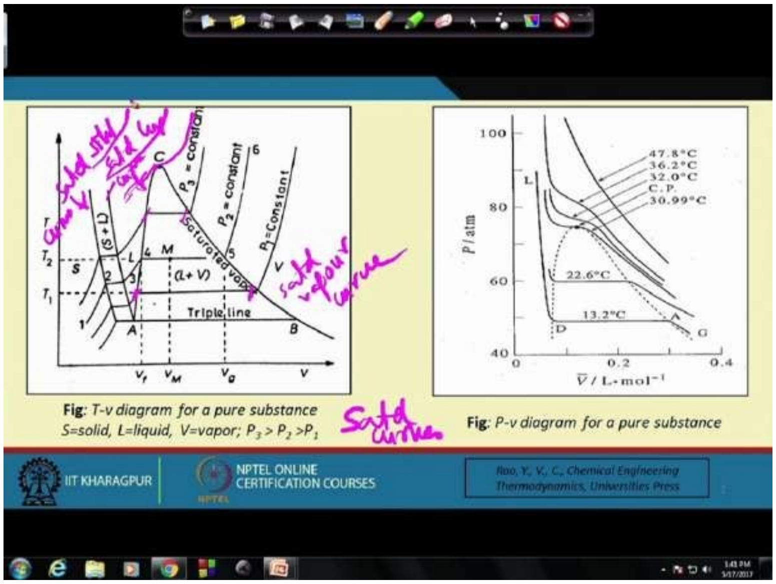


Fig: *T-v diagram for a pure substance*
S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$

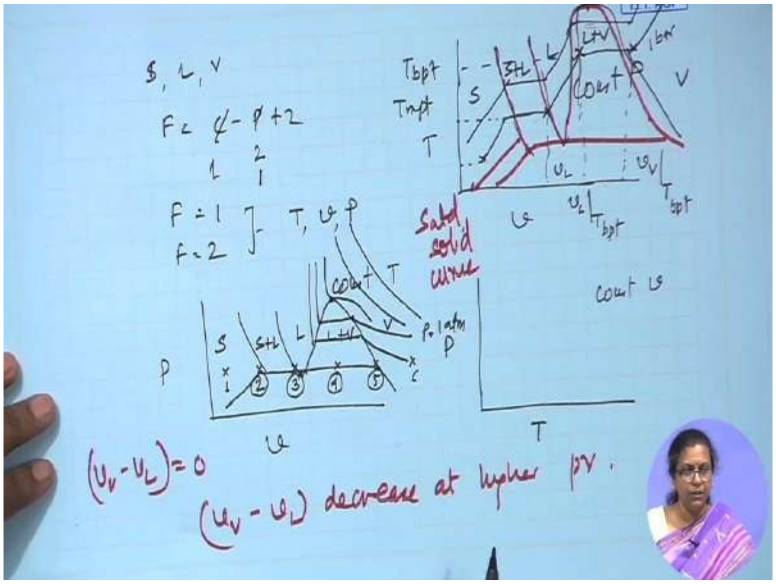
Satd curves

Fig: *P-v diagram for a pure substance*

IIT KHARAGPUR | NPTEL ONLINE CERTIFICATION COURSES

Rao, Y. V. C., Chemical Engineering Thermodynamics, Universities Press

We will be primarily confining our attention to the liquid vapor phase, so therefore we will be more or less interested in this particular portion of the Tv diagram, fine. And here what do we find? We find that as long as we are inside or we are at in a region here we find that the isobars they have free particular regions of different slopes. There is an isobar here then there is a horizontal portion and then there is another portion. So if we continue this we will find at the critical point there is going to be a horizontal inflection beyond the critical point the isobars will be something of this sort.



In the same way we can plot our Pv diagram also, we are going to start in the similar fashion that we have done here we take our substance we start heating it and then as we heat it at constant pressure initially the substance was here we heated the pressure remains constant it is here and then it changes to the vapor phase, sorry liquid phase then the liquid gets heated and then it goes to the vapor phase and then the vapor is heated to a very high temperature.

So this is what this 2 is a saturated state with of saturated solid state, this is saturated liquid state with respect to fusion, saturated liquid state with respect to vaporization, saturated vapor state this can be performed at this was possibly say at P equals to 1 atmosphere. We can keep on performing these experiments for different pressures and then finally we can draw the curves in this particular way. So in this particular case also we can we can draw the curves in this particular way we find that we are going to get something identical this is a solid-state, here also this is solid, this is solid plus liquid liquid, this is liquid plus v this is v, here also this is solid s plus L, L plus v and this is the vapor state.

Again we would like to be concentrated here if we find that the isotherms which we draw here then in that case the isotherms in this particular case it is going to be almost vertical in the liquid region because we know they are all practically incompressible and then during the change of phase we know it is more or less horizontal it is going to be horizontal curve because remember one thing change of phases occurs under isothermal isobaric conditions therefore they are horizontal both in the Tv plot as well as in the Pv plot.

And then in the vapor region it exhibits more or less a rectangular hyperbola sort of a thing. So therefore as long as we are operating at T is less that Tc we find that the saturation curve it comprises of 3 particular regions with the middle region decreasing as we go for higher and higher temperatures and finally at T equals to Tc we find that there is a horizontal inflection and beyond that they are going to have curves something of this sort.

(Refer Slide Time: 19:11)

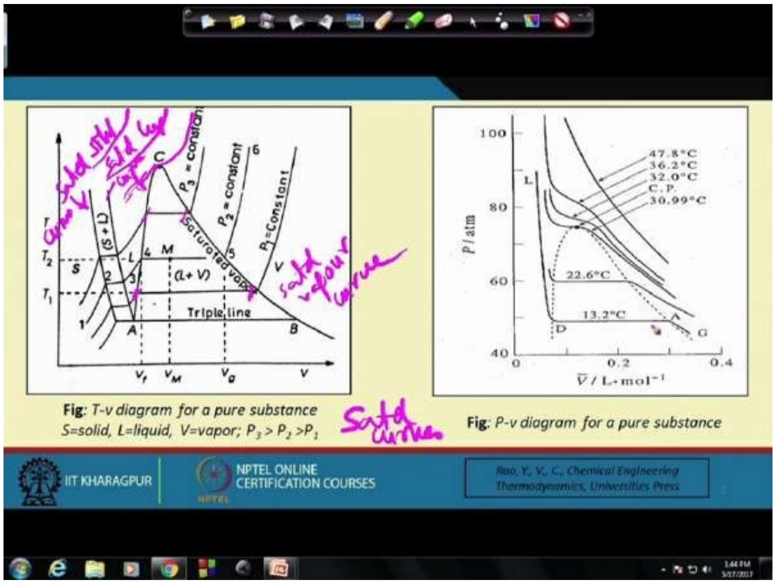


Fig: *T-v diagram for a pure substance*
S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$

Satd curves

Fig: *P-v diagram for a pure substance*

IIT KHARAGPUR

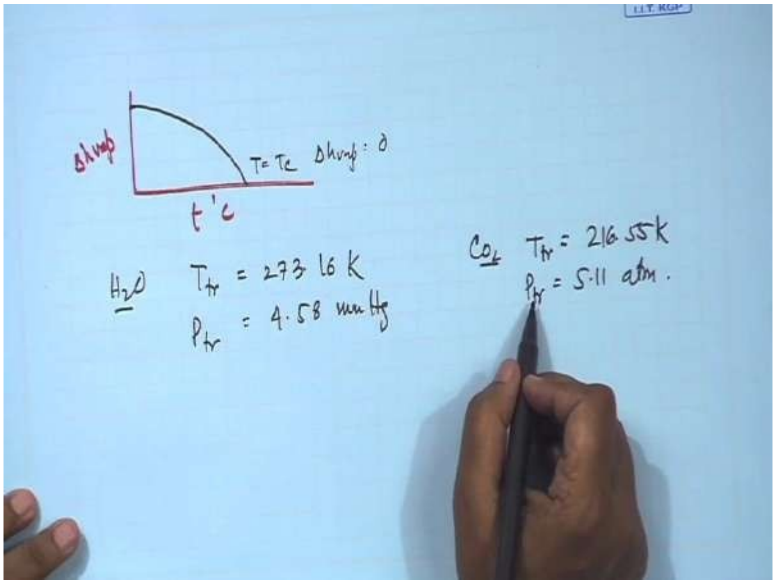
NPTEL ONLINE CERTIFICATION COURSES

Rao, Y. V. C., Chemical Engineering Thermodynamics, Universities Press

This is what I have shown in this particular figure if you see I have tried to show this, this is for carbon dioxide. Now there is one thing I have already told you about the point of termination of the liquid vapor curve, right? Liquid vapor dome, sorry, this is nothing but the critical point, what about the initial portion? Where does the liquid vapor dome or in other words where from where do this saturation curves they originate?

Now all of these curves they originate from a triple point line, if you observe this triple point line you will find that at this particular line the solid liquid and the vapor phases they coexist in equilibrium as a result of which F equals to 0 under this condition and therefore this line it is a very important constant characterizing any particular substance where it is characterized by a specific temperature, a specific pressure and a specific volume.

(Refer Slide Time: 20:23)



For instance suppose we take up 2 particular substances say water and carbon dioxide, what do we find? We find that for water the triple point pressure it is, for water T triple point this is 273.16 most of you all are aware of it, P triple point this is4.58 millimeters mercury and for carbon dioxide if you see you will find that the T triple point it is 216.55 Kelvin, P triple point this is equals to 5.11 atmospheres but does this bring any, does this strike any cord in your mind the importance of this data?

(Refer Slide Time: 21:13)

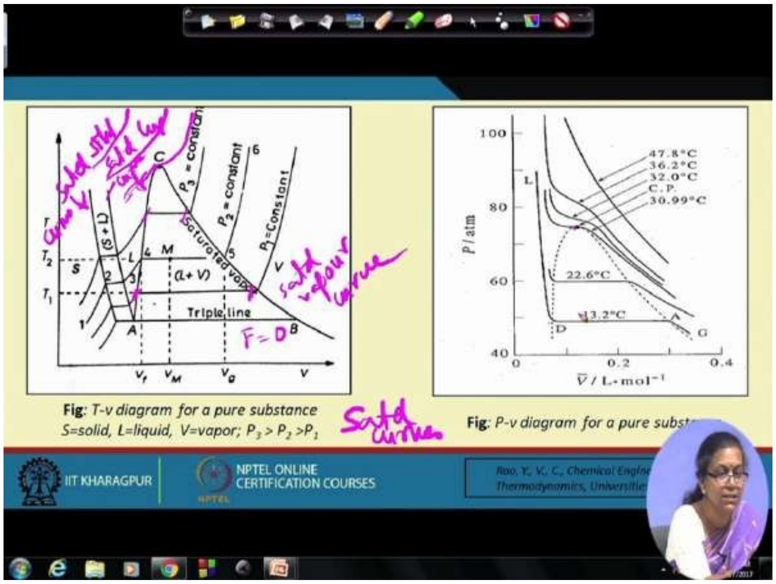


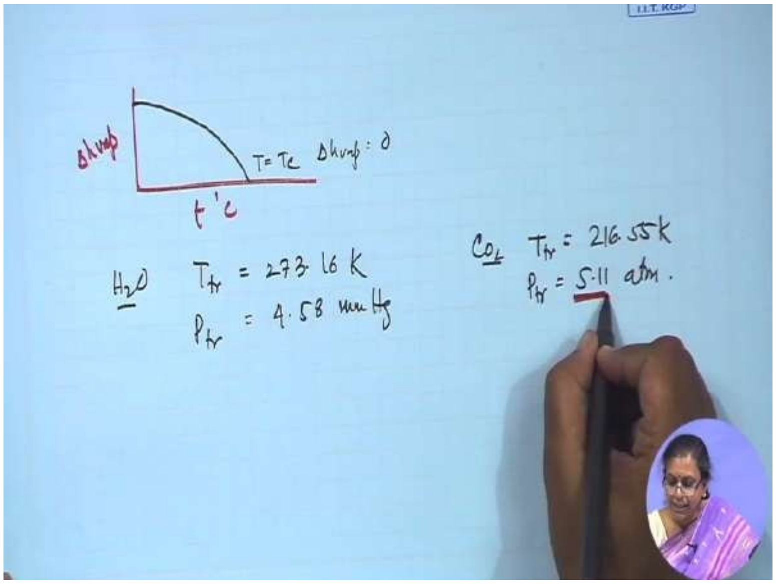
Fig: *T-v diagram for a pure substance*
S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$

Fig: *P-v diagram for a pure subst*

Rao, Y. V. C., Chemical Engine
Thermodynamics, Universitie

If you observe this data what do you find? You find that the triple point curve for carbon dioxide this particular curve here as well as here this occurs at a pressure much higher than the atmospheric pressure.

(Refer Slide Time: 21:51)



Δhvap = 0

H_2O $T_{tr} = 273.16$ K

$P_{tr} = 4.58$ mm Hg

CO_2 $T_{tr} = 216.55$ K

$P_{tr} = 5.11$ atm.

(Refer Slide Time: 22:03)

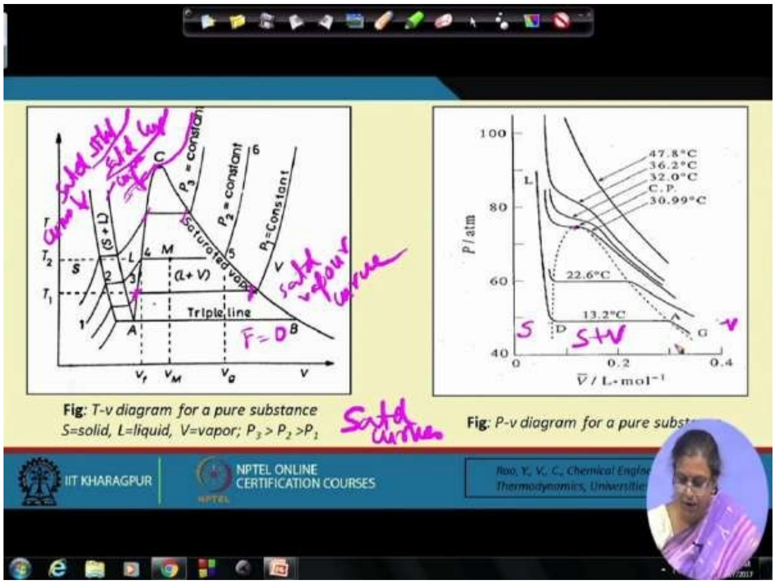


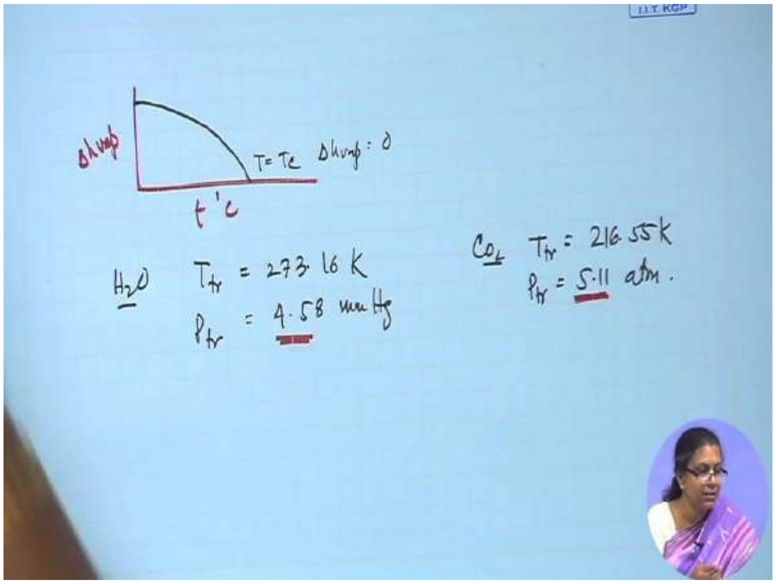
Fig: T-v diagram for a pure substance
S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$

Fig: P-v diagram for a pure subst

Rao, Y. V. C., Chemical Engine
Thermodynamics, Universitie

So therefore at atmospheric pressure where are you exactly? When you're working with carbon dioxide at atmospheric pressure you are lying in this particular region, what is this region? It is a solid here, it is a solid plus it is a vapor region here and in between this region it is marked by a solid plus vapor. So what does it imply? It implies that if you're working at a pressure below the triple point pressure then in that case you're working in this particular zone where the solid will directly be converted to the vapor phase as a result of which we will find that substances sublime if their triple point pressure is higher than the atmospheric pressure.

(Refer Slide Time: 22:14)



Δh_{vap}

$T = T_c$ $\Delta h_{vap} = 0$

t °C

H_2O $T_{tr} = 273.16$ K

$P_{tr} = 4.58$ mm Hg

CO_2 $T_{tr} = 216.55$ K

$P_{tr} = 5.11$ atm.

(Refer Slide Time: 22:17)

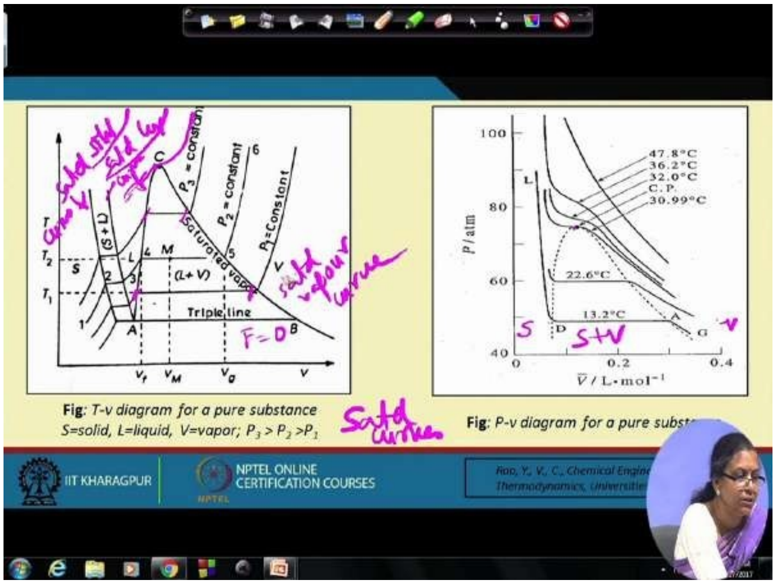


Fig: T-v diagram for a pure substance S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$

Fig: P-v diagram for a pure subst

Rao, Y. V. C., Chemical Engine
Thermodynamics, Universitie

On the contrary if the triple point pressure is much less than the atmospheric pressure then at atmospheric pressure what are you doing basically? You are operating in this particular region where you find that the solid will be converted to the liquid and the liquid then will be converted to the vapor and this gives you the answer to questions as to why some substances sublime.

In reality all substances sublime if you are operating below the triple point pressure, for example if you're working with water and you're working at a pressure of say 1 millimeters mercury that at such a great amount of vacuum then you'll find that water will also sublime. So the question of why some substances sublime is that, it's triple point pressure is either higher than atmospheric or lower than atmospheric.

(Refer Slide Time: 23:01)

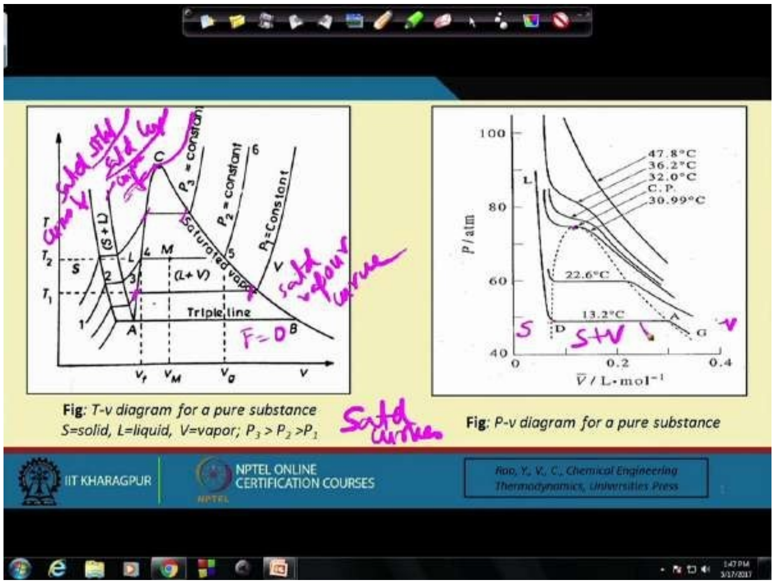


Fig: T-v diagram for a pure substance
S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$

Fig: P-v diagram for a pure substance

IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

So therefore we find that the vapor liquid dome that we have drawn here, the vapor liquid dome it starts from the triple point curve, this is the triple point curve and it extends to the critical point. Now there is one particular question which I would like to put before you, we have a triple point curve and a critical point marking the beginning and end of the vapor liquid dome, correct? The solid liquid coexistence curve also starts from the triple point curve as is very much evident from this particular figure.

But here we have not marked an end to this solid liquid coexistence region, for example here we know that both of them they merge at the critical point and beyond the critical point we have only vapor phase and the characteristics of the critical point is that if you're working above the critical point then just by mere completion we cannot reduce the or rather just by mere cooling we cannot convert a vapor to a liquid phase.

Do you have certain identical termination point for the solid liquid coexistence curve? Or does the solid liquid coexistence region or the curves they continue indefinitely? This is something that you should be wondering and here I would like to mention that there is no termination point for the solid liquid coexistence curves they keep on continuing, what is the reason behind it? The reason is, if you observe the molecule behavior of liquids and vapors you'll find that the main difference between them is about the degree of freedom of movement of the molecules in the liquids they are much more bound, in the gases they are much more free.

So therefore when we are heating a liquid, what we are doing? We are just making the molecules more free from one another we are decreasing the intermolecular attraction between them as a result of which they are getting converted to the vapor phase. It is basically a matter of the degree of the freedom of which is enjoyed by the molecules.

(Refer Slide Time: 25:24)

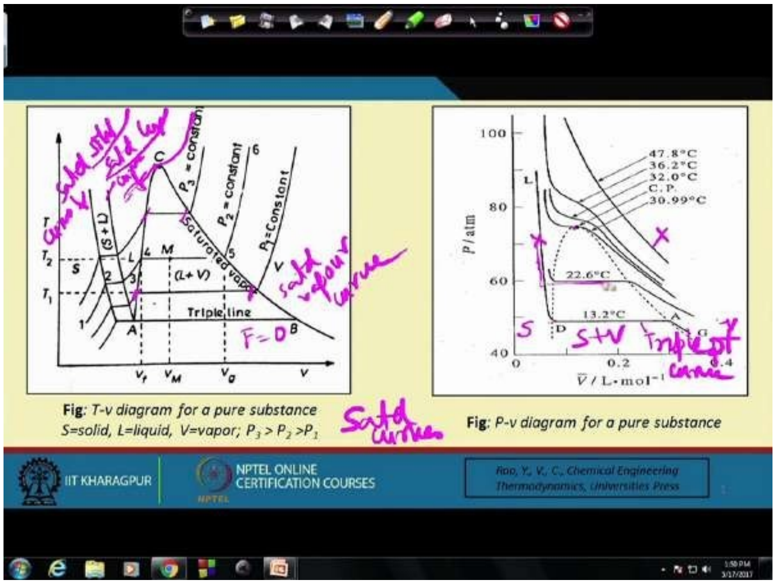


Fig: *T-v diagram for a pure substance S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$*

Fig: *P-v diagram for a pure substance*

Rao, Y., V., C., Chemical Engineering Thermodynamics, Universities Press

So therefore for such a case beyond the critical point if you're going then we find that we can very well, suppose we are in this particular region we want to come to this particular region. We can cross either follow this particular isotherm and we can perform this thing or else we can even ignore this particular discontinuous region and we can make this transition by these particular process where we find that without this particular change of phase this particular heterogeneous liquid vapor dome we can also make a gradual change from one to the other.

But when we are considering the solid liquid transition state then it is not just a matter of the degree of freedom enjoyed by the molecules. In this case actually the solid structure has to break and the liquid has to form as a result of which under this particular condition there has to be a zone of discontinuity where the solid structure starts breaking, breaks completely and forms the liquid state due to which the solid liquid coexistence curve it keeps on continuing indefinitely there is nothing like a critical point for a solid liquid coexistence curve.

(Refer Slide Time: 26:48)

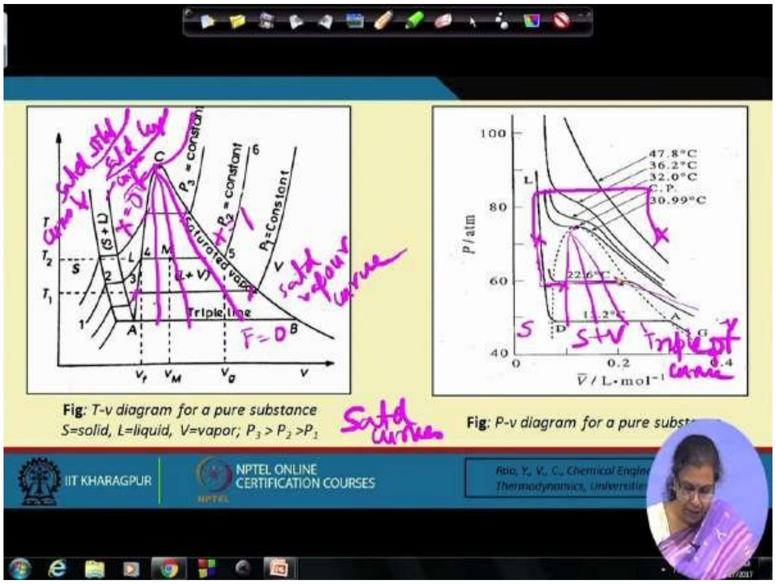


Fig: *T-v diagram for a pure substance*
S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$

Fig: *P-v diagram for a pure subst*

IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

Rao, Y., V., C., Chemical Engine
Thermodynamics, Universitie

In fact if you also consider solid-solid transitions there also we will find that there is nothing like a critical point. Well this was, one more thing before I end I would just like to remind you that these curves will not be complete unless we introduce one more information into them, what have we shown here? We have shown the pure component existence zones. We have shown the zones of existence of the 2 phases.

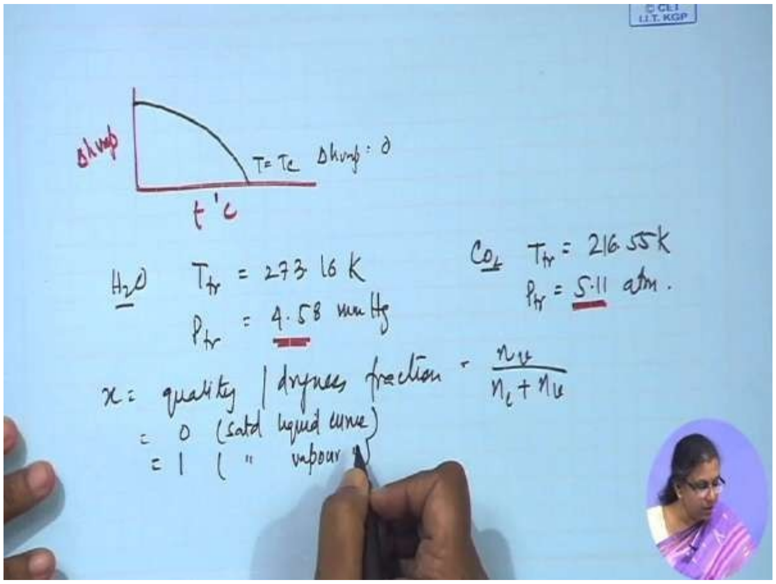
Now remember one thing, when we are working with 2 phases then it's not only the temperature and pressure that is important, in fact when you fix one the other automatically gets fixed. What is the other thing which is important here? The other thing is the proportion of liquid and the vapor which is there when you're operating inside the liquid vapor dome. So in order to complete this particular figure it is very important that we also plot along with isobars, isotherms we also plot the constant quality lines.

And remember one thing the first constant quality line is the saturated liquid zone where we know the x which is the dryness fraction which is the mass of dry vapor divided by the total mass of the moles of the liquid vapor mixture that is equal to 0 at the saturated liquid curve and it is equal to one along the saturated vapor curve. So therefore the first quality line is x equals to 0, the next quality line is x equals to 1, the intermediate quality lines can be drawn.

All these quality lines they start from the critical point and end at the triple point curve and once everything is inserted the saturated or rather the phase diagrams for pure substances are completed. Here also there should be the constant quality lines and in from these constant quality lines, suppose we are operating at this particular point we can know that pressure of that particular point, we can know the mixture volume and we can also know the temperature here and from the mixture volume we can know what is the proportion of the liquid and was the proportion of the vapor in this particular case.

So the liquid and the proportion of liquid and the vapor they can be obtained from a lever rule principle, okay. They are proportional to the distances of the horizontal portion of that point from the liquid saturated liquid curve and from the saturated vapor curve. So therefore just I would like to show how we can do this?

(Refer Slide Time: 29:08)



H_2O $T_{tr} = 273.16$ K

$P_{tr} = 4.58$ mm Hg

CO_2 $T_{tr} = 216.55$ K

$P_{tr} = 5.11$ atm.

x = quality | dryness fraction = $\frac{n_v}{n_l + n_v}$

= 0 (satd liquid curve)

= 1 (" vapour ")

We know what is x equals to? x is nothing but the quality or the dryness fraction, right? What is this quality or the dryness fraction? Suppose they're working with nv moles of vapor nl moles of liquid and then nv moles of vapor, okay. So therefore we know that this is equal to 0 as I have already mentioned because nv equals to 0 on the saturated liquid curve no matter what pressure or temperature you have operating equal to one over the saturated vapor curve.

(Refer Slide Time: 29:46)

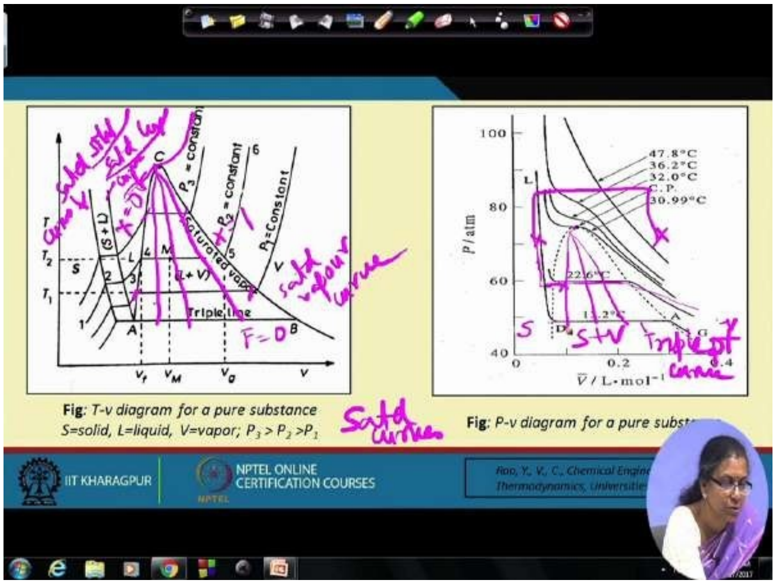
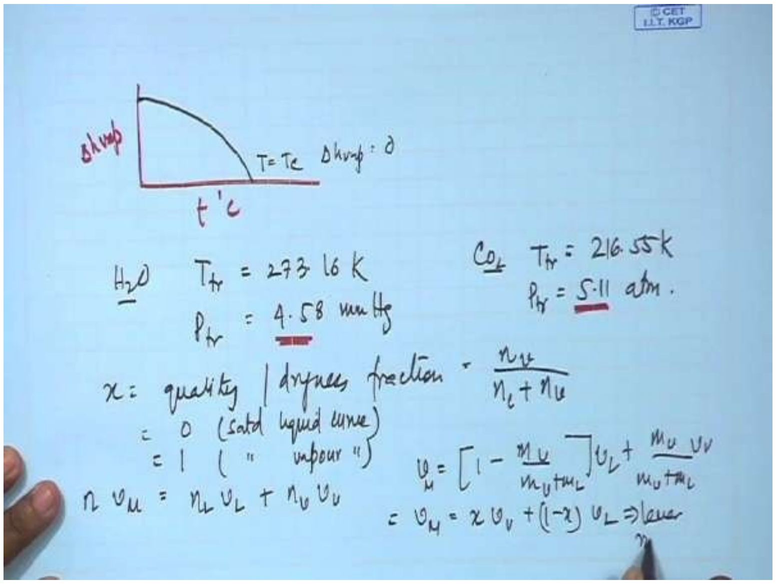


Fig: T-v diagram for a pure substance S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$

Fig: P-v diagram for a pure subst

Rao, Y. V. C., Chemical Engine… Thermodynamics, Universities…

(Refer Slide Time: 30:04)



H_2O $T_{tr} = 273.16$ K

$P_{tr} = 4.58$ mm Hg

CO_2 $T_{tr} = 216.55$ K

$P_{tr} = 5.11$ atm.

x = quality / dryness fraction $= \frac{n_v}{n_l + n_v}$

$= 0$ (satd liquid curve)

$= 1$ (" vapour ")

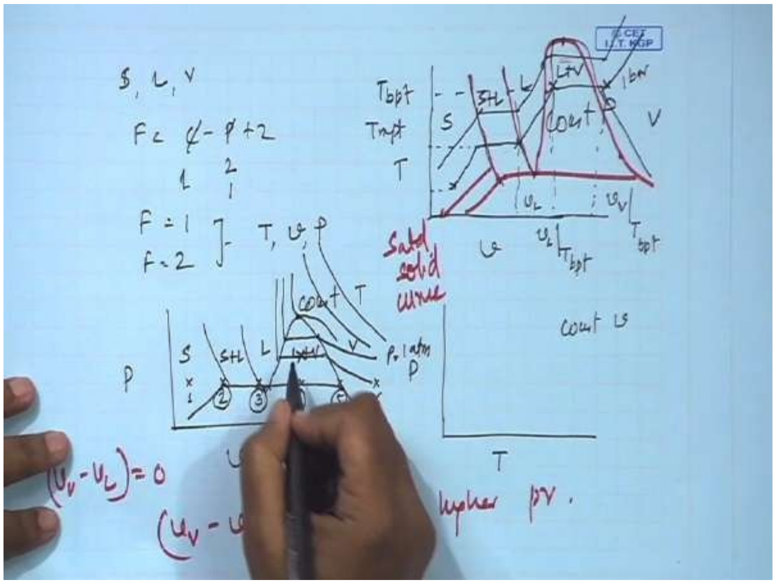
$n v_M = n_L v_L + n_v v_v$

$v_M = \left[1 - \frac{m_v}{m_v + m_L}\right] v_L + \frac{m_v v_v}{m_v + m_L}$

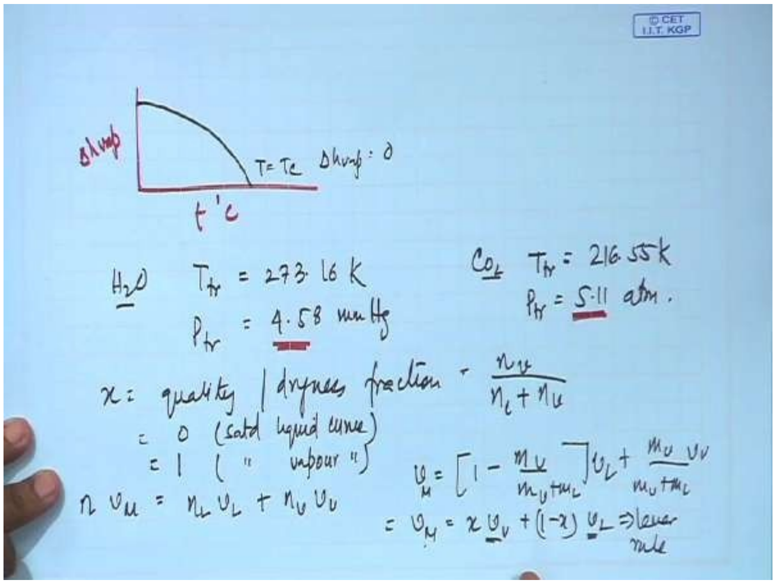
$= v_M = x v_v + (1-x) v_L \Rightarrow$ lever r

And then suppose we have located the molar volume here in this particular case, suppose say it is VM, so therefore and we are working with say n moles of the gas, right? So therefore nVM should be equal to nlVL plus nv Vv, fine. Now dividing throughout by n, what do we get? We get V is nothing but equals to 1 minus mv by mv plus mL the VL plus mv by mv plus mL Vv or in other words the V for the mixture VM which is nothing but equals to Xvv plus 1 minus x VL, right? And this has been obtained from the lever rule, so therefore by measuring the horizontal portion here.

(Refer Slide Time: 30:46)



(Refer Slide Time: 30:56)



H_2O $T_{tr} = 273.16\ K$

$P_{tr} = 4.58$ mm Hg

CO_2 $T_{tr} = 216.55\ K$

$P_{tr} = 5.11$ atm.

x = quality | dryness fraction $= \frac{n_V}{n_L + n_V}$

$= 0$ (satd liquid curve)

$= 1$ (" vapour ")

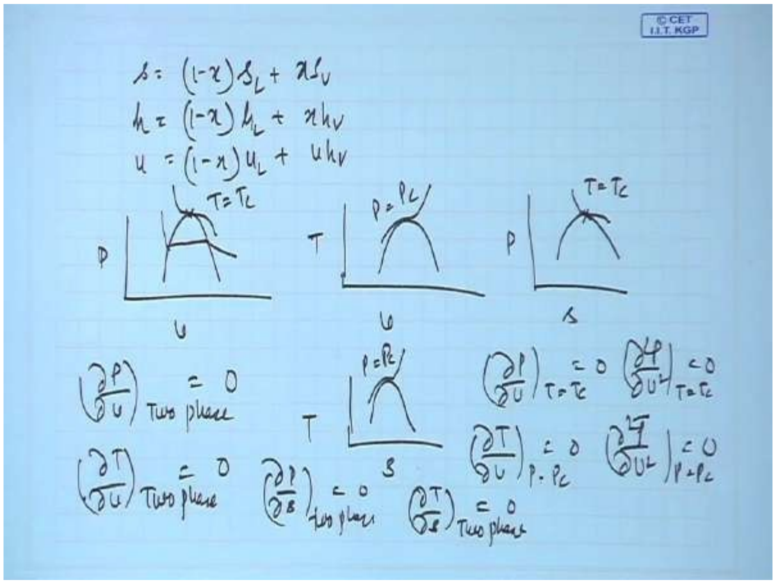
$n v_M = n_L v_L + n_V v_V$

$v_M = \left[1 - \frac{m_V}{m_V + m_L}\right] v_L + \frac{m_V}{m_V + m_L} v_V$

$= v_M = x \underline{v_V} + (1-x) \underline{v_L} \Rightarrow$ lever rule

Suppose we are at this particular position by measuring the horizontal portions, we can find out x and 1 minus x and we already know these 2 so we can find out VM from here

(Refer Slide Time: 31:13)



$s = (1-x)s_L + x s_v$

$h = (1-x)h_L + x h_v$

$u = (1-x)u_L + u h_v$

$\left(\frac{\partial P}{\partial v}\right)_{\text{Two phase}} = 0$

$\left(\frac{\partial T}{\partial v}\right)_{\text{Two phase}} = 0$

$\left(\frac{\partial P}{\partial s}\right)_{\text{two phase}} = 0$

$\left(\frac{\partial T}{\partial s}\right)_{\text{Two phase}} = 0$

$\left(\frac{\partial P}{\partial v}\right)_{T=T_c} = 0$ $\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c} = 0$

$\left(\frac{\partial T}{\partial v}\right)_{P=P_c} = 0$ $\left(\frac{\partial^2 T}{\partial v^2}\right)_{P=P_c} = 0$

And here I would like to mention that the similar relationship this additive property in fact this holds for all extensive properties of pure substances we can have s equals to 1 minus x sL plus xsv similar way we can have the same thing for enthalpy the same thing for internal energy and so on and so forth we can keep on having. So therefore from here what do I do? Till now what have I done?

I have discussed just 2 curves we will be discussing the PT curve in the next class and in all the curves that I have discussed it is important for you to know this is TV curve in all the curves you will find that at this particular point more or less we have something of this sort. In fact we can we can also plot different curves for Ps and Ts also.

Here also in the Ps curves also we find that there is a horizontal inflection at the critical point, here also we will be having a horizontal inflection at P equals to PC this is at T equals to TC, this is P equals to PC, this is T equals to TC, for all the curves we find there is a horizontal inflection and for each of the curve we know that there is going to be a horizontal portion here as a result of which for each copy can write down del P del V 2 phase equal to 0.

Del T del V 2 phase equal to 0, same applies for these 2 and we can also write down del P del V at T equals to TC equals to 0 del 2 P del v2 at T equals to Tc equals to 0. Same thing for del T del V at p equals to Pc equals to 0 del 2P sorry del 2T del V2 at P equals to PC equals to 0. So therefore this particular and similar way we can write for these also, we can write del P del s at constant at 2 phase this is also equal to 0.

Del T del s 2 phase equals to 0 and therefore, so therefore what I mean is such a relationship can be written down for any particular closed substance in the 2 phase region and at the critical point. So we will continue with our discussions regarding the graphical representations in the next class.